



2026-2 Tagungsbericht

Conference Proceedings

Processes for Resilient Supply of Carbon Carriers, Fuels
and Chemicals

October 8 - 9, 2026 | Essen



DGMK und Autor(en) haben alle Sorgfalt walten lassen, um vollständige und akkurate Informationen in diesem Buch zu publizieren. Der Verlag übernimmt weder Garantie noch die juristische Verantwortung oder irgendeine Haftung für die Nutzung dieser Informationen, für deren Wirtschaftlichkeit oder fehlerfreie Funktion für einen bestimmten Zweck. Die DGMK übernimmt keine Gewähr dafür, dass die beschriebenen Verfahren, Programme usw. frei von Schutzrechten Dritter sind.

Alle Rechte vorbehalten

© DGMK e.V., Hamburg, 2026

Für Copyright in Bezug auf das verwendete Bildmaterial siehe Quellenangaben in den Abbildungsunterschriften. Abbildungen ohne Quellenangabe sind von den Autoren.

Das Werk einschließlich aller seiner Teile ist urheberrechtlich geschützt. Jede Verwertung außerhalb der engen Grenzen des Urheberrechtsgesetzes ist ohne Zustimmung der DGMK unzulässig und strafbar. Das gilt insbesondere für Vervielfältigungen, Übersetzungen, Mikroverfilmungen und die Einspeicherung und Verarbeitung in elektronischen Systemen.

The work including all its parts is protected by copyright. Any use outside the narrow limits of the German Copyright Law without the consent of the DGMK is prohibited and punishable by law. This applies in particular to reproduction, translation, microfilming and storage and processing in electronic systems.

Umschlaggestaltung: DIE NEUDENKER®, Darmstadt | DGMK e.V., Hamburg

Titelfotografie: shutterstock.ai, generated image;

ISSN 3052-1629

ISBN 978-3-947716-84-5

<https://www.dgmk.de>

CONTENTS

Page

METHANOL SYNTHESIS

- Step-wise Technology Pathways to Decarbonization** **1**
J.-P. Bohn
- Methanol Production from Steel Mill Gases - Comparison of Plant Performance for Different Carbon Sources** **2**
J. Voß, V. Angenedt, T. Schulzke

METHANE PYROLYSIS, HYDROGEN, AMMONIA CRACKER

- From the Lab to the Field: Air Liquide's R D-driven De-Risking Strategy for the Commercialization of Ammonia Cracking Technology** **4**
S. Trunk, R. Schmidt, X. Tang, V. Ren, G. Lodier, P. Del-Gallo, M. Madelain, B. Dhungel, D. Ulber, T. Wurzel, F. Cock
- Compact and Efficient Ammonia Cracker for Decentralized Hydrogen Production** **23**
D. Gashnikova, R. Zapf, C. Hofmann, G. Kolb
- Hydrogen and Solid Carbon Production by Discharge Plasma Decomposition in Liquid-Phase Hydrocarbons** **24**
Y. Katsuragawa, H. Ueda, M. Asahara, T. Harigai, T. Miyasaka
- Inductively Heated Moving-Bed Reactors for Methane Pyrolysis** **34**
S. Schütz, G. Stubbe, S. Möhring, T. E. Müller

ELECTRIFICATION OF CHEMICAL PROCESSES

- Novel Joule-Heated Radial Reactors with Spatially Distributed Heat Generation for the Intensification of Steam Methane Reforming** **43**
L. Cozzarolo, F. Romanelli, F. Poma, M. Ambrosetti, M. Bracconi, P. Baj, T. Podolak, M. Maestri, A. Beretta, G. Groppi, B. Mello-Gabbrielleschi, B. Williams, E. Tronconi
- Decentralized Ammonia Cracking in a Resistively Heated Reactor** **45**
C. M. Watermann, F. L. Winter, M. Peters, A. Menne, B. Zeidler-Fandrich

METHANOL-TO-X, FISCHER-TROPSCH, E-FUELS, SAF

- Intensified Thermocatalytic CO₂ Conversion to Chemicals and Fuels** **50**
J. Xie
- Fuelling the Fleet: Utilizing Air Liquide's Advanced Methanol Technology to Deliver a CO₂-Based Next-Generation Marine Fuel** **51**
A. Roesch
- From Oil to Low Carbon Alcohols as Energy Carriers for Transportation and Intermediates for Chemical Production** **52**
M. Marchionna

From Methanol to Alcohols: Mechanistic Understanding of a Tandem Catalytic System for Resilient C1-Based Chemical Supply	60
<i>J. T. Groteguth, S. Stahl, J. T. Vossen, J. Exo, T. Weyhermüller, C. Lyall, J. Lowe, U. Hintermair, W. Leitner, A. J. Vorholt</i>	

Demonstration of an Integrated Power-to-liquid Plant for SAF Production using a 220 kW Co-SOEC Module	61
<i>G. Corre, A. Happ, H. Bürgmayr, M. Rubin, R. Dittmeyer</i>	

CHEMICAL RECYCLING

Industrialization of Chemical Recycling – Technical, Regulatory and Market Perspectives from OMV’s ReOil® Scale-Up Journey	62
<i>A. Leitner</i>	

Pyrolysis of PC/ABS-Blends in a gaseous Ammonia Atmosphere	63
<i>P. Rathsack, M. D. Hannak, D. Scheithauer, M. Peuker, J. Kleeberg, M. Gräbner</i>	

Intensification of the Modified OxFA Process by Evaluation of Different Reactor Concepts	64
<i>I. C. Wirth, H. Kleemiß, D. Voß, M. Poller, M. Schlüter, J. Albert</i>	

Integration of Plastic Waste Pyrolysis Oils into FCC Processes	65
<i>T. Dreising, L. Brilmayer, J. Vogt, S. Tavakkol, D. Stapf</i>	

Circular Carbon via Gasification of Complex Waste Streams	83
<i>A. Bader, L. Seidl, T. Horst</i>	

PLASMA PYROLYSIS

Electrification of Gasification Processes by Plasma Integration	84
<i>M. Gräbner</i>	

Integration of a Free-burning Plasma Arc into a Fluidized Bed Gasification System	85
<i>R. Schimpke, V. Kuznetsov, M. Gräbner, P. Pieterse, D. Uhrlandt</i>	

Enhancing Waste Gasification-based Methanol Production by Renewable Energy Integration – Hydrogen vs. Plasma	99
<i>A. Helf, F. Keller, M. Gräbner</i>	

Circular Carbon for Resilient Chemical Value Chains Enabled by Plasma Technology	114
<i>S. Renninger</i>	

POSTERSESSION

Production of Fischer-Tropsch suitable syngas for green jet-fuel through dry reforming of methane-CO₂-mixtures <i>M. Bachstädter, A. Jess</i>	115
Thermal Behavior and Runaway Analysis of Exothermic Reactions in Fixed-Bed Reactors: CO₂ Methanation as a Case Study <i>C. Bischoff, C. Kern, A. Jess</i>	116
EnerFuel – Production of Fuels and Energy Carriers from Biogenic Residues and Plastic Waste for the Development of Regional Value Chains <i>K. Rimagmos, T. Plessing</i>	117
Investigation of the Electrochemical Ethylene Glycol Oxidation using Ni-based Layered Double Hydroxides <i>I. Kohlhaas, L. Cino, C. Englezos, G. Mul, G. Katsoukis, R. Palkovits</i>	118
Two-step glycerol valorization to 1,2-propanediol as the basis for the construction of a SMART-reactor <i>P. Hassenstein, J.-D. Krueger, J. Albert</i>	119
Process Scale-Up for Tandem Catalytic Alcohol E-Fuel Production in the E-TANDEM project <i>H. Stieber, S. Popp, W. Leitner, G. Prieto, A. J. Vorholt</i>	121
Bio-based Polyesters from Itaconic Acid and L-Histidine as Sustainable Alternatives to Fossil-based Polymer Carriers <i>R. Sebers, L. Klug, E. Fulajtar, J. L. G. Nava, A. Pich, R. Palkovits</i>	122
Simulation-Driven Validation and Enhancement of Reactor Models for a Technical Fixed-bed Fischer–Tropsch Synthesis <i>L. Hentschel, C. Kern, A. Jess</i>	123
Ammonia Cracking as a Key Enabler for Resilient and Carbon-Free Energy Supply Chains in Industrial High-Temperature Processes <i>T. Schiek</i>	124
Promotion of Hydrogen Production via the Thermal Decomposition of Piperylene in the Presence of By-Product Light Hydrocarbons <i>S. Miyamoto, Y. Katsuragawa, H. Ueda, M. Asahara, T. Watanabe, S. Ohta, T. Miyasaka</i>	126
Higher Oxygenate E-Fuel Synthesis by Tandem Fischer-Tropsch Synthesis and Reductive Hydroformylation <i>S. Popp, H. Stieber, W. Leitner, G. Prieto, A. Vorholt</i>	136
Decentralized Methanol Production at Wastewater Treatment Plants: Synergies and Regulatory Challenges in the E-BO₂t Project <i>B. Bender, C. Ait Tarint, F. Voit, T. Lind</i>	137
Closing the Carbon Loop: CO₂-to-Fuel via Hybrid Catalysis <i>S. Feldhoff</i>	148

Studying Deactivation phenomena using Pd/1,2-DTBPMB in the Tandem Isomerization-Methoxycarbonylation Reaction	163
<i>N. Kumari, R. Franke, A. J. Vorholt</i>	
Plasma-assisted entrained flow gasification as a key technology for Net Zero - a review	164
<i>L. Kufferath-Sieberin, S. Fleck, U. Santo, D. Becker, M. Vogelbacher, J. Matthes, F. Scheiff</i>	
Turning Emission to Feedstock: Mapping Europe's CO₂ Market for Fuels and Chemicals	166
<i>I. Akhmetova, N. Fuchs, C. Gruber, H. Basche, S. Bernhardt, H. Lehmann</i>	
High Temperature Workflows in High Throughput Experimentation: From NH₃ Cracking and CO₂ -to-CO to Methane Pyrolysis	167
<i>M. Moll, C. Hauber, B. Mutz</i>	
Catalyst-modulated Discharge Chemistry: Tailoring electron-surface Interactions in the total Oxidation of n-butane to CO₂ over a MnO₂/CaO-coated Surface Dielectric Barrier Discharge	183
<i>J. Hiepel, T. Oppotsch, G. Hübner, P. Awakowicz, I. Korolov, M. Muhler</i>	
Influences on the Selective Catalytic Oxidation of Residual Ammonia in Ammonia Cracking Gas	184
<i>A. Sack, H.-P. Schmid, J. A. Wüning, T. Plessing, A. Jess</i>	
Comparative Simulation Study of Fuel Production Pathways from Biomass-derived Syngas	185
<i>M. E-Moghaddam, N. Dahmen</i>	
Modeling and Prediction of Phase Equilibria in Systems Containing Bio-Oil Compounds	187
<i>A. Jalalinejad, A. Funke, N. Dahmen</i>	
Minimum Achievable Cost of Methanol-to-jet Sustainable Aviation Fuel: A Bottom-up Decomposition by Optimization Measures	188
<i>A. Elwalily, V. Erfurt, M. Wenzel, L. Tafur, S. Günthner, H. Lehmann</i>	
Comparative Assessment of Fischer-Tropsch and Methanol Synthesis Pathways for Resilient Fuel Production from Sustainable CO₂ Sources	202
<i>V. Erfurt, L. Tafur, A. Elwalily, M. Wenzel, S. Günthner, H. Lehmann</i>	
Compliance of Synthetic Fuels with European Standards: The German Regulatory Perspective	203
<i>M. J. Alhnidi, N. Dahmen, M. Glaser</i>	
Revealing Resonances in Technical Dehydration of Ethanol	204
<i>M. Seifert, L. A. Lorenz, L. A. Haufe</i>	
Kinetic modelling of the Sabatier reaction over Ni/CeO₂-ZrO₂ for synthetic natural gas production	205
<i>G. Ramis, W. Da Silva Cardoso, S. Romegialli, M. Tommasi, A. Gramegna, I. Rossetti</i>	

Three-pipeline Gas Grid for Renewable Hydrogen Storage and Distribution: Integrated Power-to-gas/gas-to-power Conversion with Closed-loop Carbon Utilization	216
<i>I. Rossetti, M. Tommasi, S. Romegialli, W. Da Silva Cardoso, A. Gramegna, G. Ramis</i>	
Power2ValueChemicals – Integrated Process Development for Evaluating Electrolytically Produced CO from CO₂ for Industrial Applications	228
<i>L. Steinwachs, A. Vorholt</i>	
Bridging the Gap in MDI Value Chains: A Dual-Metric Evaluation of Circularity and Carbon Footprint from CO Production to MDI Synthesis	229
<i>T. E. Korkut, A. Uguina</i>	
Operando Spectroscopy to Investigate Molecular Catalysts in Flow	230
<i>R. Medhekar, A. Sobolev, M. Gerlach, C. Hamel, W. Leitner, A. J. Vorholt</i>	
Phosphorus-Modified Catalysts in the Dehydrogenation of n-Heptane as a Model Compound for Pyrolysis Oil Upgrading	232
<i>C. Schweiger P. Schühle</i>	
Multiscale Study of CH₄ Pyrolysis: From Kinetics to Fluidized Reactor Operation with C-valorization in the Steel Industry	233
<i>M. Orsenigo, V. Piazza, G. Dall'Osto, C. Negri, L. Castoldi, G. Groppi, M. Maestri, C. Mapelli, A. Beretta</i>	
Reconstructing the Kinetics of Biomass Pyrolysis from bio-components Contributions: Application to Rice Husk	235
<i>E. Benedetto, V. Piazza, A. Guarnieri, M. Y. Suleiman, L. C. Pariani, P. D'Arrigo, T. Faravelli, A. Frassoldati, L. Lietti, A. Beretta, P. Debiagi</i>	
Recrystallisation of Pyrolysis Carbon into Graphitic Materials	237
<i>S. Schütz, G. Stubbe, G. Bendel, G. Sorrentino, T. E. Müller</i>	
Environmental Assessment of CO₂-based Pathways to Short-Chain Alkenes	239
<i>J. H. Westerbarkei, M. Hebenbrock, V. Hagen, T. E. Müller</i>	
From Ammonia Synthesis to CO₂-based Alkenes: Repurposing Industrial Iron Catalysts	241
<i>J. H. Westerbarkei, V. Hagen, T. E. Müller</i>	
DME from Crude Methanol	243
<i>A. Schaadt, S. Feuerbach, F. Nestler, M. Gierse, R. Szolak</i>	

Step-wise Technology Pathways to Decarbonization

J.-P. Bohn

LINDE Engineering, Chemical and Process Technology Development, Pullach, Germany

Achieving deep decarbonization of large-scale chemical production assets poses a significant challenge, as existing plants are capital-intensive, and deeply integrated into complex value chains. While fully greenfield solutions offer the highest theoretical emission reduction potential, they are often limited by technology readiness, infrastructure availability, and economic constraints. As a result, step-wise technology pathways that enable gradual impactful emission reductions are emerging as a pragmatic and scalable approach towards net-zero.

This presentation discusses three representative industrial examples in which decarbonization can be implemented incrementally rather than through a single, disruptive transition. The first example focuses on methanol production, where a green hydrogen electrolyzer is added to an existing grey steam methane reforming (SMR)–based syngas plant. By partially substituting fossil-derived hydrogen with renewable hydrogen, CO₂ emissions are reduced while key assets such as large-scale methanol synthesis and downstream processing remain unaffected. Such hybrid configuration enables early deployment of electrolysis, supports learning curves and reduces risks, and can be scaled further as renewable power availability grows.

The second example addresses steam cracking, one of the most energy- and carbon-intensive processes in the chemical industry. Instead of full electrification, a single conventional fired furnace is partially replaced by an electrically heated furnace within an existing cracker complex. This selective electrification approach allows significant direct CO₂ emission reductions, while maintaining operational flexibility and minimizing retrofit risks related to power infrastructure, plant availability, and capital expenditure.

The third example illustrates feedstock decarbonization through the gradual introduction of pyrolysis-oil-based feedstocks derived from plastic waste into a conventional steam cracker. Due to feedstock availability, and process constraints, full substitution is neither realistic nor necessary in the short to medium term. However, even limited co-feeding enables meaningful fossil feedstock displacement and supports circular carbon pathways.

Together, these cases demonstrate that step-wise decarbonization strategies can deliver substantial and credible emission reductions today, while preserving asset value and enabling continuous technological and infrastructural evolution towards fully decarbonized chemical production chains.

Methanol Production from Steel Mill Gases - Comparison of Plant Performance for Different Carbon Sources

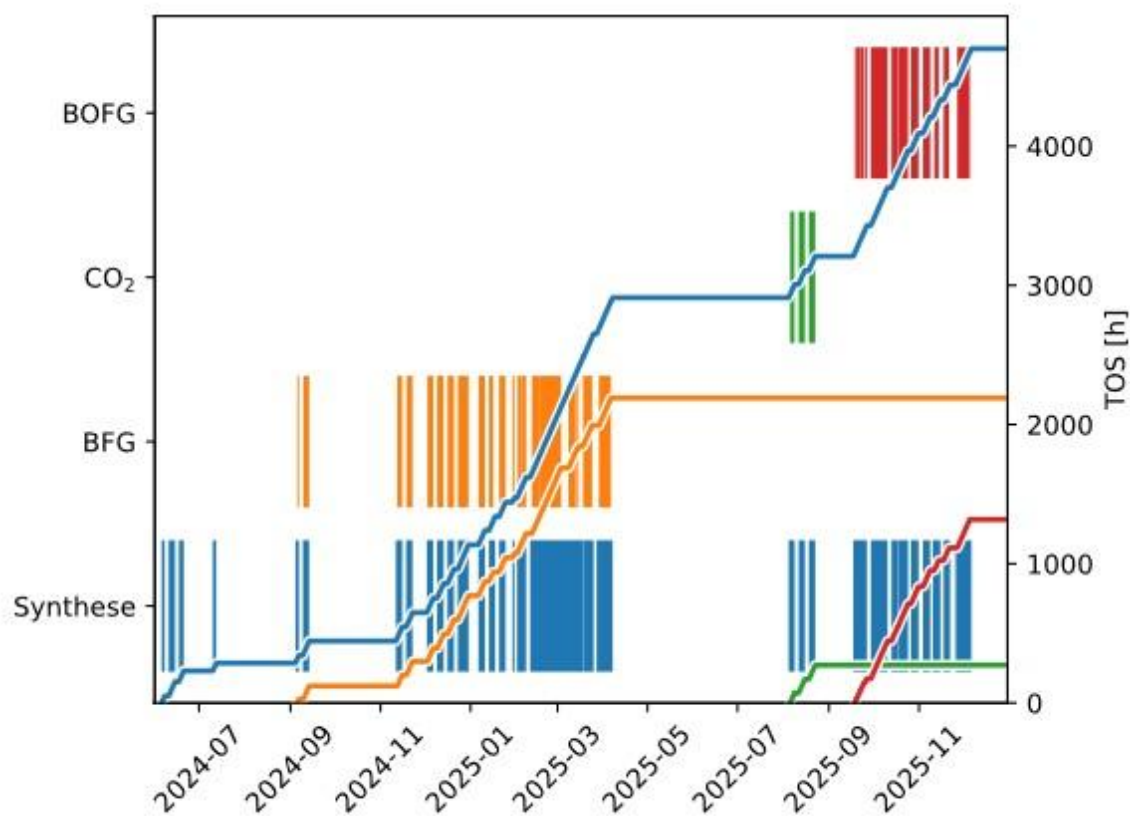
J. Voß, V. Angenedt, T. Schulzke

Fraunhofer UMSICHT, Carbon Utilization and Synfuels, Oberhausen, Germany

Within the collaborative project “Carbon2Chem” [1], a consortium from industry and academia investigates the potential for carbon sequestration from still mill off-gases and its subsequent utilization for the production of chemicals. A subproject deals with the production of methanol. The hydrogen source is a 2 MW alkaline water electrolysis. The sources for carbon oxides are blast furnace gas (BFG) and basic oxygen furnace gas (BOFG). While BOFG is mainly composed from carbon monoxide and carbon dioxide, BFG contains about 50 % nitrogen unfortunately and this dilutes the reacting gases and affects the efficiency of synthesis gas conversion. [2]

A used demonstration plant for methanol production from pure CO₂ and H₂ was procured and extended for the operation with feedgases with varying share of CO₂ and CO and additionally containing diluting inert gases like N₂ or CH₄. Online IR gas analysers for recycle gas and feedgas were added and a temperature measurement on the reactor axis with 36 measurement points. This plant with a production capacity of 50 ltrs. per day was operated with clean bottle gases on the premises of Fraunhofer UMSICHT for 3 campaigns with 1,257 operating hours in total performed with a single filling of catalyst [3] and subsequently moved to the integrated steel mill of thyssenkrupp Steel Europe in Duisburg and connected to the gas cleaning unit from the Carbon2Chem project. [4]

The demonstration plant is now operated with different carbon sources from the steel mill to compare the plant performance. The first carbon source was cleaned blast furnace gas with its nitrogen dilution. Next, the blast furnace gas is further processed in a water gas shift reaction to convert all CO to CO₂ and subsequently sequestered in an amine wash and converted in demonstration plant. The third source will be basic oxygen furnace gas from the conversion of raw iron to steel. At the end, blast furnace gas will “only” be treated in the amine wash (without prior sulfur adsorption and water gas shift) as a potential cheap cleaning system. With a single filling of commercial catalyst the accumulated TOS reached 4,701 h



Accumulated time-on-stream (TOS) with different steel-mill gases as carbon source

[5]. Liquid samples are taken during the operation and analyzed for main and by-products.

References:

- [1] Deerberg, G., Oles, M., Schloegl, R., (2018), The project Carbon2Chem, Wiley-VCH, Chem. Ing. Tech., Weinheim, 1365-1368
- [2] Schittkowski, J., Ruland, H., Laudenschleger, D., Girod, K., Kähler, K., Kaluza, S., Muhler, M., Schloegl, R., (2018), Methanol Synthesis from Steel Mill Exhaust Gases: Challenges for the industrial Cu/ZnO/Al₂O₃ Catalyst, Wiley-VCH, Chem. Ing. Tech., Weinheim, 1419- 1429
- [3] Voß, J.M., Daun, T., Geitner, C., Schlüter, S., Schulzke, T., (2022), Operating behavior of a Demonstration Plant for Methanol Synthesis, Wiley-VCH, Chem. Ing. Tech., Weinheim, 1489-1500
- [4] Voss, J., Schulzke, T., Deerberg, G., (2024), First Operation Experience of a Methanol Demonstration Plant with Steel Mill Gases, Shanghai, Presentation at 12th International Freiberg Conference, 23.-27. September 2024, Shanghai, China, IEC TU Bergakademie Freiberg
- [5] Voss, J., Schulzke, T., (2026), First Operation Results of a Methanol Demonstration Plant with real Steel Mill Gases, Wiley-VCH, Chem. Ing. Tech., Weinheim, in review

From the Lab to the Field: Air Liquide's R&D driven De-risking Strategy for the Commercialization of Ammonia Cracking Technology

S. Trunk¹, R. Schmidt¹, X. Tang¹, V. Ren², G. Lodier², P. Del-Gallo², M. Madelain², A. Duarte Tarazona², B. Dhungel³, D. Ulber⁴, T. Wurzel⁵, F. Cock⁶

¹Air Liquide Forschung und Entwicklung GmbH, Innovation Campus Frankfurt, Frankfurt, Germany

²Air Liquide Research & Development, Innovation Campus Paris, Loges en Josas, France

³Air Liquide Research & Development, Innovation Campus Delaware, Newark, United States

⁴Air Liquide Global Engineering & Construction Solutions Germany GmbH, Frankfurt, Germany

⁵Air Liquide Large Industries % Global Engineering & Construction Solutions Germany GmbH, Frankfurt, Germany

⁶Air Liquide Industries Belgium NV, NCE Cluster, Zaventem, Belgium

Abstract

The global transition toward a low-carbon energy economy is fundamentally dependent on the development of scalable, logistically viable hydrogen (H₂) carriers. Ammonia (NH₃) can become a vital carbon-free hydrogen carrier for H₂ production. Air Liquide (AL) is commercializing NH₃ Cracking technology to provide a high-capacity H₂ source with a significantly lower carbon footprint than conventional steam methane reforming. Historically, this process lacked the necessary Technology Readiness Level (TRL) for large-scale commercial adoption. AL has addressed this critical gap through a multi-year, structured Research and Development (R&D) program ("technology roadmap") designed to transition NH₃ cracking from theoretical chemical engineering to a robust, field-ready industrial reality. This work focuses on the systematic de-risking of the technology through an iterative "Lab-to-Field" methodology.

The AL R&D framework utilized a rigorous, integrated approach combining fundamental R&D laboratory science with large-scale technical validation across all relevant TR levels to bridge the gap between lab-scale research and industrial implementation in the field.

The LAB: A rigorous approach involving the deployment of R&D pilots at progressive scales, ranging from bench-scale units for rapid screening to technical-scale pilots for representative industrial testing. Applied holistically to all techno bricks: catalysts, metallic materials and combustion, this multi-scale approach allows us to accurately decouple kinetic properties (reaction and nitridation kinetics) from transport phenomena and scale effects. Additionally the work is accompanied by the validation and improvement of the analytical methods for solid materials and reactants as well as trace components. This generates robust physical data to calibrate our proprietary design tools and models with high confidence.

The FIELD: A fully integrated industrial-scale pilot dedicated to demonstrating the design's reliability, safety, performance and operability across all relevant techno bricks. By operating in a representative production environment, it serves to validate the complete NH₃ to H₂ production chain, confirming the performance and durability of critical equipment. Key analytical methodologies include Data Validation and Reconciliation (DVR) to ensure reliable datasets by rigorously closing mass and energy conservation laws to allow for a precise model calibration.

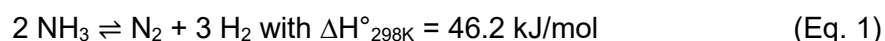
The different test campaigns have successfully elevated the technology to TRL 8. Findings from laboratory research were effectively scaled and reproduced at an industrial scale pilot at the AL Antwerp production site, confirming that efficient NH₃ conversion can be realized, that

all selected materials resist long-term operation in harsh industrial conditions and that NH₃ combustion complies with NO_x emission standards.

Ammonia cracking has been proven as a commercially viable technology through the effective implementation of this technology roadmap. This represents a critical milestone to establish NH₃ as an energy & hydrogen carrier and NH₃ cracking as a pillar of the energy transition. The technology is ready for large scale industrial deployment.

Introduction

The transition to a global hydrogen economy is fundamentally constrained by the logistical challenges of storing and transporting hydrogen. While elemental H₂ possesses a high gravimetric energy density, its exceedingly low volumetric density necessitates liquefaction at extreme cryogenic temperatures (-253 °C). This highly energy-intensive process makes long-distance maritime transport uneconomical. Consequently, NH₃ has emerged as a superior hydrogen carrier. It offers a higher volumetric hydrogen density, condenses at relatively mild conditions (-33 °C) and has a relatively low vapor pressure of around 8.5 bar @ 20 °C. Furthermore, it benefits from a mature, globally established supply chain [1]. However, utilizing NH₃ as an H₂ vector requires releasing the stored H₂ at the point of demand e.g. via catalytic decomposition:



This cracking step is highly endothermic and kinetically limited, requiring elevated operating temperatures. Until recently, the market offering for NH₃ cracking was limited to niche markets such as heavy water production or small-scale units for the metal heat treatment industry. Project developers faced a "scale-up gap", introducing unacceptable technical and financial risks for world-scale hydrogen projects. To realize NH₃ cracking for H₂ production at an industrial scale, comprehensive research must de-risk several critical "techno bricks", such as:

- **Material Selection:** Plant components must operate under severe high-pressure and high-temperature conditions facing NH₃, a very corrosive chemical. Extensive material research is essential to identify alloys resistant to the dominant degradation mechanisms of nitriding, hydrogen embrittlement and thermal creep.
- **Heat Provision:** The endothermic heat demand should be supplied via direct NH₃ combustion to lower the carbon footprint and achieve zero direct CO₂ emissions. However, this requires optimized burner designs and combustion strategies to strictly suppress the formation of harmful nitrogen oxides (NO_x and N₂O).
- **Process Gas Purification:** Because thermodynamic equilibrium prevents 100 % conversion at elevated pressures, robust downstream separation technologies must be developed to remove unconverted NH₃, formed N₂ and other impurities from the H₂ product stream to meet the required purity specifications for the different industrial applications.
- **Catalyst Selection:** Active materials must be rigorously evaluated under realistic industrial parameters rather than only at lab conditions. Specifically, long-term catalyst stability must be tested at industrial temperature, pressure and using representative industrial grade NH₃ feedstocks, which can affect the kinetic as well as catalyst stability.

At Air Liquide, all critical techno bricks have been addressed in a systematic manner to overcome the “scale-up gap”. A dedicated Technology Roadmap (TRM) with focus on the main techno bricks was created in order to accelerate the process development and its commercialisation. The TRM provides a holistic framework and connects the whole innovation chain of Air Liquide from Research & Development (R&D) towards the solution development at Engineering & Construction (E&C) and finally plant operation by Large Industries (LI). This paper presents this comprehensive framework and the initial findings of our R&D program for industrial-scale NH_3 cracking. The following section provides an overview of the TRM's general setup and our strategic approach to technology development. Subsequent sections detail the experimental methodologies and corresponding empirical results for the exemplarily selected techno-bricks. Ultimately, this work defines a validated, scalable pathway for transitioning NH_3 cracking from bench-scale concepts to commercially viable industrial-scale hydrogen production.

Air Liquide’s scale-up strategy: From the lab to the field

Scaling up an endothermic, high-temperature and high-pressure process such as catalytic NH_3 cracking to a commercial scale is a highly non-linear challenge. A commercial plant is not simply an enlarged laboratory reactor, it is a highly complex system of interdependent techno bricks that work together as one system. Attempting to bypass intermediate Technology Readiness Levels (TRL) may lead to systemic failure, since critical techno bricks, such as catalyst performance, combustion technology, material selection, process gas purification, or modelling mature at different stages of the scale-up process. A rigorous, scale-up strategy is essential to fully master the individual techno bricks and thus guarantee a sound de-risking of the technology. In the framework of the NH_3 Cracking TRM, we have built up testing capacities for all major techno bricks at various TRL levels, ranging from lab-, over technical- to even industrial-scale test benches and pilot plants. As can be seen in [Figure 1](#), the different test units are highly interconnected, which means results derived from one test unit are systematically integrated as input parameters for other test units.

The first phase of our technology development strategy is the laboratory-scale phase (up to TRL 5). The main focus at this stage is on extensive material screening and deriving kinetic expressions, regardless of the technology brick. This level of granular investigation provides the robust physical data basis necessary to calibrate proprietary modelling and design tools with high confidence. Regarding cracking catalyst screening, we conduct extensive screening of various types, active materials and suppliers to evaluate specific catalyst performance. Crucially, the catalyst's activity and initial stability are evaluated under industrial-grade NH_3 in order to quantify the inhibitory effects of impurities in the NH_3 feed on reaction kinetics. In our R&D material test bench, we test high-temperature alloys for their nitriding resistance. By testing durability at different temperatures and NH_3 concentrations, we were able to identify the most suitable alloys for specific sections of the commercial plant, taking into account factors such as mass variation and internal nitrogen diffusion. Lab-scale research on the process gas purification involves testing different adsorbent materials measuring dry and wet adsorption isotherms for N_2 , H_2 , and NH_3 . This fundamental data is the basis for scale-up simulations and the sizing of the commercial PSA unit targeting maximum hydrogen recovery and purity.

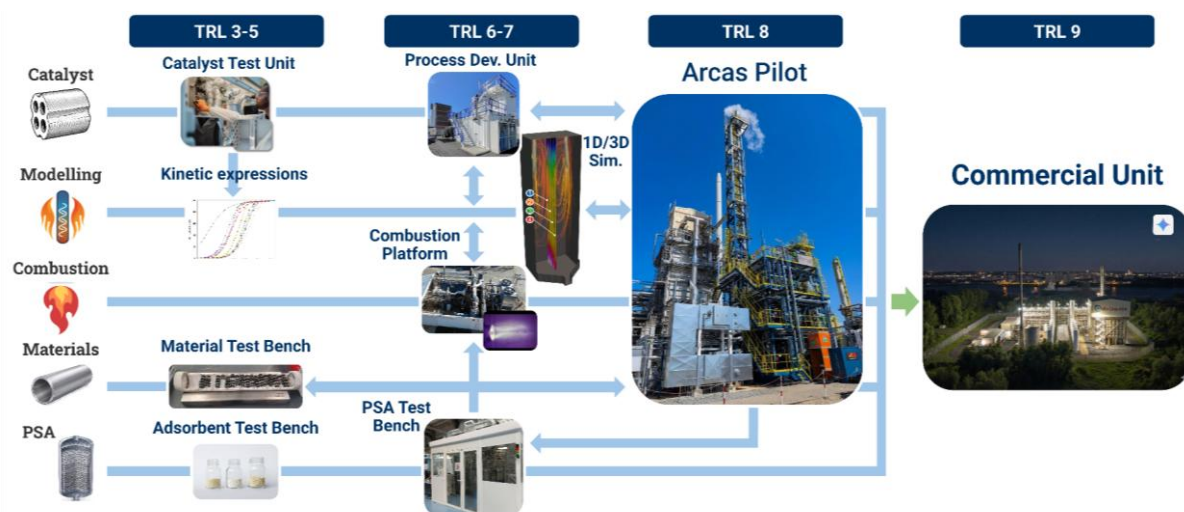


Figure 1: Graphical representation of AL's multiscale technology development strategy for the commercialization of NH₃ cracking.

At the laboratory scale, the primary goal is to study fundamental mechanisms across a broad range to derive the data basis. In contrast, at technical scale (TRL 6-7), the goal is to consider industrial fluid dynamics, macroscopic transport phenomena and hardware limitations in order to evaluate the system's behaviour under industrial-relevant conditions and scenarios. Our Process Development Unit (PDU) for catalyst testing, our Combustion Test Platform and our PSA Test Bench have explicitly been designed to study and to understand these phenomena in detail. In the context of catalyst testing, establishing industrial relevance entails continuously testing a packed bed of full-size catalyst pellets within a tubular reactor at elevated reaction temperatures and pressures over an extended test duration. This setup characteristically introduces real-world operational challenges, such as pressure drop, thermal gradients, and mass transport limitations. The combustion characteristics of NH₃, including crucial combustion parameters such as flame stability, emissions, and heat transfer, are studied using full-scale industrial burners. As the commercial fuel is expected to vary significantly depending on the implementation location, NH₃ can be blended in the Combustion Test Platform with natural gas, H₂, CO₂ and N₂. Very process specific blends include PSA off-gases, the byproduct gas streams released during the regeneration (depressurization and purging) of a PSA system. Conclusions about their compositions can be drawn from the adsorption experiments conducted at the PSA Test Bench. This test bench was upgraded to handle NH₃ containing streams and is used to optimize the complex multi-step pressure cycle and the sizing of the adsorbent layers of a full scale industrial PSA.

Up to TRL 7, each test facility—whether the PDU for catalyst testing, the material test bench, the PSA test bench for adsorption, or the combustion platform—is designed to develop and optimize one specific, individual technological building block in a highly controlled environment. As mentioned above, results derived from these test units are systematically integrated as input parameters for other test units, but they are not combined in one system, which is at the end crucial for the final de-risking of a new technology. That is why ARCAS, our TRL 8 industrial-scale NH₃ cracking pilot plant is the cornerstone of our technology development. Located in the Port of Antwerp and started up in 2025 [2], this facility is a fully integrated and operational pilot plant installed in an industrial area and designed specifically to ensure that all experimental results from lab- & technical-scale test benches and pilot plants are directly scalable and relevant to commercial plant designs. Key analytical methodologies include Data Validation and Reconciliation (DVR) to ensure reliable datasets by rigorously enforcing mass and energy conservation laws to allow for a precise data analysis and model calibration.

Applying the above described rigorous, integrated approach combining fundamental R&D lab- and technical-scale science with industrial-scale validation across all relevant TRL levels, we bridge the gap between R&D lab research and industrial implementation in the field. The following sections will provide a more detailed overview of our “from the lab to the fields” scale-up approach, using selected technology bricks as examples.

Metallic Material Testing

Many corrosion mechanisms in the H₂ production industry are well understood, except for a specific phenomenon that occurs in the NH₃ Cracking process [3, 4]. At high temperatures and under an NH₃ atmosphere, process components suffer from nitrogen diffusion inside the metallic matrix [5]. This phenomenon is called nitridation. It has been well documented in surface treatment applications to increase wear and corrosion resistance [6]. However, increasing the hardness of materials by introducing Nitrogen into the metal matrix over long periods can lead to severe embrittlement and loss of containment in equipment operating at high temperatures and pressures. In addition, ablation and reduction in wall thickness over time can happen as well [7]. In an industrial NH₃ Cracker, nitridation is not the only mechanism causing damage. High flow velocities, thermal cycling and creep can also have an impact on the failure of metallic components such as heat exchangers, reactor tubes or the plant periphery in general. Moreover, the interaction between all these mechanisms can lead to an accelerated degradation, which must be assessed in detail.

A test bench dedicated to high-temperature nitridation was developed at Air Liquide's Innovation Campus Paris. This facility was designed to test materials at high temperatures and high pressures in an NH₃ atmosphere. Several different high-temperature-resistant materials were selected for testing in the pilot. To evaluate the performance of alloys in a high-temperature NH₃ environment, a multifaceted testing strategy was employed. This strategy integrates macroscopic kinetic analysis to measure specific mass variation and nitrided thickness after exposure for different durations. Cross-sectional microscopic characterisations of exposed samples provide a thorough study of the nitridation-induced degradation process. [Figure 2](#) shows exemplarily the experimental results for two different materials tested showing a lower (Alloy A) and a higher (Alloy B) resistance to nitridation. This test approach is designed to not only rank the performance of different materials, but also to understand the underlying corrosion mechanisms and assess their resilience to process-relevant variations.

These lab-scale tests are complemented by industrial-scale material testing at our industrial-scale pilot plant. Industrial operation introduces inner tube pressure, potential creep and thermal cycling due to varying operating conditions to the material test campaign. The provision of both intermediate inspections (visual and videoscope) and destructive testing of the cracker tubes themselves after the campaign offers a unique and comprehensive understanding of the material's integrity throughout its service life. To verify our lab-scale results, numerous additional material samples were placed throughout the whole ARCAS pilot. Strategically placing various sample types, including tensile, hot tensile, creep, toughness, and metallurgy test samples within the cracker tubes further increased our understanding of how materials behave in different process environments. The ability to extract and analyze these

samples after extended exposure provides critical insights into the long-term degradation mechanisms. Integrated temperature measurements (tube skin temperatures and temperatures inside the cracker tube) and online gas stream composition analysis enable precise correlation between process conditions and observed material degradation. Unlike lab-scale tests, this direct exposure within an industrial setting allows for the observation of combined effects such as nitridation, high-temperature creep and thermal cycling.

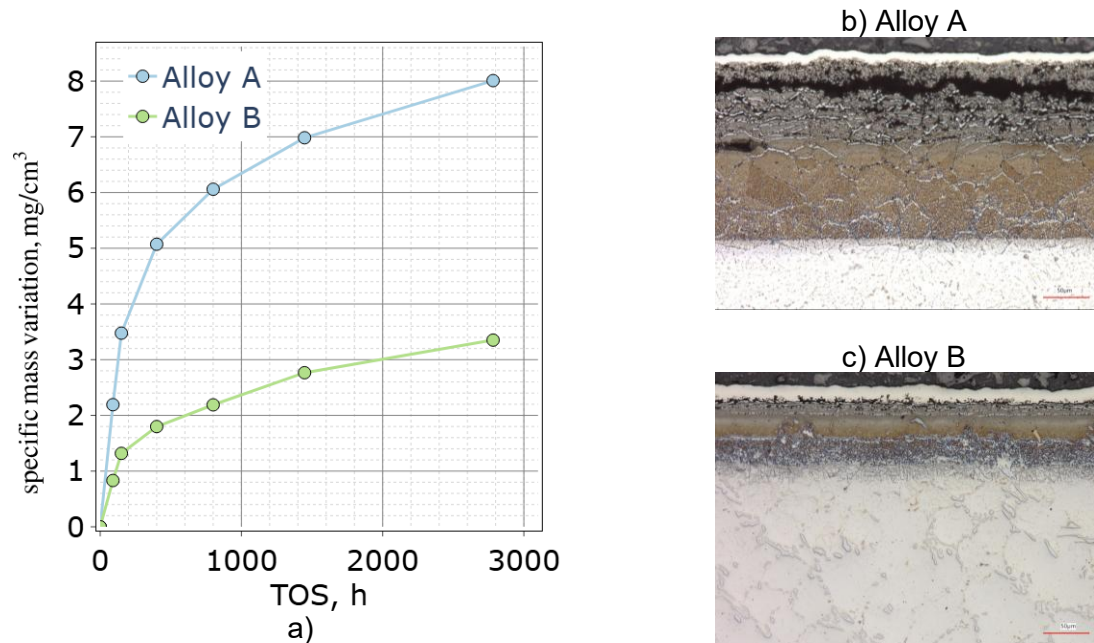


Figure 2: Characterization outputs from lab pilot testing with a) specific mass variation evolution for 2 alloys, b) optical microscopy cross section of Alloy A and c) optical microscopy cross section of Alloy B.

To demonstrate the severity of these typically combined effects, a tubular sample was subjected to testing within the ARCAS pilot plant. The conditions of high temperature, high NH_3 concentration and severe thermal cycling resulted in a catastrophic material failure (see [Figure 3](#)). Subsequent analysis of this sample made it possible to assess the impact of thermal fatigue on nitridation identifying a specific damage mode, which is illustrated in [Figure 3 c](#)). For this specific material, the thermal cycling introduced severe thermal stress, which led to the embrittlement of the protective nitrided outer layers. Consequently, deeper, fresh material was nitrided, causing the delamination of nitrided sublayers over time and resulting in catastrophic material failure. These findings are crucial for ensuring the robustness of the material selection for industrial crackers operating under similar conditions.

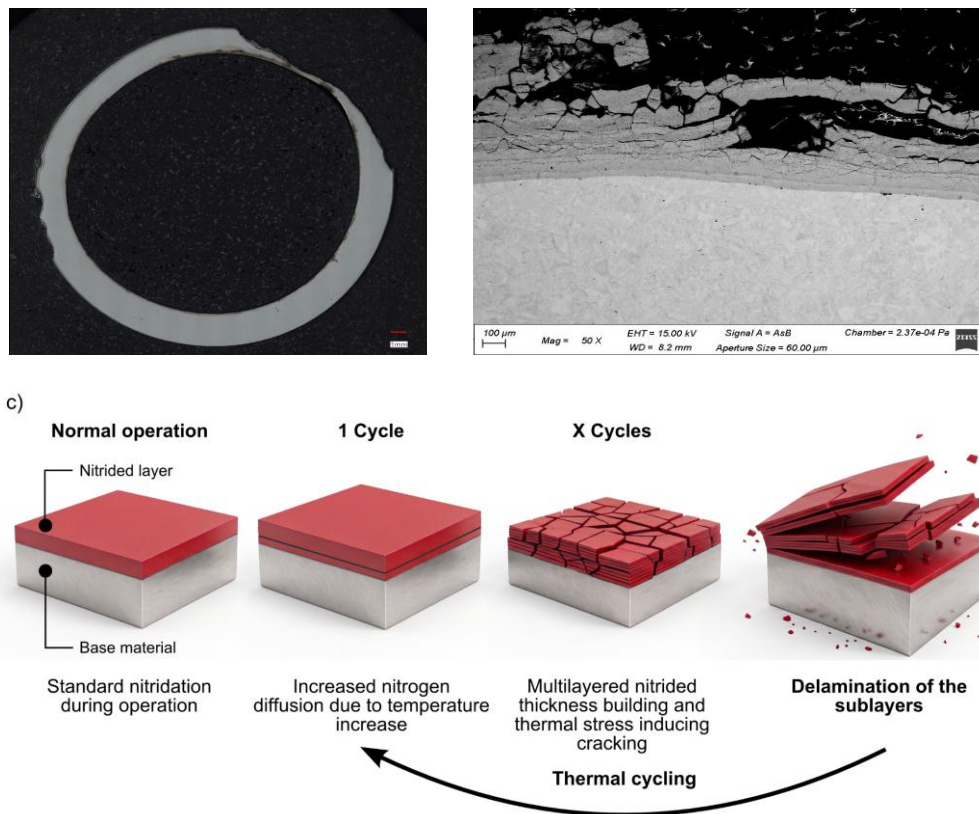


Figure 3: a) Optical microscopy of the section of the sample tube, b) SEM image of the damaged nitrided layer c) Failure scenario during thermal cycles.

NH₃ Combustion

Since NH₃ is both a hydrogen carrier and an energy carrier, the endothermic heat demand for the NH₃ cracking process can be met by using it as a fuel. Using renewable or low-carbon NH₃ as fuel can therefore further reduce the carbon footprint of the H₂ produced. However, this presents several technical challenges, such as flame stability and the emission of nitrogen oxides (NO_x and N₂O). The lower flame stability of NH₃ compared to conventional fuel like natural gas is primarily due to its narrow flammability range and lower laminar burning velocity [8], as well as its higher ignition energy [9]. The presence of fuel-bound nitrogen in NH₃ can potentially lead to significantly more NO_x emissions and literature shows 1-2 orders of magnitude higher NO_x when compared to natural gas [10, 11].

In order to design new or to retrofit existing furnaces for NH₃ fuel, Air Liquide invested in NH₃ combustion capabilities at Innovation Campus Delaware, Delaware, USA (see [Figure 4](#)). Since the modification of our combustion test platform, hundreds of test points at different conditions have been performed. Along with conventional fuels and NH₃, the test facility is also capable of hydrogen firing, with firing rates up to 2 MW. The furnace itself is 2.4 m in diameter and 6.7 m in length. At the front face of the furnace, a large opening is provided for mounting different industrial burners. Several viewports, probe access ports, camera ports and thermocouple ports are available to enable required measurements.



Figure 4: Combustion test platform with NH_3 combustion capability at Innovation Campus Delaware (top) with NH_3 tank (bottom left) and NH_3 flow control skid (bottom right).

For burner tests with different fuel blends, natural gas, H_2 , CO_2 and N_2 are available at the combustion test platform. To supply NH_3 , a bulk tank with a capacity of around 2 t of NH_3 was installed next to the test facility (see [Figure 4](#), bottom left). To enable the vaporization of anhydrous NH_3 , the tank system consists of a vaporizer that provides a continuous stream of NH_3 gas up to a combustion capacity of 2 MW. Flow control skids complying with NFPA standard for NH_3 and H_2 were added to the existing ones for natural gas and oxygen to enable safe firing of the fuel blends (see [Figure 4](#), bottom right). Either air or oxygen can be used as oxidant depending on the test requirement. Air can be preheated up to 450°C , to enable testing at realistic process conditions. This unique setup enables continuous variation of the fuel mixture, allowing all industrial-relevant fuels to be mixed and tested [12].



Figure 5: Natural Gas (left) and NH_3 flames (right) using full scale burners

As mentioned previously, hundreds of tests have been carried out with various full scale burners (1-2 MW) with the aim of determining flame stability, emissions and heat transfer characteristics for the whole operating envelope to be used in commercial plants. Several theoretical assumptions were validated but also unexpected results regarding flame stability and flue gas compositions were obtained. Small amounts of NH_3 in the fuel mixture are almost one to one converted into NO_x emission and lead to higher NO_x in NH_3 combustion compared to hydrocarbon combustion. However, the NO_x emissions do not scale proportionally with the NH_3 content in the fuel. Functional relationships have been established between process-specific burner design, operating parameters and emissions. The NO_x level of the optimized combustion solution is such that stringent emission limits can be achieved with a combination of low NO_x burners and an enhanced de NO_x system. Higher NO_x emissions during NH_3 combustion can be understood according to the fuel- NO_x kinetic pathway. The NO_x emission level varies with process parameters in a different manner than hydrocarbon combustion. For example, the air to fuel ratio has a more pronounced influence, whereas the influence of the combustion air preheat and flame temperature is less important. Furthermore, the formation of N_2O can be avoided by the appropriate selection of combustion parameters for the process-specific burner design and furnace.

Ammonia combustion was demonstrated at the test facility both for fuel-staged and air-staged burners. A wealth of measurement data has been generated and practical knowledge, for example on flame scanner adaptation, has been gathered. The test revealed that flame stability varies significantly with combustion parameters, especially the fuel composition and NH_3 duty contribution, but also combustion temperature. The large variations in parameters in the test program reveal a stable and safe operating window for NH_3 combustion. New combustion safeguards have been developed for the industrial furnace, including the one of the ARCAS pilot plant. Using the burners tested at the R&D platform demonstrates that data from the R&D combustion test platform can be scaled up to commercial fireboxes. Air Liquide E&C is now using the detailed test results and analytical data for the design of Steam Methane Reformer revamps and new NH_3 Crackers.

NH_3 Cracking Catalyst

As seen from the reaction equation (Eq.1) the equilibrium for the endothermic NH_3 cracking is favored by high temperatures and low pressures. At 1 bar full NH_3 conversion, i.e. 98%, is thermodynamically possible at 350 °C. At elevated pressure of 20-40 barg full NH_3 the same conversion requires 650 to 687 °C. In view of the industrial operation this conflicts with the preferred elevated pressures—resulting in smaller equipment, and low operation temperatures—reducing the energy consumption. For industrial application the NH_3 cracking

activation energy needs to be lowered using a catalyst. Numerous catalytic systems are described in the literature, a recent overview is provided by [13, 14]. In general the activity of catalytic active materials can be ranked as follows [15]:



The ranking of active metal reactivities outlines that the best catalysts for NH_3 synthesis are not optimal for NH_3 cracking. Also the role of the support and promoters should not be underestimated for the final NH_3 cracking activity.

Research showed that the rate determining step in the mechanism is often either [13, 15]:

- N-H bond cleavage: $\text{NH}_3(\text{ads}) \rightarrow \text{NH}_2(\text{ads}) + \text{H}(\text{ads})$
- Combinative desorption of N: $2 \text{N}(\text{ads}) \rightarrow \text{N}_2$

For the most active metals Ni and Ru both steps have similar activation energies so that neither of them is significantly limiting.

For latest developments in catalyst development and the variety of investigated combinations of active elements, dopants and support materials it is referred to the review of Ding et al. [13] and Lucentine et al. [14].

For the industrial application the catalyst must satisfy mainly three criteria:

- Acceptable reaction rates
- Long-term stability (mechanical stability in the catalyst bed and chemical stability)
- Commercial availability

As solution provider and operator, our research is focused on the industrial application of developed catalyst systems. Hence, we concentrated on testing various Ni and Ru catalysts developed and manufactured by known catalyst suppliers or active catalyst developers.

Like in the whole TRM, the work was organized on different levels:

1. R&D lab-scale:
 - a. Screening tests
 - b. Kinetic Tests
2. R&D technical-scale pilot:
 - a. Near industrial conditions in controlled environment
3. Industrial-scale pilot:
 - a. Industrial conditions

R&D lab-scale screening and kinetics

Tests of Ni- and Ru-based catalysts were conducted in a small test reactor which allowed for the analysis of small particles in the range of 1-2 mm under isothermal conditions and pressures up to 30 barg at a partner lab. If the investigated catalyst had a larger size, the pellets were crushed and sieved.

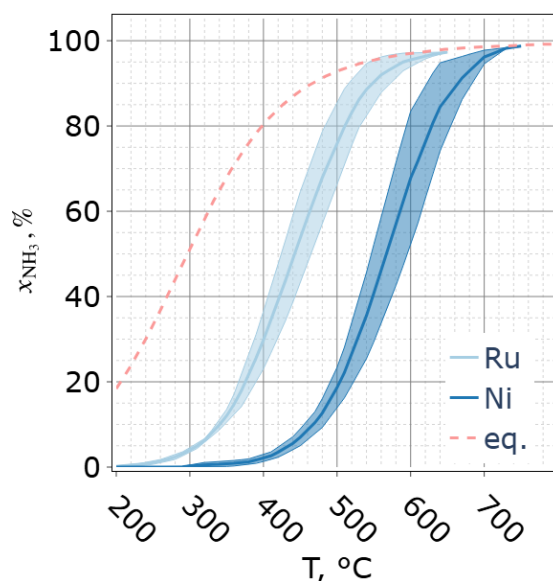


Figure 6: Conversion of NH_3 over Ni and Ru catalysts at 30 barg.

As the most promising catalytic systems the work concentrated on Ru and Ni based catalysts. [Figure 6](#) provides the outcome of the screening test at 30 barg. As expected Ru catalysts excel with a high performance at lower temperatures. On the other hand, Ni catalysts reach equilibrium at 750 °C having a conversion of 99 %. From the equilibrium curve it is obvious that at high pressures for high conversion above >98 % temperatures of more than 650 °C are required. Considering the recommended maximum operation T of many Ru catalysts being around 550-580 °C [16], results in a maximum conversion of only ~97 %. Together with their high price, for industrial large scale application the more robust solution for high T conversion are Ni catalysts. Hence the tests in the R&D pilot unit focused on Ni catalysts.

The temperature limitation of the Ru catalysts is not fully intuitive at the first moment. Using the Tammann and Hüttig temperatures, at 0.5 and 0.3 T_{melt} respectively, it can be concluded that Ru ($T_{\text{melt}} = 2334$ °C) based catalysts have better temperature stability compared to Ni ($T_{\text{melt}} = 1455$ °C) ones. However in general the maximum operation T for Ru catalysts is lower. Both metals are affected by the Gibbs-Thomson effect when the particle size is in the nano scale range, leading to a melting-point depression and vapour pressure increase. Consequently smaller particles suffer in greater extends from particle growth/sintering [17]. For maximal activity an optimal particle size for Ru is 1.8 - 7 nm, dependent on the shape of the Ru particles [18]. The real size of the active centers is close to the optimal one with 6 nm for 1.5 % Ru/ Al_2O_3 [19]. For Ni active centers density functional theory revealed an optimal size of 3.1 - 3.6 nm [20]. However due to the higher amount of material larger crystallines are formed, Atsumi et al. report 26.7 - 27.9 nm for 10 % Ni/ Al_2O_3 [21]. The smaller Ru particle can explain at least partly the lower maximum operation temperature due to stronger melting point depression compared to larger Ni particles. But it must be emphasised, for the stability of the final catalyst product beside the size of the crystallines other factors are important like the interaction strength between active center & support and amount of available material / active surface. Especially when comparing the amount of active material Ni catalysts often have an order of magnitude higher metal loadings compared to Ru ones.

The data from the lab scale experiments were utilized to adapt a kinetic model for the application in proprietary cracker design tools.

R&D technical-scale pilot plant

Catalyst testing at lab-scale with powder or crushed catalyst provides valuable insights for catalyst screening, general stability and the kinetics. However the test conditions differ significantly from the industrial operation. The catalyst pellets are placed in a tube and heat is provided by firing. Depending on the operation conditions (T_{inlet} , p , GHSV, heat flux profile) a temperature profile forms within the catalyst bed which influences the overall conversion. Furthermore based on the local temperature and gas composition different aging or inhibition mechanisms might be pre-dominant.

To test the most prominent catalyst close to industrial conditions a new technical-scale pilot plant (process demonstration unit) at Innovation Campus Frankfurt, Germany, is used. Being able to fit full catalyst particles at $T_{\text{max}} = 950\text{ }^{\circ}\text{C}$ and up to 40 barg the unit is able to cover the expected industrial operation envelope. [Figure 7a](#) shows an outside view of the test bench and [Figure 7b](#) the core equipment: the heated reactor. Using independent electrical heating zones we can simulate different heat flux profiles in the unit to mimic industrial operation. Evaluation of the results is based on two main parameters, the T-profile of the catalyst bed and the NH_3 conversion determined utilizing GC and Raman Spectroscopy.



a)



b)

Figure 7: R&D pilot scale “Process Development Unit” (PDU), a) outside view, b) reactor with electrical heaters.

The observed temperature profiles for NH_3 cracking are as expected for an endothermic process. As depicted in [Figure 8a](#), at high inlet temperatures the temperature in the catalyst drops in the first part of the bed where the reaction's heat consumption outweighs the heat transfer into the system, a characteristic minimum temperature is observed. Further in the bed the temperature rises towards the outlet temperature. For comparison lower inlet temperatures were used as well, in this case a steady temperature increase is observed, see [Figure 8a](#). If the catalyst ages this influences the reaction rate and hence the T-profile in the reactor, as shown in [Figure 8b](#) is the minimum temperature increasing from start to end of the campaign.

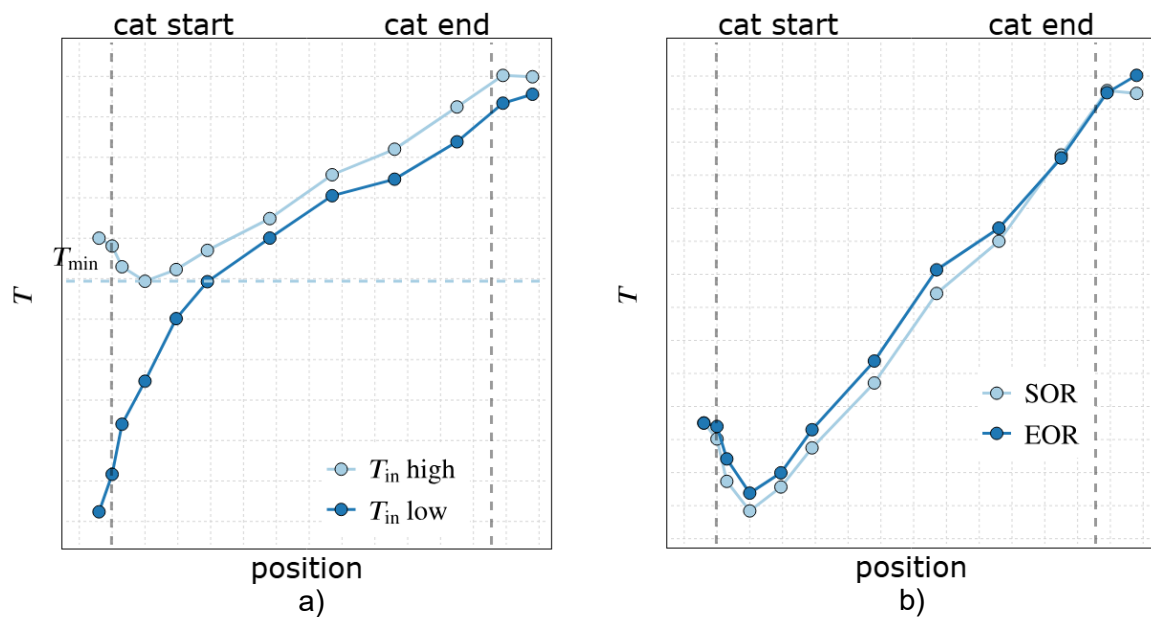


Figure 8: T profiles in R&D pilot unit for a) high & low inlet temperature and b) at start-of-run (SOR) and end-of-run (EOR) of a campaign

Operating at high outlet temperature the cracked gas is in or very close to equilibrium. In detail the temperature approach to equilibrium (ΔT_{app}) for the cases shown in [Figure 8a](#) is between -7 to $+9$ K. That a slight positive temperature approach is observed can result from small errors in the assumed outlet temperature and uncertainties in the composition measurement. At high temperature and flat equilibrium conversion profile, already small deviations in the gas composition result in a noticeable change in the calculated approach to equilibrium. Under equilibrium conditions the catalyst's long term stability is hard to evaluate because decreasing activity might still result in an equilibrium conversion. Therefore the unit is operated on a regular basis in a kinetically limited regime, the so-called "Reference Point". The "Reference Point" was defined at the beginning of the test campaign, targeting at $\Delta T_{app} \sim -260$ K based on the high outlet temperature. To achieve the conversion the outlet temperature T_{Ref} was determined experimentally..

The performance, illustrated as the approach to equilibrium ΔT_{app} , over time for two test campaigns executed in our PDU are shown in [Figure 9a](#) and b. [Figure 9a](#) reveals that in this campaign no significant aging of the catalyst was observed. The approach to equilibrium stayed close to 0 at industrial conditions and was stable at the reference point. In comparison, the campaign shown in [Figure 9b](#) provides an example where the catalyst performance decreases with increasing time-on-stream (TOS). This result underlines the importance of tests performed as close as possible to industrial conditions meaning high pressure, a representative temperature profile and industrial-grade NH_3 .

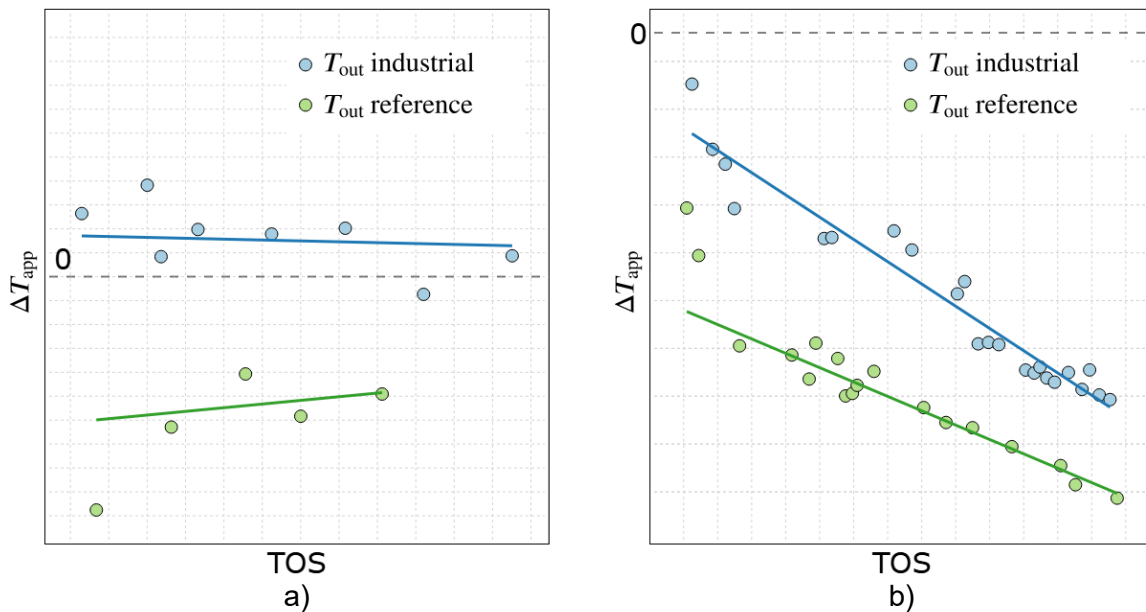


Figure 9: Time history of approach to equilibrium ΔT_{app} for two test campaigns showing a) stable conversion and b) dropping performance. Y axis are scaled to show the industrial and reference in meaningful scale (the ratio of slopes ratio is conserved).

Process Gas Purification

The NH_3 Cracking process is concluded with the process gas purification, which is used to recover the H_2 product. H_2 purification is a core Air Liquide competency backed by more than 15 years of proprietary Pressure Swing Adsorption (PSA) technology and hundreds of industrial references worldwide, primarily in steam methane reforming. However, the gas composition produced from NH_3 cracking presents a unique challenge. Typical syngas contains hydrogen, carbon monoxide, carbon dioxide and methane. In contrast, the stream exiting an NH_3 cracker is a high-pressure mixture predominantly composed of H_2 and N_2 in a 3:1 ratio, alongside critical traces and unconverted NH_3 .

The scientific literature highlights the complexities of removing these impurities. For instance, foundational reviews on hydrogen purification from NH_3 decomposition [22, 23] and established works on general H_2 purification by PSA [24] underscore the need for specific adsorption materials. Furthermore, extensive research on NH_3 adsorption characteristics across various sorbents, including activated alumina [25] and ion-exchanged zeolites [26, 27, 28], dictates strict selection criteria. Building on these academic foundations, our purification sequence is strictly ordered based on molecular affinities to protect the core separation process. The process initiates with a dedicated guard layer engineered for its high capacity to adsorb H_2O and NH_3 , ensuring the gas is thoroughly dried and residual NH_3 is trapped to protect downstream materials. Following this, the bulk of the separation relies on a high-performance microporous material, which has been extensively tested and selected as the optimal medium for the complex separation of N_2 from H_2 to achieve > 99.99 % H_2 purity.

To bridge the gap between theoretical material science and commercial deployment, we rely on a rigorous validation workflow. By collaborating with partners such as the University of Edinburgh we gather highly accurate pure gas capacity data. Specifically, NH_3 isotherms for different adsorbents (see [Figure 10](#)) were measured across a wide temperature range, showing significant differences in the adsorbent's performances. This raw data is

mathematically regressed to create accurate Adsorbent Identity Cards (AIC), which are then fed into internal adsorption simulation software to evaluate separation performance.

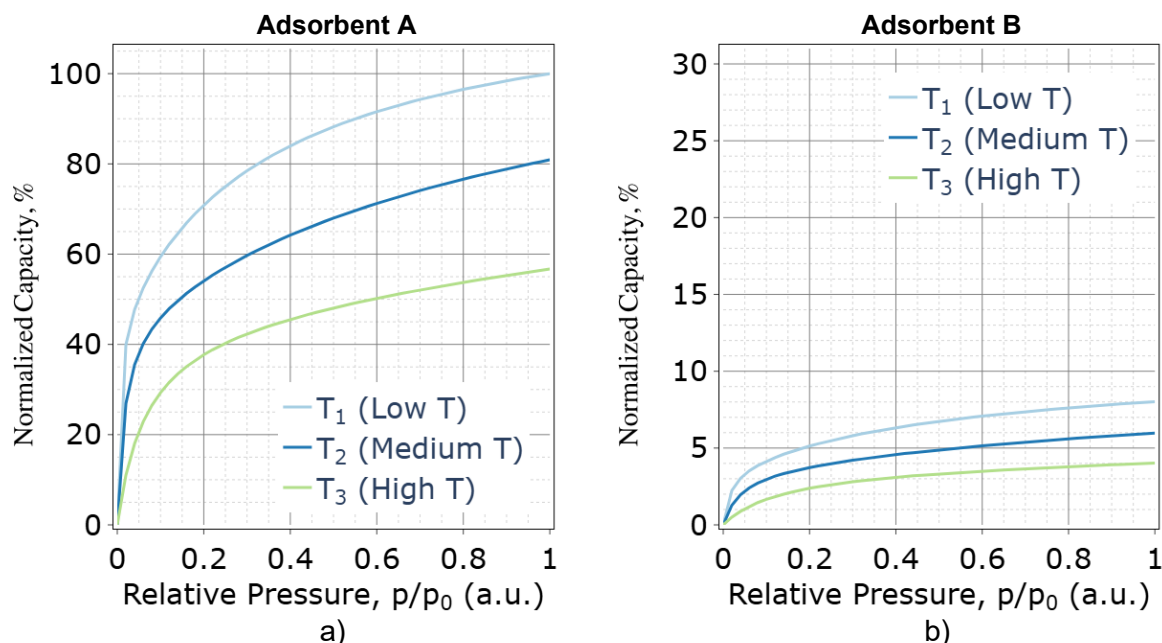


Figure 10: Experimental NH_3 isotherms for adsorbent A and B.

Once the baseline data model is built, its representativeness is checked and calibrated against the dynamic realities of a technical-scale test bench. Our R&D H_2 PSA test bench at Innovation Campus Paris, France was upgraded to handle NH_3 and replicate the complex multi-step pressure cycle of a full scale industrial PSA. By comparing simulation predictions against experimental data, we ensure the model captures physical reality.

Finally, these validated AIC are transferred to our E&C teams. This workflow from lab-scale characterization to pilot-plant validation to engineering design allows E&C to size the commercial PSA units with absolute confidence, guaranteeing optimized H_2 recovery, strict purity specifications, and highly reliable, long-term operation.

ARCAS pilot - AL's industrial-scale NH_3 cracking pilot plant

As mentioned in the previous sections, the ARCAS pilot is the cornerstone of our technology development, bridging the gap between R&D lab- & technical-scale testing and full industrial deployment. The ARCAS pilot plant (see [Figure 11](#)) comprises several key industrial-scale components, including an upstream feed preparation system, a firebox of industrial dimensions with industrial reactor tubes and burners, a versatile fuel system, a waste heat recovery system with enhanced DeNO_x section, each essential for replicating and studying a full production cycle. ARCAS pilot also served as an intensive materials science laboratory for metallic materials and cracking catalysts, applying stable, long-term, high-temperature-induced material aging conditions, and exploring the full operational range for future NH_3 Crackers.

At the heart of the industrial-scale pilot lies a firebox of industrial dimensions. Although there are fewer cracker tubes than in a full commercial plant, they are of industrial size and specifications. This ensures that heat transfer, material stress and reaction kinetics are

representative of a commercial operating unit. By exploring the comprehensive operating envelope of the ARCAS pilot, we were able to compile a robust dataset for calibrating our in-house simulation tools by systematically varying the load and reaction temperatures. In addition to testing different catalyst products in different operating windows, the unit was fitted with specific metallic test samples at different locations to cover the full spectrum of temperature and gas composition conditions. Upon completion of the test campaign after more than 4000 hours of safe operation, critical metallic equipment and the materials samples were removed from the plant for destructive and physicochemical analyses. This step was crucial to validate the corrosion kinetics established in R&D, to assess the impact of nitridation on mechanical properties and to verify the mechanical integrity of the equipment.



Figure 11: ARCAS - Air Liquide's world's first industrial-scale NH_3 cracking pilot unit.

Industrial burners provide the heat for the endothermic cracking reaction, enabling the accurate study of various fuel types and combustion efficiencies under relevant conditions. The integrated, highly flexible fuel system allows for extensive testing of various fuel mixtures, including combinations of N_2 , H_2 and NH_3 . This capability provides invaluable data on the combustion characteristics, energy efficiency, heat emissions profile and suppression of NO_x formation. Thanks to the pilot's extensive analytical equipment, we were able to collect a large set of robust and accurate experimental data for various industrial operating conditions.

But transitioning NH_3 cracking to world-scale commercial deployment requires not only bridging the technological gap between lab- and technical-scale research to industrial implementation, it also requires transitioning developed safe & reliable operation philosophies to the industrial scale. While core unit operations of an industrial NH_3 Cracker share design similarities with traditional Steam Methane Reforming (SMR), handling industrial amounts of pressurized liquid and gaseous NH_3 at high temperatures introduces unique toxicity and operational hazard profiles that necessitate specialized safeguards. For practical plant design and daily operations, robust secondary containment, isolation, and pressure relief systems

form essential safeguards. Medium-inventory pressurized liquid equipment, such as feed vaporizers and surge drums, should minimize large liquid-phase flanged connections and be surrounded by containment bunds, deflection walls and flange guards to limit aerosol dispersion in case of a leak. Double Block and Bleed (DBB) isolation is mandated for upset isolation, online maintenance and leak mitigation. Automated Emergency Shutdown (ESD) isolation and controlled gas-phase depressurization logic triggered by process monitoring, gas detection or manual intervention must ensure rapid and safe fallback transitions during release events. Operating procedures and plant design must explicitly mitigate two-phase liquid hammering, cold embrittlement during nitrogen purging, and thermal expansion of trapped liquid NH_3 via dedicated Thermal Safety Valves (TSVs). Due to NH_3 toxic and explosive properties and environmental impact, safety releases and drains shall be routed to a dedicated flare system and mixing with water- or steam-containing streams should be avoided. All these safeguards in the plant design and the operation philosophy have been validated during our test campaign at ARCAS pilot.

Overall, the Arcas test campaign was successful in de-risking the entire NH_3 Cracking process chain. Additional key procedures, including start-up, shutdown, as well as catalyst reduction and oxidation, were validated alongside the full control philosophy and complex loops. The industrial pilot plant confirmed the performance and stability of several catalyst products under industrial conditions. The data gathered at the combustion test platform formed the basis of a highly efficient abatement strategy that has now been proven by the ARCAS pilot to achieve greater than 99% NO_x reduction in operation and N_2O mitigation. This concrete track record demonstrates that NH_3 -fired crackers can meet the most stringent global environmental permitting standards. Ultimately, this extensive, long-term campaign provided the final dataset required to calibrate and validate our internal design tools successfully, thus securing the engineering basis for future commercial plants [29].

Summary and Conclusions

The primary obstacle to industrial, large-scale NH_3 cracking for H_2 production has been the "scale-up gap"—the technical and financial risk associated with moving from lab- and technical-scale testing to robust industrial operations in the field. By employing our rigorous, integrated "from the lab to the field" scale-up and de-risking methodology, we have successfully bridged this gap. By separately studying fundamental process steps in the lab and validating them through technical-scale platforms, we developed the physical data basis necessary for high-confidence tools development and process design. This multi-scale technology roadmap allowed for the systematic de-risking of critical techno bricks, such as the cracking catalyst, the metallic material durability under harsh nitriding conditions and NH_3 combustion within environmental permitting standards.

Finally, all the technobricks were combined in the industrial pilot ARCAS. Beyond technical scalability, the ARCAS pilot plant has validated through more than 4.000 hours of safe operation that NH_3 cracking is ready for large-scale industrial deployment. We proved all critical safeguards for managing NH_3 unique toxicity & hazard profile including specialized containment and automated emergency shutdown logic. The implemented stringent environmental abatement strategies guarantee operation within the strict permitting standards.

Bibliography

- [1] FGE NexantECA: "Ammonia as a Hydrogen Carrier". In: Technology and Costs:

Technoeconomics - Energy & Chemicals, TECH 2023S7, (2023).

- [2] Air Liquide Group, World first: Air Liquide's innovative technology converts Ammonia into Hydrogen at industrial scale, paving the way for new low-carbon supply chains, Paris, France, November 13, 2025.
<https://www.airliquide.com/group/press-releases-news/2025-11-13/world-first-air-liquides-innovative-technology-converts-ammonia-hydrogen-industrial-scale-paving-way>
- [3] Holland, M. L. et al.: "Metal dusting failures in methane reforming plant". In: International Journal of Pressure Vessels and Piping, Volume 66, Issues 1–3 (1996), pp. 125-133.
- [4] Davies, M.: "Corrosion by Ammonia". In: Corrosion: Environments and Industries, ASM International. (2006), pp. 727-735.
- [5] Tjokro, K.: "Comparison of internal nitridation reactions in ammonia and in nitrogen". In: Oxid Met 44 (1995), pp. 453-474.
- [6] Homerberg, V. O. et al.: "Case-Hardening with Ammonia Gas". In: Transactions of the American Society of Mechanical Engineers, 53(7) (1931), pp. 1-6.
- [7] Chakravartty, J. K. et al.: "Microstructural and mechanical properties of service exposed Alloy 625 Ammonia cracker tube removed after 100 000 h". In: Materials Science and Technology 28 (6) (2012), pp. 702 - 710.
- [8] Valera-Medina, A. et al.: "Preliminary study on lean premixed combustion of ammonia-hydrogen for swirling gas turbine combustors". In: Int. J Hydrogen Energy 42(38) (2017), pp. 24495-24503.
- [9] Kobayashi, H. et al.: "Science and technology of ammonia combustion". In: Proc Combust Inst, 37(1) (2019), pp. 109–133.
- [10] Mashruk, S. et al.: "Evolution of N₂O production at lean combustion condition". In: NH₃/H₂/air premixed swirling flames, Combust. Flame, 244 (2022), 112299.
- [11] Rocha, R. C. et al.: "Combustion and Emission Characteristics of Ammonia under Conditions Relevant to Modern Gas Turbines". In: Combust. Sci. Technol., 193 (14) (2021), pp. 2514–2533.
- [12] Dungal, B. et al.: "Ammonia combustion for large furnaces". In: Nitrogen+Syngas, 389 (2024), pp. 45-49.
- [13] Ding, X. et al.: "Ammonia synthesis and cracking: Thermocatalytic versus electrochemical approaches". In: Green Energy & Environment, Vol 11, Issue 3 (2026), pp.603-629.
- [14] Lucentini, I. et al.: "Review of the Decomposition of Ammonia to Generate Hydrogen.". In: Ind. Eng. Chem. Res., 60 (51) (2021), pp. 18560–18611.
- [15] Ganley, J. et al.: "A Priori catalytic activity correlations: the difficult case of hydrogen production from ammonia". In: Catalysis Letters, 96(3) (2004), pp. 117-122.
- [16] Spatolisano, E. et al.: "Catalysts for unlocking H₂ production from NH₃: A process design perspective". In: Appl. Catal. A: Gen., 710, (2026), Article: 120670.
- [17] Hansen, T. W. et al.: "Sintering of catalytic nanoparticles: particle migration or Ostwald

- ripening”? In: *Acc Chem Res.* 20, 6(8) (2013), pp. 1720-1730.
- [18] Karim, A. M. et al.: “Correlating Particle Size and Shape of Supported Ru/ γ -Al₂O₃ Catalysts with NH₃ Decomposition Activity”. In: *J. Am. Chem. Soc.*, 131 (34) (2009), pp. 12230-12239.
 - [19] Casu, S.: “Ruthenium-Based catalysts and ammonia cracking: precious metal figures prominently in the energy equation”. In: *Catal Rev*, 6–11 (2022).
 - [20] Duan, X. et al.: “Structure sensitivity of ammonia decomposition over Ni catalysts: A computational and experimental study”. In: *Fuel Processing Technology*, Vol 108 (2013), pp. 112-117.
 - [21] Atsumi R. et al.: “Effects of Steam on Ni/Al₂O₃ Catalysts for Ammonia Decomposition.” In: *Ind. Eng. Chem. Res.* 53 (45) (2014), pp. 17849–17853.
 - [22] Lamb, K. E. et al.: “Ammonia for hydrogen storage; A review of catalytic ammonia decomposition and hydrogen separation and purification”. In: *International Journal of Hydrogen Energy*, 44(7) (2019), pp. 3580-3593.
 - [23] Lin, L. et al.: “Techno-economic analysis and comprehensive optimization of an on-site hydrogen refueling station system using ammonia: hybrid hydrogen purification with both high H₂ Purity and high recovery”. *Sustainable Energy & Fuels*, 4(6) (2020), pp. 3006-3017.
 - [24] Sircar, S. et al.: “Purification of Hydrogen by Pressure Swing Adsorption”. In: *Separation Science and Technology*, 35(5), (2000), pp. 667-687.
 - [25] Saha, D. et al.: “Characteristics of Ammonia Adsorption on Activated Alumina”. In: *Journal of Chemical & Engineering Data*, 55(12) (2010), pp. 5587–5593.
 - [26] Shiralkar, V. et al.: “Sorption of ammonia in cation-exchanged Y zeolites: Isotherms and state of sorbed molecules”. In: *Journal of Colloid and Interface Science*, 108(1) (1985), pp. 1-10.
 - [27] Helminen, J. et al.: “Comparison of sorbents and isotherm models for NH₃-gas separation by adsorption”. In: *AIChE Journal*, 46(8), (2000), pp. 1541–1555.
 - [28] Lui, C. Y. et al.: “Ammonia Adsorption on Ion Exchanged Y-zeolites as Ammonia Storage Material”. In: *Journal of the Japan Petroleum Institute*, 46(5) (2003), pp. 301–307.
 - [29] Prost, L. et al.: “Unlocking Low-Carbon Hydrogen: Air Liquide’s Breakthrough in Ammonia Cracking”. In: *Nitrogen+Syngas Expoconference*, Barcelona, Spain, 10.-12. February 2026.

Compact and Efficient Ammonia Cracker for Decentralized Hydrogen Production

D. Gashnikova, R. Zapf, C. Hofmann, G. Kolb

Fraunhofer Institute for Microengineering and Microsystems IMM, Mainz, Germany

Hydrogen is a key compound for the reduction of CO₂ emissions and the ongoing energy transition. According to current forecasts, Germany will not be able to cover its energy demand with inland production of renewable electricity. Therefore, it will be dependent on imports of energy chemically converted to hydrogen from other countries, such as Australia, Chile or Africa. However, the long-distance transport of hydrogen poses certain safety and security risks. In contrast, hydrogen carriers such as ammonia and methanol are already produced in large amounts and can be easily transported via the existing infrastructure. In this regard, ammonia with its high hydrogen content of 18 wt.% is seen as the most promising carbon-free hydrogen carrier. At the application site, ammonia must then be decomposed over catalyst to hydrogen and nitrogen, which requires compact and efficient cracking technology.

In this work, we present our reactor concept for decentralized hydrogen production from ammonia, which is based on the microstructured plate heat exchangers coated with catalyst. By applying catalytic coatings [1] instead of conventional fixed beds, the negative impact of mass transport limitations can be avoided, also allowing us to reach one of the highest catalytic activities reported in the literature [2]. Moreover, heat transport to the catalyst during endothermic ammonia cracking can be significantly improved in such microstructured reactors. This allows the ammonia cracker to be operated at lower temperatures compared to conventional technology (e.g. 650°C-700°C vs. 800-1000°C), thus also reducing the risk of material and catalyst damage. Depending on the application, the heat supply to the microstructured reactor can be achieved in different ways. For mobile applications, the hot exhaust gas from a combustion engine can be utilized for reactor heating. Alternatively, the concept of integrated catalytic heating can be applied. In this case, the hydrogen containing off-gas from hydrogen purification or fuel cells is combusted inside heat exchanger channels coated with the combustion catalyst [3]. The high energy efficiency of 90% in combination with stable and efficient catalyst formulations enable the significant size reduction of the ammonia cracker by 90% or more. The operation of the developed ammonia cracker was already demonstrated for 50 kW electric power equivalent. Further scaling up of the technology to 200 kW is currently ongoing, thus broadening the possible application areas.

References:

- [1] T. Weißenberger et al., (2024), Catalyst coatings for ammonia decomposition in microchannels at high temperature and elevated pressure for use in decentralized and mobile hydrogen generation, *Catalysts*, 14, 104.
- [2] H. Pennemann et al., (2013), Optimization of Wash-Coating Slurries as Catalyst Carrier for Screen Printing into Microstructured Reactors, *Chem. Eng. Technol.*, 36, 1033.
- [3] S. Blauth et al., (2024), Multi-Scale Simulation of a Novel Integrated Reactor for Hydrogen Production by Ammonia Decomposition, *Chem. Ing. Tech.*, 96, 627.

Hydrogen and Solid Carbon Production by Discharge Plasma Decomposition in Liquid-Phase Hydrocarbons

Y. Katsuragawa¹, H. Ueda¹, M. Asahara¹, T. Harigai¹, T. Miyasaka¹,

¹Gifu University, Gifu, Japan

Abstract

Methane (CH₄) decomposition is a promising route for turquoise hydrogen (H₂) production because it produces H₂ and solid carbon without direct carbon dioxide (CO₂) emissions. Plasma-assisted methane decomposition enables localized energy input near the electrodes and along the discharge path and is therefore of interest for the direct use of liquid hydrocarbons as feedstocks for H₂ production. In this study, the decomposition characteristics of gaseous methane, liquid heptane at ambient temperature, and liquefied methane under cryogenic conditions were experimentally investigated. The hydrogen yields were compared among the three reaction environments, and the morphology and elemental composition of the generated solid carbon were characterized. The hydrogen yields for gaseous methane, liquid heptane, and liquefied methane were 0.064, 0.168, and 0.029, respectively. The hydrogen yield obtained under the liquefied-methane condition was lower than those obtained under the other conditions, although hydrogen was generated even in the cryogenic liquid-phase reaction environment. The lower hydrogen yield of liquefied methane compared with gaseous methane may be attributed to the use of a portion of the discharge energy for local heating and vaporization of liquefied methane, as well as heat transfer from the discharge region to the surrounding cryogenic liquid. The discharge-sustaining times for gaseous methane, liquid heptane, and liquefied methane were approximately 59, 40, and 120 s, respectively. SEM observations revealed that carbon produced in liquefied methane had an irregular agglomerated morphology composed of fine particles, differing from the relatively spherical carbon obtained by thermal decomposition of methane at 1200°C. These results confirm hydrogen and solid carbon production in a cryogenic liquefied-methane reaction medium and suggest that the feedstock species, phase state, and thermal environment are associated with differences in hydrogen production and carbon morphology.

Introduction

In recent years, hydrogen (H₂) has attracted increasing attention as a promising energy carrier toward the realization of a carbon-neutral society because it does not directly emit carbon dioxide (CO₂) during combustion. Currently, steam reforming of natural gas is widely used for H₂ production; however, this process generates CO₂ during the production stage. Therefore, reducing CO₂ emissions associated with H₂ production is essential for the widespread utilization of H₂. In this context, turquoise H₂ production, in which methane (CH₄) is decomposed into H₂ and solid carbon, has attracted considerable attention. Methane decomposition theoretically produces no direct CO₂ emissions and enables carbon to be recovered in solid form, making it a promising low-carbon H₂ production method [1].

Noncatalytic thermal decomposition of methane generally requires temperatures of approximately 1000 °C or higher, resulting in substantial energy consumption for heating and maintaining the temperature of the entire reactor [2]. In contrast to conventional thermal decomposition, in which the entire reaction field is heated, plasma-based methods can locally supply high energy to regions near the electrodes and along the discharge path. Such localized energy input reduces the need to maintain the entire reaction medium at a uniformly high temperature and may contribute to reactor downsizing. Previous studies on turquoise H₂ production have mainly focused on gaseous feedstocks such as CH₄ and natural gas. Meanwhile, direct utilization of hydrocarbons that exist as liquids at ambient temperature, as well as waste oils, as feedstocks for H₂ production has also been investigated [3]. Such

approaches are expected to provide opportunities for integrating H₂ production with the effective utilization of underutilized hydrocarbon resources.

When plasma is generated directly in a liquid hydrocarbon, bubbles formed within the liquid, gas–liquid interfaces, electrode surfaces, and discharge paths interact with one another, resulting in a reaction environment that differs from that in the gas phase [4]. The liquid phase contains substantially more hydrocarbon per unit volume than the gas phase. Therefore, applying localized plasma energy to such a high-density reaction medium may increase H₂ production per unit reactor volume. On the other hand, electrical breakdown may be more difficult to initiate in the liquid phase than in the gas phase, potentially making the formation of a stable discharge path more challenging.

The above characteristics of liquid-phase plasma can also be considered for methane-based feedstocks. Maintaining methane at a high density in the liquid phase may enable the development of a reaction system that combines a dense reaction medium with localized energy input. However, because methane exists as a gas at ambient temperature, cryogenic cooling is required to maintain it in the liquid phase. Natural gas, whose principal component is methane, is already transported and stored in a liquefied state as liquefied natural gas (LNG), suggesting the possibility of utilizing such a liquefied feedstock directly as a reaction medium. Therefore, it is necessary to investigate cryogenic liquid-phase conditions relevant to LNG utilization, such as liquefied methane. Because liquefied methane contains a much larger amount of methane per unit volume than gaseous methane, localized energy input into this high-density reaction medium may, as in ambient-temperature liquid hydrocarbons, increase H₂ production per unit reactor volume. However, under cryogenic liquid-phase conditions, a portion of the discharge energy may be consumed by localized heating and vaporization of the liquefied methane and by heat transfer to the surrounding cryogenic liquid. Furthermore, the formation of a stable discharge path itself may become difficult within the liquid phase. Nevertheless, if a plasma reaction field can be formed directly in LNG, which is already transported and stored in a liquefied state, this approach could potentially lead to a new H₂ production process integrated with the existing LNG supply infrastructure.

Several approaches to plasma decomposition of liquid hydrocarbon feedstocks have been investigated. These include supplying liquid fuels to a gas-phase plasma reaction field after vaporization [5], bringing liquid-film hydrocarbons into contact with plasma [6], and plasma decomposition of hydrocarbons in a preheated Ar atmosphere [7]. Direct generation of electrical discharges inside liquid hydrocarbons has also been investigated. Wang et al. generated pulsed discharges directly in liquid *n*-hexadecane and reported that the discharge mode changed with the applied voltage and electrode gap, accompanied by changes in hydrocarbon conversion and product selectivity [8]. Chung et al. generated plasma directly in liquid hexane and benzene and simultaneously produced H₂ and solid carbon. They also reported that the generated carbon consisted of fine particles smaller than 10 nm and exhibited a high specific surface area [9]. Furthermore, Lim et al. directly generated AC plasma in hydrocarbons that are liquid at ambient temperature, including hexane, cyclohexane, benzene, toluene, and xylene, and demonstrated that the discharge frequency affected bubble formation, product distribution, and energy efficiency. They also reported that inducing liquid flow around the electrodes altered the contact between the reactants and the plasma, allowing the product selectivity and energy efficiency to be controlled [10]. These studies demonstrate that H₂ and carbonaceous products can be produced through plasma decomposition in which liquid hydrocarbons themselves are directly used as the reaction medium.

In contrast to these ambient-temperature liquid hydrocarbons, CH₄ liquefies below approximately 111 K at atmospheric pressure; therefore, the use of liquefied methane results in a cryogenic reaction environment that differs substantially from conventional liquid-phase hydrocarbon systems. Although direct plasma generation in liquid hydrocarbons has previously been reported, the decomposition of liquefied methane in a cryogenic liquid-phase reaction environment remains insufficiently understood.

Therefore, in this study, gas-phase methane, liquid heptane, and liquefied methane were investigated to compare the H₂ yields obtained under different reaction conditions. The ambient-temperature liquid phase was considered with a view toward the direct utilization of waste oils and other underutilized liquid hydrocarbons, whereas the cryogenic liquid phase

was investigated for the potential development of processes that directly utilize liquefied hydrocarbons as reaction media. Furthermore, because the carbon generated during H₂ production is a solid byproduct whose properties may vary depending on the reaction conditions, the morphology and elemental composition of the carbon produced by the plasma reactions were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The morphology and elemental composition were compared with those of carbon produced by thermal decomposition of methane at 1200 °C to evaluate differences in carbon characteristics among the reaction conditions.

Experimental Methods

In this study, discharge decomposition experiments were conducted under three different reaction conditions—gas-phase methane, ambient-temperature liquid-phase heptane, and cryogenic liquid-phase methane—to compare the effects of the hydrocarbon reaction environment on plasma discharge and H₂ production. The experimental conditions are summarized in Table 1.

Table 1 Experimental condition used for plasma decomposition of gaseous methane, liquid heptane, and liquefied methane. The same electrode configuration and high-voltage power supply were used for the three reaction environments.

Parameter	Gaseous methane	Liquid heptane	Liquefied methane
Feedstock	CH ₄	C ₇ H ₁₆	CH ₄
Phase	Gas	Liquid	Cryogenic liquid
Electrode gap [mm]	1	1	1
N ₂ carrier-gas flow rate [ml/min]	100	100	100
Maximum power-supply voltage [kV]	20	20	20
Maximum power-supply current [mA]	10	10	10

Gas-phase discharge experiment

Figure 1 shows a schematic of the experimental apparatus used for the gas-phase discharge experiment. In the gas supply system, methane (CH₄) and nitrogen (N₂) were depressurized using pressure regulators and supplied to the reaction section through mass flow controllers. Initially, N₂ was introduced into the reaction section to purge the residual air from the test tube, thereby preventing the formation of a CH₄–air mixture. After the replacement with N₂ was completed, a short-duration discharge was generated under an N₂ atmosphere to confirm the normal operation of the electrodes and the high-voltage power supply (maximum voltage: 20 kV; maximum current: 10 mA). Subsequently, CH₄ was supplied to the reactor to replace the N₂ atmosphere. After the gas replacement was completed, a high voltage was applied across the electrodes to generate a discharge in the gas phase and initiate the reaction.

The gaseous products were analyzed by gas chromatography (GC) to determine the gas composition. Inside the reactor, a sharpened stainless-steel rod was installed at the top of the reactor, and a stainless-steel tube was installed at the bottom. These components were connected to the high-voltage power supply and used as electrodes. This configuration was designed to facilitate discharge formation by supplying the carrier gas directly to the electrode gap and thereby forming a gas phase in the region where the discharge occurred. N₂ was used as the carrier gas. During the discharge, the discharge duration and the deposition behavior of solid carbon on the electrode surfaces were observed. After the discharge experiment, the solid products remaining on the electrodes and inside the reactor were collected and characterized.

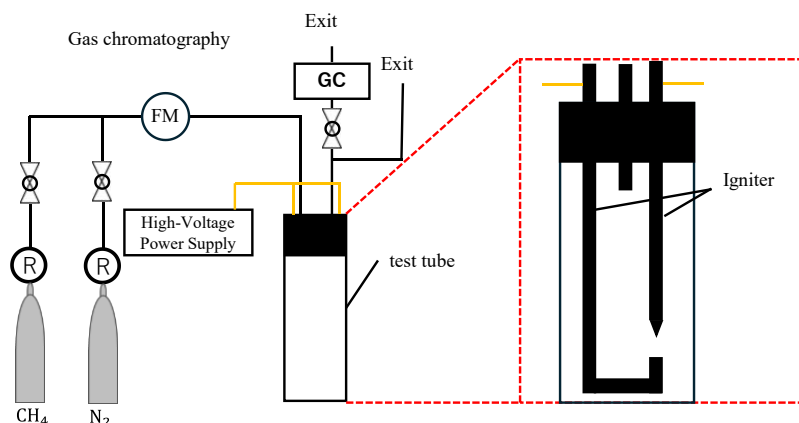


Fig. 1 Schematic diagram of the experimental apparatus for plasma decomposition of gaseous methane. Methane and N_2 were supplied to the reactor through mass-flow controllers, and plasma was generated between the upper stainless-steel rod electrode and the lower tubular electrode. The product gas was discharged from the upper outlet for gas chromatographic analysis.

Discharge experiment in liquid hydrocarbon

Figure 2 shows a schematic of the experimental apparatus used for the ambient-temperature liquid-phase discharge experiment. Liquid heptane was used as the reaction medium at ambient temperature. In the liquid-phase experiment, N_2 was supplied through a SUS tube installed at the bottom of the test tube to generate bubbles between the electrodes, thereby creating conditions favorable for the formation of a discharge path inside the bubbles or near the gas–liquid interface. Bubble formation and the resulting liquid-phase flow were also intended to remove carbon deposited between the electrodes and thereby suppress electrical shorting. Furthermore, the electrode gap was oriented vertically so that the generated bubbles could readily detach from the electrode gap and rise upward owing to buoyancy. The flow induced by the rising bubbles was expected to suppress the accumulation of generated carbon between the electrodes.

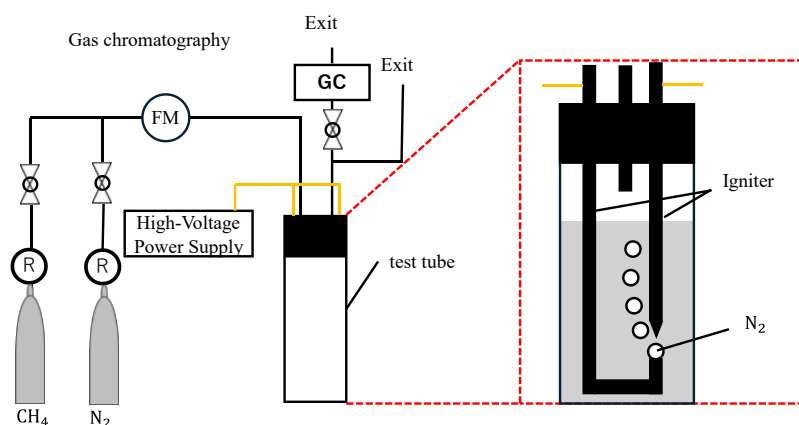


Fig. 2 Schematic diagram of the experimental apparatus for plasma decomposition of liquid heptane. N_2 was introduced through the lower tubular electrode to form bubbles between the vertically arranged electrodes, where plasma discharge was generated in or near the gas–liquid interface.

Discharge experiment under cryogenic conditions

Figure 3 shows a schematic of the experimental apparatus used under cryogenic liquid-phase conditions. Prior to the experiment, N_2 was supplied to the reactor to purge the residual air, after which CH_4 was introduced to replace the N_2 atmosphere. The test tube containing the reaction section was then immersed in a stainless steel (SUS) vessel filled with liquid nitrogen. Methane was condensed by cooling the outer wall of the reactor with liquid nitrogen, thereby

producing a predetermined amount of liquefied methane. During liquefaction, the volume of methane decreases to approximately 1/588 of its gaseous volume, which may create a sub-atmospheric pressure inside the test tube and induce backflow of air through the outlet. Therefore, a check valve was installed at the test-tube outlet to prevent the ingress of air. After the predetermined amount of liquefied methane had been obtained, a high voltage was applied across the electrodes to generate the discharge. Because flammable liquefied methane was handled in this experiment, the amount of liquefied methane retained in the reactor was limited to less than 100 mL to minimize the amount of methane that could be released in the event of rapid vaporization.

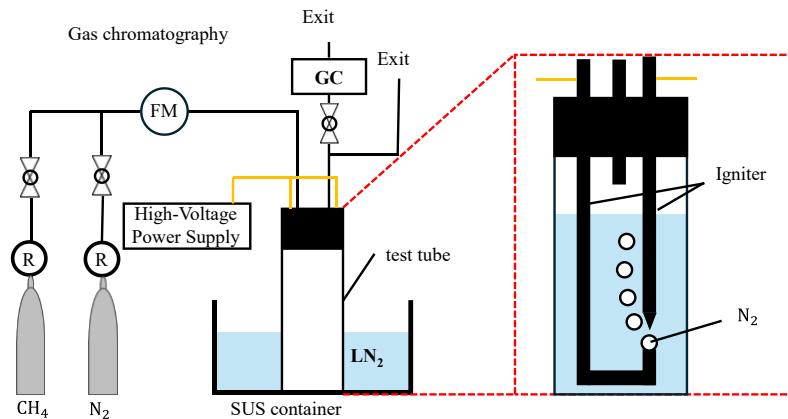
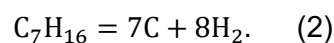
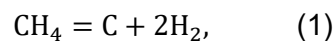


Fig. 3 Schematic diagram of the experimental apparatus for plasma decomposition of liquefied methane under cryogenic conditions. Methane supplied to the reactor was condensed by cooling the reactor in a liquid-nitrogen bath, and plasma discharge was generated between the electrodes immersed in the liquefied-methane reaction environment. A check valve was installed at the gas outlet to prevent air backflow during methane liquefaction.

Experimental conditions and evaluation methods

Assuming that methane and heptane are completely decomposed into H_2 and solid carbon, the overall reactions can be expressed by



These equations represent simplified overall reactions. In actual plasma reactions, hydrocarbon molecules are not converted directly into H_2 and solid carbon through a single reaction pathway; rather, multiple reaction pathways involving intermediate species, such as radicals and lower-molecular-weight hydrocarbons, are expected to occur. Therefore, in this study, Eqs. (1) and (2) were used to define the theoretical amounts of H_2 obtainable from methane and heptane, respectively.

To evaluate discharge sustainability, the discharge duration was defined as the time from the initiation of the discharge until the discharge was terminated by electrical shorting caused by the accumulation of generated carbon between the electrodes. During plasma decomposition of hydrocarbons, the generated carbon was observed to bridge the electrode gap and form an electrically conductive path, resulting in termination of the discharge. Therefore, the discharge duration was used as an indicator of continuous operability. In addition, the generated H_2 was measured using gas chromatography (GC), and the H_2 yield was calculated by

$$Y_{H_2-CH_4} = \frac{x_{H_2}}{2-x_{CH_4}}, \quad (3)$$

$$Y_{H_2-C_7H_{16}} = \frac{x_{H_2}}{8-7x_{C_7H_{16}}}. \quad (4)$$

Results and Discussion

Plasma discharge behavior under different reaction conditions

Figure 4 shows the appearance during plasma discharge and after the reaction in gas-phase methane, liquid heptane, and liquefied methane under the conditions listed in Table 1. Under the liquefied-methane condition, frost formed on the outer wall of the reactor, preventing direct observation of the discharge region; therefore, only an external view of the reactor is shown in Fig. 4(c).

In the gas-phase methane experiment, a localized discharge accompanied by intense light emission was observed between the electrodes. After the reaction, black solid products were found to have deposited near the electrodes. The accumulation of these products between the electrodes likely formed an electrically conductive path, eventually causing electrical shorting and terminating the discharge.

In the heptane experiment, bubbles were formed between the electrodes during the discharge and were observed to rise upward. As the reaction proceeded, the entire liquid became black and turbid, and black solid products were widely dispersed throughout the liquid phase after the reaction. Under the liquid-phase condition, the observed bubble rise and liquid motion may have transported carbon generated near the electrodes into the bulk liquid. Such carbon transport may suppress the formation of carbon bridges between the electrodes and thereby delay the occurrence of electrical shorting.

Although direct observation of the reactor interior was difficult under the liquefied-methane condition owing to frost formation on the reactor surface, intense light emission similar to that observed for gas-phase methane and heptane was confirmed. In addition, carbon was observed at the bottom of the reactor after the experiment. Together with the H_2 detected by GC, these observations indicate that methane decomposition occurred even under cryogenic liquid-phase conditions. Further development of visualization techniques suitable for cryogenic environments will be necessary to clarify the reaction behavior in greater detail.

These observations indicate differences in the distribution of solid products between the gas- and liquid-phase conditions. In particular, under liquid-phase conditions, bubble formation and the resulting liquid-phase flow may contribute to the transport of generated carbon. The relationship between bubble-induced liquid motion, carbon transport, and discharge sustainability remains to be clarified.

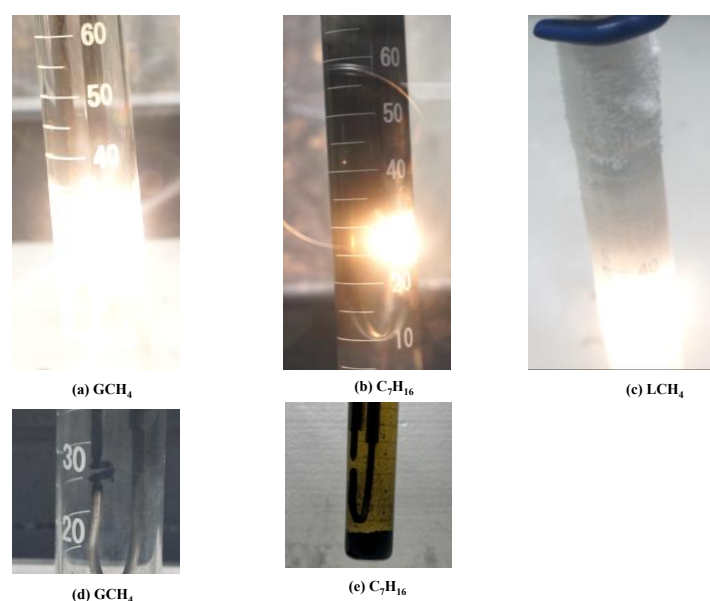


Fig. 4 Photographs of the reactor and products during and after plasma decomposition under different reaction conditions: (a) plasma discharge in gaseous methane, (b) plasma discharge and bubble formation in liquid heptane, (c) external view of the reactor during the liquefied-methane experiment, in which frost formation obscured direct observation of the discharge region, (d) carbonaceous deposits on the electrode after plasma decomposition of gaseous methane, and (e) black solid products dispersed in liquid heptane after plasma decomposition.

Hydrogen production characteristics

Figure 5 shows the H_2 yields obtained under the different reaction conditions. The H_2 yields for gas-phase methane (GCH_4), liquefied methane (LCH_4), and liquid heptane (C_7H_{16}) were approximately 0.064, 0.029, and 0.168, respectively. Under the present experimental conditions, liquid heptane exhibited the highest H_2 yield.

A comparison between gas-phase methane and liquefied methane, which are based on the same hydrocarbon feedstock, showed that the H_2 yield from liquefied methane was lower than that from gas-phase methane. Under the liquefied-methane condition, methane near the electrodes may have been locally heated by the discharge, potentially causing vaporization. Therefore, a portion of the discharge energy may have been used for local heating and vaporization of the liquefied methane or transferred from the discharge region to the surrounding cryogenic liquid. Consequently, under the present experimental conditions, the fraction of the discharge energy effectively utilized for hydrocarbon decomposition may have decreased, resulting in a lower H_2 yield for liquefied methane than for gas-phase methane. Nevertheless, H_2 production was confirmed even under cryogenic liquid-phase conditions, demonstrating that H_2 can be produced using liquefied methane as the reaction medium.

Heptane exhibited a higher H_2 yield than both gas-phase and liquefied methane. Because the heptane and methane experiments differed in both feedstock species and phase state, the higher H_2 yield obtained with heptane cannot be attributed solely to the liquid-phase reaction environment. Differences in molecular structure and decomposition pathways may also have contributed to the observed H_2 yield.

Overall, the H_2 yield depended not only on phase state but also on feedstock species and the thermal environment. The direct comparison between gaseous and liquefied methane suggests that cryogenic phase-change and heat-transfer processes may reduce the fraction of discharge energy available for methane decomposition.

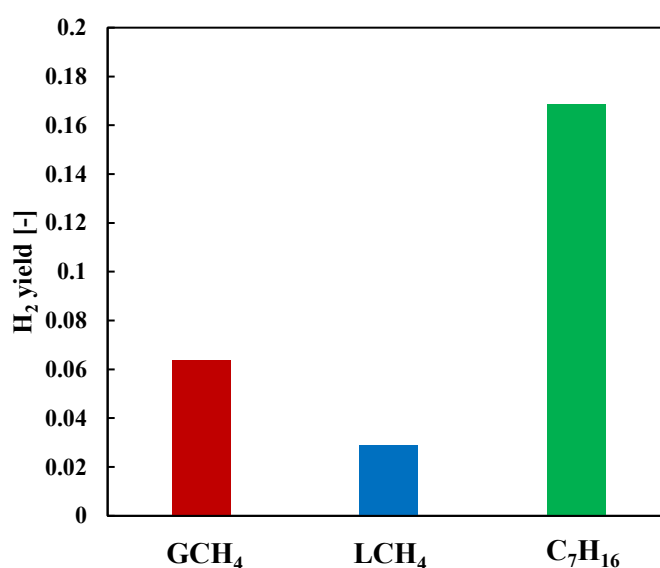


Fig. 5 Dimensionless hydrogen yield obtained from plasma decomposition of gaseous methane (GCH_4), liquefied methane (LCH_4), and liquid heptane (C_7H_{16}), calculated from the gas composition measured by gas chromatography.

Discharge duration and carbon deposition

Figure 6 shows the discharge duration under each reaction condition. The discharge durations for gas-phase methane (GCH_4), liquefied methane (LCH_4), and liquid heptane (C_7H_{16}) were approximately 59 s, 120 s, and 40 s, respectively. LCH_4 exhibited the longest discharge duration, whereas C_7H_{16} exhibited the shortest.

For C_7H_{16} , although the highest H_2 yield was obtained as described, the discharge duration was the shortest. In addition, as shown in fig.4, black solid products were dispersed throughout the liquid phase after the heptane reaction. The presence of dispersed carbon particles may

have altered the electrical characteristics of the liquid phase and contributed to the formation of conductive paths between the electrodes. However, the electrical conductivity of the liquid and the formation process of conductive carbon paths were not measured in the present study. Therefore, the mechanism responsible for the relatively short discharge duration in liquid heptane cannot be identified from the present results.

In contrast, LCH₄ exhibited the longest discharge duration but the lowest H₂ yield. This result indicates that, under the present experimental conditions, a longer discharge duration did not directly correspond to a higher H₂ yield. A portion of the discharge energy under the LCH₄ condition may have been used for local heating and vaporization or transferred to the surrounding cryogenic liquid. However, the relationship between these energy-transfer processes, carbon formation, and discharge duration remains unclear because the amount and formation rate of carbon were not quantified.

The discharge duration for GCH₄ showed an intermediate value between those for LCH₄ and C₇H₁₆. These results show that the discharge duration differed among the three reaction conditions, although the factors governing these differences have not yet been clarified. Further visualization of bubble behavior, carbon transport, and carbon accumulation near the electrodes will be required to clarify the discharge termination mechanism. In addition, the development of reactor and electrode configurations that suppress carbon accumulation between the electrodes will be important for achieving long-term stable discharge operation.

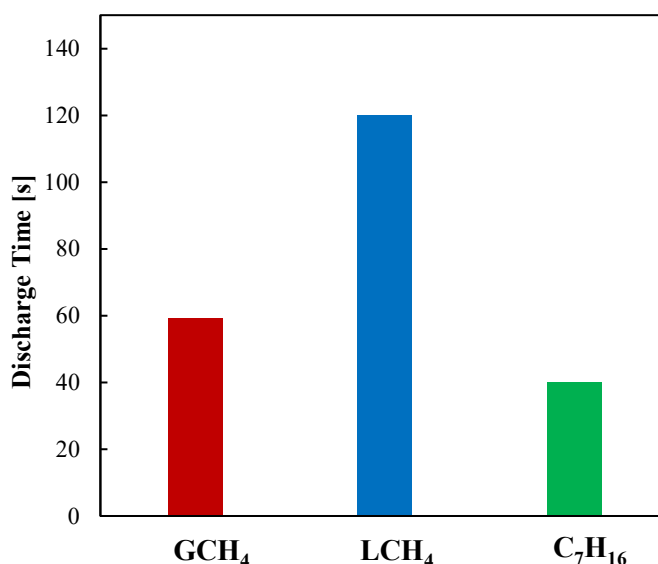


Fig. 6 Discharge duration measured during plasma decomposition of gaseous methane (GCH₄), liquefied methane (LCH₄), and liquid heptane (C₇H₁₆). The discharge duration was defined as the elapsed time from the initiation of discharge to its termination under each reaction condition.

Morphology and elemental composition of carbon products

Figure 7 shows SEM images of the solid carbon obtained from plasma reactions in liquefied methane and gas-phase methane, as well as from thermal decomposition of methane at 1200°C. The carbon generated in liquefied methane exhibited an irregular agglomerated structure composed of fine particles, which differed from the relatively spherical carbon produced by thermal decomposition of methane at 1200°C. This difference suggests that the reaction environment may influence the growth and aggregation processes of the carbon particles.

In plasma reactions, a localized high-energy field is formed over a short period of time; therefore, carbon is expected to form under temperature histories and residence times that differ from those in conventional thermal decomposition. The agglomerated morphology may reflect rapid cooling of carbon formed near the discharge region; however, the particle formation and cooling histories were not directly measured.

Table 2 summarizes the EDX analysis results. The carbon mass fractions of the samples obtained from liquefied methane, gas-phase methane, and thermal decomposition of methane at 1200°C were 99.1, 99.8, and 99.3 wt.%, respectively. These results confirm that carbon is the predominant element in the analyzed regions under all reaction conditions.

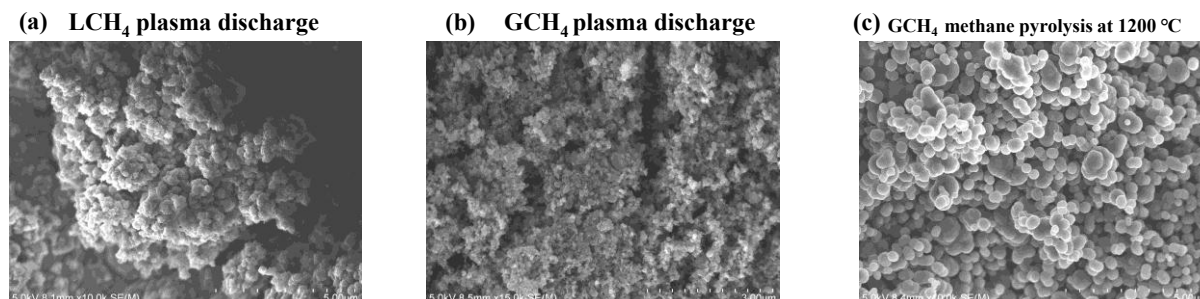


Fig. 7. SEM images of solid carbon obtained from (a) plasma decomposition of liquefied methane, (b) plasma decomposition of gaseous methane, and (c) thermal decomposition of methane at 1200°C.

Table 2 EDX analysis results of carbon products obtained under different reaction conditions.

	LCH ₄	GCH ₄	1200°C CH ₄
Carbon[wt. %]	99.1	99.8	99.3

Conclusions

In this study, discharge decomposition experiments were conducted using gas-phase methane, ambient-temperature liquid heptane, and cryogenic liquid-phase methane to compare the effects of different reaction conditions on H₂ production characteristics, discharge sustainability, and the characteristics of the generated carbon. The main findings are summarized as follows.

1. The H₂ yields for gas-phase methane, liquefied methane, and liquid heptane were approximately 0.064, 0.029, and 0.168, respectively, confirming H₂ production under all reaction conditions. In particular, H₂ production was successfully achieved using liquefied methane as a cryogenic liquid-phase reaction medium. However, the H₂ yield from liquefied methane was lower than that from gas-phase methane. This result suggests that a portion of the discharge energy may have been used for local heating and vaporization of liquefied methane or transferred from the discharge region to the surrounding cryogenic liquid, thereby reducing the fraction of energy available for methane decomposition.
2. The discharge durations for gas-phase methane, liquefied methane, and liquid heptane were approximately 59 s, 120 s, and 40 s, respectively, with liquefied methane exhibiting the longest discharge duration. In contrast, heptane, which exhibited the highest H₂ yield, showed the shortest discharge duration, indicating that discharge duration and H₂ production performance are not simply proportional. Bubble formation and liquid-phase motion were observed under the liquid-phase conditions; however, their relationship with carbon transport and discharge termination remains to be clarified.
3. Comparison of the solid products obtained from liquefied methane, gas-phase methane, and thermal decomposition of methane at 1200°C showed that the carbon generated in liquefied methane exhibited an irregular aggregated structure composed of fine particles, whereas the carbon produced by thermal decomposition at 1200°C exhibited a relatively spherical morphology. EDX analysis also confirmed that carbon was the predominant element in the analyzed regions of all samples. These results suggest that the temperature history of the reaction field and the cooling environment after carbon formation may influence the growth and aggregation behavior of the carbon particles.

Overall, this study confirmed that plasma discharge and H₂ production are possible even in liquefied methane under cryogenic liquid-phase conditions and showed differences in H₂ production, discharge-sustaining time, and carbon morphology among the tested conditions. Future work will focus on visualizing the discharge, bubble dynamics, and carbon deposition behavior and on investigating the effects of electrode conditions. These studies will clarify the relationship between the transport and accumulation of generated carbon and discharge stability, with the aim of establishing reactor design guidelines that achieve both high H₂ production performance and long-term stable discharge operation.

Acknowledgments

This research received partial support from the Research Foundation for the Electrotechnology of Chubu(REFEC).

References

- [1] Mokashi M, Bhimrao Shirsath A, Lott P, Müller H, Tischer S, Maier L, et al. Understanding of gas-phase methane pyrolysis towards hydrogen and solid carbon with detailed kinetic simulations and experiments. *Chemical Engineering Journal* 2024;479:147556. <https://doi.org/10.1016/J.CEJ.2023.147556>.
- [2] Muradov N. Hydrogen via methane decomposition: an application for decarbonization of fossil fuels. *Int J Hydrogen Energy* 2001;26:1165–75. [https://doi.org/10.1016/S0360-3199\(01\)00073-8](https://doi.org/10.1016/S0360-3199(01)00073-8).
- [3] Zhang G, Yao Y, Wang W, Zhang X. Hydrogen production from waste insulating oil based on DBD plasma (laboratory scale). *Journal of the Energy Institute* 2026;125:102280. <https://doi.org/10.1016/J.JOEI.2025.102280>.
- [4] Laosombut T, Field TA. Plasma Cracking of Liquid Hydrocarbons at Room Temperature for Efficient Production of Hydrogen. *Plasma Chemistry and Plasma Processing* 2026 46:3 2026;46:48-. <https://doi.org/10.1007/S11090-026-10643-X>.
- [5] Tang Y, Yao Q, Zhuo J, Li S. Plasma-assisted pyrolysis and ignition of pre-vaporized n-heptane, iso-octane and n-decane. *Fuel* 2021;289:119899. <https://doi.org/10.1016/J.FUEL.2020.119899>.
- [6] Wandell RJ, Bresch S, Hsieh K, Alabugin I V., Locke BR. Formation of alcohols and carbonyl compounds from hexane and cyclohexane with water in a liquid film plasma reactor. *IEEE Transactions on Plasma Science* 2014;42:1195–205. <https://doi.org/10.1109/TPS.2014.2304183>.
- [7] Xu S, Jin D, Song F, Wu Y. Experimental investigation on n-decane plasma cracking in an atmospheric-pressure argon environment. *Plasma Science and Technology* 2019;21. <https://doi.org/10.1088/2058-6272/AB104E>.
- [8] Wang L, Sun B, Zhu X, Xin Y, Yan Z. Study on n-hexadecane cracking with introducing water by pulsed discharge in liquid. *Fuel* 2021;293:120400. <https://doi.org/10.1016/J.FUEL.2021.120400>.
- [9] Chung KH, Shiung Lam S, Park YK, Kim SJ, Jung SC. Application of liquid-phase plasma for the production of hydrogen and carbon from the plasma-induced cracking of liquid hydrocarbons. *Fuel* 2022;328:125297. <https://doi.org/10.1016/J.FUEL.2022.125297>.
- [10] Lim N, McFarland E, Gordon MJ. AC Plasmas Directly Excited in Liquid-Phase Hydrocarbons for H₂ and Unsaturated C₂ Hydrocarbon Production. *J Am Chem Soc* 2024;147:397. <https://doi.org/10.1021/JACS.4C11174>

Inductively Heated Moving-Bed Reactor for Methane Pyrolysis

S. Schütz^{1,2}, G. Stubbe¹, S. Möhring¹, T. E. Müller^{2,*}

¹VDEh-Betriebsforschungsinstitut GmbH (BFI), Düsseldorf, Germany

²Carbon Sources and Conversion, Ruhr-Universität Bochum, Germany

Abstract

The electrification of high-temperature chemical processes requires heating concepts that deliver electrical energy efficiently and selectively to the reaction zone. Induction heating meets this requirement by generating heat directly within electrically conductive reactor materials. This contribution demonstrates its application to counter-current moving-bed methane pyrolysis and to the subsequent upgrading of the solid carbon co-product. Calcined acetylene coke served simultaneously as the induction susceptor and as a continuously moving substrate for carbon deposition. At 1200 °C, methane conversion reached 98.5% during quasi-steady operation without observable reactor blockage. The favourable operating behaviour is consistent with direct heat generation within the carbon bed, preferential deposition on the hottest coke particles, and continuous removal of agglomerated material from the reaction zone. The absence of internal electrodes further facilitates solids transport. In a second application, inductively heated melt recrystallisation transformed amorphous pyrolysis carbon into thin graphitic particles; Raman spectroscopy indicated a highly ordered graphitic structure. The results show how induction heating can combine high-temperature reaction engineering with the directed management and upgrading of solid carbon co-products.

Introduction

Making the chemical industry sustainable requires a fundamental transformation of both its raw-material base and its energy supply. Decarbonisation of energy-intensive industries requires coordinated changes in process technologies, energy supply, infrastructure and policy [1]. The sector still depends heavily on fossil resources, which serve not only as fuels for generating process heat but also as carbon feedstocks for fuels, polymers and other chemical products.

In a sustainable energy system, renewable electricity must be used directly where possible but also converted into chemical energy carriers where storage, transport or molecular feedstocks are required [2]. Sustainable chemical production therefore requires the combined use of circular and renewable carbon sources, renewable energy and resource-efficient processes.

The geographic availability of renewable electricity and the energetic losses associated with its conversion determine which Power-to-X pathways can provide energy and chemical feedstocks most efficiently [3]. Hydrogen occupies a central position in these pathways, but its environmental performance depends strongly on the production route and the associated energy and feedstock supply; methane pyrolysis may provide a low-carbon route when the required process energy is supplied with a sufficiently low carbon footprint [4].

This challenge is shared by the wider energy-intensive basic-materials industry, including the chemical, refractory-materials, gas, non-ferrous-metals, glass, ceramics, steel and cement industries. New processes are required that avoid or substantially reduce process-related greenhouse-gas emissions. Although these sectors differ in their products and process chains, they share a need for high-temperature heat, carbon-containing raw materials or reducing agents.

Within the chemical industry, the project SynGas2Ethene illustrated how the transformation of

carbon feedstock and energy supply can be combined [5]. The production of ethene from synthesis gas derived from industrial recycling streams and renewable carbon sources provides an alternative to the established fossil-based value chain. Supplying the required process energy from renewable sources can enable substantially more sustainable production pathways for carbon-based platform chemicals.

Alongside the substitution of fossil feedstocks, the provision of process heat is therefore a central element of industrial transformation. As wind and solar energy enter the energy system predominantly in the form of electricity, power-to-heat technologies provide a direct route for integrating renewable energy into chemical processes (Fig. 1). This is particularly relevant for highly endothermic and high-temperature reactions, for which efficient and spatially controlled energy transfer remains challenging. Against this background, the present contribution examines induction heating as a means of generating heat directly within the reaction zone, using methane pyrolysis and the subsequent upgrading of its solid carbon co-product as case studies.

Existing linear value chain

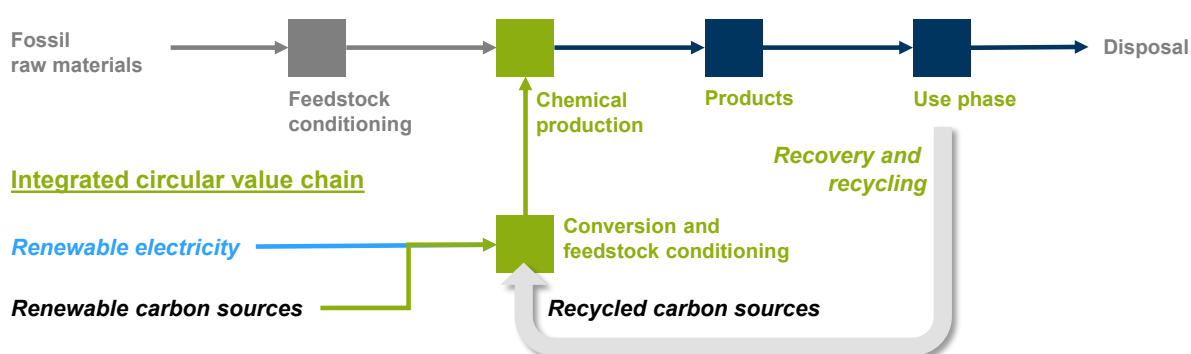


Figure 1: Transformation from a linear, fossil-based value chain to an integrated circular production system. Renewable electricity together with renewable or recycled carbon sources replaces fossil inputs, while recovery and recycling close material loops.

Power to Heat as a Tool for the Transformation of the Chemical Industry

The electrification of process heat is an important route for replacing fossil-fuel combustion in energy-intensive industries. It is particularly attractive for high-temperature reactions, for which both the required energy density and efficient heat transfer into the reaction zone are challenging.

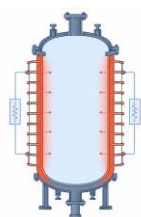
Electric reactor heating can be implemented through three principal concepts (Fig. 2).

- (i) The first is indirect heating through electrically heated reactor walls. Resistance-heating elements transfer heat to the reactor wall, from which it reaches the reaction volume by conduction, convection and radiation. Although this concept can often be integrated into established reactor designs, the attainable heating rate and temperature distribution remain constrained by heat transfer through the wall. Moreover, the reactor wall is exposed to the highest temperatures, which may accelerate material degradation and promote undesired deposition.
- (ii) A second approach is the direct electrical heating of the catalyst, catalyst support or another solid reactor component. Electrical energy is converted into heat within the reaction zone by resistive, microwave or induction heating. This reduces the heat-transfer distance and allows the temperature of the reactive solid to exceed that of the surrounding reactor wall or gas phase. Heat can therefore be supplied selectively where the reaction occurs. Depending on the heating principle, however, the solid must possess suitable electrical, dielectric or magnetic properties.

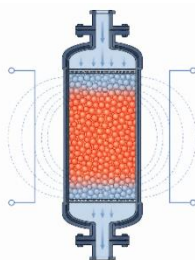
(iii) The third concept is the direct heating of the reaction gas, for example by an electric arc or plasma torch. Such systems can provide very high temperatures and heating rates and are therefore particularly attractive for strongly endothermic gas-phase reactions. Their application may nevertheless be associated with steep temperature gradients, high local energy densities and the formation of highly reactive plasma species, which can affect reaction selectivity.

Among these approaches, induction heating combines contact-free electrical-energy transfer with direct heat generation in an electrically conductive solid. It is therefore particularly suitable for high-temperature gas–solid reactions (Fig. 2, centre) in which the solid simultaneously serves as an induction susceptor, a reactive material or a substrate for product deposition.

**Indirect heating
through reactor walls**



**Direct heating of catalyst,
support or solid bed**



**Plasma-torch heating
of the reaction gas**

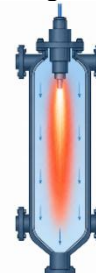


Figure 2: Principal power-to-heat pathways for electrifying high-temperature chemical reactors: indirect heating through reactor walls (left), direct heating of the catalyst, catalyst support or solid bed (centre), and direct plasma-torch heating of the reaction gas (right). The highlighted regions indicate where electrical energy is converted into heat.

Inductively Heated Reactors

Induction heating is a versatile approach for local heat management in catalytic and reactive systems [6,7]. It is based on the contact-free transfer of electrical energy through an alternating electromagnetic field. An alternating current passing through an induction coil generates a time-dependent magnetic field that induces eddy currents in an electrically conductive material inside the coil. The electrical resistance of this material converts the induced currents into heat. In ferromagnetic materials, magnetic hysteresis may additionally contribute to heat generation. The material coupled to the electromagnetic field is referred to as the susceptor. Heating efficiency depends on the frequency and strength of the electromagnetic field and on the electrical conductivity, magnetic permeability, geometry and dimensions of the susceptor.

Figure 3 summarises the reactor configurations considered in this work for integrating inductive heat generation with the reactive phase. The catalyst itself may act as the susceptor, or catalyst and susceptor may be combined within a composite particle. Alternatively, catalyst particles may be deposited on the surface of a susceptor or applied as a catalytic shell around a susceptor core. If a conventional catalyst support is required, the susceptor can be incorporated into the supported catalyst particle or brought into contact with it as a separate particulate phase. Susceptor and catalyst particles may also be physically mixed within a fixed, fluidised or moving bed.

These configurations differ in the distance over which heat must be transferred from the susceptor to the active sites. Integrating catalyst and susceptor within the same particle enables highly localised heat generation and minimises heat-transfer limitations. Physically mixed beds provide greater flexibility in independently selecting and replacing the catalyst and susceptor but require heat transfer between separate particles. The appropriate configuration therefore depends on electromagnetic coupling, catalyst stability, particle transport and the required temperature distribution.

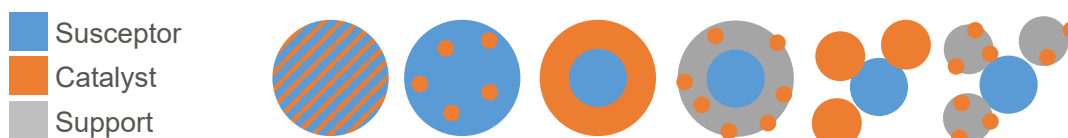


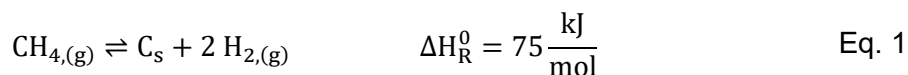
Figure 3: Conceptual framework developed in this work for combining susceptors and catalyst particles in inductively heated reactors: multifunctional catalyst–susceptor composites, catalyst particles dispersed on a susceptor, a catalytic shell around a susceptor core, supported catalysts incorporating a susceptor, and physical mixtures of susceptor particles with unsupported or supported catalyst particles. Blue denotes the susceptor, orange the catalyst and grey the catalyst support.

Methane Pyrolysis using an Inductively Heated Reactor

Methane pyrolysis is an option for hydrogen production without the direct formation of CO₂. Within future hydrogen supply chains, it offers the possibility of producing hydrogen and a separable solid carbon co-product from methane [8]. The overall reaction is shown in Eq. 1. When heated in the absence of oxygen, methane dissociates into solid carbon and hydrogen. The reaction does not proceed in a single elementary step but through a radical chain initiated by C–H bond cleavage [9]. The resulting hydrocarbon radicals undergo further reactions and successive dehydrogenation until macroscopic carbon particles containing little residual hydrogen are formed.

Hydrogen transport infrastructure entails thermodynamic and environmental trade-offs between repurposed natural-gas pipelines and newly constructed hydrogen pipelines [10]. Comparative assessments indicate that transporting methane and converting it into hydrogen by integrated methane pyrolysis may, under comparable conditions, be favourable relative to long-distance hydrogen transport [11].

Methane pyrolysis (Eq. 1) is endothermic and generally requires temperatures of 800–1000 °C or above to achieve technically relevant equilibrium conversions and reaction rates [12].



Concepts for heating the reactor include indirectly electrically heated wall reactors, moving-bed reactors heated by electric current supplied through immersed electrodes, bubble columns containing electrically heated molten metal, and plasma reactors [12,14]. The solid carbon co-product tends to form at the hottest locations and on pre-existing carbon surfaces. Deposition on reactor internals can cause catalyst deactivation, obstruct gas or solids transport and ultimately result in severe reactor blockage [14,15].

An inductively heated counter-current moving bed of carbon particles provides a means of directing carbon deposition onto a particulate solid phase that is continuously withdrawn from the reaction zone. Building on reactor design and process development conducted within the FfPaG project [13], an experimental reactor based on this concept was designed and constructed at BFI (Fig. 4).

A steel feed hopper for the carbon particles was connected to a quartz-glass tube with an inner diameter of 80 mm and a length of 750 mm. The tube passed through an induction coil with a diameter and height of 120 mm. A high-frequency generator produced an alternating magnetic field at approximately 950 kHz and supplied up to 25 kW in the induction coil. Calcined acetylene coke with a particle diameter of 2–3 mm served as the carbon precursor and the induction susceptor. The lower end of the tube was connected to a steel product hopper containing a movable piston. Lowering the piston increased the available volume and allowed the particles to descend through the tube under gravity, creating a moving bed within the induction zone. Natural gas was introduced at the lower end of the quartz tube, whereas the

product gas exited above the feed hopper, establishing counter-current gas flow. A small nitrogen purge maintained an inert atmosphere in the product hopper. The temperature in the induction zone was measured by infrared pyrometry and controlled by adjusting the induction power.

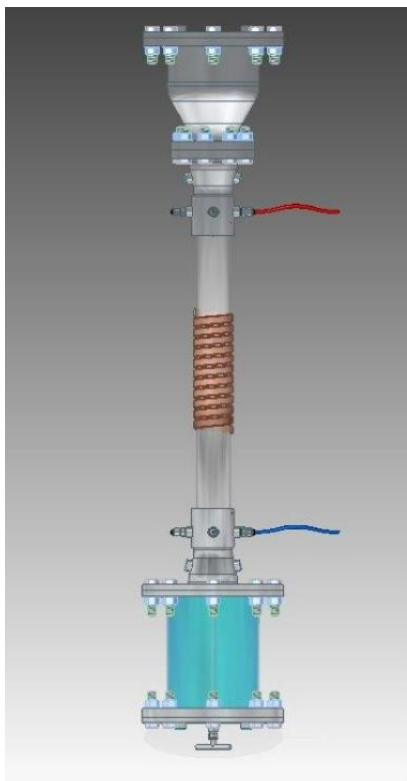


Figure 4: Schematic representation of the inductively heated counter-current moving-bed reactor.

Under representative operating conditions, the reactor was operated at a reaction temperature of 1200 °C and a natural-gas feed of 100 NL h⁻¹. The bed moved downward at 170 mm h⁻¹, corresponding to a particle mass flow of 1.32 kg h⁻¹. Maintaining this temperature in the non-insulated reactor required a power input of 4.4 kW (Fig. 5). The close-up of the particles in the induction zone indicated uniform heating, with no visible signs of blockage.

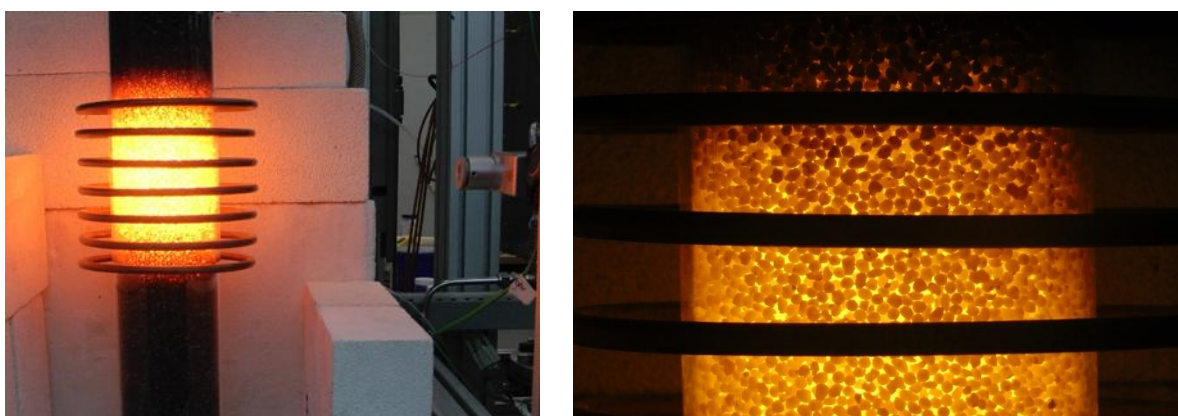


Figure 5: Inductively heated methane pyrolysis in the BFI moving-bed reactor with infrared temperature measurement and control (left); close-up of the heated calcined-acetylene-coke particles in the induction zone (right).

Figure shows the volume fractions of methane (red) and hydrogen (blue) in the product gas as functions of time on stream. The corresponding methane conversion increased rapidly during the first 12 min, reaching approximately 85%. It then increased more gradually to 98.5% after 75 min. This near-complete conversion was maintained for the remaining 25 min,

consistent with quasi-steady operation.

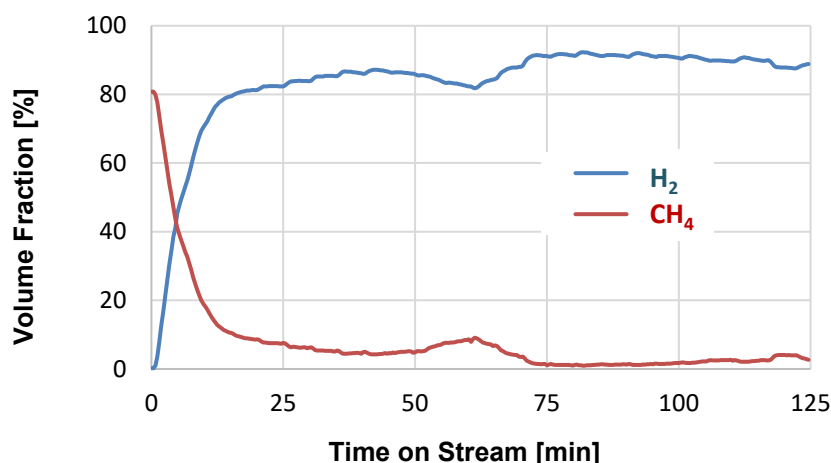


Figure 6: Dry volume fractions of H₂ and CH₄ in the product gas during operation of the inductively heated counter-current moving-bed reactor. The remaining volume fraction is predominantly N₂ arising from feed-gas dilution. The steady-state composition is consistent with near-complete methane conversion.

The results demonstrate the feasibility of inductively heated counter-current moving-bed methane pyrolysis. Near-complete methane conversion was achieved and maintained without critical reactor blockage. The favourable operating regime can be rationalised by three design features of the reactor concept [13].

- (i) Calcined acetylene coke acts as the induction susceptor, so heat is generated directly within the moving carbon bed. The carbon particles consequently form the primary heated region of the reactor. Together with the tendency of pyrolytic carbon to deposit on pre-existing carbon surfaces, this promotes product deposition on the coke particles rather than on the reactor wall.
- (ii) The continuous downward movement of the bed transports carbon-coated particles out of the reaction zone. The counter-current gas flow simultaneously brings the methane-rich feed into contact with the hottest carbon particles.
- (iii) Induction heating does not require electrodes inside the moving bed. Solids transport is therefore not obstructed by internal electrical contacts, and agglomerates can be withdrawn with the moving carbon phase rather than becoming trapped within the reaction zone.

Melt-Recrystallisation of Pyrolysis Carbon in an Inductively Heated Reactor

To contribute to climate protection, the carbon co-product of methane pyrolysis must either be incorporated into material cycles that prevent or substantially delay its return to the atmosphere as CO₂ [16] or stored durably. The economic and ecological competitiveness of methane pyrolysis is therefore strongly influenced by the value and intended use of the co-produced carbon [17]. Although methane-pyrolysis carbon can exhibit high chemical purity, its nanoscale, mesoscale and macroscale morphology frequently limits its use in established carbon-black applications [14].

Melt recrystallisation offers a route for transforming amorphous pyrolysis carbon into higher-value graphitic materials [18]. The process is based on dissolving amorphous pyrolysis carbon in molten metal, followed by controlled precipitation during cooling (Fig. 7). Under oxygen-free conditions, graphitic material precipitates at the surface of the molten metal. In the present

setup, induction heating provides precise thermal control and may additionally induce electromagnetic movement of the molten phase.

SEM images (Fig. 7, insets) reveal thin graphitic crystals with diameters of approximately 100 μm and thicknesses below 5 μm . Raman spectroscopy suggests a highly ordered graphitic structure.

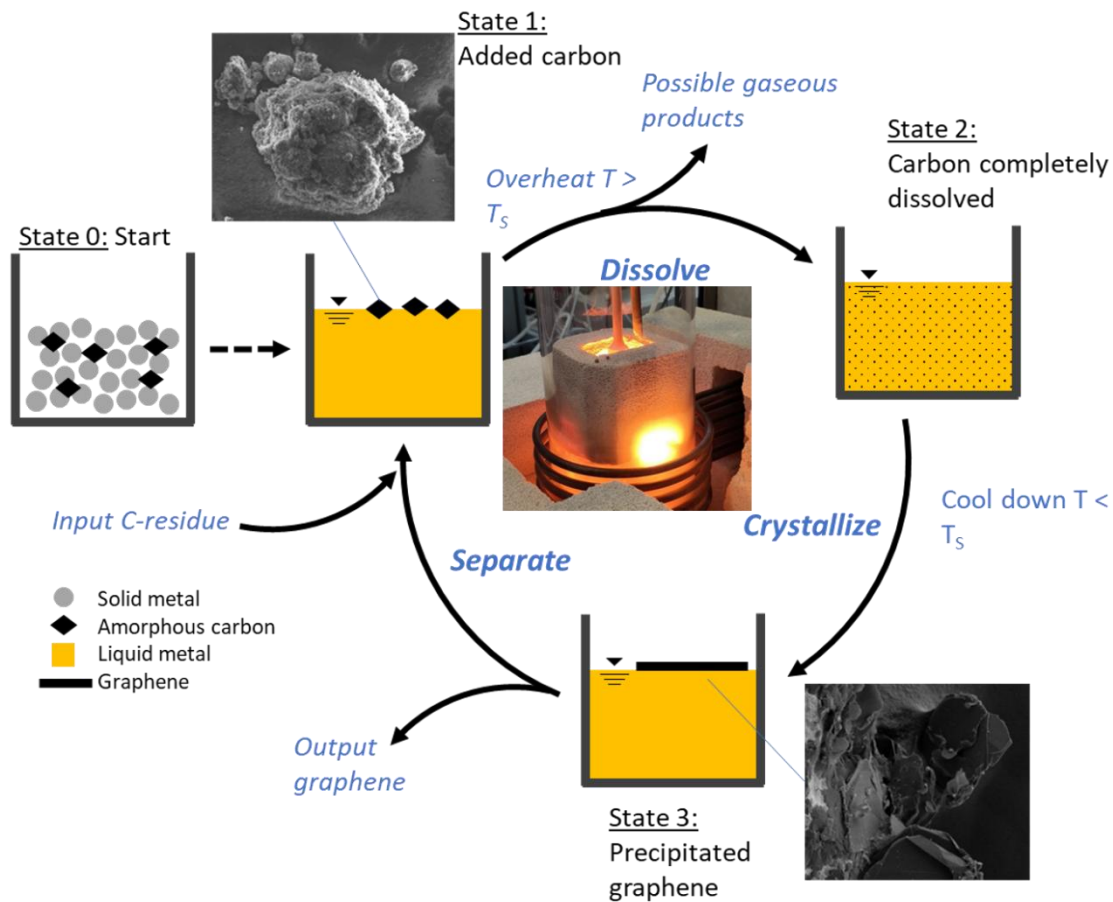


Figure 7: Inductively heated molten-metal recrystallisation process for transforming amorphous pyrolysis carbon into graphitic materials. The insets show representative graphitic crystals obtained after controlled cooling of the melt.

During cooling, bright, flat particles became visible on the surface of the molten metal (Fig. 8). Their appearance is consistent with the precipitation of graphitic carbon from the carbon-saturated melt. The image illustrates the formation of graphitic material on the melt surface; a detailed time-resolved analysis of particle nucleation, growth and surface coverage will be reported separately.

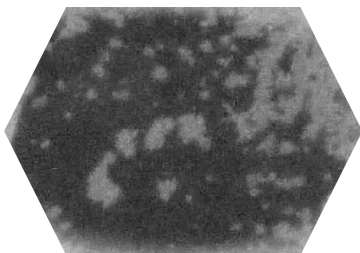


Figure 8: Representative greyscale image of the molten-metal surface during cooling. Bright, flat particles are visible against the darker molten phase, providing a qualitative observation of graphitic-material formation at the melt surface.

Conclusions

Electrification of process heat is a central route for integrating renewable electricity into energy-intensive, high-temperature chemical processes. Induction heating is particularly suited to this purpose because it generates heat directly within electrically conductive reactor materials, thereby enabling local and selective energy supply. In counter-current moving-bed methane pyrolysis, calcined acetylene coke served simultaneously as the induction susceptor and as a substrate for carbon deposition. At 1200 °C, methane conversion reached 98.5% and was maintained under quasi-steady operation without observable reactor blockage. The same heating principle supported molten-metal recrystallisation, transforming amorphous pyrolysis carbon into thin graphitic particles. Together, these results demonstrate how induction heating can couple high-temperature reaction engineering with the directed management and upgrading of solid carbon co-products, thereby extending its relevance beyond heat supply alone.

Acknowledgements

The presented work was funded by the federal government of Germany through the projects SynGas2Ethene, FfPaG and RekCarb.

References

1. C. Bataille, M. Åhman, K. Neuhoﬀ, L. J. Nilsson, M. Fishedick, S. Lechtenböhmer, B. Solano-Rodriguez, A. Denis-Ryan, S. Stiebert, H. Waisman, O. Sartor, S. Rahbar, A review of technology and policy deep decarbonization pathway options for making energy-intensive industry production consistent with the Paris Agreement, *Journal of Cleaner Production* 187, 960–973 (2018). DOI: 10.1016/j.jclepro.2018.03.107.
2. R. Schlögl, Chemical energy storage enables the transformation of fossil energy systems to sustainability, *Green Chemistry* 23, 1584–1593 (2021). DOI: 10.1039/D0GC03171B.
3. M. Hermesmann, K. Grübel, L. Scherotzki, T. E. Müller, Promising pathways: The geographic and energetic potential of power-to-x technologies based on regeneratively obtained hydrogen, *Renewable and Sustainable Energy Reviews* 138, 110644 (2021). DOI: 10.1016/j.rser.2020.110644.
4. M. Hermesmann, T. E. Müller, Green, turquoise, blue, or grey? Environmentally friendly hydrogen production in transforming energy systems, *Progress in Energy and Combustion Science* 90, 100996 (2022). DOI: 10.1016/j.pecs.2022.100996.
5. T. Liese, I. Graef, F. Heck, V. Hagen, T. E. Müller, Produktion von Ethen aus Recycleströmen und erneuerbaren Kohlenstoffquellen als eine nachhaltige und ökonomische Route zu Grundbausteinen der chemischen Industrie - SynGas2Ethene, Final Report, Technische Informationsbibliothek, Hannover (2025). DOI: 10.34657/27229.
6. W. Wang, G. Tuci, C. Duong-Viet, Y. Liu, A. Rossin, L. Luconi, J.-M. Nhut, L. Nguyen-Dinh, C. Pham-Huu, G. Giambastiani, Induction Heating: An Enabling Technology for the Heat Management in Catalytic Processes, *ACS Catalysis* 9 (2019) 7921–7935. DOI: 10.1021/acscatal.9b02471.
7. C. Kuhwald, S. Türkhan, A. Kirschning, Inductive heating and flow chemistry—a perfect synergy of emerging enabling technologies, *Beilstein J. Org. Chem.* 18 (2022) 688–706. DOI: 10.3762/bjoc.18.70.
8. T. E. Müller, Supply Chains for Hydrogen and Carbon Dioxide for Sustainable Production of Base Chemicals, in Á. Banyai (Ed.), Supply Chain - Perspectives and Applications, Ch. 2, pp. 27-68 IntechOpen (2024). DOI: 10.5772/intechopen.114031.

9. C.-J. Chen, M.H. Back, R. A. Back, The Thermal Decomposition of Methane. I. Kinetics of the Primary Decomposition to $C_2H_6+H_2$; Rate Constant for the Homogeneous Unimolecular Dissociation of Methane and its Pressure Dependence, *Canadian Journal of Chemistry*, 53, 3580-3590 (1975). DOI: 10.1139/v75-516.
10. C. Tsiklios, M. Hermesmann, T. E. Müller, Hydrogen transport in large-scale transmission pipeline networks: Thermodynamic and environmental assessment of repurposed and new pipeline configurations, *Applied Energy* 327, 120097 (2022). DOI: 10.1016/j.apenergy.2022.120097.
11. C. Tsiklios, M. Hermesmann, P. Stumm, T. E. Müller, Comparative analysis of hydrogen vs. methane pipeline transport systems with integrated methane pyrolysis for low-carbon hydrogen supply, *Applied Energy* 383, 125276 (2025). DOI: 10.1016/j.apenergy.2025.125276.
12. S. Schneider, S. Bajohr, F. Graf, T. Kolb, Verfahrensübersicht zur Erzeugung von Wasserstoff durch Erdgas-Pyrolyse, *Chemie Ingenieur Technik*, 92, 1023-1032 (2020). DOI: 10.1002/cite.202000021.
13. A. Bode, C. Anderlohr, J. Bernat, D. Flick, F. Glenk, D. Klingler, G. Kolios, F. Scheiff, A. Wechsung, M. Hensmann, S. Möhring, G. Stubbe, C. Lizandara, A. Lange de Oliveira, S. A. Schunk, V. Göke, J. Hunfeld, D. Mihailowitsch, S. Pleintinger, H. Posselt, M. C. Weikl, H.-J. Zander, N. Antweiler, K. Büker, M. Eckbauer, M. Krüger, P. Marek, K. Rodermund, U. Janhsen, H. Mittelstädt, C. Möllers, D. W. Agar, A. Munera-Parra, Feste und fluide Produkte aus Gas – FfPaG, Final Report (2018). DOI: 10.2314/GBV:1010173073.
14. S. R. Patlolla, K. Katsu, A. Sharafian, K. Wei, O. E. Herrera, W. Mérida, A review of methane pyrolysis technologies for hydrogen production, *Renewable and Sustainable Energy Reviews*, 181, 113323 (2023). DOI: 10.1016/j.rser.2023.113323.
15. T. Becker, M. Richter, D. W. Agar, Methane pyrolysis: Kinetic studies and mechanical removal of carbon deposits in reactors of different materials, *International Journal of Hydrogen Energy*, 48, 2112-2129 (2023). DOI: 10.1016/j.ijhydene.2022.10.069.
16. P. Tomkins, T. E. Müller, Evaluating the carbon inventory, carbon fluxes and carbon cycles for a long-term sustainable world, *Green Chemistry*, 21, 3994-4013 (2019). DOI: 10.1039/C9GC00528E.
17. O. Machhammer, A. Bode, W. Hormuth, Ökonomisch/ökologische Betrachtung zur Herstellung von Wasserstoff in Großanlagen, *Chemie Ingenieur Technik*, 87, 409 (2015). DOI: 10.1002/cite.201400151.
18. S. Wölfelschneider, M. Hensmann, D. Panke, T. E. Müller, Graphene Nanoparticles from Amorphous Carbon via Molten Metal Recrystallization, *ACS Sustainable Resource Management*, 2, 1643 (2025). DOI: 10.1021/acssusresmgt.4c00366.

Novel Joule-Heated Radial Reactors with Spatially Distributed Heat Generation for the Intensification of Steam Methane Reforming

L. Cozzarolo¹, F. Romanelli¹, F. Poma¹, M. Ambrosetti¹, M. Bracconi¹, P. Baj², T. Podolak², M. Maestri¹, A. Beretta¹, G. Groppi¹, B. Mello-Gabbrielleschi³, B. Williams³, E. Tronconi¹

¹Politecnico di Milano, Dipartimento di Energia, Laboratory of Catalysis and Catalytic Processes, Milan, Italy, ²Air Liquide Global E&C Solutions Poland S.A., Kraków, Poland, ³Air Liquide Forschung und Entwicklung GmbH, Frankfurt am Main, Germany

Introduction

Electrification of catalytic reactors is a promising route to decarbonize energy-intensive processes. Steam methane reforming (SMR), the main industrial hydrogen production route, requires high heat inputs and suffers from strong thermal gradients due to mismatch between heat supply and reaction heat demand.

To overcome this, two novel Joule-heated radial reactor concepts are proposed: EMERALD [1] and NEPER [2]. Both designs exploit a spatially distributed heat generation tailored to the endothermic reaction demand. EMERALD combines radial electric current (Figure 1A) with centrifugal gas flow through an annular packed foam bed, generating a heat profile decaying as $1/r^2$. NEPER, instead, features tangential current flow (Figure 1B) while maintaining the same power density distribution, offering improved electrical design and scalability.

Methods

The reactor concepts were investigated through combined modeling and experiments. A hierarchical modeling approach [3] linked detailed 3D CFD simulations to reduced 1D/2D porous-media models [4].

Experimental validation was carried out in a lab-scale reactor (0.1 L) using Rh catalyst particles ($dp=1\text{mm}$), packed into SiSiC internals (i.e., foams and POCS) acting as resistive heating elements. Radial temperature profiles were measured via thermocouples, and outlet composition via MicroGC. The reactor wall temperature was externally controlled.

Results and discussion

Preliminary 1D simulations under industrially relevant conditions show that conventional axial Joule-heated reactors develop a pronounced cold spot at the inlet, while radial configurations largely suppress it due to spatially distributed Joule heating matching the reaction heat demand. The radial layout also reduces pressure drop.

Experimental investigation of the EMERALD configuration showed that temperature profiles are governed by the net heat flux, with methane conversion approaching thermodynamic equilibrium. The highest methane conversion achieved was 71%. Both reduced-order models and detailed CFD simulations accurately reproduce the observed behavior.

While EMERALD confirms the effectiveness of the radial concept, it presents limitations related to electrical connections. These are addressed in the NEPER design, which features tangential current flow and enables higher operating temperatures - and consequently almost complete methane conversion - while preserving the same optimal power density profile. Corresponding experimental results for the NEPER configuration are reported in Figure 1C.

Conclusions

Two novel electrified radial structured reactor concepts for SMR have been developed and validated. EMERALD demonstrates tailored heat generation and cold-spot suppression, while NEPER improves electrical management and enables higher-temperature operation. Together, they highlight the strong

potential of spatially distributed Joule heating for process intensification and low-carbon hydrogen production. Scale-up studies are ongoing.

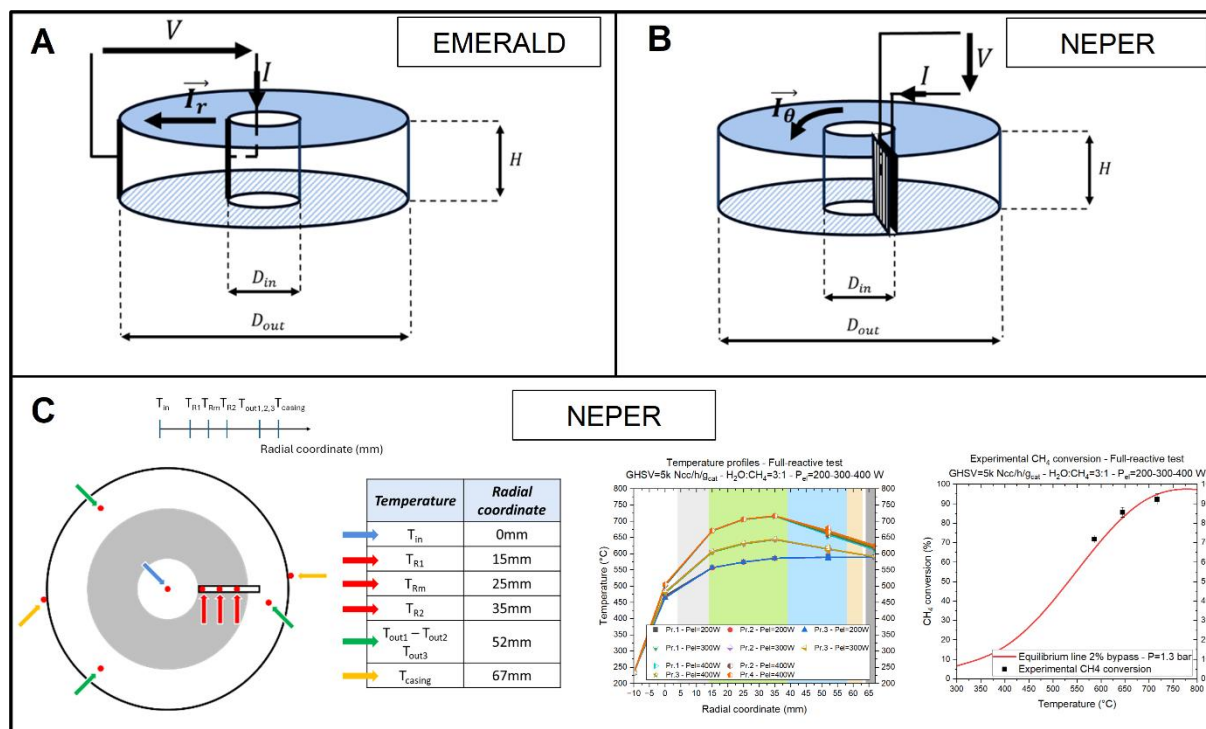


Figure 1. A) EMERALD electrical scheme B) NEPER electrical scheme C) NEPER experimental results

References:

- [1] Patent EMERALD - IT202100026456A1; EP4415857A1
- [2] Patent Application NEPER - EP26156436.3
- [3] Giulia Ferri, Matteo Ambrosetti, Alessandra Beretta, Gianpiero Groppi, Enrico Tronconi, (2024), Experimental investigation and 2D mathematical modelling of copper foams packed with Rh-Al₂O₃ catalysts for the intensification of methane steam reforming, Catalysis Today, Article 114386, 426, <https://doi.org/10.1016/j.cattod.2023.114386>
- [4] Daniele Micale, Claudio Ferroni, Riccardo Uglietti, Mauro Bracconi, Matteo Maestri, (2022), Computational Fluid Dynamics of Reacting Flows at Surfaces: Methodologies and Applications, Chemie Ingenieur Technik, 634-651, 94, <https://doi.org/10.1002/cite.202100196>

Decentralized Ammonia Cracking in a Resistively Heated Reactor

C. M. Watermann, F. L. Winter, M. Peters, A. Menne, B. Zeidler-Fandrich
Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT,
Oberhausen, Germany

Abstract

Ammonia cracking is a promising route for decentralized, low-emission hydrogen supply, as ammonia combines a high hydrogen density with established storage and transport infrastructure. This contribution focuses on the development of catalyst and reactor concepts for NH_3 decomposition in a resistively heated fixed-bed reactor. The work is embedded in the Fraunhofer flagship project AmmonVektor and addresses the catalytic cracking step, the behaviour of cobalt-based catalyst systems on conductive carbon supports, and the electrically heated reactor design. The objective is to evaluate whether direct electrical heating can reduce thermal inertia, improve dynamic controllability and enable efficient hydrogen production at small to medium scale. Catalyst performance is assessed with respect to ammonia conversion, temperature dependence and stability, while the reactor concept is investigated as an electrified alternative to conventionally heated systems. Initial findings indicate that optimized catalyst formulations in resistively heated fixed beds can achieve high ammonia conversion. The results highlight the potential of coupling tailored ammonia cracking catalysts with electrified reactor concepts and identify remaining development needs in catalyst durability, structured catalyst design, reactor scale-up and integration into decentralized hydrogen supply systems.

Introduction

The transition toward renewable energy systems requires hydrogen supply chains that are technically robust, economically viable and compatible with fluctuating renewable electricity. While molecular hydrogen is attractive as a carbon-free energy carrier, its direct storage and transport are limited by low volumetric density, high compression or liquefaction requirements and the need for dedicated infrastructure. Ammonia provides an alternative carbon-free hydrogen carrier because it combines high volumetric hydrogen density with existing large-scale storage and transport infrastructure and can be decomposed into nitrogen and hydrogen [1–3]. The cracking reaction, $2 \text{NH}_3 \rightleftharpoons \text{N}_2 + 3 \text{H}_2$, is endothermic and equilibrium-limited; therefore, catalyst activity, heat supply and reactor design jointly determine the achievable conversion, product quality and system efficiency [4,5]. In decentralized applications, these requirements become even more pronounced because reactors must operate flexibly, respond to variable demand and remain compact, safe and efficient.

Although ruthenium-based catalysts are frequently discussed as highly active benchmark systems for ammonia decomposition, base-metal catalysts such as nickel- and cobalt-based materials are of particular interest for scalable decentralized applications because they offer potential advantages in cost, availability and robustness [5,6]. Their performance, however, depends strongly on active metal dispersion, support interaction, pore structure, reducibility and resistance to sintering or deactivation under reaction conditions. In previous work on cobalt supported on activated carbon, the catalyst precursor was shown to strongly affect cobalt particle formation: nitrate-derived catalysts formed well-dispersed particles below 10 nm and reached 94% NH_3 conversion at 600 °C, whereas acetate-derived materials formed substantially larger cobalt agglomerates and were markedly less active [7]. For electrified reactor concepts, the catalyst cannot be considered independently from the heat-supply strategy. The thermal conductivity, electrical properties and geometry of the catalyst bed or structured support influence local temperature profiles, heat-up behaviour and the risk of hot spots or cold zones. Consequently, the present work addresses catalyst development in direct connection with the intended reactor environment rather than treating catalyst and reactor optimization as separate tasks.

Research Objective and Scope

This work addresses the development of decentralized ammonia cracking technology for flexible, low-emission hydrogen provision within an ammonia-based energy system. The objective is to develop and evaluate NH_3 cracking concepts for small to medium-scale applications supplied by renewable electricity and integrated into local energy infrastructures. Upstream ammonia synthesis and downstream hydrogen use are considered only as boundary conditions in order to maintain a clear focus on cracking technology, reactor operation and system integration.

Within the AmmonVektor project framework, decentralized cracking is evaluated as the link between ammonia logistics and local hydrogen demand. The specific focus of the present manuscript is the coupled design of catalyst formulation and resistively heated reactor hardware for ammonia decomposition.

State of the Art in Catalytic Ammonia Cracking

Catalytic ammonia cracking has been intensively investigated using noble-metal and transition-metal catalyst systems. Reviews of ammonia decomposition emphasize that the reaction is structure-sensitive and that catalyst performance is controlled by active metal identity, metal particle size, promoter chemistry and support properties [5,8]. Ruthenium is generally regarded as one of the most active metals for ammonia decomposition, particularly at lower temperatures, but its high cost and limited availability motivate the development of alternative catalyst families. Nickel-based catalysts are attractive for technically relevant systems because they are comparatively inexpensive and robust, although they often require higher temperatures than ruthenium catalysts. Cobalt-based materials and cobalt-containing mixed systems are also relevant because they may offer favorable nitrogen binding and dissociation properties depending on support and promoter selection [6,9]. Recent literature emphasizes that catalyst performance is not governed by the active metal alone but by the interplay between metal particle size, support basicity, electronic metal-support interactions, promoter effects and reactor-specific heat and mass transport limitations.

Direct electrical heating has recently gained attention as a process-intensification strategy for endothermic catalytic reactions because it can reduce the distance between heat generation and the catalytic reaction zone. Badakhsh et al. demonstrated compact ammonia decomposition by Joule heating of a catalytic foam reactor, reporting high power density and reforming efficiency in a small reactor volume [10]. This supports the broader hypothesis that electrified reactor concepts can be particularly suitable for decentralized ammonia cracking, provided that the catalyst bed is electrically conductive, thermally homogeneous and catalytically stable.

In the present work, we focus on electrically conductive carbon-based catalyst supports because they combine catalyst-support functionality with the requirements for direct resistance heating. Carbon materials provide high thermal and electronic conductivity, large surface areas that can promote high metal dispersion, and basic surface properties that may facilitate nitrogen desorption during ammonia decomposition. Our previous study identified cobalt on activated carbon as a promising non-noble metal catalyst system for ammonia cracking, with cobalt showing more favourable interaction with carbon supports and higher ammonia conversion than comparable nickel- or iron-based catalysts. However, the available literature on Co/C catalyst systems remains comparatively limited and has mainly addressed the influence of different carbon supports, such as activated carbons, carbon nanotubes and mesoporous carbons, on catalytic performance [7].

Methodological Approach

The methodological approach combines catalyst development, resistive reactor testing and process-oriented evaluation. Catalyst systems are selected based on their catalytic activity for

ammonia decomposition, compatibility with conductive carbon supports and suitability for direct electrical heating.

Catalyst Development

The catalyst development focuses on cobalt-based formulations supported on electrically conductive carbon materials. The central hypothesis is that non-noble metal catalysts can provide sufficient activity and durability for decentralized ammonia cracking when active phase, support structure and reactor heating concept are developed together. Catalyst candidates are compared under identical operating conditions in order to distinguish intrinsic catalytic behavior from reactor-related effects.

The previous activated-carbon study provides a useful baseline because it showed that smaller, better-incorporated cobalt particles prepared from nitrate precursors led to substantially higher NH_3 conversion than acetate-derived catalysts, while deactivation at elevated temperature was associated with methanation of the carbon support [7]. The follow-up study extends this concept from activated carbon to graphite felt and promoted cobalt catalysts. In that work, graphite felt was less active than activated carbon in the unpromoted state because of its low surface area and likely lower cobalt dispersion, but Ba and La promotion strongly improved Co/GF activity and enabled stable NH_3 conversion for at least 150 h time on stream at 500 °C [11]. These findings make Ba- and La-promoted Co/GF particularly relevant lead systems for resistively heated ammonia cracking.

Resistively Heated Reactor Concept

The reactor concept investigated in this work is a resistively heated fixed-bed system for ammonia cracking. In contrast to externally heated tubular reactors, direct electrical heating is intended to introduce heat close to or within the reaction zone. This approach can reduce heat-transfer resistances, shorten heat-up times and improve controllability during partial-load operation. For an endothermic reaction such as ammonia decomposition, the spatial matching of heat supply and reaction rate is critical: insufficient local heat input can limit conversion, whereas excessive local heating may accelerate catalyst deactivation or cause undesired temperature gradients. Carbon-based catalyst supports are therefore attractive because they can combine electrical conductivity with catalytic support functionality; however, their stability against methanation under hydrogen-rich conditions must be considered carefully [7,11]. The reactor should therefore be evaluated not only by outlet conversion but also by its thermal response. Relevant parameters include electrical power input, heating rate, axial and radial temperature profiles, bed conductivity, pressure drop and the relation between supplied electrical energy and produced hydrogen. The accepted Co/GF study showed that graphite felt provided more uniform heating than activated carbon granules in initial ohmic-heating experiments, most likely because the fabric-like felt structure enabled better electrical contact and a more homogeneous current distribution [11].

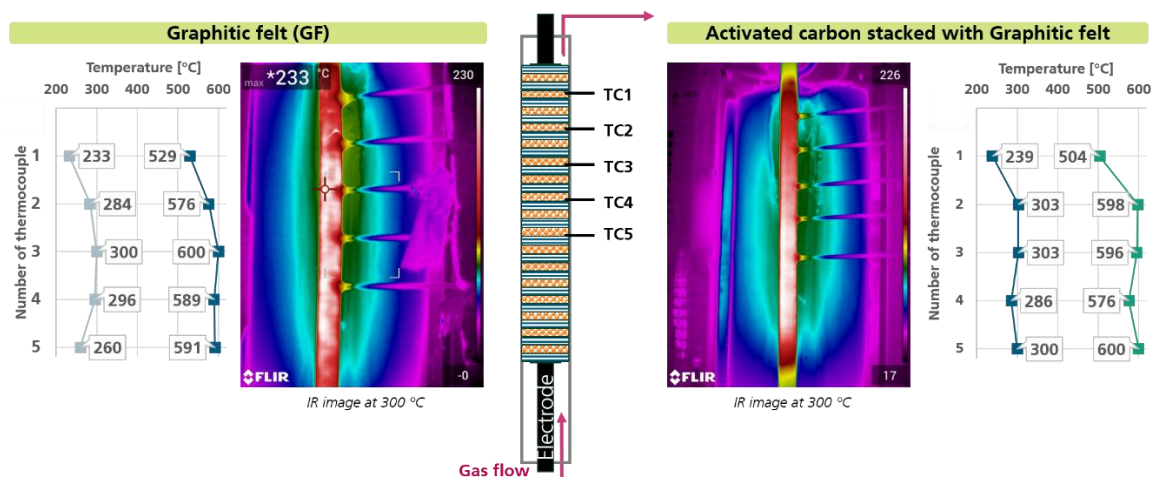


Figure 1. Resistive heating of conductive carbon-based catalyst configurations. Left: direct

electrical heating of graphite felt as a structured, electrically conductive support. Right: heating of activated carbon stacked with graphite felt, where the graphite felt provides electrical contact and heat generation while the activated carbon contributes a high-surface-area catalyst bed.

Based on the previous planning for resistive heating, the ohmic reactor concept has been scaled up to a DN100 configuration with a reactor length of 40 cm and axial current flow through the fixed bed. The design allows variable bed dimensions, ranging from a minimum bed height of 5 cm, corresponding to approximately 0.4 L of bed volume, to a maximum bed height of 20 cm, corresponding to approximately 1.6 L. This flexibility enables systematic investigation of the influence of bed height, electrical contact and catalyst loading on the thermal behaviour of the reactor.

Current work therefore focuses on the electrical characterization of this scaled reactor setup, including the determination of maximum achievable temperatures, the resulting temperature distribution within the bed and the dynamic response to changes in electrical load. In addition, a first pressureless ammonia cracking experiment with cobalt on activated carbon is being conducted to evaluate the basic catalytic functionality of the scaled resistively heated system under initial operating conditions.

Membrane-assisted reactor configurations may provide an additional route for process intensification by shifting the equilibrium through selective hydrogen removal. In the present study, however, they are considered as a future development step rather than as part of the primary reactor concept.

Process Evaluation, Safety and System Integration

Process evaluation is used as a supporting element rather than as the main focus of this presentation. The central scientific question remains how catalyst formulation and resistive reactor heating affect ammonia conversion, hydrogen yield and dynamic operation. Nevertheless, basic process metrics are required to assess whether the reactor concept is technically meaningful for decentralized hydrogen supply. These include the specific electrical energy demand per unit of hydrogen produced, heat losses, achievable product gas composition and the extent of downstream purification needed to meet the requirements of the intended application.

Safety aspects related to localized ammonia storage and handling are analyzed to derive design and operational guidelines. These include measures for leak prevention and detection, ventilation, emergency concepts, integration of safety distances, operational training and interfaces with regulatory requirements. Because decentralized applications may be located close to industrial users, mobility hubs or local energy systems, safety and public acceptance are central criteria.

Experimental Data Evaluation

The evaluation of the experimental data is presented in detail in our two publications. [7,11]

Initial Results and Discussion

Initial results show that electrically conductive cobalt catalysts can be operated in resistively heated reactor concepts for ammonia decomposition. In the accepted Co/GF study, blank graphite felt showed a more homogeneous temperature profile than activated carbon during ohmic heating, and a proof-of-concept experiment demonstrated NH_3 conversion over a directly resistance-heated Co/GF catalyst bed [11]. In small-scale indirect heating experiments, Ba- and La-promoted Co/GF were the most promising formulations because they combined substantially improved activity with stable performance for at least 150 h time on stream at 500 °C [11]. These findings support the use of promoted Co/GF as a reference system for further reactor-scale experiments under direct electrical heating.

System analyses indicate that decentralized cracking supplied by regionally produced or imported ammonia can be competitive with compressed or liquefied hydrogen distribution in

selected industrial and mobility applications. Competitiveness is most likely where ammonia logistics are already available, hydrogen demand is sufficiently continuous, and waste heat can be integrated into the local energy concept. These findings highlight the importance of evaluating cracking technology not only at the reactor level but also within complete supply chains.

Conclusions and Outlook

This work demonstrates the relevance of coupling catalyst and reactor development for decentralized ammonia cracking in resistively heated fixed-bed systems. Cobalt-based catalysts on conductive carbon supports represent scalable alternatives to noble-metal systems, while direct electrical heating offers a route toward compact, controllable and dynamically operable reactor hardware. The activated-carbon study establishes precursor-controlled cobalt dispersion as a key factor for catalytic activity [7], whereas the graphite-felt study shows that Ba- and La-promoted Co/GF can combine improved activity, long-term stability and suitability for direct resistance heating [11]. Together, these findings support the further development of conductive carbon-supported cobalt catalysts and scaled resistively heated reactor concepts for decentralized hydrogen production from ammonia. Future work will focus on catalyst durability under dynamic operation, optimization of structured catalyst configurations, reactor scale-up and integration with downstream hydrogen purification and local energy systems.

References

- [1] J. Andersson and S. Grönkvist, Large-scale storage of hydrogen, *Int. J. Hydrogen Energy*, 2019, 44, 11901–11919.
- [2] S. Giddey, S. P. S. Badwal, C. Munnings and M. Dolan, Ammonia as a renewable energy transportation media, *ACS Sustain. Chem. Eng.*, 2017, 5, 10231–10239.
- [3] C. Zheng, B. Guan, J. Guo, T. Su, J. Zhou, J. Chen, Y. Zhang, Y. Yuan, W. Xie, N. Zhou and Z. Huang, Research status, optimization strategies, and future prospects of ammonia decomposition catalysts for CO_x-free hydrogen, *Ind. Eng. Chem. Res.*, 2023, 62, 11305–11336.
- [4] D. J. Deka, B. Boruah, G. Lee and K. G. Rappé, Recent advances in ammonia decomposition technologies for hydrogen production, *Energy Fuels*, 2025, 10802–10852.
- [5] I. Lucentini, X. Garcia, X. Vendrell and J. Llorca, Review of the decomposition of ammonia to generate hydrogen, *Ind. Eng. Chem. Res.*, 2021, 60, 18560–18611.
- [6] Z. Lendzion-Bieluń, U. Narkiewicz and W. Arabczyk, Cobalt-based catalysts for ammonia decomposition, *Materials*, 2013, 6, 2400–2409.
- [7] F. L. Winter, P. Diehl, P. Telaar, C. M. Watermann, S. Kaluza, M. Muhler, U.-P. Apfel and B. Zeidler-Fandrich, Influence of the catalyst precursor for cobalt on activated carbon applied in ammonia decomposition, *Catal. Today*, 2024, 429, 114502.
- [8] E. García-Bordejé, S. Armenise and L. Roldán, Toward practical application of H₂ generation from ammonia decomposition guided by rational catalyst design, *Catal. Rev.: Sci. Eng.*, 2014, 56, 220–237.
- [9] L. Torrente-Murciano, A. K. Hill and T. E. Bell, Ammonia decomposition over cobalt/carbon catalysts: effect of carbon support and electron donating promoter on activity, *Catal. Today*, 2017, 286, 131–140.
- [10] A. Badakhsh, Y. Kwak, Y.-J. Lee, H. Jeong, Y. Kim, H. Sohn, S. W. Nam, C. W. Yoon, C. W. Park and Y. S. Jo, A compact catalytic foam reactor for decomposition of ammonia by the Joule-heating mechanism, *Chem. Eng. J.*, 2021, 426, 130802.
- [11] F. L. Winter, L. Riebel, C. M. Watermann, S. Kaluza, M. Muhler, U.-P. Apfel and B. Zeidler-Fandrich, On the role of carbon supports and promoters in joule-heated cobalt-catalyzed ammonia decomposition, accepted manuscript, 2026.

Intensified thermocatalytic CO₂ conversion to chemicals and fuels

J. Xie

Green Chemical Reaction Engineering, Engineering and Technology Institute Groningen,
University of Groningen, The Netherlands

CO₂ hydrogenation to chemicals and fuels has the potential to reduce CO₂ emissions while displacing fossil resources. Yet, the chemical inertness of CO₂ makes its direct conversion to C₂₊ hydrocarbon products fundamentally challenging, requiring C₁ intermediates such as CO or methanol [1]. This keynote lecture explores both routes for process-intensified CO₂ conversion: the CO-mediated via integration of reverse water–gas shift (RWGS) with Fischer-Tropsch synthesis (FTS), and the methanol-mediated conversion to hydrocarbons.

The first part focuses on iron- and cobalt-based catalysts for CO₂/CO/H₂ conversion to C₂₊ hydrocarbons. Iron catalysts are intrinsically bifunctional, catalyzing both RWGS and FTS, and therefore offer the possibility of direct CO₂ conversion in a single reactor. However, exploiting this bifunctionality requires balancing CO formation and consumption rates, hydrocarbon chain growth, and methane suppression. Using carbon-supported potassium-promoted iron-based catalysts, I will show how catalyst characteristics and process parameters such as CO₂ conversion influence reaction pathways and overall performance [2,3]. In contrast, cobalt catalysts predominantly hydrogenate CO₂ to methane, motivating a different approach to process integration. Using a conventional titania-supported metallic cobalt catalyst, I will showcase the boundary conditions under which CO₂ behaves as an inert component, and those under which it becomes reactive, in CO₂/CO/H₂ feeds entering a cobalt-catalyzed FTS reactor [4]. These results provide insight into when conventional staged configurations are necessary and when more integrated reactor concepts may be feasible.

The second part addresses methanol-mediated conversion to light olefins, focusing on the methanol-to-olefins (MTO) process. Using a series of isomorphically substituted AEI-type zeotypes (MAPO-18, M = Si, Mg, Co, Zn), I will demonstrate how framework composition and acidity influence MTO performance under CO₂/CO/H₂ co-feeds [5]. In particular, I will discuss how H₂ promotes catalyst activity but can also hydrogenate olefins, while CO suppresses this undesired reaction over Brønsted acid sites. I will discuss the challenges of bridging conventional MTO chemistry with oxygenate-mediated CO_x conversion and provide an assessment of methanol, dimethyl ether, and ketene as potential oxygenate intermediates [6].

Together, these studies illustrate how reaction engineering, catalyst design, reactor and process integration must be considered collectively to unlock efficient and selective conversion of CO₂ to chemicals and fuels.

[1] Ye, R. P. et al. *Nat. Commun.* 10 (2019) 5698.

[2] W. Meng, B. C. A. de Jong, H. van de Bovenkamp, G. Boer, G. L. Bezemer, A. I. Dugulan, J. Xie. *Chem. Eng. J.* 489 (2024) 151166.

[3] W. Meng, R. Rocks, A. I. Dugulan, J. Xie. *J. CO₂ Util.* 111 (2026) 103543.

[4] B. C. A. de Jong, K. T. Rommens, T. Rosner, P. van den Tempel, L. Rohrbach, G. L. Bezemer, H. J. Heeres, M. Saeys, C. Vogt, J. Xie. *ACS Catal.* 15 (2025) 10946.

[5] J. Xie, D. S. Firth, T. Cordero-Lanzac, A. Airi, C. Negri, S. Øien-Ødegaard, K. P. Lillerud, S. Bordiga, U. Olsbye, *ACS Catal.* 12 (2022) 1520.

[6] J. Xie, U. Olsbye, *Chem. Rev.* 123 (2023) 11775.

Fuelling the Fleet: Utilizing Air Liquide's Advanced Methanol Technology to Deliver a CO₂-Based Next-Generation Marine Fuel

A. Rösch

Air Liquide Global E&C Solutions Germany

Methanol is a powerful component for any CCUS strategy and can decarbonize energy intensive industries and transportation, thus accelerating the transition towards a low-carbon economy.

Air Liquide as a global leader in gases, technologies and services for the industry offers a unique energy transition technology portfolio comprising the world-class LurgiTM Methanol and CO₂ capture technologies. The track record of more than 50 Methanol plants and 60 years of excellence and innovation in Methanol technology make Air Liquide Engineering & Construction a partner of choice that unlocks efficient and reliable Methanol production for its customers. Beyond the continuous optimization and innovation of its industrialized Methanol processes, Air Liquide's most recent R&D activities comprise the [M²ARE](#)^{*} project which is unlocking a fully renewable value chain for cost-effective production of maritime Methanol tailored to the requirements of global shipping.

Air Liquide integrates syngas generation, CO₂ capture, Electrolysis and Methanol production into comprehensive low-carbon Methanol solutions. In all of these fields, Air Liquide leverages leading technologies including Lurgi LP MethanolTM and Lurgi MegaMethanolTM for large-scale production, as well as renewable Lurgi PowerMethanolTM and biogenic Methanol production. As a one-stop shop for Methanol plants, Air Liquide offers solutions that help achieve CO₂ reduction goals while producing Methanol from various feedstocks in a cost-effective way.

This presentation focuses on producing Methanol from CO₂ and renewable hydrogen. Air Liquide is unique in that it offers the entire technology chain, from CO₂ capture to electrolysis and finally, Methanol synthesis. This comprehensive approach culminates in fully integrated and flexible Lurgi PowerMethanolTM plants, essential for cost-effective e-Methanol production using fluctuating renewable energy sources.

** This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement number 101136080.*

From Oil to Low Carbon Alcohols as Energy Carriers for Transportation and Intermediates for Chemical Production

Mario Marchionna

Società Chimica Italiana, Past President Industrial Chemistry Division, Milano, Italy

Abstract

A few considerations, regarding the chain of production, transport and use of the energy carriers, make us realize that the success that Oil matured over the years as energy source cannot be attributed only to its great availability and the relatively cheap price but also to the ease with which liquid hydrocarbon derivatives can be transported, stored and distributed for their final use because of their optimal energy density per unit of volume.

Unlike most energy sources that are directed to electric power generation, oil production is mainly devoted to the transportation market and a significant minor part to petrochemistry.

Of course, the effects on the environment are significant and make Oil less appealing, especially in the longer term, calling for the identification of less emitting substitutes but with the same peculiar properties; consequently, a huge effort is being devoted worldwide to develop several innovative decarbonized energy/carbon carriers which may constitute the base for producing sustainable low-carbon fuels and may also represent a key to decarbonize chemical productions.

Among them, a few alternative synthetic carriers, such as alcohols (methanol, ethanol and even butanols) are increasingly attractive, as potential key intermediates for Sustainable Aviation Fuels (SAF) and as a possible base for a more decarbonized petrochemistry (or carbo-chemistry).

On one side, within the SAF landscape, Alcohol-to-Jet (AtJ) is an emerging pathway positioned as early commercial scale, offering high feedstock flexibility and compliance with aviation fuel specifications. On the other hand, the use of bio-ethanol as the raw material for producing ethylene and, ultimately, as a possible key intermediate for the industrial organic chemistry of the next decades will be discussed. Similar results could be achieved also through Methanol to Olefins (MTO) technology by employing "low carbon" methanol.

Introduction - Oil and its Energy Carriers

The fossil fuels have provided about 80% of total energy consumption for more than 100 years [1]. Looking ahead, although renewables are the energy source with the highest growth rate, they will still play an important role, due to their higher energy density, their reliability and affordability, the ever-growing need for energy worldwide (furtherly exacerbated by AI adoption), and the high current exposure to these sources, not easily substitutable in the low-medium term.

The various phases involved from generation to the end-use of an energy carrier constitute its 'life cycle'. The basic operations involved in the life cycle of an energy carrier are (Fig. 1): a) generation using the primary source; b) transport; c) storage (when required); d) distribution; e) end-use (with consequent impact on the environment, both in local terms in the form of emissions, and in global terms of impacting the climate as main contributors of CO₂ into the atmosphere [1]). Furthermore, the primary energy carrier could be transformed into a secondary energy carrier more tuned with the final end use. The operations are not necessarily carried out in the aforementioned order; for example, storage could even precede transport or could be carried out at the same time as the final use (as in the case of motor traction). Linking energy sources with the market therefore entails technological and strategic choices as far as the processes for obtaining the carriers, the logistics of the sources and the end-uses are concerned. Obviously, also the environmental impact is a decisive factor.

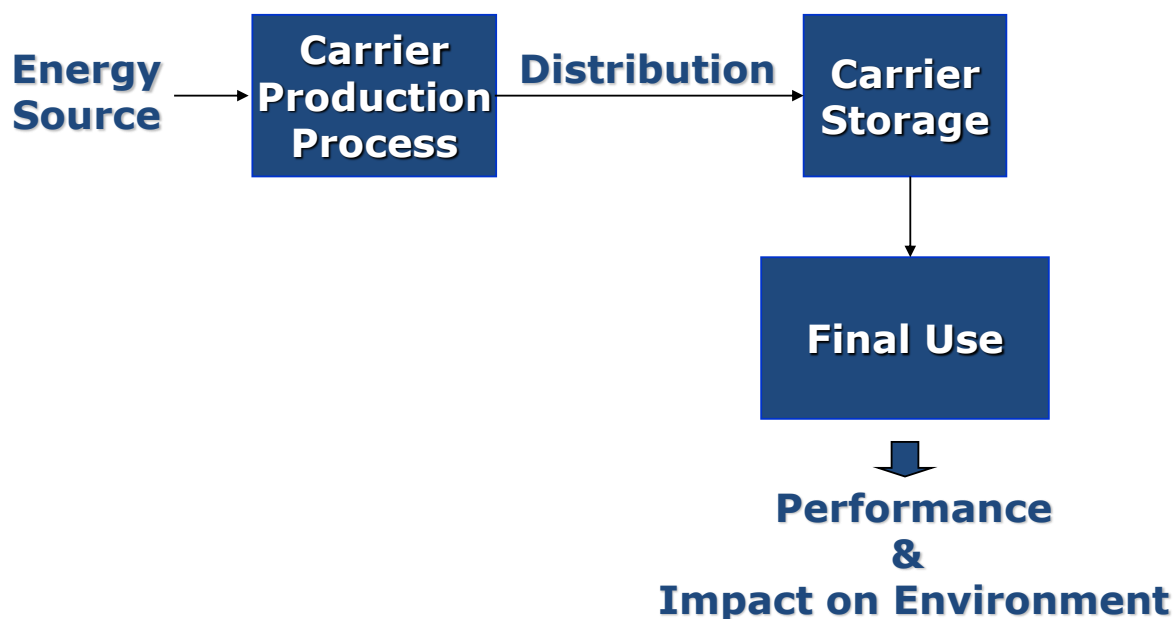


Fig. 1: Life cycle of an energy carrier

Oil carriers are dedicated to well-defined uses; for example, the use of gasoline, jet fuel and of diesel oil is dominant in the motor traction.

These brief considerations make us realize that the success that oil has had as an energy source cannot be attributed only to its great availability but also, and perhaps above all, to the ease with which liquid hydrocarbon derivatives can be transported, stored and distributed for their final use. In fact, their liquid state enables their energy density per unit of volume to be optimized, and this has great advantages for the storage and the distribution of the carrier.

In principle, an ideal energy carrier could be represented by a liquid with a relatively high boiling point (above 80 °C) and a low melting point (below -40 °C); such carriers would remain liquid under any climatic condition and at various altitudes. In fact, gasoline and diesel gasoil are good examples; their physical properties are almost ideal for applications in the transportation field as they optimize all downstream phases of production of the energy carrier, from transport to storage and to the final use. But this observation must not be considered as conclusive, otherwise there would be no explanation of the great success that natural gas is having: economic and environmental aspects play an important role.

As previously anticipated, Oil is peculiar among the different energy sources as it is specifically devoted to mobility and as the main raw material for petrochemistry. In addition, unlike most energy sources that are directed to electric power generation, Oil production is mainly devoted to the transportation market and a significant minor part to petrochemistry.

Oil is not so easily substitutable although its environmental impact will have to be reduced, a partial limitation could be achieved by introducing systems aimed at reducing CO₂ emissions, such as Carbon Capture & Storage but other solutions need to be devised.

In perspective, Oil will be less dominant in mobility, also due to the advent of electric vehicles; will slow down as vehicles get more efficient [6] and more electric. However, its potential decline will be very slow as the electric vehicles penetration will have to face the need of substituting a huge fleet of light duty vehicles equipped with conventional engines; presumably it will not have the same impact on heavy duty vehicles. On the other side, its substitution will be much more difficult in the aviation and in the maritime transportation sectors; for aviation it will be mandatory to seek for liquid alternatives. On the petrochemical side, Oil will remain central to the petrochemical industry, as also shown by new mega-projects in Saudi Arabia for the direct conversion of crude oil into petrochemical derivatives, which try to maximize the conversion to petrochemical products and less to fuels. Obviously, any effective alternative solution based on renewable feedstock would be welcome.

In the search for potential alternatives, in this article attention is focused on alcohols. Alcohols have a very long tradition as fuels [3]; Ethanol has been used for internal combustion engines since their invention in the early 1900s (Ford Model T) but soon neglected due to its cost; however, nowadays, ethanol is widely used worldwide by combining the octane-enhancing effect with the desired production from renewable sources. Also, Methanol is a well-known alternative, but ethanol is generally the most preferred alcohol due to its better stability, water tolerance, smaller risk of corrosion, and lower toxicity. Methanol has been used for the direct blending, but only in China, due to the market condition with high gasoline demand and large-scale availability of methanol produced from low-cost local coal. As regards higher alcohols, also Bio-butanol, a mixture of n-butanol and isobutanol, is another potentially attractive compound for gasoline, also due to its renewable nature. In the following, we shall try to understand if low carbon alcohols could represent a real answer at least to a partial substitution of Oil in its different uses.

Low Carbon Alcohols as Energy Carriers

Alcohols might be attractive in the near future because they present similar features to the Oil's energy carriers and they can be produced in a sustainable manner. Innovative liquid carriers such as methanol and ethanol have almost ideal characteristics (Table 1), and they can be also useful intermediates both for petrochemistry and transportation scopes. They are among the leading options, offering practical and increasingly advanced means to reduce emissions across both on- and off-road applications. They represent two of the most mature and promising options, with bioethanol taking the lead as the most commonly used biofuel [4].

	UNIT	GASOLINE	DIESEL	BIODIESEL	ETHANOL	METHANOL
CHEMICAL STRUCTURE		$C_nH_{2,1n}$	$C_nH_{1,87n}$	R-COOCH ₃	C ₂ H ₅ OH	CH ₃ OH
DENSITY IN LIQUID STATE	kg/m ³	750	831	870	790	790
CETANE NUMBER			40-55	49		
OCTANE NUMBER		90-100			110	119
BOILING POINT	°C	40-200	180/350	260-370	78.5	65
LOWER HEATING POWER (MASS)	MJ/kg	45	43.5	36	27	20
LOWER HEATING POWER (VOLUME)	MJ/l	33.7	36.1	31	21	16
SELF IGNITION	°C		316			464

Table 1: Chemical-physical and motor properties of various energy carriers [2]

Both the alcohols can be used directly as fuels, even for the marine sector [5-7]; they can be added to conventional fuels as boosters or full components or can be transformed into other transportation fuels, through different pathways, i.e. methanol to gasoline or alcohols to jet fuels.

Methanol

Methanol is industrially manufactured in world-scale plants using a two-step process based on the catalytic conversion of synthesis gas produced from natural gas or coal with a global demand, in 2025, higher than 100 million tons. At present, methanol is mostly used as a chemical intermediate for the synthesis of formaldehyde, acetic acid and solvents. The efficient production technology via syngas, in fact, allows it to be exploited optimally in terms of carbon and hydrogen use; when produced on a large scale (7,500-10,000 Mt/d) from low-cost gas, the cost of production can be very low.

An emerging and more environmentally attractive approach is based on the production of syngas from biogenic sources or from waste, or from CO₂ hydrogenation to e-fuels [8-10]. For example, the gasification of biomass and waste produces synthesis gas (a mixture of CO and H₂), the traditional feedstock for methanol production. Of course, in these cases significant experience at scale has still to be achieved.

As regards the petrochemical side, methanol can be transformed into olefins, mainly ethylene and propylene, through the well-known MTO (Methanol to Olefins) process, a technology that, when biomass is used as the starting point, is also referred to as BTO, biomass to olefins. As an intermediate for petrochemistry, in China, several plants based on MTO technology have been built. This strategic choice has been driven by the country's growing demand for ethylene and propylene. But this does not necessarily mean it moves in the direction of decarbonization. Quite the opposite: the methanol that is then converted into olefins comes from the gasification of fossil coal, which is certainly no more sustainable than oil or natural gas.

Being a liquid fuel, methanol is far easier to transport and store, even if its hydrophilous nature may lead to some problem; it can be useful for various applications in the energy field:

- As a component for gasoline.
- As fuel for fuel cells in which methanol can feed the cells directly or indirectly through the formation of hydrogen.
- As an indirect reserve of hydrogen which could be easily obtained from methanol through reforming. Applications of this type can be found, for example, with the Topsoe Methanol To Shift (MTS) process in which the methanol is fed in a hydrogen plant directly to the Water/Gas Shift reaction, maximizing the production of hydrogen.
- As an intermediate for fuels: as early as the 80s, the conversion of methanol was proposed with zeolitic catalysts in gasoline (Mobil process) but that approach rapidly became costly because of the collapse of the price of crude as from 1986. Now, this process could attract some fresh interest following the pinpointing of catalysts that enable ethylene and/or propylene to be synthesized selectively and then converted into quality fuels by means of the oligomerization of these olefins. In this respect, the synergy between the MTO process and the succeeding conversion of the olefins to jet through oligomerization is evident.
 - More recently, the Alcohol to Jet (AtJ) route, see also later, has attracted novel interest in the production of Sustainable Aviation Fuels (SAF) [11]. As of August 2025, Methanol to Jet (MtJ) projects under development represent around 1.8 million tonnes per year of future SAF capacity with over 60 Mt of announced capacity across e-methanol, bio-methanol and low-carbon methanol by 2030. China leads with about half of global projects, followed by Europe and North America [12], for example the Essar project is a typical one [13].

Ethanol

Ethanol can be synthesized by the hydration of ethylene with an acid catalyst but much more commonly is produced by conventional fermentation and distillation of a large variety of organic materials like sugars (sugarcane and sugar beet), grains (corn, wheat, etc), starches (cassava, potatoes) or cellulosic material (wood or bio-wastes). Clearly the choice of the possible feedstock is a function of the plant location; typically, bio-ethanol is produced from sugarcane in Brazil, from corn in the US, and from sugar beet, feed wheat, barley, and some maize in Europe. At present, sugarcane is the preferred feedstock since it has the lowest cost, the best emission balance of greenhouse gases, and production cost competitive with gasoline.

Brazil and the US are the largest producers of ethanol.

Together with the traditional processes, this enormous demand for ethanol is pushing for the development of new technologies to convert biomass wastes (agricultural residues, forestry, consumer and industrial streams) into fermentable sugars (second-generation biofuels) [14]. Global ethanol production is significant: around 110 billion liters in 2025, or 87 million tonnes (Mt). Considerable reductions in cost and improvements in energy yield can derive from using advanced biotechnological processes and innovative separation methods (by means of membranes).

As regards petrochemicals production, it is realistic to think that many plastics, fibers, rubbers, and engineering polymers will continue to be produced until around the middle of the century from the traditional basic Oil-derived chemical intermediates: ethylene, propylene, butenes, butadiene, benzene, toluene, and xylenes. In this context, it is worth asking whether their current production processes could be replaced by others based on renewable feedstock. It is difficult to imagine that, in the medium to long term, all current petrochemical production can be supplied with renewable feedstocks. It seems more likely that many of the products currently made from petrochemicals will instead be replaced by different products obtained from renewable raw materials.

From a chemical standpoint, one of the simplest ways to replace fossil-based ethylene seems to be to start with bioethanol [15]. After all, the conversion of ethanol to ethylene is a simple acid-catalyzed reaction that has already been practiced industrially, albeit on a limited scale. Once ethylene has been produced, its derivatives can continue to be manufactured as they are today, with the difference that they would be products obtained from renewable sources [16].

From a sustainability standpoint, cellulosic bioethanol represents an important improvement over traditional bioethanol, when used as a fuel, compared with fossil-derived gasoline; however, the costs are high compared with bioethanol from sugarcane and corn.

Fermentation has also been successfully applied to convert off-gases from steel plants, rich in CO and H₂, into ethanol. The technology was developed by LanzaTech, a New Zealand company that has applied it in several steel plants in China and India and is also building one in Belgium at an ArcelorMittal steelwork [16]. According to LanzaTech, off-gases from steelworks and refineries could provide a significant amount of ethanol: 30 × 10⁹ and 5 × 10⁹ gallons per year respectively, which means 104 Mt/year of ethanol [17]. Today, however, this technology is applied in only 6 plants, which together produce 300,000 t/year of ethanol.

Another, entirely chemical, route for producing ethanol from biomass and waste has been developed and applied by the Canadian company Enerkem, which built a plant in Edmonton (Canada) [15].

In principle, we cannot rule out that bioethanol may become in the future one of the main building blocks of industrial chemistry. It remains to be verified, however, whether a sufficient quantity of feedstocks is available to produce it.

It is therefore foreseeable that, to produce bioethanol for the chemical industry, as for biofuels, it will be necessary to rely on waste biomass.

SAF (Sustainable Aviation Fuels) Production Routes

Moving from the petrochemical application to the transportation fuels and more precisely to the aviation fuels, SAF can be produced through different routes, depending on whether the feedstock is of biological origin (bio-jet) or derived from the reduction of CO₂ with green H₂ (e-kerosene).

SAF is an entirely compatible, drop-in alternative for existing aircraft and airport infrastructure. It meets the same range of operational specifications as conventional Jet A1, which looks it performs the same (or better) as its fossil equivalent, while being produced by more benign sources, such as waste carbon sources that exist above the ground [17].

Bio-jet production technologies include [18]:

- Hydroprocessed Esters and Fatty Acids (HEFA)
- Alcohol-to-Jet (AtJ), which involves dehydration of bio-alcohols to olefins, followed by oligomerization, hydrogenation, and fractionation
 - o including methanol upgrading to jet fuel via Methanol-to-Olefins (MtO), and successive oligomerization, hydrogenation, and fractionation
- Biomass gasification to syngas, which can then be converted through Fischer–Tropsch (FT) synthesis to produce hydrocarbon mixtures subsequently isomerized and fractionated.

Among these routes, HEFA is currently the most mature technology, with several industrial scale plants already in operation. Alcohol to Jet (AtJ) and gasification/FT routes follow in terms of technological readiness, although they are still at an earlier stage of deployment.

These pathways differ mainly in the type of biomass employed. HEFA are typically produced from vegetable oils - preferably from non-food oilseeds or crops grown on marginal land - as well as from waste and residual lipids such as used cooking oil and animal fats.

Alcohol-to-Jet (AtJ) is an emerging pathway positioned as early commercial scale, offering high feedstock flexibility and compliance with aviation fuel specifications. AtJ routes rely on bio-alcohols (e.g., ethanol, methanol, even butanols) obtained via fermentation, but also from syngas-based routes as from gasified waste streams, including municipal solid waste (MSW) and biomass residues [19-20]. AtJ leverages existing bioalcohols production infrastructure.

AtJ technology benefits from mature components (dehydration, oligomerization and hydrotreating) and flexible feedstock options. On the other side, it still remains an energy-intensive process, although a bit less with respect to Fischer Tropsch and also more selective as regards carbon efficiency. Its exothermic upgrading steps enable heat internal recovery, low utilities and high jet yields with limited light-hydrocarbon formation unlike FT systems, which generate more methane.

For example, taking ethanol as the alcohol reference, the AtJ technology is split into four discrete processes, which enable the end-to-end conversion of any ethanol source into a drop-in commercial SAF blending component [17].

1. Dehydration: ethanol is dehydrated over a catalyst to form ethylene. In the case of methanol this process is substituted by an MTO process, while for higher olefins than ethanol, the process is still a dehydration.
2. Oligomerization: the ethylene produced is catalytically converted to mixtures that maximize the composition in the C₈-C₁₆ range needed for jet fuel.
3. Hydrogenation: the longer chain alkenes are then treated with hydrogen over catalyst, which saturates the olefin to form paraffins (alkanes). This helps to improve stability, reduce reactivity, and meet jet fuel specifications.
4. Fractionation: the paraffins, now in the form of a hydrocarbon mixture of varying chain lengths, are split into different fractions of product based on their boiling points, with the intent of isolating the fraction useful suitable for jet fuel. The remainder of the

mixture is heavier than jet fuel and generally used as component for a renewable diesel output.

Among bio based SAFs, HEFAs are already commercially available and used in blends with fossil jet fuel. Their production is well established, but they face a fundamental constraint: the limited availability of sustainable lipid feedstocks, which will likely prevent very high production volumes.

Other bio-jet fuel technologies such as AtJ are not subject to the same feedstock limitations. In fact, the availability of biomass wastes and residues offers significant potential; an IEA report [21] estimates that total biomass resources - including MSW, agricultural residues, and forestry residues - could reach 130–240 EJ of energy equivalent by 2060.

Final remarks

In conclusion, the following preliminary considerations may be advanced:

- Alcohols may represent an environmentally attractive and versatile alternative to the oil-derived energy carriers (gasoline, diesel, jet as fuels) for transportation.
- Methanol and Ethanol can be also a sustainable feedstock for petrochemistry, thus partially replacing Oil also in this scope.
- Alcohols can be directly used as fuels (also for different transportation categories) or can be converted to selected mixtures such as SAF, through AtJ process.
- A lot of AtJ projects are currently underway, starting both from ethanol and from methanol [22-28].
- The liquid nature of alcohols is ideal for their manipulation, transportation and storage. Due to the latter aspect, their production phase can be decoupled by the following conversion step (e.g. AtJ), thus making the overall production process much more flexible.
- Economics will remain the most important obstacle to their full development. Improvements, especially in the phase of production of the “low carbon” alcohols are needed in the near future: “The most important near-term action is to have first-of-a-kind facilities at scale, facilities that are in the range of thousands of tons per year, to start the cost reduction journey”, as reported by Lee Beck from HIF [5].

References

- 1) M. Marchionna. *La Chimica & l'Industria* **2**, 18 (2019).
- 2) M. Marchionna. in *Encyclopedia of Hydrocarbons*, ed. Treccani, 3th Vol., 4.1, 301 (2007).
- 3) M. Di Girolamo, M. Brianti, M. Marchionna. *Ullmann's Encyclopedia of Industrial Chemistry*, DOI: 10.1002/14356007.a18_037.pub3, Article Online Posting date: October 6, 2017.
- 4) T. Anderson. *Hydrocarbon Processing online*, January issue (2026).
- 5) A. Tullo. *Chemical & Engineering News*, 26 (2025, February 24).
- 6) Z. Skoufa. *Decarbonisation Technology*, 37 November issue (2024).
- 7) *Hydrocarbon Processing online*, June 12th (2026).
- 8) *Hydrocarbon Processing online*, April 27th (2026).
- 9) *Hydrocarbon Processing online*, October 1st (2025).
- 10) *Hydrocarbon Processing online*, October 24th (2025).
- 11) E.D. Hafizoglu, T. Ozpercin, A. Zahidova, V. Mutlu. *Decarbonisation Technology*, 56 February issue (2026).
- 12) *Hydrocarbon Processing online*, January 23rd (2026).
- 13) *Hydrocarbon Processing online*, May 20th (2026).
- 14) T. Guha. *Hydrocarbon Processing online*, May issue (2026).
- 15) C. Perego, M. Ricci. *La Chimica & l'Industria* **1**, 10 (2025).
- 16) F. Burton. *Decarbonisation Technology*, 25 November issue (2025).
- 17) D. Bloch. *Decarbonisation Technology*, 5 August issue (2025).
- 18) C. Perego, R. Millini. *La Chimica & l'Industria* **4**, to be published (2026).

- 19) W. Shiflett. *Digital Refining, Catalysis 2025*, 31 March issue (2025).
- 20) J. Nava. *Hydrocarbon Processing online*, January issue (2026).
- 21) *Technology Roadmap – Delivering Sustainable Bioenergy*, IEA report (2017)
- 22) *Hydrocarbon Processing online*, March 3rd (2026).
- 23) *Hydrocarbon Processing online*, March 31st (2026).
- 24) *Hydrocarbon Processing online*, May 11th (2026).
- 25) *Hydrocarbon Processing online*, June 29th (2026).
- 26) *Hydrocarbon Processing online*, April 14th (2026).
- 27) *Hydrocarbon Processing online*, September 30th (2025).
- 28) *Hydrocarbon Processing online*, May 1st (2026).

From Methanol to Alcohols: Mechanistic Understanding of a Tandem Catalytic System for Resilient C1-Based Chemical Supply

J. T. Groteguth¹, S. Stahl¹, J. T. Vossen¹, J. Exo¹, T. Weyhermüller¹, C. Lyall², J. Lowe², U. Hintermair², W. Leitner^{1,3}, A. J. Vorholt¹

¹Max Planck Institute for Chemical Energyconversion, Mülheim an der Ruhr, Germany, ²University of Bath, Bath, United Kingdom, ³RWTH Aachen University, Institute of Technical and Macromolecular Chemistry, Aachen, Germany

The annual production of more than 12 million tonnes of aldehydes via olefin hydroformylation underscores the central role of this homogeneous catalytic process in the chemical industry — serving as a key entry point to alcohols, plasticizers, and a broad range of value-added chemicals.[1] However, the conventional process relies on synthesis gas (CO/H₂), whose supply is tied to large-scale, centralized infrastructure and predominantly fossil carbon sources. As the chemical industry seeks more flexible and resilient supply chains, alternative C1 feedstocks are gaining strategic importance.[2]

Methanol — increasingly accessible from renewable and distributed production routes — offers a compelling alternative. The methanolation reaction exploits methanol as an in situ syngas source, integrating methanol reforming and olefin hydroformylation into a single, atom-efficient tandem process.[2] Applied to 1-octene as a model substrate, the system delivers alcohol yields of up to 80% with outstanding linear selectivity (l:b = 93:7), a rhodium-based turnover number exceeding 17,000, and operation under mild conditions (<10 bar total pressure). Successful scale-up from 5 mL to a 250 mL miniplant demonstrates the robustness and industrial viability of the approach.[2]

Building on these results, this contribution presents mechanistic investigations of the tandem system using multinuclear operando FlowNMR spectroscopy. By directly monitoring catalyst speciation and key reaction intermediates under working conditions, this study aims to establish a molecular-level understanding that guides the rational design of future methanol-based processes for the resilient supply of carbon carriers and chemicals.

References:

[1] Shu Tao, Da Yang, Minmin Wang, Guangxun Sun, Gaoyan Xiong, Wenwen Gao, Youzhi Zhang and Yuan Pan, (2023), Single-atom catalysts for hydroformylation of olefins, CellPress, iScience, 106183, 26/3, <https://doi.org/10.1016/j.isci.2023.106183>, 2023-03-17, College of Chemistry and Chemical Engineering, China University of Petroleum

[2] Sebastian Stahl, Jeroen T. Vossen, Stephan Popp, Walter Leitner, Andreas J. Vorholt, (2025), Methanolation of Olefins: Low-Pressure Synthesis of Alcohols by the Formal Addition of Methanol to Olefins, Wiley VHC, Angewandte Chemie International Edition, e202418984, 64, <https://doi.org/10.1002/anie.202418984>, 2024-11-19, Max Planck Institute for Chemical Energyconversion

Demonstration of an integrated power-to-liquid plant for SAF production using a 220 kW Co-SOEC module

G. Corre¹, A. Happ², H. Bürgmayr², M. Rubin², R. Dittmeyer²

¹Karlsruher Institut für Technologie, Institut für Mikroverfahrenstechnik (IMVT), Eggenstein, Germany,

²Karlsruher Institut für Technologie, Eggenstein, Germany

E-fuels are anticipated to play a significant role in the decarbonisation of sectors that are difficult or impractical to electrify, including aviation and maritime transport. Co-SOEC technology provides an energy-efficient pathway for producing the syngas required for synthesis processes such as Fischer–Tropsch conversion. However, the realisation of industry-relevant scale Co-SOEC-based PtL plants is necessary to validate the technological potential and assess its performance under practical operating conditions.

In this work, a Co-SOEC system was successfully integrated into a PtL plant employing Fischer–Tropsch synthesis. The 220 kW Co-SOEC module, developed by Sunfire, was coupled to a compressor and a flare, demonstrated highly reliable and stable syngas production, with straightforward tuning of the H_2/CO ratio and overall efficiency of 85%. The compressed syngas was directly utilised in the synthesis process, enabling the validation of the complete process chain and the production of syncrude. Furthermore, the recycling of Fischer–Tropsch off-gas back into the Co-SOEC was demonstrated, providing an efficient means of enhancing carbon utilisation and improving the overall system efficiency.



Co-SOEC module at KIT's PtX Lab

Industrialization of Chemical Recycling – Technical, Regulatory and Market Perspectives from OMV's ReOil® Scale-Up Journey

A. Leitner

Innovation & Technology, OMV AG, Vienna, Austria

Chemical recycling is increasingly recognised as an essential complement to mechanical recycling for processing post-consumer polyolefin waste streams that cannot be effectively recycled through conventional routes. However, the transition from pilot and demonstration facilities to commercially viable industrial assets remains one of the greatest challenges facing the circular plastics economy. This paper presents OMV's experience gained during the development and industrialisation of the proprietary ReOil® technology, highlighting key technical learnings, regulatory requirements, and market dynamics shaping future deployment.

ReOil® converts mixed post-consumer polyolefin waste into circular hydrocarbon feedstocks through a continuously operated pyrolysis process integrated into refinery and petrochemical infrastructure. Following more than fifteen years of development, the technology progressed from laboratory and pilot-scale operation to the industrial ReOil® Plant in Schwechat, Austria. Continuous operation at nominal design capacity has validated critical scale-up assumptions, including feedstock flexibility, refinery integration, pyrolysis oil upgrading, and product certification pathways.

Beyond technology, the future of chemical recycling in Europe is strongly influenced by regulation. Ongoing discussions surrounding the Packaging and Packaging Waste Regulation (PPWR) and associated mass-balance methodologies will affect investments and market development.

Market developments reveal a growing divergence between Europe and China. While regulatory uncertainty and slower project development have tempered European growth, China has positioned chemical recycling as a strategic industrial priority, supported by substantial investments and rapid capacity expansion.

The paper concludes that successful industrialisation of chemical recycling requires the alignment of technology, regulation, and business models. OMV's ReOil® journey demonstrates that technical feasibility has been established, while future deployment will depend on robust regulatory frameworks, effective refinery integration, disciplined scale-up, and market demand.

Pyrolysis of PC/ABS-Blends in a gaseous ammonia atmosphere

P. Rath sack¹, M. D. Hannak¹, D. Scheithauer¹, J. Kleeberg^{1,2}, M. Gräbner^{1,2,3}

¹Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Circular Carbon Technologies, Freiberg, Germany, ²TU Bergakademie Freiberg (TUBAF), Institute of Energy Process Engineering and Chemical Engineering (IEC), Freiberg, Germany, ³TU Bergakademie Freiberg (TUBAF), Center for Efficient High Temperature Processes and Materials Conversion (ZeHS), Freiberg, Germany

Polycarbonate/Acrylonitrile Butadiene Styrene (PC/ABS) blends are widely used in sectors such as electronics and automotive because of their excellent impact strength and thermal resistance. However, mechanical recycling of these materials is difficult, as it often causes thermal degradation and a resulting loss of key properties. Chemical recycling, especially pyrolysis, represents a promising alternative. In this process, PC/ABS is thermally decomposed in the absence of oxygen, producing valuable monomers or structurally related compounds such as bisphenol A (BPA) or phenol. The pyrolysis behavior of condensation polymers like PC differs from that of addition polymers such as polyolefins, because bond cleavage occurs specifically at functional groups rather than randomly along the polymer backbone. These functional groups also serve as reactive sites for reagents introduced into the gas phase.

In this study, we investigated the effect of ammonia addition on PC pyrolysis as a gaseous reagent by varying its concentration at constant temperature and by varying the temperature at constant ammonia concentration. The experiments were conducted on the gram scale in a laboratory fixed-bed reactor, where the meltable polymer was placed in a crucible and exposed to a reactive gas flow from top to bottom. The pyrolysis products were transferred from the reactor to a condensation system within seconds, and the non-condensable gases were analyzed using at-line gas chromatography. The condensates were subsequently characterized in detail by GC-FID and comprehensive two-dimensional gas chromatography-mass spectrometry (GCxGC-MS).

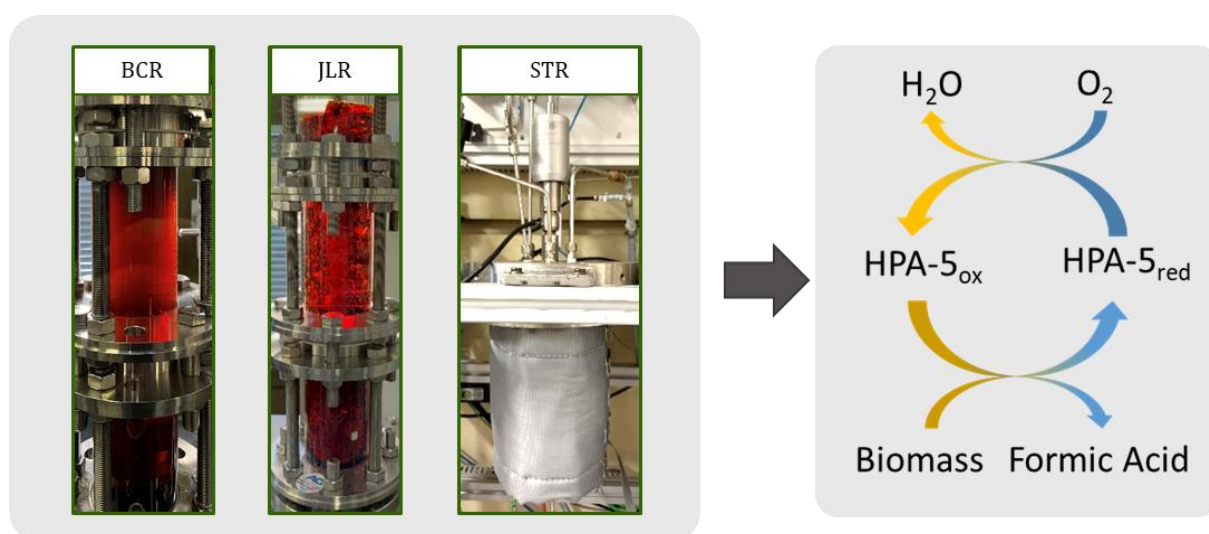
The results show that the formation of a coked residue, which usually occurs during the pyrolysis of PC, can be almost completely suppressed. At the same time, the yield of the liquid products and the desired target species can be significantly increased. In the presentation, the results including detailed analyses will be disclosed. Furthermore, a hypothesis about the reactions that take place will be presented.

Intensification of the Modified OxFA Process by Evaluation of Different Reactor Concepts

I. C. Wirth¹, H. Kleemiß², D. Voß¹, M. Poller¹, M. Schlüter², J. Albert¹

¹University of Hamburg, Hamburg, Germany, ²Technische Universität Hamburg, Hamburg, Germany

Lignocellulosic biomass, the structural component of woody plant cell walls, is a renewable and carbon-neutral resource. Currently, lignocellulosic biomass accounts for approx. 16% of total waste generation in Europe, yet only 77% of this biomass is recycled. In light of this and the increasingly challenging geopolitical landscape, there is growing interest in using lignocellulose as a raw material for the chemical industry to combat climate change and reduce dependence on fossil raw materials.¹ This paradigm shift presents new challenges for catalytic chemistry. While simple heterogeneous catalysts suffice for gas-solid systems converting fossil resources, the structural complexity of biomass requires gas-liquid multiphase systems, placing significantly higher demands on catalysts.^{2,3} The BioValCat project (Enhanced Biomass Valorization by Engineering of Polyoxometalate Catalysts) aims to develop versatile homogeneous catalytic processes for the selective transformation of lignocellulose into industrially viable valorization technologies. The project is based on the OxFA process, in which biomass is oxidized with O₂ to formic acid, which is widely used in industry, such as in the textile industry.⁴ The process is a gas-liquid multiphase system that relies heavily on the transport of oxygen in the liquid phase, which can be a limiting factor. This study investigates how mass transfer and the catalytic conversion of biomass to formic acid can be improved through different reactor setups and chemical system modifications. Key hardware and chemical parameters were systematically varied to identify the main drivers of process intensification. Three different model substrates representing the major components of lignocellulosic biomass and three different solvent systems were investigated to vary the chemical system. To vary the hardware parameters, three reactor systems with nearly identical geometric dimensions but different phase-mixing mechanisms were implemented and their performance was compared. Depending on the system, the phase mixing is achieved by using a stirrer, a nozzle, or a sparger. The reactor concepts investigated include the stirred-tank reactor (STR), which is classically used for OxFA processes.⁴ The jet loop reactor (JLR), selected due to promising results for the glycerol oxidation reported by Wirth et al.³ and the bubble column reactor (BCR), which was chosen for investigation due to its simple construction, which requires neither moving parts nor additional components within the reactor. This comprehensive study provides significant insights into the process intensification of the homogeneously catalyzed biomass oxidation, thereby laying the foundation for the scalable, safe, and economical production of formic acid from biomass.



Graphical abstract.

Integration of Plastic Waste Pyrolysis Oils into FCC Processes

T. Dreising, L. Brilmayer, J. Vogt, S. Tavakkol, D. Stapf

¹Institute for Technical Chemistry (ITC), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Abstract

Chemical recycling of plastic waste via pyrolysis offers a potential pathway to reduce fossil resource consumption and recover value from otherwise non-recyclable waste streams. While plastic-derived pyrolysis oils are widely discussed as alternative feedstocks for steam crackers, their integration into Fluid Catalytic Cracking (FCC) has received comparatively little attention, particularly with regard to process integration and industrial operating constraints.

This study investigates the technical and environmental implications of co-processing a well-characterized LDPE-derived pyrolysis oil in conventional FCC and Deep Catalytic Cracking (DCC) configurations using process simulation and life cycle assessment. An industrial FCC model was developed in Aspen HYSYS, calibrated, and assessed against published industrial reference data. Increasing shares of pyrolysis oil in the respective conventional refinery feedstocks were subsequently evaluated with respect to product distribution, reactor–regenerator heat balance, and process integration.

Under controlled cracking conditions, increasing substitution of conventional feedstock with pyrolysis oil shifts the product distribution toward lighter hydrocarbons while reducing light cycle oil formation. Under conventional FCC operation, the additional conversion is expressed primarily as increased gasoline production, whereas olefin-oriented DCC operation more effectively converts the resulting gasoline-range intermediates into LPG and propylene. Increasing pyrolysis oil substitution simultaneously reduces coke formation and regenerator heat release, resulting in higher catalyst circulation requirements and a progressively narrowing thermal operating window. A co-processing ratio of 10 wt.% was therefore selected as a conservative representative scenario for the environmental assessment. Additional adaptations to feed injection and downstream gas recovery may be required, particularly under DCC conditions.

From a product perspective, co-processing does not substantially change the climate change impact of propylene production relative to the corresponding fossil reference configurations. From a waste-treatment perspective, however, net climate change impacts of 0.13 and 0.02 kg CO₂-eq per kg LDPE were obtained for FCC and DCC co-processing, respectively, compared with 1.35 kg CO₂-eq for waste treatment by incineration with energy recovery. Overall, the results demonstrate the potential of existing FCC infrastructure as a flexible platform for integrating recycled carbon into refinery and petrochemical value chains, with DCC providing additional opportunities to direct the product slate toward light olefins when petrochemical feedstock production is prioritized.

1. Introduction

The transition toward a circular and climate-neutral chemical industry requires a fundamental transformation of today's fossil-based carbon supply chains. While global demand for plastics is expected to continually grow over the coming decades, achieving a more sustainable and resilient carbon supply will require the progressive integration of recycled and renewable feedstocks alongside conventional fossil resources [Geyer2017, Bachmann2023]. Future petrochemical production therefore requires technologies capable of processing a broader spectrum of alternative feedstocks while maintaining process stability, product quality and economic competitiveness. Existing refinery assets are expected to play a key role in this transition by providing resilient and flexible conversion pathways for circular carbon carriers.

Among the available recycling technologies, chemical recycling via plastic waste pyrolysis has attracted considerable attention as a complementary route to mechanical recycling for mixed, contaminated and otherwise non-economically recyclable plastic waste streams [Stallkamp2023, Kumagai2025]. Instead of recovering polymers directly, pyrolysis converts waste plastics into hydrocarbon mixtures that can be reintroduced into existing petrochemical production. Consequently, plastic-derived pyrolysis oils are increasingly regarded as promising secondary feedstocks capable of reducing the demand for virgin fossil resources while retaining carbon within the chemical value chain [Bachmann2023, Hennig2025].

To date, most industrial activities and scientific investigations have focused on integrating plastic pyrolysis oils into steam crackers. This pathway enables the direct recovery of light olefins for polymer production but requires comparatively narrow feed specifications and exhibits limited tolerance toward contaminants and heavy hydrocarbon fractions, which can be particularly challenging when processing mixed plastic waste streams [Abdulrahman2026]. Here, Fluid Catalytic Cracking (FCC) represents a potentially attractive alternative integration route. FCC is one of the largest catalytic conversion processes in modern refineries, with a global installed conversion capacity exceeding 700 Mt per year while offering significantly greater flexibility regarding feed composition and boiling range [Vogt2015]. At the same time, the expected long-term decline in transportation fuel demand and the growing demand for light olefins are driving the transformation of FCC units from predominantly fuel-producing assets toward increasingly petrochemical-oriented operation [Al-Samhan2022, Akah2015]. Deep Catalytic Cracking (DCC) represents one example of an FCC extension, using higher cracking severity and modified catalyst formulations to enhance the production of light olefins. These developments position FCC units as potential key enablers for integrating circular carbon feedstocks into existing refinery infrastructure while strengthening the resilience of petrochemical carbon supply by combining greater feedstock flexibility with the ability to adapt the product slate to changing demand.

Despite this potential, FCC co-processing of plastic pyrolysis oils remains considerably less investigated than steam cracking. Previous studies have primarily focused on laboratory-scale catalytic experiments or product yield characterization, whereas comparatively little attention has been paid to industrial operating constraints, process integration and system-wide environmental performance [Büchele2022, Mastry2023, Dorazio2023]. In particular, comprehensive assessments combining industrial process simulation with life cycle assessment remain scarce.

The present work addresses these research gaps by investigating the co-processing of plastic pyrolysis oil in conventional FCC and DCC configurations using industrially representative process simulation and environmental assessment. This initial study deliberately employs a well-characterized LDPE-derived pyrolysis oil as a simplified model feedstock. The use of a chemically well-defined feed enables the systematic investigation of fundamental process interactions without the additional complexity introduced by contaminants and strongly varying feed compositions. Using an assessed conventional FCC model and a comparative DCC configuration, the influence of increasing pyrolysis oil substitution on product distribution,

catalyst and energy requirements, and operational constraints is analyzed for both conventional fuel-oriented FCC operation and olefin-oriented DCC operation. Finally, the environmental implications of both process configurations are evaluated using life cycle assessment.

2. Methodology

The methodological framework adopted in this study combines process simulation with environmental assessment to evaluate both the technical implications and the environmental impacts of integrating plastic pyrolysis oil into existing FCC units. First, a conventional FCC model and an olefin-oriented DCC configuration were established and calibrated using literature data representative of industrial operation. Subsequently, a well-characterized LDPE-derived pyrolysis oil was introduced into both process configurations at different substitution ratios. Besides analyzing changes in product distribution under controlled operating conditions, additional simulations were carried out under industrially representative process constraints to assess the process-level implications of increasing pyrolysis oil integration. Finally, the resulting process configurations were assessed using life cycle assessment to quantify their environmental performance.

2.1 FCC process modeling

Process simulations were performed in Aspen HYSYS V15 using the integrated FCC reactor model based on the industrially established 21-lump kinetic approach. The model describes the catalytic cracking reactions between predefined hydrocarbon lumps while simultaneously accounting for catalyst circulation, regenerator heat balance and the overall thermal integration of the FCC process. The selected modeling approach therefore enables the investigation of both reaction chemistry and process-level interactions under industrially relevant operating conditions.

Two different FCC configurations were investigated. The first represents a conventional gasoline-oriented FCC operation, while the second represents a DCC configuration designed to maximize light olefin production through increased reaction severity and modified catalyst formulation. The conventional FCC model was calibrated against representative operating data from a commercial Asia Pacific FCC unit with an annual feed capacity of 800,000 t reported by Chang et al. [Chang2012]. The conventional refinery feed was represented by a blend of vacuum gas oil (VGO) and atmospheric gas oil (AGO) based on the corresponding feed characterization. Missing data were completed by further literature data [Letzsch2015, Sadeghbeigi2020]. Calibration was considered successful when the deviation between the theoretical and apparent heat of cracking remained below 5% [Chang2012]. The DCC configuration was derived from the calibrated conventional FCC model using deasphalted oil (DAO) as the conventional feedstock, with feed properties taken from Deng et al. The model was calibrated to the operating point reported by Deng et al., which featured a higher catalyst-to-oil ratio, elevated reactor outlet temperature, ZSM-5 addition, and complete heavy cycle oil recycling [Deng2002, Letzsch2015]. The resulting key parameters for both models are displayed in Table 1.

Table 1: Key parameters of the FCC and DCC configurations used in Aspen HYSYS modeling.

Parameter	Unit	FCC	DCC
Riser height	m	36.7	36.7
Riser diameter	m	1	1
Riser gas residence time	s	3.7	3
Catalyst	-	A/F-3	A/F-3 + ZSM-5
Catalyst inventory	t	150	150
Catalyst-to-oil ratio	-	10.4	12.5
Riser outlet temperature	°C	518	564
Regenerator temperature	°C	680	700
Conventional feedstock	-	VGO/AGO blend	DAO
Feed preheat temperature	°C	175	250
Feed mass flow rate	t/h	103	103
Feed steam	t/h	5.2	24.2
Stripper steam	t/h	5	5
Regenerator air flow rate	m ³ /h	105,000	120,000

After calibration using the reference operating point reported by Chang et al., the model's predictive capability was assessed using additional operating conditions covering a range of riser outlet temperatures reported in the same study [Chang2012]. Owing to the limited availability of detailed industrial reference data for commercial DCC units, the DCC model could not be assessed to the same extent and should therefore be regarded primarily as a comparative process model intended for analyzing relative trends between conventional FCC and DCC operation.

2.2 Pyrolysis oil characterization

In order to investigate the fundamental influence of pyrolysis oil on FCC operation, a chemically well-defined LDPE-derived pyrolysis oil from Netsch et al. was selected as a model feedstock [Netsch2025]. Unlike pyrolysis oils originating from mixed plastic waste, the selected feed contains virtually no heteroatoms or inorganic contaminants, thereby enabling the isolated investigation of hydrocarbon chemistry without interference from chlorine-, nitrogen-, oxygen- or metal-containing contaminants. The hydrocarbon composition was determined by GC×GC analysis within the accessible boiling range as described by Netsch et al. [Netsch2025]. Additionally, the composition was grouped into 30 °C boiling point intervals. For fractions boiling above 450 °C, for which reliable GC×GC compositional information was unavailable, a purely paraffinic composition was assumed based on the characterization reported by Dorazio et al. [Dorazio2023]. Figure 1 presents the resulting distillation curve together with the temperature-resolved hydrocarbon class distribution of the LDPE-derived pyrolysis oil. Based on these boiling-point-dependent hydrocarbon class distributions, the individual fractions were assigned to the corresponding hydrocarbon lumps used by the FCC kinetic model. Although simplified compared to real post-consumer pyrolysis oils, this approach establishes a well-defined reference system that enables systematic analysis of process interactions before extending the methodology to increasingly complex waste-derived feedstocks.

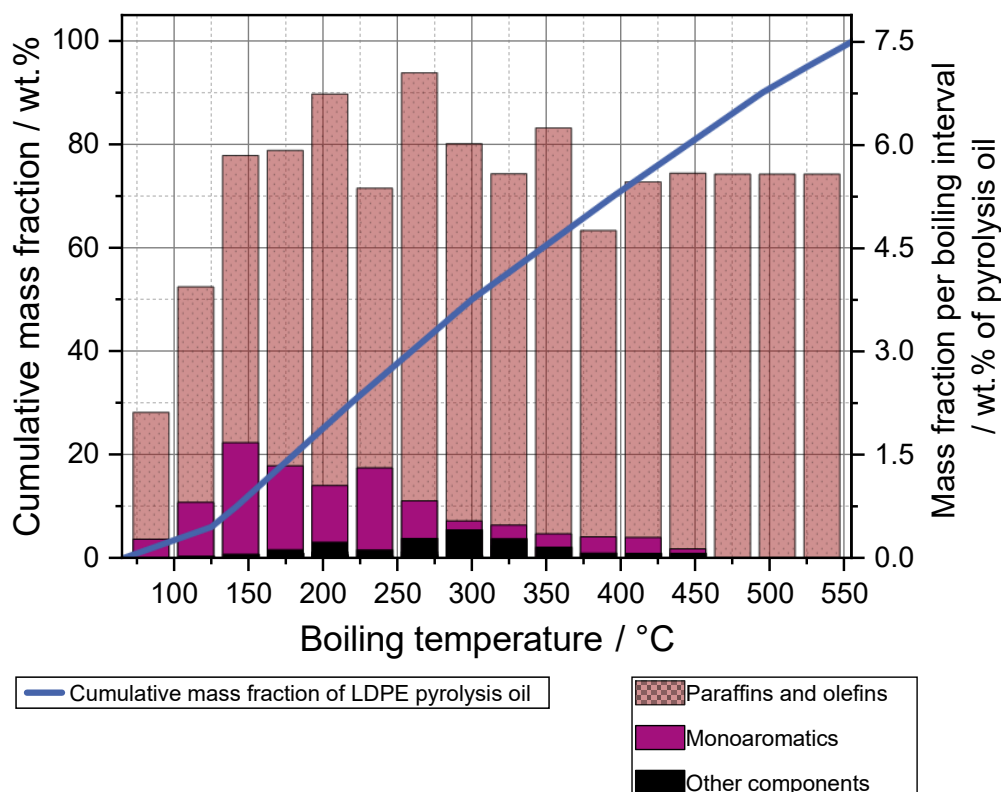


Figure 1: Distillation curve and temperature-resolved hydrocarbon composition determined by GC×GC analysis. Hydrocarbon compositions for boiling temperatures above 450 °C were assumed to be entirely paraffinic according to Dorazio et al. [Dorazio2023].

2.3 Simulation strategy

The simulation strategy comprised two complementary approaches to distinguish intrinsic feedstock effects from process limitations arising during industrial FCC operation. For all co-processing simulations, increasing fractions of the respective conventional feedstock were substituted by LDPE-derived pyrolysis oil. In the first approach, product yields and selectivities were investigated under controlled reactor conditions by systematically varying reactor outlet temperature (ROT), catalyst-to-oil ratio and pyrolysis oil substitution rate while intentionally decoupling these parameters from the thermal constraints of the integrated reactor–regenerator system. This methodology is conceptually analogous to laboratory-scale Micro Activity Test and Advanced Cracking Evaluation experiments, which are designed to isolate the catalytic influence of feedstock composition under well-defined reaction conditions [Dorazio2023, Mastry2023]. Consequently, changes in product distribution can primarily be attributed to differences in feedstock chemistry.

In the second approach, the complete industrial FCC process was considered by maintaining the thermal coupling between the reactor and regenerator together with catalyst circulation and auxiliary process requirements represented in the process model. This approach therefore captures the principal process-level interactions governing the thermal operating window. Additional equipment-related constraints associated with feed handling, injection, and downstream gas recovery were assessed qualitatively based on the simulated feed and product properties and relevant literature.

This two-stage methodology enables a clear distinction between fundamental catalytic feedstock effects and engineering constraints associated with industrial FCC implementation. While the first approach facilitates direct comparison with laboratory-scale studies reported in the literature, the second captures the process-level interactions that govern the thermal and operational integration of pyrolysis oil co-processing.

2.4 Life cycle assessment

The environmental performance of the investigated process configurations was evaluated using life cycle assessment in accordance with ISO 14040 and ISO 14044. Two complementary perspectives with different system boundaries and functional units were considered to assess both the environmental performance of pyrolysis oil co-processing from a product perspective and the potential of the overall process route as a chemical recycling option for plastic waste.

For the product-based assessment, the functional unit was defined as the production of 1 kg of propylene. The system boundary included the upstream production of the conventional refinery feedstocks. Due to the absence of suitable background datasets for the VGO and AGO fractions, their production through atmospheric and vacuum distillation of crude oil was modeled using existing Aspen HYSYS refinery models. For the environmental assessment of the DCC configuration, the upstream burden of the DAO feed was approximated using the same VGO/AGO inventory as in the conventional FCC case to provide a consistent basis for comparison. This approximation was considered reasonable because the DAO and FCC reference feeds exhibited similar characteristics within the applied process representation. The energy demand associated with downstream gas recovery and propylene separation was determined using additional Aspen HYSYS models and included in the foreground inventory.

For the waste-treatment assessment, the system boundary was extended to include the complete chemical recycling route from LDPE waste to refinery products. The functional unit was defined as 1 kg of LDPE waste treated, consistent with common practice in waste-management life cycle assessment [Hennig2025]. The plastic waste was first processed by pyrolysis, yielding a pyrolysis oil, pyrolysis gas and pyrolysis residue. Pyrolysis mass balances were based on experimental data [Netsch2025], while the process energy demand was assumed to correspond to 10% of the lower heating value of the feedstock [Netsch2024]. Pyrolysis gas was energetically utilized in a gas engine, whereas the solid pyrolysis residue was treated by municipal solid waste incineration (MSWI). The resulting pyrolysis oil was subsequently used as a co-feed in the developed FCC and DCC process models. As the waste treatment reference process, incineration of LDPE plastic waste in an MSWI plant with energy recovery was used. Electricity and district heat recovery were calculated using net efficiencies reported by ITAD [ITAD2023].

Foreground inventories were derived from the Aspen HYSYS simulations, while background processes were modeled using the ecoinvent 3.10 cut-off database. Climate change impacts were quantified as Global Warming Potential over a 100-year time horizon (GWP100) using the Environmental Footprint (EF) 3.1 method [AndreasiBassi2023]. Plastic waste entered the recycling system under a zero-burden assumption.

For the product-based assessment, multifunctionality throughout the refinery process chain was addressed by mass allocation following the allocation logic recommended by PlasticsEurope for steam-cracker processes. For each individual process, feedstock-related burdens were allocated by mass across all resulting products, whereas process energy demand and direct process emissions were allocated by mass across the respective main products [PlasticsEurope2017].

For the waste-treatment assessment, system expansion was applied by crediting the substitution of conventionally produced refinery products and recovered energy. Refinery-product credits were based on the corresponding products from the respective 100% conventional-feed FCC or DCC reference configuration, whereas credits for recovered electricity and district heat were derived from the ecoinvent database [Wernet2016]. The complete co-processing system, including the required fossil co-feed, was considered. All refinery products generated in the corresponding co-processing case were credited by substitution of their conventional production routes, thereby accounting for both the fossil

feedstock required for co-processing and the complete product output of the FCC or DCC unit.

3. Results and Discussion

The developed modeling framework was applied to systematically investigate the integration of LDPE-derived pyrolysis oil into conventional FCC and DCC operation. This chapter first evaluates the capability of the process models to reproduce industrially representative operating conditions before analyzing the influence of pyrolysis oil on product distribution under controlled cracking conditions. Subsequently, the practical implications of increasing pyrolysis oil integration are assessed by considering industrial operating constraints, followed by an environmental evaluation of the investigated process configurations using life cycle assessment. This structure enables a clear distinction between model performance, fundamental feedstock effects, engineering limitations and the resulting environmental implications.

3.1 Model performance assessment

Before investigating the influence of pyrolysis oil on FCC operation, the performance of the developed process models was assessed using published industrial operating data. The purpose of this assessment was not to establish universally valid representations of commercial FCC units, but to demonstrate that the implemented models reproduce the characteristic operating behavior and product distribution with sufficient accuracy for the subsequent comparative analysis.

Figure 2 compares the simulated product yields of the conventional FCC configuration with the reference data reported by Chang et al. [Chang2012]. Data for the C3 fraction at 560 °C are not depicted due to missing literature data. Overall, the model reproduces the literature product distribution with good agreement. The gasoline yield is reproduced closely over most of the investigated temperature range. Larger deviations occur for LCO and, at high cracking severity, for the C3 fraction. Overall, the calculated conversion agrees well with the industrial reference data. Given the simplified lumped kinetic approach and the limited availability of detailed industrial process information, the agreement is considered sufficient to investigate relative changes caused by pyrolysis oil co-processing, rather than to predict individual product yields under all operating conditions with high precision.

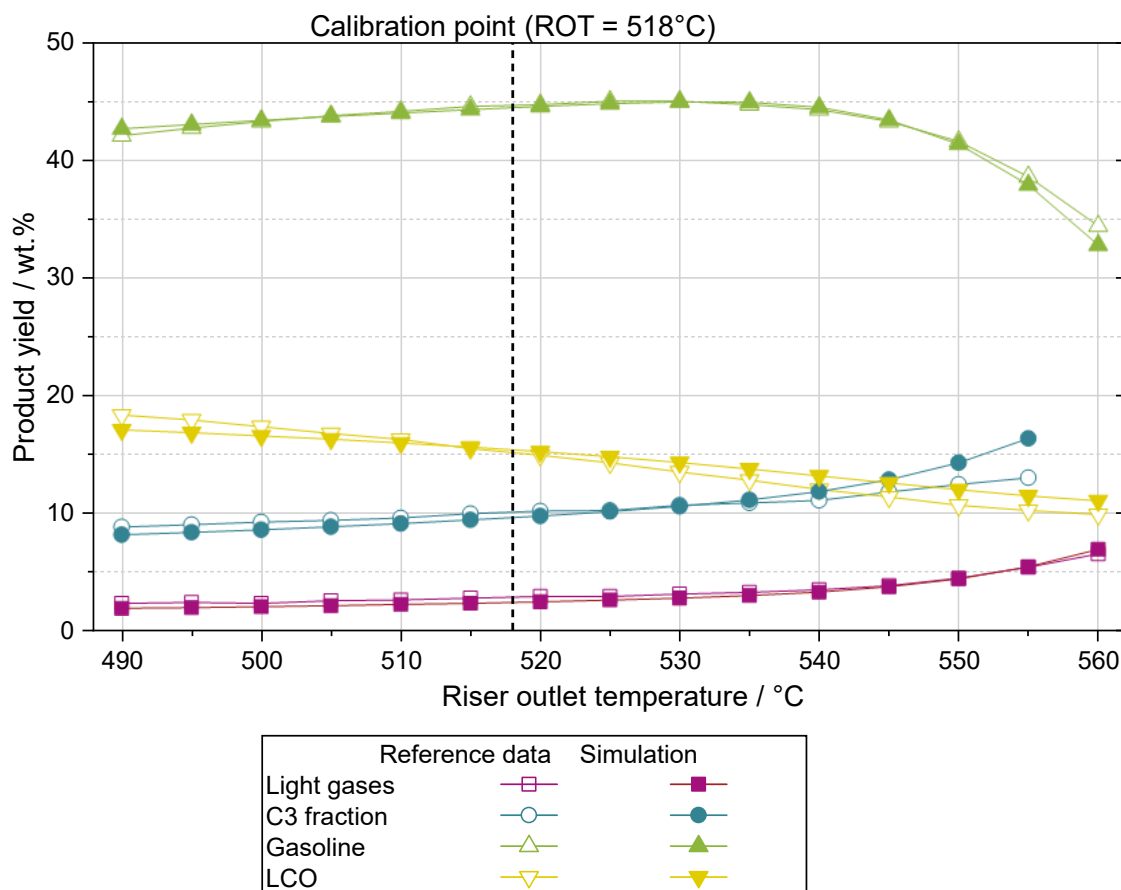


Figure 2: Comparison of modeled product yields with literature data for the conventional FCC model over a reactor outlet temperature (ROT) range of 490–560 °C. Literature data adapted from Chang et al. [Chang2012]. The dashed vertical line indicates the ROT (518 °C) used for model calibration.

The DCC configuration was calibrated with the operating point reported by Deng et al. [Deng2002], using representative DCC operating conditions derived from Deng et al. and Letzsch et al. [Deng2002, Letzsch2015]. Compared with the conventional FCC configuration, considerably fewer reference data are publicly available for DCC operation, preventing an independent performance assessment over a broader operating range. Consequently, the DCC model should primarily be interpreted as a comparative process model that captures the characteristic trends of olefin-targeted high-severity operation rather than as a broadly assessed representation of a specific commercial DCC unit. Nevertheless, the simulated product distribution exhibits the expected shift toward increased light-olefin production and reduced gasoline yields, providing an appropriate basis for the comparative evaluation of pyrolysis oil co-processing under representative DCC conditions.

Overall, both process models provide a suitable modeling framework for analyzing the impact of pyrolysis oil integration on product distribution and process operation. The following sections therefore focus on the relative effects of increasing pyrolysis oil substitution on product distribution and process performance rather than on the absolute prediction of individual product yields.

3.2 Reaction behavior under controlled cracking conditions

To isolate the intrinsic influence of LDPE-derived pyrolysis oil on FCC reaction behavior from process-related limitations, the different feed mixtures were first evaluated under a common matrix of controlled cracking conditions by systematically varying the riser outlet temperature (ROT) and catalyst-to-oil ratio (C/O). Four feed compositions were investigated, consisting of the conventional FCC feed and co-processing scenarios containing 10, 20 and 30 wt.%

pyrolysis oil. The investigated parameter range extends from conventional FCC conditions to high-severity conditions approaching those applied in DCC operation, thereby allowing the influence of cracking severity to be assessed independently of DCC-specific differences in catalyst formulation, feedstock, and process configuration.

Figure 3 illustrates the calculated yields of propylene, gasoline and light cycle oil (LCO) as functions of cracking severity. Regardless of feed composition, all investigated mixtures exhibit the characteristic response of catalytic cracking to increasing ROT and C/O. Propylene production increases continuously, whereas LCO formation decreases as heavier hydrocarbons are converted into lighter products. Gasoline exhibits the typical intermediate-product behavior: at ROTs of 520 and 540 °C, its yield initially increases with C/O before reaching a maximum and declining at higher severity. At 560 °C, gasoline yields decrease over most of the investigated C/O range, indicating that secondary cracking toward lighter gaseous products already predominates. These severity-dependent trends are consistent with experimental FCC studies, which report increasing propylene formation and decreasing LCO yields with increasing temperature and catalyst-to-oil ratio, while gasoline passes through a maximum as secondary cracking becomes dominant [Li2007, Acosta-López2025].

At a given ROT and C/O ratio, increasing pyrolysis oil substitution systematically shifts the product distribution toward gasoline-range hydrocarbons while reducing LCO formation. The increase in propylene yield is comparatively smaller than the changes observed for gasoline and LCO. This behavior can be attributed to the compositional differences between the LDPE-derived pyrolysis oil and the conventional FCC feed. As discussed in Section 2, the pyrolysis oil consists predominantly of paraffinic and olefinic hydrocarbons and exhibits a boiling distribution shifted toward lower temperatures compared with the conventional FCC feed. Consequently, a considerable fraction of its components already lies within or close to the gasoline boiling range and requires fewer cracking steps to form gasoline-range products than the heavier and more aromatic components of the conventional FCC feed. At the same time, replacing part of the high-boiling conventional FCC feed reduces the amount of material contributing to the LCO boiling range, explaining the systematic decrease in LCO yield. Under conventional FCC conditions, only part of the additional gasoline-range material undergoes further secondary cracking, limiting the corresponding increase in propylene production. These observations are in good agreement with previous experimental investigations of polyolefin-derived pyrolysis oils, which likewise reported increased gasoline production accompanied by reduced LCO yields during FCC co-processing [Bücheler2022, Passamonti2012].

Overall, under the investigated conditions, the primary effect of LDPE-derived pyrolysis oil is a shift in product selectivity toward gasoline-range hydrocarbons and away from middle-distillate fractions. Importantly, the resulting increase in gasoline yield does not solely arise from additional conversion, as a considerable fraction of the full-range pyrolysis oil already falls within the gasoline boiling range. This raises the question whether upstream fractionation of full-range pyrolysis oil could enable a more targeted utilization of individual boiling-range fractions. The evaluation of such fractionation strategies is beyond the scope of the present study. For the investigated full-range feed, however, the additional gasoline-range material represents an intermediate product pool that could be utilized more effectively in process configurations specifically designed to intensify secondary gasoline cracking.

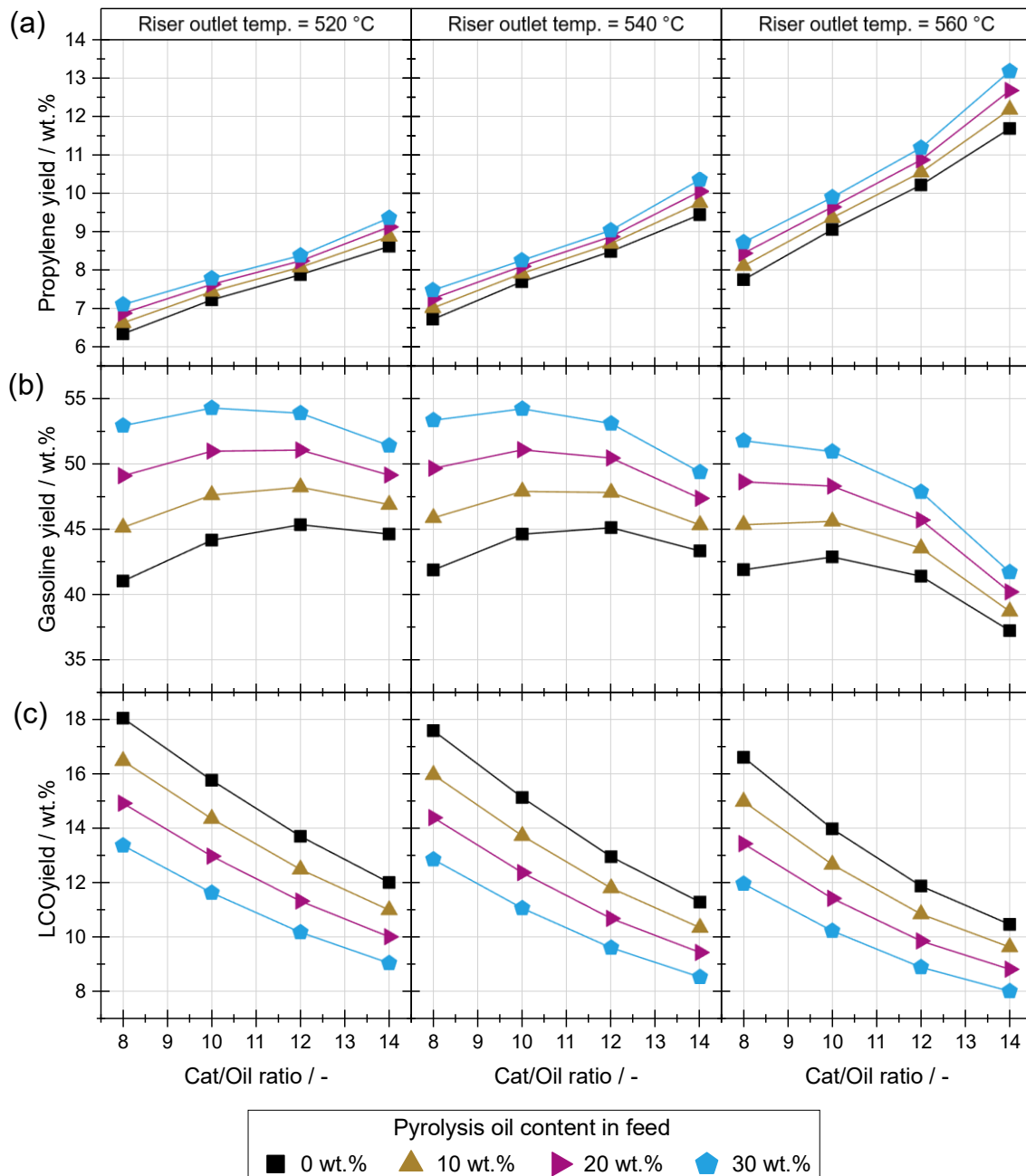


Figure 3: Simulated product yields under controlled FCC cracking conditions as a function of catalyst-to-oil ratio, riser outlet temperature (ROT), and the share of LDPE-derived pyrolysis oil in the feed: (a) propylene, (b) gasoline, and (c) light cycle oil (LCO).

3.3. Co-processing under industrial constraints

To investigate whether the favorable reaction behavior identified in Section 3.2 persists under industrially representative process constraints, the co-processing of LDPE-derived pyrolysis oil was evaluated under representative operating conditions for both conventional FCC and Deep Catalytic Cracking (DCC). Unlike conventional FCC, DCC is specifically designed to maximize the conversion of gasoline-range hydrocarbons into light olefins by operating at higher cracking severity. Beyond reaction chemistry, however, industrial implementation is additionally constrained by the thermal balance of the FCC unit and may impose additional requirements on the surrounding refinery infrastructure.

The influence of increasing pyrolysis oil substitution on the key operating parameters of both

process configurations is presented in Figure 4. Increasing the pyrolysis oil co-processing ratio reduces coke formation under both FCC and DCC conditions (Figure 4d), thereby decreasing the heat released during catalyst regeneration. At the same time, the lower boiling range and reduced cracking requirement of the pyrolysis oil decrease the specific heat demand of the cracking reactions (Figure 4c), partially compensating for the lower heat generation in the regenerator. Nevertheless, the reduction in coke-derived heat progressively lowers the regenerator temperature (Figure 4a). To maintain the specified riser outlet temperature, the catalyst-to-oil ratio must therefore be increased (Figure 4b), indicating higher catalyst circulation requirements and a progressively narrowing operating window.

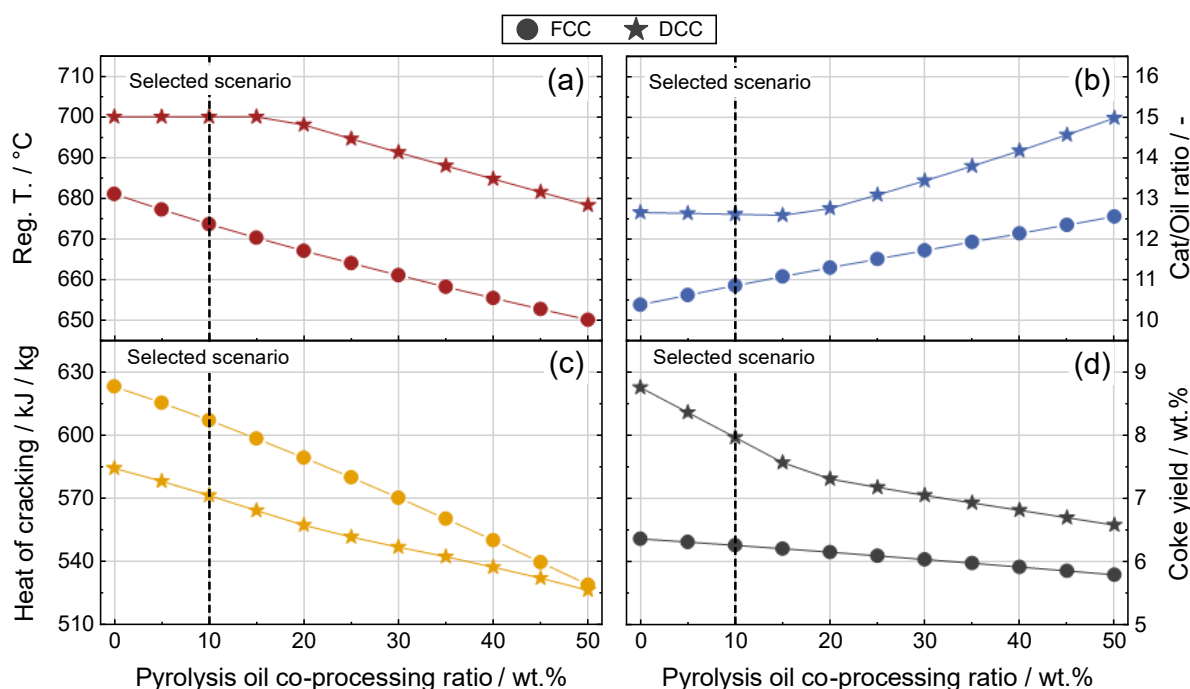


Figure 4: Influence of pyrolysis oil co-processing ratio on key operating parameters under conventional FCC (●) and DCC (★) conditions: (a) regenerator temperature, (b) catalyst-to-oil ratio, (c) heat of cracking, and (d) coke yield. The vertical dashed line indicates the selected scenario at a pyrolysis oil co-processing ratio of 10 wt.%.

The thermal response differs between the two process configurations. Under conventional FCC conditions, the regenerator temperature decreases continuously with increasing pyrolysis oil substitution. Under DCC conditions, the regenerator temperature initially remains nearly constant because the decreasing heat surplus can be compensated by reducing the duty of the catalyst cooler. Once this operational reserve is increasingly consumed, the regenerator temperature also begins to decline, accompanied by a stronger increase in the required catalyst-to-oil ratio. The reactor–regenerator heat balance therefore represents the primary process-level constraint on increasing pyrolysis oil substitution in the investigated configurations.

The corresponding changes in product distribution are summarized in Figure 5. Increasing pyrolysis oil substitution shifts the product slate toward lighter products in both process configurations, as reflected by increasing gasoline yields, decreasing LCO yields, and, particularly under DCC conditions, increasing light-olefin production. Under conventional FCC operation, this effect is dominated by a pronounced increase in gasoline yield (Figure 5a), whereas LPG (Figure 5b) and propylene (Figure 5c) yields remain nearly constant. Under DCC conditions, gasoline production increases only moderately, while LPG and propylene yields increase more distinctly, indicating more extensive secondary cracking of gasoline-range intermediates at the higher cracking severity. The LCO yield decreases continuously with increasing pyrolysis oil substitution in both configurations (Figure 5d), reflecting the progressive shift away from middle-distillate products. Consequently, the characteristic

selectivity trends identified under controlled cracking conditions are retained under industrially representative operation, while the differences between FCC and DCC become increasingly pronounced. While conventional FCC primarily retains the additional conversion as gasoline, DCC more effectively exploits the resulting gasoline-range intermediate pool for light-olefin production.

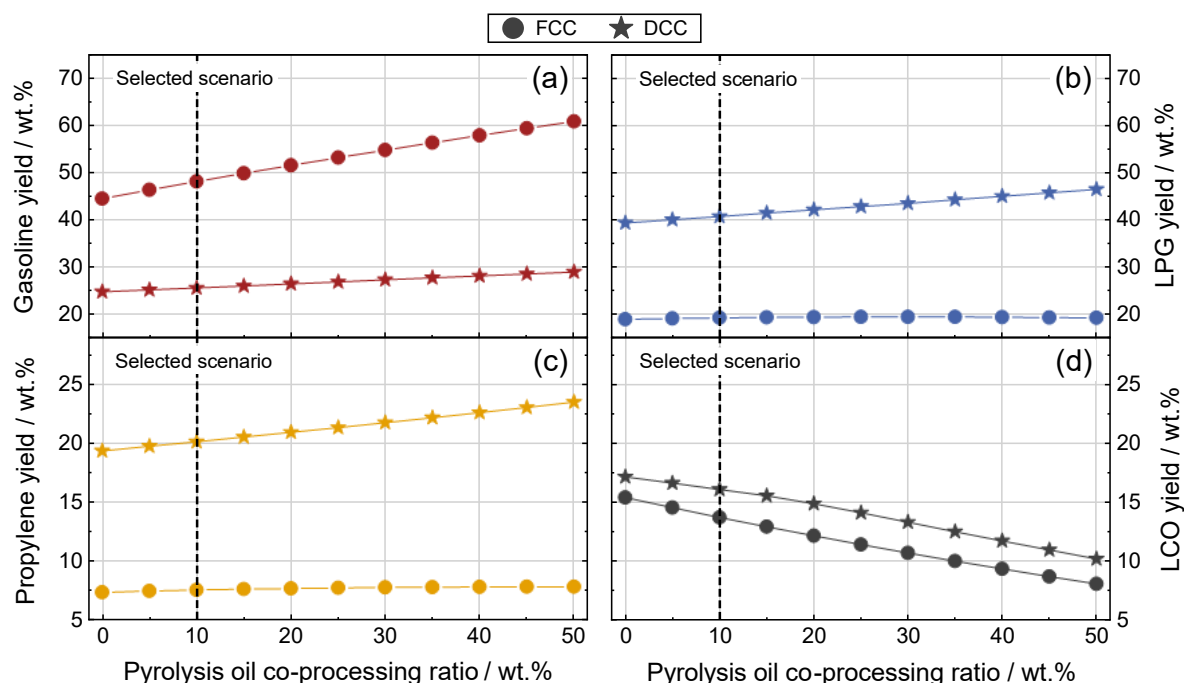


Figure 5: Influence of pyrolysis oil co-processing ratio on the simulated product yields under conventional FCC (●) and DCC (★) operating conditions: (a) gasoline, (b) liquefied petroleum gas (LPG), (c) propylene, and (d) light cycle oil (LCO). The vertical dashed line indicates the selected scenario at a pyrolysis oil co-processing ratio of 10 wt.%.

Beyond the reactor–regenerator heat balance, implementation of pyrolysis oil co-processing may therefore require adaptations to both upstream feed handling and downstream product recovery. As indicated by the broad boiling distribution shown in Figure 1, the investigated full-range pyrolysis oil combines comparatively volatile components with a substantial high-boiling fraction. Depending on feed pressure and preheating conditions, these components may partially vaporize upstream of the feed injection nozzles, potentially resulting in two-phase flow and altered atomization behavior. At the same time, the high-boiling fraction still requires efficient vaporization upon contact with the regenerated catalyst. Consequently, direct blending with the conventional feed may require adaptation of the preheating and injection system. Separate feed introduction represents one potential option for maintaining independent control of pyrolysis oil temperature and atomization conditions, as demonstrated for the co-processing of pyrolysis-derived alternative feedstocks in FCC units [Pinho2017]. Moreover, the higher conventional feed-preheat temperature applied in the DCC configuration further increases the potential for premature vaporization of the volatile pyrolysis-oil fraction and therefore strengthens the case for independently controlled feed introduction.

Additional constraints may arise in the downstream gas-recovery section. Increasing LPG and propylene production raises the amount of light hydrocarbons that must be processed, potentially increasing the load on the wet-gas compressor and subsequent gas-recovery equipment [OrtegaGarcía2024]. This aspect becomes particularly relevant for olefin-oriented DCC operation, for which the present simulations predict substantially higher LPG and propylene yields. These considerations underline the trade-off associated with olefin-oriented DCC operation, which more effectively converts the additional gasoline-range material into LPG and propylene while simultaneously increasing the requirements placed on both feed conditioning and downstream gas recovery.

Considering the combined effects on the reactor–regenerator heat balance, product distribution and the additional equipment-integration considerations discussed above, a co-processing ratio of 10 wt.% was selected as a conservative representative scenario for the subsequent environmental assessment. At this substitution level, the simulations retain sufficient thermal operating margin while already capturing the characteristic product-selectivity effects of pyrolysis oil co-processing. The selected ratio should therefore not be interpreted as a general technical limit, but as a process- and feed-specific scenario suitable for assessing the environmental implications of industrial co-processing.

3.4. Environmental assessment

The environmental implications of the selected 10 wt.% co-processing scenario were evaluated from two complementary perspectives. First, a product-based assessment quantified the climate change impact associated with the production of 1 kg of propylene. Second, a waste-treatment perspective compared the full chemical recycling route with the conventional incineration of 1 kg of LDPE waste. The two assessments therefore address different questions and should not be interpreted as directly comparable results.

Figure 6a presents the product-based climate change impacts of the conventional and co-processing scenarios under FCC and DCC conditions. All investigated catalytic cracking scenarios exhibit impacts between 1.30 and 1.46 kg CO₂-eq per kg of propylene. For comparison, the conventional steam-cracking route exhibits an impact of 1.95 kg CO₂-eq per kg of propylene [Dellenbach2023]. Because the underlying system boundaries and allocation procedures are not fully harmonized, this value should primarily be interpreted as an external plausibility benchmark rather than as a direct process comparison. The comparatively low impacts obtained for the FCC and DCC configurations may partly reflect the integrated heat supply of the reactor–regenerator system and the distribution of process burdens across a broad product slate through mass-based allocation.

DCC operation exhibits a higher climate change impact than conventional FCC operation. The higher cracking severity increases coke formation, steam consumption and electricity demand, particularly for the regenerator air blower and wet-gas compressor. In addition, the higher catalyst replacement requirement increases the contribution associated with catalyst production. These additional burdens are only partially compensated by heat recovery from the catalyst cooler.

The substitution of 10 wt.% of the conventional feed by LDPE-derived pyrolysis oil does not substantially change the product-based climate change impact relative to the corresponding fossil reference configurations. Co-processing increases the overall conversion in both process configurations and consequently the total output of product streams considered in the mass-based allocation. The environmental burdens associated with feedstock production and FCC operation are therefore distributed over a larger product mass, reducing the burden allocated to each individual product, including propylene. This allocation effect is particularly relevant because the increase in propylene yield itself remains comparatively small under conventional FCC conditions.

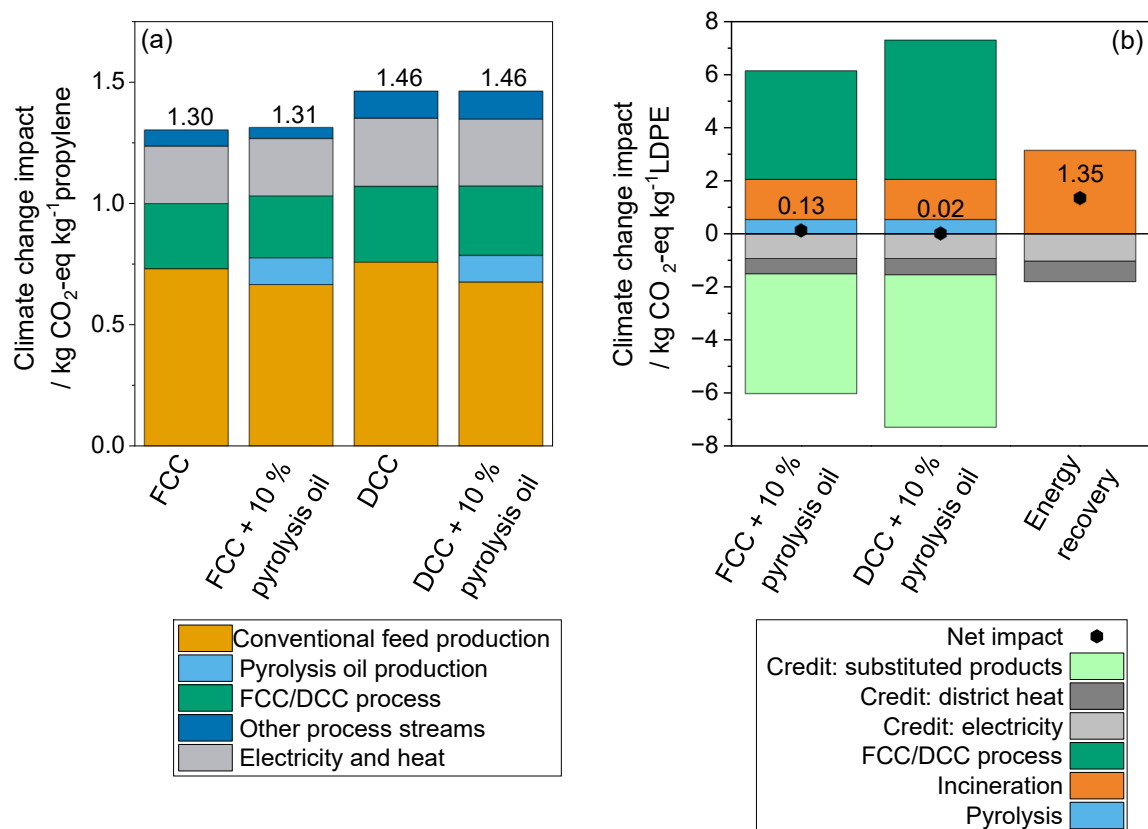


Figure 6: Climate change impacts of the 10 wt.% pyrolysis oil co-processing scenarios: (a) product-based assessment under FCC and DCC conditions, using 1 kg of propylene as the functional unit; (b) waste-treatment assessment of the FCC and DCC routes compared with direct LDPE incineration with energy recovery, using 1 kg of LDPE as the functional unit. Positive contributions represent process-related burdens, whereas negative contributions indicate credits. Black markers indicate the net climate change impact.

In addition, the reduced coke yield lowers direct CO₂ emissions from coke combustion in the regenerator. These favorable effects are counterbalanced by the upstream burdens associated with pyrolysis oil production, as only part of the LDPE feedstock is recovered as pyrolysis oil, while the remaining fractions are converted into pyrolysis gas and solid residues. Considering the simplified representation of pyrolysis-oil production, coproduct treatment and mass allocation applied in this study, the product-based climate impacts of the fossil and co-processing configurations should therefore be regarded as essentially equivalent rather than as evidence of a significant environmental improvement. Co-processing nevertheless enables the incorporation of recycled carbon into the FCC product slate without a relevant increase in the climate impact of propylene production.

A different conclusion is obtained when the complete recycling route is assessed from the perspective of waste LDPE treatment. As shown in Figure 6b, direct incineration results in a net climate change impact of 1.35 kg CO₂-eq per kg of LDPE, including credits for the generated electricity and district heat. In contrast, the FCC and DCC co-processing routes achieve net impacts of 0.13 and 0.02 kg CO₂-eq per kg of LDPE, respectively. This corresponds to reductions of up to 1.32 kg CO₂-eq per kg of LDPE compared with incineration.

Within the applied system boundaries, the substantial reduction is primarily attributable to the different fate of the carbon contained in the LDPE waste. During incineration, the polymer carbon is directly oxidized to CO₂, whereas chemical recycling transfers a large fraction of the carbon into refinery and petrochemical products that substitute conventionally produced equivalents. The resulting product credits outweigh most of the burdens associated with pyrolysis and FCC processing. DCC achieves a slightly lower net impact than conventional

FCC because its altered product distribution results in greater substitution credits, which compensate for the additional process burden associated with the more severe operating conditions.

Taken together, the two assessment perspectives provide a nuanced environmental interpretation. From a product perspective, the favorable effects of increased conversion, allocation over a larger product output and reduced coke combustion approximately compensate for the additional upstream burden of pyrolysis oil production. From a waste-management perspective, however, chemical recycling through FCC or DCC co-processing provides a substantial climate benefit compared with the energetic utilization of LDPE waste. The magnitude of this benefit remains dependent on the pyrolysis-oil yield, energy integration and the methodological treatment of substituted products.

3.5. Limitations and implications

The quantitative results of this study are specific to the investigated full-range LDPE-derived pyrolysis oil and the selected FCC and DCC configurations. In addition, olefinic pyrolysis-oil components were represented by the corresponding paraffinic lumps because dedicated olefin reaction pathways were unavailable, which may underestimate olefin retention in the product streams. Consequently, the identified product shifts, thermal constraints and selected co-processing ratio of 10 wt.% should not be interpreted as universally applicable.

Further uncertainty arises from the modeling approach. The conventional FCC model was assessed over a broader operating range using available reference data, whereas the DCC configuration was calibrated to a single industrial reference point and should therefore primarily be interpreted as a comparative trend model. Moreover, the detailed design and capacity limitations of the feed-injection and downstream gas-recovery systems were outside the scope of the process model. The corresponding integration requirements discussed in Section 3.3 should therefore be interpreted as potential engineering constraints rather than quantified operating limits.

The environmental results are likewise dependent on the applied system boundaries and methodological assumptions, including the zero-burden treatment of plastic waste, mass-based allocation and credits for substituted conventional products. The magnitude of the waste-treatment benefit is influenced by the treatment of downstream product use. Carbon transferred into fuel-range products will ultimately be released as CO₂ if these products are combusted, meaning that substitution of conventional fuels does not avoid the corresponding end-use carbon emissions but primarily replaces their conventional production. In contrast, the fraction transferred into petrochemical intermediates enters material value chains, although its ultimate climate impact remains dependent on the subsequent product life cycle and end-of-life treatment. Furthermore, the upstream burden of the DAO feed used in the DCC process model was approximated by the VGO/AGO inventory used for the conventional FCC case, introducing additional uncertainty into the absolute environmental comparison between the two configurations.

Despite these limitations, the results indicate that FCC may provide a complementary integration route for broad-boiling pyrolysis oils that are less compatible with more feed-sensitive petrochemical processes. The observed dependence of product selectivity and thermal balance on feed composition further suggests that upstream fractionation could enable a more targeted distribution to suitable conversion routes. Future work should therefore investigate the influence of pyrolysis-oil composition and fractionation on FCC and DCC integration.

4. Conclusions

This study evaluated the co-processing of full-range LDPE-derived pyrolysis oil in conventional FCC and DCC units by combining refinery-scale process modeling with life cycle assessment. The FCC model reproduced the relevant product-yield trends over a broad operating range, whereas the DCC configuration was applied as a comparative trend model under industrially representative conditions.

Under controlled cracking conditions, increasing pyrolysis oil substitution shifted the product distribution from heavier fractions toward gasoline-range hydrocarbons. This behavior was attributed to the lower boiling range and predominantly paraffinic and olefinic composition of the pyrolysis oil. Under conventional FCC conditions, the additional conversion was therefore apparent mainly as increased gasoline production, while the increase in light-olefin yield remained limited. DCC operation exploited these gasoline intermediates more effectively and resulted in a more pronounced increase in LPG and propylene yields owing to DCC's higher cracking severity.

The reactor–regenerator heat balance emerged as the principal process limitation with increasing pyrolysis oil substitution. Increasing pyrolysis oil substitution reduced coke formation and the associated heat release during catalyst regeneration, resulting in lower regenerator temperatures and higher catalyst circulation requirements. A co-processing ratio of 10 wt.% was consequently selected as a conservative representative scenario that retains sufficient thermal operating margin while capturing the characteristic product-selectivity effects of pyrolysis oil co-processing. Additional adaptations to feed injection and downstream gas recovery may be required, particularly for olefin-oriented DCC operation. This co-processing ratio is specific to the investigated full-range LDPE pyrolysis oil and should not be interpreted as a universal limit for other feedstocks or fractionated pyrolysis oils.

From a product perspective, the climate change impact of propylene production remained essentially unchanged within the assumptions and simplifications of the assessment. The favorable effects of increased conversion, mass allocation over a larger product output and reduced coke combustion were approximately balanced by the additional burdens of pyrolysis oil production. From a waste-treatment perspective, however, the complete chemical recycling route provided a substantial climate benefit compared with direct LDPE incineration within the applied system boundaries, as a larger share of the waste carbon was transferred into refinery products that substituted conventionally produced equivalents.

Overall, the results demonstrate that existing FCC infrastructure can provide a flexible platform for integrating plastic-waste-derived feedstocks into established refinery and petrochemical value chains. Its ability to accommodate different feedstocks and adjust the product slate between fuel-range products and petrochemical intermediates may strengthen carbon-supply resilience through greater feedstock and product flexibility. DCC provides additional opportunities to direct the product slate toward light olefins when petrochemical feedstock production is prioritized.

References

- Abdulrahman, A. J. et al. Advancing circular plastics: hydrotreatment of pyrolysis oils for high-yield ethylene production. *Waste Management* 211, (2026).
- Acosta-López, J. G. et al. Unravelling Vacuum Gas Oil Catalytic Cracking: The Influence of the Catalyst-to-Oil Ratio on FCC Catalyst Performance. *Catalysts* 15, (2025).
- Akah, A. & Al-Ghrami, M. Maximizing propylene production via FCC technology. *Applied Petrochemical Research* 5, (2015).
- Al-Samhan, M. et al. Prospects of refinery switching from conventional to integrated: An opportunity for sustainable investment in the petrochemical industry. *Fuel* 310, (2022).
- Andreas Bassi, S. et al. Updated Characterisation And Normalisation Factors For The Environmental Footprint 3.1 Method; Publications Office of the European Union, (2023).
- Bachmann, M. et al. Towards circular plastics within planetary boundaries. *Nature Sustainability* 6, (2023).
- Büchle, M. Heavy residues and pyrolysis oils as feedstocks in the FCC process for a more sustainable production of olefins and high-octane gasoline. TU Wien (2022).
- Chang, A.-F. et al. *Refinery Engineering Integrated Process Modeling and Optimization*. Wiley-VCH, (2012).
- Dellenbach, D.; Fröhlich, T. Unsaturated hydrocarbons production, steam cracking operation, average; propylene, RER, Allocation, cut-off, ecoinvent database 3.10; Ecoinvent Association, (2023).
- Deng, R. et al. Experimental Study of the Deep Catalytic Cracking Process in a Downer Reactor. *Industrial & Engineering Chemistry Research* 41, (2002).
- Dorazio, L. & Fu, J. Transforming refineries' opportunities through FCC. Digitalrefining PTQ Q4 2023, (2023).
- Geyer, R. et al. Production, use, and fate of all plastics ever made. *Science Advances* 3, (2017).
- Hennig, M. et al. Entrained-Flow Gasification for the Utilization of Pyrolysis Oil from Mixed Plastic Waste. *ACS Sustainable Chemistry & Engineering* 13 (2025).
- ITAD – Interessengemeinschaft der Thermischen Abfallbehandlungsanlagen in Deutschland e.V. ITAD Jahresbericht 2022/23; (2023). <https://www.itad.de/ueber-uns/mehr/jahresbericht/itadjahresbericht-2022-2023>.
- Kumagai, S. et al. Chemical Feedstock Recovery Through Plastic Pyrolysis: Challenges and Perspectives Toward a Circular Economy. *ChemSusChem* 18, (2025).
- Letzsch, W. Fluid Catalytic Cracking (FCC) in Petroleum Refining. in *Handbook of Petroleum Processing*. Springer International Publishing, (2015).
- Li, X. et al. Effects of Temperature and Catalyst to Oil Weight Ratio on the Catalytic Conversion of Heavy Oil to Propylene Using ZSM-5 and USY Catalysts. *Journal of Natural Gas Chemistry* 16, (2007).
- Mastry, M. C. et al. Processing renewable and waste-based feedstocks with fluid catalytic cracking: Impact on catalytic performance and considerations for improved catalyst design. *Frontiers in Chemistry* 11, (2023).
- Netsch, N. et al. Thermogravimetric study on thermal degradation kinetics and polymer interactions in mixed thermoplastics. *Journal of Thermal Analysis and Calorimetry* 150 (2024).
- Netsch, N. et al. Chemical characterization of mixed plastic pyrolysis oils relevant for cracker reintegration by advanced two-dimensional gas chromatography. *Fuel Processing Technology* 280, (2025).
- Ortega García, F. D. J. & Mar Juárez, E. Polyethylene waste co-processing in fluid catalytic cracking plants. *Cleaner Engineering and Technology* 19, (2024).
- Passamonti, F. J. & Sedran, U. Recycling of waste plastics into fuels. LDPE conversion in FCC. *Applied Catalysis B: Environmental* 125, (2012).
- Pinho, A. D. R. et al. Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production. *Fuel* 188, (2017).

PlasticsEurope. PlasticsEurope recommendation on Steam Cracker allocation. (2017), https://plasticseurope.org/wp-content/uploads/2021/12/PlasticsEurope_recommendation_on_Steam_Cracker_allocation-_Juillet_2018.pdf.

Sadeghbeigi, R. *Fluid Catalytic Cracking Handbook: An Expert Guide to the Practical Operation, Design, and Optimization of FCC Units*. 4th ed., Butterworth-Heinemann, (2020).

Stallkamp, C. et al. Economic and environmental assessment of automotive plastic waste end-of-life options: Energy recovery versus chemical recycling. *Journal of Industrial Ecology* 27, (2023).

Vogt, E. T. C. & Weckhuysen, B. M. Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis. *Chemical Society Reviews* 44, (2015).

Wernet, G. et al. The ecoinvent database version 3 (part I): overview and methodology. *International Journal of Life Cycle Assessment* 21 (9), (2016).

Circular Carbon via Gasification of Complex Waste Streams

A. Bader¹, L. Seidl², T. Horst³

¹BASF SE, Global Technology Basic Petrochemicals, Ludwigshafen am Rhein, Germany, ²BASF SE, Process Development Petrochemicals, Ludwigshafen am Rhein, Germany, ³BASF SE, BASF Renewable Carbon, Ludwigshafen am Rhein, Germany

The transition toward a circular and climate-neutral chemical industry requires technologies capable of converting complex waste streams into valuable secondary raw materials. Gasification has emerged as a promising pathway because it can accommodate a broad variety of carbon-containing residues, including those that are incompatible with mechanical or molecular recycling technologies. Demonstrating the recyclability of diverse feedstocks through gasification is therefore essential to closing industrial carbon loops and reducing reliance on fossil resources.

Within this context, two representative pilot studies were conducted to explore the gasification behavior of complex residual materials. Automotive Shredder Residue (ASR) and post-consumer adsorption hygiene products (AHP) such as diapers were investigated as illustrative examples for highly heterogeneous, conventionally non-recyclable waste streams. The AHP gasification project demonstrated the successful production of stable synthesis gas, confirming its technical feasibility even for highly complex feedstocks. The ASR gasification project extended beyond syngas generation and demonstrated the full conversion pathway from heterogeneous waste to value-added chemical products. The produced synthesis gas was further processed into Fischer–Tropsch intermediates and ultimately converted into polyurethane (PU) used in automotive steering wheels, thereby closing the loop from end-of-life automotive waste to high-value polymer products. This demonstrates that gasification can serve as a robust recycling route for complex waste materials that currently lack viable alternatives and can integrate seamlessly into existing chemical value chains.

Beyond the two example feedstocks examined here, additional gasification initiatives are underway to investigate a wider range of residues—including mixed plastics, composite packaging waste, textile fractions, and biomass-derived industrial by-products. Furthermore, electrification of gasification is being explored as a promising approach to enable higher carbon recycling rates through improved process control and energy efficiency. While this emerging technological pathway offers significant potential, it is currently still in the research and development stage and requires further validation prior to industrial implementation.

Keynote – Electrification of Gasification Processes by Plasma Integration

M. Gräbner^{1,2,3}, R. Schimpke^{1,3}

¹TU Bergakademie Freiberg, IEC - Institute for Energy Process Engineering and Chemical Engineering, Freiberg, Germany, ²Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Division Energy and Process Engineering – Circular Carbon Technologies, Freiberg, Germany, ³TU Bergakademie Freiberg, ZeHS - Center for Efficient High Temperature Processes and Materials Conversion, Freiberg, Germany

The keynote will address the question of how renewable electricity can be integrated into gasification processes for converting low-grade, high-ash waste with the lowest possible intrinsic CO₂ generation, while maintaining high-quality syngas and stable operation [1].

The presentation will focus on the technical feasibility and performance potential of allothermal plasma-assisted gasification in two representative reactor concepts, using a fixed-bed gasifier equipped with a H₂O thermal torch and a fluidized-bed gasifier with internal electric arc as building blocks for electrified circular carbon technologies.

A technology survey [2] identified arc plasmas as being suitable for integration on a large scale into slagging and fluidized-bed systems. Based on this, two experimental platforms were realized. In the fixed-bed system, a non-transferred arc plasma using pure steam as the plasma gas is used for gasification of carbonaceous waste products (e.g. graphite, plastics, GFRP/CFRP and waste wood) at temperatures above 1300 °C. In the fluidized bed, a free-burning arc [3] was integrated into the internal circulation zone of a sewage sludge gasifier that was operated with steam and CO₂. Test campaigns assessed stationary operation, syngas yield and composition, arc stability, and electrode erosion under autothermal and allothermal conditions.

The results demonstrate that plasma-assisted gasification can consistently convert low-grade, high-ash feedstocks into high-quality syngas while directly integrating electrical power. In the fixed-bed concept, syngas production was governed by the water–gas shift and the Boudouard reaction. In the fluidized bed, the integrated arc maintained high internal temperatures, achieving high conversion rates, high gas quality and reducing slagging. Optimizing the power supply and electrode geometry enabled increased plasma powers and extended stable operation.

Overall, electrified, plasma-assisted gasification appears to be a promising key technology for circular carbon systems, enabling the highest possible carbon efficiency.

KEYWORDS

Circular Carbon Technology, Chemical Recycling, Gasification, Electrification, Plasma integration

[1] Helf, A., Keller, F., Gräbner, M. 2026. Electrification of gasification-based chemical recycling - A techno-economic assessment, *Energy Conversion and Management* 353, 121181.

[2] Kuznetsov, V.A., Gräbner, M., Schimpke, R., Uhrlandt, D., Richter, A. 2026. Systematic evaluation of gasifiers driven by the high-enthalpy plasma supply, *Fuel* 417, 138538.

[3] Pieterse, P., Gonzalez, D., Najam, A., Schimpke, R., Gräbner, M., Uhrlandt, D. 2025. Towards plasma-enhanced gasification: Investigating free-burning carbon arcs in molecular gas mixtures, *Plasma Physics and Technology* 12 (1), p. 52-55.

Integration of a free-burning plasma arc into a fluidized-bed gasification system

R. Schimpke^{1,2}, V. A. Kuznetsov¹, M. Gräbner^{1,2,3}, P. J. Pieterse⁴, D. Uhrlandt⁴

¹Institute of Energy Process Engineering and Chemical Engineering, TU Bergakademie Freiberg, Freiberg, Germany

²Center for Efficient High Temperature Processes and Materials Conversion, TU Bergakademie Freiberg, Freiberg, Germany

³Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Division Energy and Process Engineering – Circular Carbon Technologies, Freiberg, Germany

⁴Leibniz Institute for Plasma Science and Technology e.V., Greifswald, Germany

Abstract

Syngas production from secondary feedstock by means of plasma-assisted gasification covers a wide field of technologies with different development states from lab to industrial scale. This contribution presents the development and integration of a DC plasma arc system into the COORVED pilot-scale plant to make this fluidized bed gasifier ready for allothermal sewage sludge gasification along with high-value syngas production. The whole work was conducted within the framework of the PhosCOOR project. Its primary objective was to create reaction conditions that favor thermochemical phosphorus release into the gas phase through strongly reducing conditions and high temperatures by means of electrical energy input, independent of the gasification agent composition.

Three plasma generation techniques have been considered for the integration in the gasification plant: radio-frequency plasma, microwave plasma and an arc plasma. A comparison based on literature research resulted in the choice of a free-burning arc plasma, due to its high temperatures, avoided contamination of the gasification products and neglectable cooling efforts. Its integration into the existing autothermal gasification plant is described in detail as well as preliminary investigations to define the operating parameters.

Experimental campaigns included a comparison of autothermal and allothermal (plasma-assisted) gasification modes. The feasibility of stable plasma-assisted operation over an extended time frame was demonstrated. The results show the successful development of a new plasma-enhanced fluidized-bed gasification principle and reveal that plasma-assisted gasification enables high syngas qualities with CO₂ concentrations down to 14 vol% (dry, N₂-free) compared to 45 vol% in an autothermal operation mode, even for low-quality feedstocks. An increase of the H₂/CO ratio from 1.1 (autothermal) to 1.9 for a plasma-assisted operation mode highlight the potential of plasma-assisted gasification. The results underline the potential of plasma technology to decouple process temperature from gasification agent composition, opening new avenues for process optimization and contributing to resource circularity and sustainable waste management.

1. Introduction

The integration of plasma technology into solid fuel gasification provides a promising advancement in the field of waste-to-products conversion by means of sustainable syngas production. Plasma-assisted gasification leverages the extreme temperatures (up to 10,000 °C) generated by ionized gas (plasma) to decompose organic and inorganic materials in order to produce syngas (a mixture of mainly H₂, CO, H₂O and CO₂), with minimal formation of tars and hazardous by-products. Plasma-driven gasification opens up the potential of converting electrical energy into chemical energy while enabling the gasification of feedstocks with low calorific value. It also allows precise control over reaction conditions, independent of the calorific value or moisture content of the feedstock. This enables a wide variety of waste materials, including hazardous, heterogeneous, and high-ash feedstocks like sewage sludge, municipal solid waste, and industrial residues to be chemically recycled. In turn, this offers a

pathway to recover energy and materials from waste streams that would otherwise be disposed of, supporting both economic and environmental goals.

Plasma gasification enables high process efficiency and the production of clean, high-calorific syngas suitable as fuel gas or for chemical synthesis, reduction processes or hydrogen production. The high temperatures enable the vitrification of inorganic residues into a stable, glass-like slag [1] that can be used in construction materials, reducing landfill dependency.

This technology is particularly attractive for the treatment of challenging waste streams such as sewage sludge, which is rich in inorganic matter, pathogens, and valuable nutrients like phosphorus — a highly demanding element where Germany and most European countries are completely dependent on imports from a few regions prone to supply disruptions [2].

Plasma-assisted gasification offers a technically viable and environmentally advantageous pathway for syngas production from sewage sludge, having the potential of combining chemical energy recovery with valorization of ash elements. While challenges related to energy efficiency and cost remain, ongoing research and pilot projects—particularly in Germany [3], [4], [5] and the UK [6]—demonstrate its potential. With stringent EU and national regulations driving phosphorus recovery, plasma integration into gasification systems is well positioned to play a key role in the sustainable management of sewage sludge and the transition towards a circular bioeconomy.

In this work a fluidized bed gasifier will be introduced, in which sewage sludge already has been successfully gasified in several autothermal gasification runs, as was reported by Ginsberg et al. [7]. The main intention of this work was to upgrade the gasifier by a plasma source to introduce additional energy into the system and further increase the reduction potential of the process and increase the syngas quality. Three principal plasma-generation technologies are suitable for providing the energy densities required for gasification: radio-frequency (RF), microwave (MW), and arc plasma [8]. These technologies can operate over different pressure ranges, scales, energy densities, and efficiencies, and they may be used either to heat the gasifying medium or to interact directly with the solid feedstock. A short overview is given in the next section.

2. Comparison of main plasma-generation technologies

2.1. Radio-frequency plasma [8].

RF plasma is generated by inductively or capacitively coupled electromagnetic fields. The electric or magnetic field accelerates electrons, which then transfer energy to heavy particles through elastic collisions, ionization, excitation, and dissociation. Large-scale RF torches commonly operate near 13.6 MHz, although the precise frequency depends on the torch design and operating conditions.

RF torches are electrodeless and can operate from near-thermal-equilibrium conditions to cold-plasma modes. They can use almost any plasma-forming gas and offer long operating lifetimes because the plasma does not contact electrodes. The absence of electrode erosion also prevents contamination of the processing medium, which is beneficial when a high-temperature, chemically pure reactive gas is required.

In an inductively coupled torch, the plasma is formed inside a nonconductive tube located near an induction coil. The tube protects the coil from the plasma and heat flux, but cooling the coil and tube increases heat losses and reduces overall efficiency. Because the coil and plasma are separated by the tube and a boundary layer, only part of the electromagnetic field is coupled into the plasma. For induction torches below 50 kW, the plasma-to-coil diameter ratio is typically 0.6–0.7, with a corresponding overall efficiency of approximately 50% for argon at pressures of 1–5 bar [9], [10].

2.2. Microwave plasma [8]

MW plasma is generated by electromagnetic waves whose wavelength is comparable to or smaller than the plasma dimensions. Commercial systems commonly use magnetrons operating at 2.45 GHz, corresponding to a wavelength of approximately 12.2 cm. Like RF plasma, MW plasma may operate in either near-equilibrium or non-equilibrium modes.

MW plasma torches can be coupled through cavities, waveguides, or surface waves. With appropriate ignition and excitation-mode selection, coupling efficiency can reach more than 99%, although this figure describes electromagnetic coupling rather than total plasma-generation efficiency. Overall efficiency is reduced by losses in the discharge tube, power source, and other torch components.

Cavity coupling is typically produced inside a microwave-transparent discharge tube, commonly made from quartz, which passes through a waveguide. Swirling gas is often used to stabilize the plasma flow. Solid-state amplifiers provide greater frequency stability and potentially better tuning, whereas magnetrons generally offer better efficiency and a more favorable output-power-to-cost ratio. Magnetron-based systems have been scaled to approximately 75 kW [11], with steam injection providing an additional thermal input of 60 kW.

MW coupling is strongest at relatively low plasma enthalpy. As plasma enthalpy increases, more microwave power is reflected because the plasma behaves increasingly like a radiating antenna. In gasification applications, the introduction of reactive particles can locally cool the discharge and reduce coupling efficiency. Although individual industrial microwave generators are commonly rated at up to approximately 100 kW, industrial microwave systems can achieve substantially higher total power levels through the combination of multiple generators, with large-scale implementation requiring increasingly complex power distribution, coupling, and system integration

2.3. Arc plasma [8]

Arc plasmas are thermal discharges that generally produce higher mass-average temperatures than RF and MW systems. A distinction must be made between different configurations. In a transferred arc, the arc is maintained either between two open electrodes and is free burning in the reaction chamber, or between a torch electrode and the feedstock or treated material, which acts as the counter-electrode and must be conductive. In a non-transferred arc torch, the arc is sustained between electrodes inside a discharge chamber, while a gas flow carries the plasma energy out of the torch into the process area or onto the treated material.

Thermal arc plasmas are usually close to local thermodynamic equilibrium because electron and gas temperatures differ by less than approximately 20%, even in low-power discharges. Arc generators can theoretically operate at pressures up to 25 MPa, power levels up to 50 MW, and efficiencies up to 95%, with electrode lifetimes exceeding 1000 hours [12]; however, these maximum values cannot generally be achieved simultaneously. At high plasma enthalpy, typically around 5000–6000 K, practical efficiencies are often 60–75% and electrode lifetimes may fall to 25–100 hours due to cooling losses and electrode erosion.

Most of the approaches to plasma gasification described in the literature use either plasma torches with non-transferred arcs or the plasma melting approach where the feedstock is utilized as the counter-electrode. The former is hampered by the need to add plasma gas and high cooling requirements, whereas the latter can only be applied in slagging gasification processes using conductive slag as counter-electrode. By comparison, applications involving open transferred arcs in gasification processes have hardly been studied. Free burning arcs between open electrodes are often subject to significant fluctuations. However, this characteristic can be utilized to achieve high energy injection and a broad distribution of energy in the reaction zone.

The use of graphite electrodes for free burning arc operation has the advantage that the

inevitable electrode erosion does not introduce contaminants such as metal vapor into the process. In addition, graphite electrodes are a standard good to manufacture and need little or no cooling, and the overall efficiencies can increase substantially. For these reasons and since it is a volumetric rather than directed heat supply, a free-burning plasma arc with graphite electrodes has been identified as a perfect match for fluidized bed gasification.

3. Reactor Design

The COORVED reactor (CO₂ Reduction by Innovative Gasifier Design) is a test-scale gasifier which is adapted to represent the so-called internal circulation (INCI) principle for experimental operation [13]. It benefits from the use of an internally circulating fluidized-bed principle (INCI). It can be described as a gas–solid flow arrangement in which material is transported upward in a central region and returned downward through an outer annular region, rather than being circulated through an external loop. Key features of the bench-scale COORVED reactor involve a thermal capacity of up to 100 kW, the operation at atmospheric pressure, and a single central nozzle for the gasification agent injection to induce the circulation [14] [15] [16].

The simplified flow diagram in Figure 1 divides the plant functionally into four main regions: the gasifier itself, including three reaction zones, gas cleaning, and gas disposal. The process is initially described in the following according to autothermal operation.

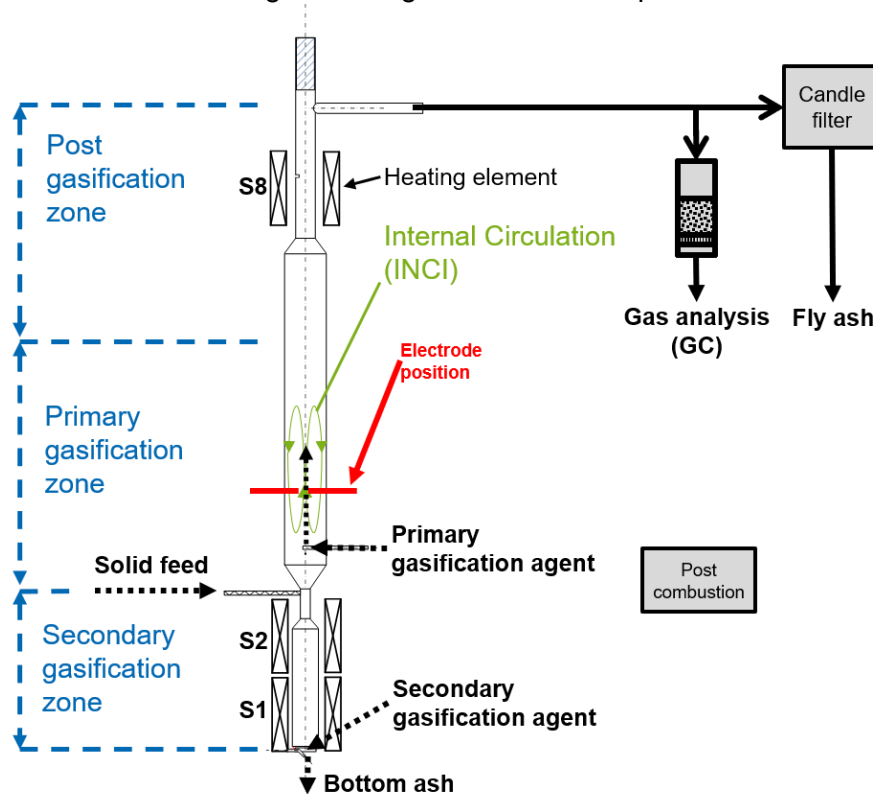


Figure 1 Simplified schematic of the COORVED gasification process

The COORVED reactor is 6 m tall with inner diameters of 250 mm in the secondary zone, 320 mm in the primary zone, and a 75 mm wide narrow section in between. It consists of nine segments where sections S1, S2 and S8 are equipped with electrical heaters. All segments include temperature and pressure measurement devices. As it is common practice, especially in the case of fluidized bed gasifiers, pressure sensor ports are purged with nitrogen to avoid vapor condensation. The reactor is heated up to 900°C using electrical heating and a natural gas start-up burner, before it switches to autothermal mode. The reactor operates at a maximum gauge pressure of 100 mbar with a mass input for low-calorific feedstock of 5–20 kg/h which is fed by a combination of a star feeder with a screw conveyer into the reactor.

It is discharged into the hot narrow section between the primary and the secondary reaction zone, as can be seen in Figure 1.

The primary and secondary gasification agents can be mixtures of oxygen, carbon dioxide, and steam. Nitrogen and argon can also be added as purging gases or as tracer gas for product gas volume flow determination. Combustible gases like CH_4 , CO , and H_2 can additionally be introduced. All permanent gases and water for the steam supply are measured and regulated via mass flow controllers and preheated. Ash is discharged by a screw conveyor at the bottom of the secondary zone, with the discharge rate controlled by pressure differences and a radiometric bed level detection. Fly ash is separated in an insulated candle filter. Eventually, the filtered syngas is fed into a post combustion unit.

3.1. Primary Gasification in the Fluidized Bed Zone

The feedstock introduced in the narrow section below the primary gasification zone is fluidized or entrained by the product gas from the secondary gasification zone. It is then transported into the primary gasification zone where a fluidized bed forms with generating the typical spout pattern of the particle circulation. The vertically upward-injected primary gasification agent containing oxygen induces the internal circulation zone in the center, known as a "jetting fluidized bed" [17], [18]. This promotes strand formation, improves gas mixing, and favors gasification reactions. Exothermic oxidation reactions dominate in this area, with local temperatures exceeding $2,000\text{ }^\circ\text{C}$ directly above the primary gasification agent nozzle. The recirculation of hot particles homogenizes temperatures, protects the reactor wall from local hot spots, promotes ash agglomeration, and improves heat and mass transfer. Reactor wall temperatures between $1,000$ and $1,200\text{ }^\circ\text{C}$ are typically achieved. Once agglomerates reach a critical size, they settle from the fluidized bed into the underlying fixed bed in the secondary zone.

3.2. Secondary Gasification in the Fixed Bed Zone

The lower reactor part contains a moving-bed zone as a downstream reaction stage. It mainly serves to convert residual carbon contained in ash agglomerates that remain unreacted after the fluidized bed stage, using the secondary gasification agent. The countercurrent flow acts as internal heat recovery, heating the gasification agent and cooling the bottom ash.

3.3. Post-Gasification in the Upper Reactor Zone

The post-gasification in the upper reactor area further increases carbon conversion in fine particles. The extended residence time of gas and solid particles in this zone enhances conversion efficiency. Target gas temperatures in the post-gasification zone are in the range of $1000\text{--}1100\text{ }^\circ\text{C}$ (non-slagging).

3.4. Gas Cleaning and Post-Treatment

The product gas leaves the reactor at temperatures between 600 and $750\text{ }^\circ\text{C}$, is cooled convectively, and then cleaned, with fly ash being separated by the above-described system. For product gas quality analysis, a slipstream is extracted at the raw gas outlet and fed to a gas chromatograph. To determine the dry syngas volume flow rate, $0.5\text{ m}^3/\text{h}$ (STP) of argon is added to the raw gas stream at the outlet, where it serves as a tracer gas.

4. Heat Supply via Arc Plasma

Whilst many of the previous approaches to plasma gasification have sought to apply a thermal plasma directly to the feedstock, a new approach is being pursued here. The central focus of

adapting the COORVED plant was the provision of sufficient heat within the reactor by the arc plasma to sustain the gasification reaction in the primary gasification zone. The aim was to reduce the addition of oxygen as far as possible while still achieving high local temperatures in the main reaction zone. This was intended to lower partial oxidation reactions of the carbon and reduce the CO₂ content in the syngas while creating a high reduction potential of the gas. Hence, the basic idea is to convert the autothermal process into an allothermal process while retaining the internally circulating fluidized-bed principle (INCI). In this way additional electrical energy is introduced to increase the quality and energy content of the produced syngas.

To implement this approach, a non-transferred free-burning direct current (DC) plasma arc with graphite electrodes was integrated into the COORVED plant. The integration of a free-burning arc plasma system into the fluidized bed reactor posed a range of significant technical challenges. One of the foremost issues was the selection of suitable electrode materials and geometries. Graphite electrodes were ultimately chosen due to their ability to withstand high temperatures in a harsh chemical environment. In addition, carbon released through electrode erosion is oxidized to carbon monoxide, thereby contributing a valuable syngas component rather than introducing metallic contaminants, as would occur with metal electrodes. Despite these advantages, electrode erosion and oxidation—particularly in gas atmospheres with high elemental oxygen content such as carbon dioxide—remained critical concerns. To mitigate these effects and to avoid condensation, the electrode inlets are gas-purged during heating and autothermal operation modes and their dimensions were optimized. It was ultimately determined that continuous electrode feeding is necessary to compensate for electrode consumption and facilitate extended operation for more than 30 hours.

Another key challenge was the design of an adjustable electrode positioning system. The electrodes were mounted on linear motors, allowing precise control over the distance between the electrode tips. This adjustability was essential for maintaining arc stability, as the arc characteristics and power input are highly sensitive to electrode spacing. The ability to dynamically adjust the electrode gap enabled the system to respond to changing process conditions and maintain stable arc operation on time-scales of minutes.

In addition, the electrical integration of the plasma system required a robust, current-controlled power supply and an inductor connected in series to stabilize the arc and accommodate the extreme voltage fluctuations and rapid load changes inherent to free-burning arc operation. The plasma arc system was successfully incorporated into the existing plant control infrastructure, with new interfaces of the distributed control system (DCS). This integration enabled continuous monitoring and adjustment of the electrode positions during operation, with average plasma power ranging from 10 to 20 kW.

4.1. Preliminary Investigations with Non-Transferred DC Plasma Arc

As part of preliminary studies, the suitability of an arc source for integration into the COORVED plant was examined. The goal was to evaluate the electrical and plasma-physical properties of different gas atmospheres and the stability of various electrode configurations, in order to derive an appropriate design for later operation in the gasifier. Various electrode configurations were considered to promote arc elongation through the arc's self-generated magnetic field, thereby increasing the arc length and average arc voltage and enabling higher power transfer at a given current.

Initially, investigations at INP reported in [19], examined arc properties in various process-relevant gas mixtures containing CO₂, CO, and H₂ at different partial pressures. Experiments were conducted at pressures up to 1.5 bar (abs.) and currents of 70–200 A, with power levels up to 40 kW. The high power levels at moderate current were mainly associated with erratic arc elongation and voltage spikes of up to about 1 kV. Subsequent experiments with the Trumpf/Hüttinger TruPlasma DC 3050 power supply investigated different electrode materials and geometries, CO₂ and N₂ gas atmospheres, and series of inductances between 1 and 15 mH. These investigations provided the basis for determining the required inductance and

electrode configuration for stable arc operation.

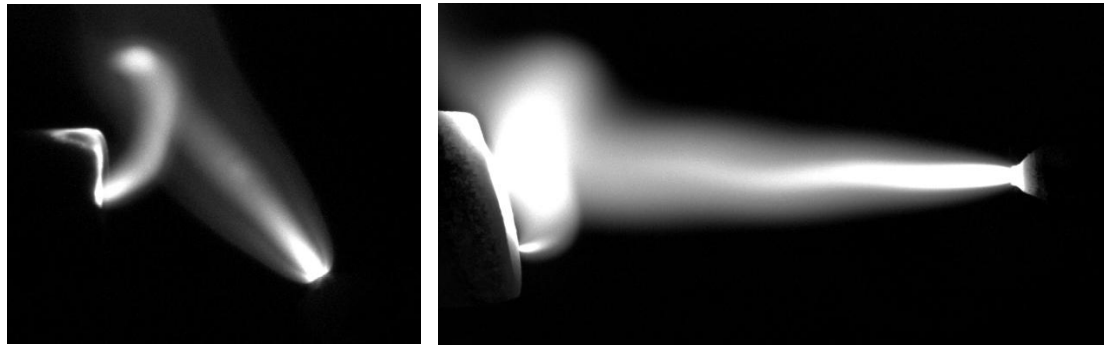


Figure 2 Exemplary highspeed images of the arc in the test setup with a 30 mm anode and a 9 mm cathode a) in N_2 at 90 A and 40 mm electrode distance and b) in CO_2 at 125 A and 80 mm distance.

The results showed that an arc between graphite electrodes with increased diameters in nitrogen could only be operated with poor stability. Higher arc stability was achieved by reducing the cathode diameter promoting the formation of an arc jet. With this configuration an arc in nitrogen could be operated at currents of up to 100 A and electrode distances of up to 40 mm. In CO_2 , currents of up to 90 A and electrode distances of up to 100 mm were achieved, with averaged voltages of around 300 V and average powers of up to 25 kW. Examples of arc images are shown in Figure 2.

Significant electrode erosion was observed, especially in carbon dioxide. For the graphite anode, a material loss of about 22 g/h was determined, while the cathode showed a loss of about 9 g/h. It was concluded that longer operating times would require either larger electrode cross-sections or continuous electrode feeding [19].

Overall, the preliminary investigations showed that stable continuous operation requires arc stability, limitation of voltage spikes, suitable electrode geometries, and control of electrode erosion. Consequently, additional control concepts and improved power regulation were planned.

4.2. Integration of the Plasma System into the COORVED Pilot Plant

After the pre-studies, the integration of the electrode system into the existing plant was accomplished. The mentioned voltage fluctuations and the resulting need for rapid power adjustment was handled by the selected power supply as it tolerates voltage spikes and ensures stable operation in current-controlled mode. The basic structure and position of the plasma system in the reactor are shown in Figure 3. Two graphite electrodes (anode and cathode) are inserted into the reaction chamber through horizontally aligned, opposing ports. The electrodes are driven by linear motors and can be moved along their axes, allowing precise adjustment of the electrode tips and their distance from each other. The greater the distance, the higher the voltage drop across the arc and the higher the electrical power input. This setup allows process heat to be supplied electrically and in a defined spatial location, while the gas phase can be used to control local reaction conditions. The choice of electrode diameter substantially influences arc stability, electrical power range, and electrode wear. Under operating conditions, the graphite electrodes are exposed to both oxidation by oxygen ions and erosion due to extremely high local temperatures. For this reason, the electrode inlets are additionally purged with nitrogen.

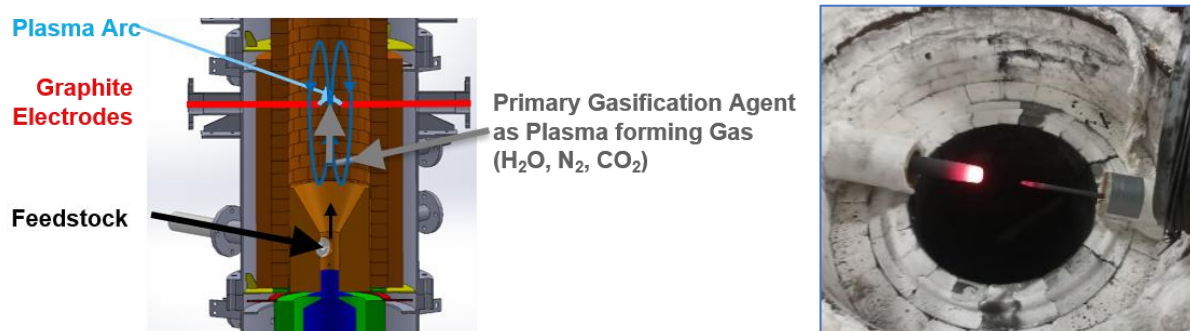


Figure 3: Plasma system of the COORVED reactor. Left: schematic, Right: installed state on the open, unbricked reactor

5. Evaluation of plasma-assisted sewage sludge gasification

To systematically investigate the influence of the gasification atmosphere on the syngas quality, an experimental campaign was conducted using sewage sludge as feedstock under two distinct operational modes: autothermal and plasma-assisted operation mode (allothermal primary gasification). Table 1 shows the different process parameters that were set for the test trials representing different levels of oxygen supply characterized by the oxygen or equivalence ratio λ , which describes the ratio of molecular oxygen supply to the process versus the stoichiometric demand for complete oxidation. To evaluate the process conditions, three different sets of process parameters were defined and kept constant, one in the autothermal and two in plasma-assisted mode. These periods of constant process conditions are classified as set points (SP), resulting in three SPs for evaluation – one autothermal (SP 1) and two plasma-assisted (SP 2-1, SP 2-2). Each mode was selected to explore specific aspects of gasification behavior, syngas quality, and process stability during sewage sludge gasification.

Table 1: Process parameters during sewage gasification

		Autothermal	Plasma-assisted		
		SP 1 O ₂ /H ₂ O 1200 °C 32.8 (kW _{th})	SP 2-1 H ₂ O 1000 °C 32.8 + 19.8 (kW _{th} + kW _{el})	SP 2-2 H ₂ O 915 °C 33.7 + 22.1 (kW _{th} + kW _{el})	
	Comp.				Unit
Sewage sludge		9.1	9.1	9.3	kg/h
Agents Secondary Zone	O ₂	0.8	0.8	0.4	m ³ /h (STP)
	CO ₂	-	-	-	m ³ /h (STP)
	H ₂ O	1.2	1.0	1.0	kg/h
	N ₂	0.6	0.6	0.83	m ³ /h (STP)
Agents Primary zone	O ₂	3.2	-	-	m ³ /h (STP)
	H ₂ O	1.0	0.8	0.8	kg/h
	N ₂	-	-	-	m ³ /h (STP)
Purge gas	N ₂	4.4	4.4	4.6	m ³ /h (STP)
Plasma	$\dot{Q}_{Pl}$	-	16.5	16.3	kW _{Pl}
Oxygen ratio	λ	0.60	0.12	0.06	-

The sewage sludge sample was delivered in a pre-dried and granular form and subsequently ground to a particle size of $x < 400 \mu\text{m}$, with a median diameter of $x_{50} = 99 \mu\text{m}$. Table 2 lists its ultimate and proximate analyses.

Table 2: Ultimate and Proximate Analysis of the Sewage Sludge

		Content	Unit
ultimate analysis	C	33.1	Wt% (ar)
	S _c	0.3	
	H	4.7	
	O	19.7	
	N	5.3	
proximate analysis	Moisture	11.1	Wt% (ar)
	Ash (815 °C)	25.8	
	Volatiles	54.1	
	C _{fix}	9.0	
	LHV	13,053	kJ/kg (ar)

In the case of autothermal mode, the reactor was operated using only the chemical energy of the sewage sludge and the exothermic reactions with the gasification agents (oxygen and steam) to maintain the necessary temperatures. The heat required for gasification was mainly generated internally by partial oxidation of the fuel, with almost no external energy input beyond initial start-up and preheating. This mode, described as SP 1, served as a reference for evaluating the baseline performance of the reactor, including temperature profiles and syngas composition under conventional autothermal gasification conditions.

In contrast, during plasma-assisted mode, electric energy was supplied to the primary zone by means of the plasma arc system. Only the secondary zone remained operated with oxygen and steam as gasification agents. The oxygen supply was varied in this zone to reduce the overall oxygen ratio from $\lambda = 0.12$ (SP 2-1) to $\lambda = 0.06$ (SP 2-2).

6. Results

The composition of the Ar- and N₂-free raw gas and the resulting syngas yield are illustrated in Figure 4. The three investigated evaluation periods of the different SPs are illustrated by red colored areas. Additionally, within each SP a time frame called reference point (RP) has been selected for evaluation where the most stable operating conditions were present (green area). The oxygen ratios, syngas yields, the specific gas compositions and the cold gas efficiencies (CGE) at the RPs are shown in Table 3, whereas the CGE is defined as the ratio of the chemical energy contained in the produced raw gas to the chemical energy supplied with the gasification feedstock.

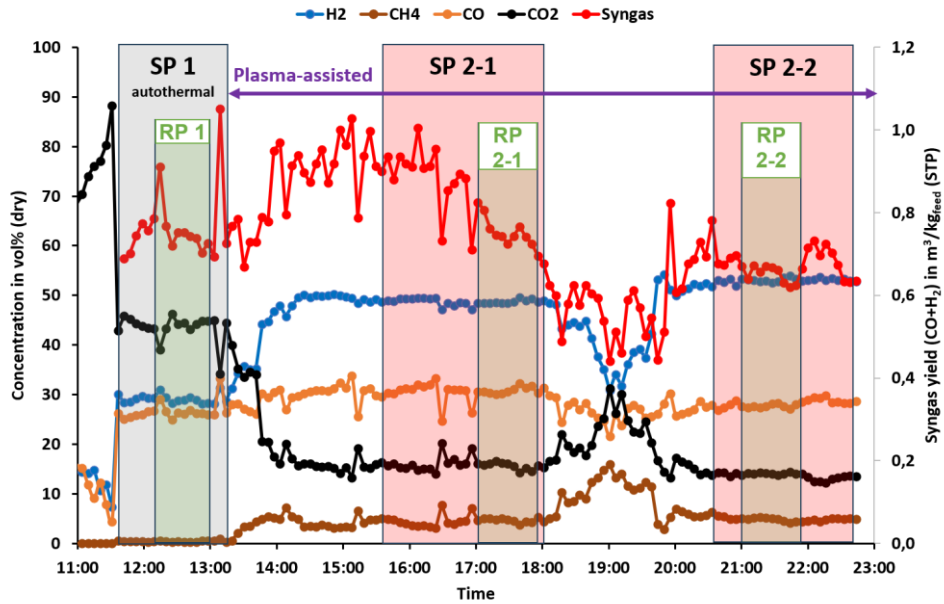


Figure 4: Dry Raw Gas Composition (N₂/Ar-free) and Syngas Yield (H₂+CO) during Sewage Sludge Gasification

6.1. Autothermal Operation

In the autothermal reference operation, a thermochemical duty of 33 kW (3.6 kW/kg_{Feed}) was introduced by the sewage sludge, with oxygen and steam as gasification agents and an oxygen ratio of $\lambda = 0.6$ (see Table 3). The results showed a comparatively unfavorable syngas compositions, e.g. for methanol synthesis. The syngas contained 28.9 vol% hydrogen and 26.2 vol% carbon monoxide at the RP, corresponding to a H₂/CO ratio of 1.1 and a CGE of 42,8 %. Although the autothermal mode enables a high syngas yield, the relatively high CO₂ content of 44.5 vol% and low H₂/CO ratio generate a syngas quality that needs elaborate gas treatment for syntheses applications.

Table 3: Evaluation of the reference points in autothermal and plasma-assisted modes

	Autothermal	Plasma-assisted		
	RP 1 O ₂ /H ₂ O 1200 °C 32.8 + 2.5 (kW _{th} + kW _{el})	RP 2-1 H ₂ O 1000 °C 32.8 + 19.8 (kW _{th} + kW _{el})	RP 2-2 H ₂ O 915 °C 33.7 + 22.1 (kW _{th} + kW _{el})	
Air ratio	0.60	0.12	0.06	
Syngas Flow rate	6.7	6.8	6.1	m ³ /h (STP, dry)
Syngas yield (H ₂ +CO)	0.74	0.75	0.65	m ³ /kg _{feed} (STP, dry)
H ₂	28.9	48.8	53.3	Vol% (dry)
CO ₂	44.5	15.6	14.1	
CO	26.2	30.9	27,8	
CH ₄	0.4	4.7	4.8	
CGE	42.8	62.1	52.7	%

6.2. Plasma-assisted Allothermal Operation

Plasma-assisted solid fuel gasification of sewage sludge proved to be easier to handle than maintaining a stable arc in gases with high oxygen contents, since the high carbon content of the sewage sludge creates strongly reducing conditions. Free oxygen atoms/radicals preferentially react with the reactive carbon, thereby largely suppressing oxidation reactions at the electrodes potentially stabilizing arc operation. Nevertheless, after approximately 8 h 45 min of plasma operation, the plasma arc became increasingly unstable and extinguished intermittently. Figure 5 shows two camera images of the arc during the gasification of sewage sludge. These were taken through the optical access port, which allows imaging of approximately 55 mm of the reactor cross-sectional width. In the image on the left of Figure 5, the electrode tips and the arc can be seen during ignition. In the image on the right of Figure 5, the plant is in operation at approximately 15 kW electrical power. The distance between the electrode tips is about 105 mm, which prevents the electrode ends from being visible. Feedstock dust particles were observed throughout the imaged section during operation, based on the recorded high-speed image sequences and videos. These particles appear predominantly in plume-like or streak-like formations, with their movement towards the arc indicated by corresponding shadow movements and alternating dark and bright regions in the image sequences. The relevant particle structures are visible on the left-hand side of the right-hand image. In addition, larger particles can be seen on the right-hand side, indicating agglomerates that may have formed from ash fractions molten in the arc.

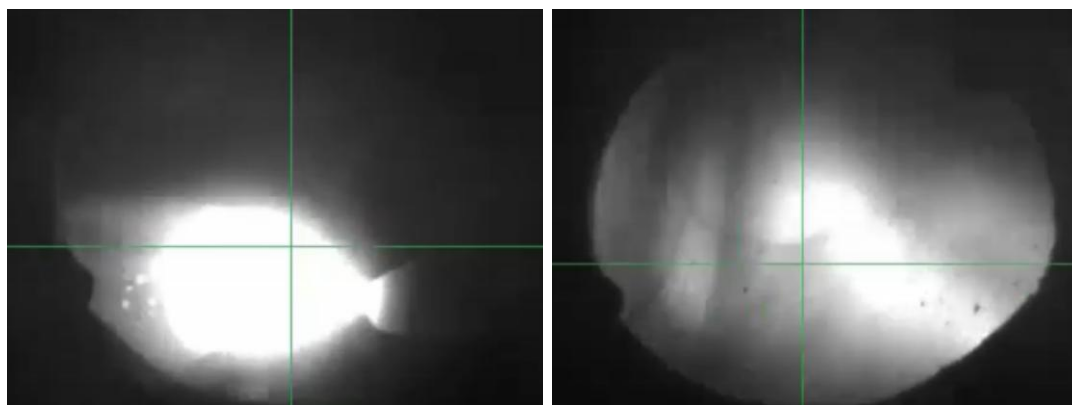


Figure 5: Camera images of the Arc during the Gasification of Sewage Sludge.

During the two set points for plasma-assisted sewage sludge gasification (SP2-1 and SP2-2), the fuel mass flow rates were similar to that of the autothermal mode at 9.1 and 9.3 kg/h, respectively. The arc plasma was operated with an average current of 85 A, with a mean arc voltage of about 150 V despite considerable voltage fluctuations, and an average plasma power of about 16.4 kW_{PI}, resulting in a specific energy input of about 1.8 kWh/kg_{Feed}. One main outcome of the plasma-assisted gasification was the reduction in carbon dioxide concentration to 14.1 vol% for RP 2-2. Additionally, increased hydrogen and carbon monoxide concentrations were measured. Consequently, the syngas quality was improved significantly by switching from autothermal to plasma-assisted gasification. H₂/CO ratios of 1.6 (RP 2-1) and 1.9 (RP 2-2) were achieved. The syngas yield, however, remained similar or decreased slightly, which is also confirmed by the CGE with a maximum of 62.1 % in RP 2-1.

The operating parameters that have been set for SP 2-1 and SP 2-2 are in a range of thermodynamically favorable conditions for an increased phosphorus release. However, it was not possible to conclusively demonstrate phosphorus release at either operating point. Furthermore, heat losses, a solid mass flow rate of more than 9 kg/h, and a maximum plasma power of approximately 16.4 kW_{PI}, resulted in reduced temperatures in the bottom of the primary gasification zone. In addition, these temperatures were strongly influenced by recurring extinction of the arc. It was found out that adjustments of the technical parameters of the power supply and the sewage sludge mass flow rate helped to avoid these arc instabilities.

It turned out that there seems to be an optimum solid loading per arc power at comparably low feeding rates. In turn this reduces the capacity of the reactor system while having heat losses at the same level. Hence, setting the gasification parameters with the target of maximizing the phosphorus release and optimizing the ratio of plasma power to feedstock mass flow rate are subject to further investigation and optimization.

7. Conclusion

With the target of increasing the syngas quality as well as the reduction potential in the main reaction zone a free-burning plasma arc was chosen and developed for the integration into an existing fluidized bed gasifier. A combination of a Trumpf/Hüttinger TruPlasma DC 3050 power supply with an inductive coil has proven its suitability for this application to ensure reliable, current-controlled operation.

As a result of the integration of the plasma system into the fluidized bed gasifier, two distinct and stable plasma-assisted sewage sludge gasification modes were reached. The main knowledge obtained from the experiments can be summarized as follows:

- Enhanced operational flexibility and process control.
- The plasma-assisted operation mode enabled precise control of the reactor temperature and decoupled the heat supply from the oxidation reactions, allowing for operation under strongly reducing conditions.
- Stable plasma operation in CO₂ was achieved with a current of 90 A and electrode distances up to 100 mm, resulting in averaged voltages around 300 V and averaged powers up to 25 kW.
- Stable plasma-assisted sewage sludge gasification with an operation time of more than 8 h 45 min.
- Syngas quality in comparison to autothermal operation mode:
 - H₂/CO ratio increased from 1.1 (autothermal) to 1.9 for a plasma-assisted operation mode.
 - Syngas yield maintained at around 6.8 m³/kg_{feed} (STP) or slightly reduced to 6.1 m³/kg_{feed} (STP)
 - CGE increased from 42.8 to 62.1 %
 - CO₂ concentration reduced from 45 to 14 vol% while H₂ rose up to 53 vol%
- Initial operating experience suggests that there is an optimal ratio of arc power to sewage sludge mass flow rate for achieving stable operation, which is found in the reactor's low-power range. Increasing the plasma power could have a positive effect on cold gas efficiency in the future.
- Despite thermodynamically favorable conditions, it was not possible to conclusively demonstrate phosphorus release at either operating point.
- The plasma-assisted gasification mode was particularly important for investigating the effects of high-temperature, externally driven gasification on syngas quality, as well as for testing the operational stability of the plasma-assisted system.

Conclusively, a free-burning arc plasma has a great potential to be utilized in industrial applications. It is allowing for a reliable plasma-driven gasification within the demanding environment of a fluidized bed reactor.

Acknowledgement

This work was funded by the German Federal Ministry of Economic Affairs and Climate Action (BMWK) under grant number 03EE5086. The authors gratefully acknowledge the funding.

Literature

- [1] K. Moustakas, D. Fatta, S. Malamis, K. Haralambous, and M. Loizidou, "Demonstration plasma gasification/vitrification system for effective hazardous waste treatment," *J Hazard Mater*, vol. 123, no. 1–3, pp. 120–6, Jan. 2005, doi: 10.1016/j.jhazmat.2005.03.038.
- [2] E. Franke, S. Shalnev, J. Jahn, T. Pietschner, and M. Gräbner, "Experimental investigations of thermochemical phosphorus release behavior from sewage sludge under inert and reducing conditions," *Journal of Cleaner Production*, vol. 493, p. 144687, Feb. 2025, doi: 10.1016/j.jclepro.2025.144687.
- [3] S. Righi, F. Baioli, A. Contin, and D. Marazza, "TO-SYN-FUEL Project to Convert Sewage Sludge in Value-Added Products: A Comparative Life Cycle Assessment," *Energies*, vol. 18, no. 19, p. 5283, Oct. 2025, doi: 10.3390/en18195283.
- [4] W. Gebhard, S. Zant, J. Neidel, A. Apfelbacher, and R. Daschner, "Conversion of Sewage Sludge with Combined Pyrolysis and Gasification via the Enhanced Carbon-To-X-Output Technology".
- [5] "Projekt Havelstoff," Sep. 2021.
- [6] M. Materazzi and R. Taylor, "Plasma-Assisted Gasification for Waste-to-Fuels Applications," *Ind. Eng. Chem. Res.*, vol. 58, no. 35, pp. 15902–15913, Jan. 2019, doi: 10.1021/acs.iecr.9b01239.
- [7] T. Ginsberg, J. Hannes, J. Kleeberg, T. Liese, J. Schaefer, and C. Wolfersdorf, "Gasification of sewage sludge in the Freiberg COORVED lab scale unit for in-situ recovery of Phosphorus," in *International Freiberg Conference*, 2018.
- [8] V. A. Kuznetsov, M. Gräbner, R. Schimpke., D. Uhrlandt, and A. Richter, "Systematic evaluation of gasifiers driven by the high-enthalpy plasma supply," *Fuel*, vol. 417, p. 138538, Aug. 2026, doi: 10.1016/j.fuel.2026.138538.
- [9] M. I. Boulos, "The inductively coupled R.F. (radio frequency) plasma," *Pure and Applied Chemistry*, vol. 57, no. 9, pp. 1321–1352, Jan. 1985, doi: 10.1351/pac198557091321.
- [10] I. Matveev, S. Matveyeva, and S. Zverev, "Experimental Investigations of the APT-60 High-Pressure Inductively Coupled Plasma System on Different Plasma Gases," *IEEE Trans. Plasma Sci.*, vol. 42, no. 12, pp. 3891–3895, Jan. 2014, doi: 10.1109/TPS.2014.2362414.
- [11] H. S. Uhm, Y. H. Na, Y. C. Hong, D. H. Shin, C. H. Cho, and Y. K. Park, "High-Efficiency Gasification of Low-Grade Coal by Microwave Steam Plasma," *Energy Fuels*, vol. 28, no. 7, pp. 4402–4408, Jan. 2014, doi: 10.1021/ef500598u.
- [12] P. G. Rutberg, V. A. Kuznetsov, V. E. Popov, A. N. Bratsev, S. D. Popov, and A. V. Surov, "Improvements of Biomass Gasification Process by Plasma Technologies," in *Pretreatment Techniques for Biofuels and Biorefineries*, Z. Fang, Ed., in Green Energy and Technology., Berlin, Heidelberg: Springer Berlin Heidelberg, 2013, pp. 261–287. doi: 10.1007/978-3-642-32735-3_12.
- [13] B. Meyer *et al.*, "Method and device for the entrained-flow gasification of solid fuels under pressure." Google Patents, Apr. 15, 2010.
- [14] R. Schimpke, A. Laugwitz, M. Schurz, S. Krzack, and B. Meyer, "Flow pattern evaluation of the internal circulation gasifying principle," *Fuel*, vol. 147, pp. 221–229, May 2015, doi: 10.1016/j.fuel.2014.12.039.
- [15] M. Schurz, A. Laugwitz, S. Krzack, and B. Meyer, "Comparison of Two Coal-Gasifier-Designs with Moving-Bed and Internal-Circulating-Fluidized-Bed Configuration in One Reactor," *TOEFJ*, vol. 10, no. 1, pp. 48–67, Aug. 2017, doi: 10.2174/1876973X01710010048.
- [16] P. A. Nikityuk and B. Meyer, *Gasification processes: modeling and simulation*. John Wiley & Sons, 2014.
- [17] A. Laugwitz and B. Meyer, "New Frontiers and Challenges in Gasification Technologies," in *Gasification Processes*, John Wiley & Sons, Ltd, 2014, pp. 305–328. doi: 10.1002/9783527673186.ch11.
- [18] A. Laugwitz, "Detailed analyses and numerical modeling of a new multi-staged fluidized-bed gasifier," 2018.

- [19] P. Pieterse, D. Gonzalez, A. Najam, R. Schimpke, M. Gräbner, and D. Uhrlandt, "Towards plasma-enhanced gasification: Investigating free-burning carbon arcs in molecular gas mixtures," *PPT*, vol. 12, no. 1, pp. 52–55, Aug. 2025, doi: 10.14311/ppt.2025.1.52.

Enhancing Waste Gasification-based Methanol Production by Renewable Energy Integration – Hydrogen vs. Plasma

A. Helf¹, F. Keller¹, M. Gräbner^{1, 2, 3}

¹TU Bergakademie Freiberg, IEC, Freiberg, Germany,

²Fraunhofer IKTS, Energie- und Verfahrenstechnik - Kohlenstoff-Kreislauf-Technologien, Freiberg, Germany,

³Zentrum für effiziente Hochtemperatur-Stoffwandlung (ZeHS), Freiberg, Germany

Abstract

Gasification-based chemical recycling offers a route for valorizing mixed and contaminated waste streams that are unsuitable for mechanical recycling, but conventional process chains suffer from substantial carbon losses through intrinsic CO₂ formation during gasification and downstream syngas conditioning. Electrification can counteract these losses through direct process electrification or indirect integration of electrolytic hydrogen. This work investigates how these pathways affect carbon recovery, economic performance and the classification of waste-derived methanol under the European Renewable Energy Directive (RED).

Three waste-to-methanol process chains are compared for a representative refused-derived fuel sorting residue: non-electrified oxygen-blown gasification, plasma-assisted gasification and gasification with downstream electrolytic H₂ integration. Thermodynamic process modeling in Aspen Plus is combined with techno-economic and greenhouse gas assessment. The configurations are evaluated based on carbon recovery, product energy yield, CAPEX, OPEX, levelized cost of methanol production and net present value. In addition, the influence of renewable-electricity availability and feedstock biogenic carbon content on the production of Recycled Carbon Fuels, Advanced Biofuels and Renewable Fuels of Non-Biological Origin is assessed.

Electrification increases carbon recovery from approximately 52% in the non-electrified reference to about 82% for plasma-assisted gasification and nearly 99% for H₂ integration. Plasma electrification provides the more favorable conventional techno-economic performance, combining increased carbon recovery with comparatively limited additional investment and electricity demand, whereas H₂ integration is constrained by electrolysis CAPEX and power consumption. However, consideration of RED fuel classifications substantially affects the economic comparison. Increasing renewable-electricity availability improves the profitability of both electrified configurations, while increasing biogenic feedstock content particularly favors H₂ integration through the combined production of Advanced Biofuels and RFNBO. Under the current regulatory framework, direct renewable-electricity input to plasma gasification does not contribute to RFNBO production, limiting the corresponding market benefit. Scenario analyses show that both RFNBO eligibility of plasma-based electricity input and flexible electrolytic H₂ production can significantly change the relative economic performance.

The results demonstrate that the preferred electrification pathway depends not only on process efficiency and cost, but also on feedstock carbon origin, renewable-electricity availability and regulatory fuel classification. Plasma-assisted gasification is particularly promising for plastic-rich waste streams, while flexible H₂ integration becomes increasingly attractive at higher biogenic carbon fractions and high availability of eligible renewable electricity.

Introduction

Gasification-based chemical recycling presents a promising pathway for the treatment of heterogeneous and contaminated waste streams that are not suitable for mechanical recycling. In addition to its feedstock flexibility, gasification offers product flexibility as the produced syngas can serve as an intermediate for a wide variety of chemical products. However, the high-temperature conversion process and subsequent product gas conditioning suffer from significant carbon losses. Typically heated by partial oxidation, CO₂ is formed during gasification. Additionally, downstream conditioning of the syngas for chemical utilization, e.g., methanol (MeOH) synthesis, usually requires water–gas shift (WGS), forming further CO₂ that is subsequently removed. Consequently, conventional plastic waste-to-methanol process chains retain only about 30–60% of feedstock carbon to the methanol product.

Electrification can counteract these carbon losses by replacing partial oxidation-based process heat or by introducing electrolytic hydrogen into the process chain. Direct electrification can be realized through electric heating or plasma integration, while indirect electrification integrates hydrogen from electrolysis into gas conditioning or synthesis [1]. Particularly for chemical recycling, electrification has been highlighted as a promising approach to increase carbon circularity, provided that low-emission electricity is available [2].

Plasma-assisted gasification (PAG) offers high energy densities and temperatures as well as the possibility to decouple the gasification heat supply from partial oxidation. Previous investigations demonstrate high feedstock flexibility and effective destruction of tars and other harmful components. However, high electricity demand, scalability, electrode lifetime and investment cost remain major challenges [3]. Indirect electrification via electrolytic hydrogen avoids part or all of the WGS reaction and thus allows a larger fraction of feedstock carbon to be retained for synthesis. Its implementation is, however, strongly dependent on electricity and electrolyzer costs.

Previous investigations of biomass- and waste-to-methanol processes indicate that direct electrification can perform favorably compared to indirect electrification, while hydrogen integration can achieve very high carbon recovery at increased cost [4,5]. Flexible operation of electrolysis during periods of low electricity prices has therefore been proposed as an option to improve economic viability [6]. Nevertheless, quantitative comparisons between direct and indirect electrification specifically for gasification-based chemical recycling remain limited.

While gasification is considered a process that can enable chemical recycling of heterogeneous waste streams, methanol as the resulting product is not directly addressed by current circularity legislation focusing on recycled plastic content. For example, recycling quotas under the German Packaging Act [7] primarily target the incorporation of recycled plastic into new plastic products and therefore do not currently provide a direct incentive for gasification-based methanol production. Consequently, the economic value of gasification-based chemical recycling depends not only on its ability to recover waste carbon, but also on regulatory frameworks that recognize the substitution of fossil carbon in applications beyond plastics production.

More direct market incentives are provided by the Renewable Energy Directive (RED) through requirements on the greenhouse gas (GHG) intensity and minimum shares of renewable and recycled fuels. These requirements can increase the market value of alternative fuels and thereby provide business case opportunities for methanol produced from waste-derived and renewable carbon. A particularly relevant market is maritime transportation, where methanol is emerging as an alternative fuel and regulatory requirements under the FuelEU Maritime framework create increasing demand for low-GHG fuel options [8,9]. The applicability of the RED framework therefore introduces an additional dimension to the assessment of gasification-based methanol beyond carbon recovery and conventional production cost.

Hence, the present investigation comparatively assesses the valorization of plastic waste sorting residues via methanol production using non-electrified gasification, plasma-assisted gasification and downstream hydrogen integration. The process chains are modeled in Aspen Plus to generate heat and material balances and subsequently evaluated from a techno-economic perspective. The central objective is to determine how direct and indirect electrification perform with regard to carbon recovery and economic viability and to identify suitable pathways for reducing process-related CO₂ formation, under consideration of the environmental and economic framework given by the Renewable Energy Directive.

Methodology

Concept definition and process balancing

Three process configurations are investigated. The reference configuration (no-EL) comprises autothermal oxygen/steam gasification followed by raw gas purification, WGS conditioning, acid gas removal and methanol synthesis. In the directly electrified configuration (PLAS), steam plasma fully replaces partial oxidation as the heat source for gasification. Consequently, no oxygen is used as gasification agent. WGS remains necessary to obtain the required syngas composition for methanol synthesis, which limits the maximum carbon recovery achievable exclusively through plasma integration.

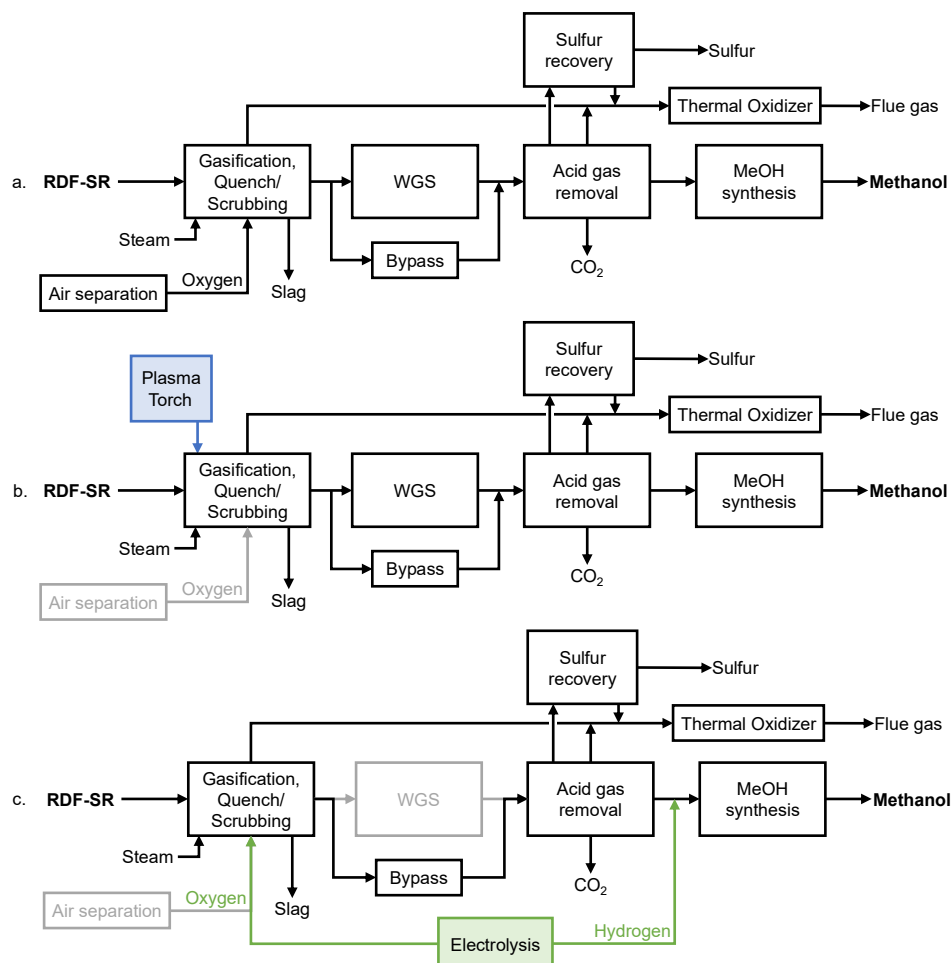


Figure 1: Configuration overview, a. no-EL – non-electrified waste gasification, b. PLAS – plasma-assisted waste gasification (direct electrification), c. H₂ – waste gasification with downstream hydrogen integration (indirect electrification)

For indirect electrification, hydrogen is integrated downstream of an oxygen-based gasification process before methanol synthesis. The WGS unit is fully bypassed and the resulting hydrogen deficit is compensated by electrolytic hydrogen. In the H_2 configuration, hydrogen input is adjusted to enable maximum carbon recovery. As the typical shift unit is not able to perform reverse WGS, maximum carbon recovery is limited by the CO_2 tolerance of the methanol synthesis unit. In this investigation, CO_2 contents are sufficiently low to allow for almost full carbon recovery via a conventional methanol synthesis.

The comparative analysis is based on heat and material balances from feedstock to methanol including the relevant auxiliary facilities. A sorting residue from lightweight packaging waste is selected as feedstock. This stream consists primarily of mixed plastics that cannot be separated into single-type plastic streams and is currently typically incinerated in the German waste management system. Due to its origin from plastics, the carbon content of this feedstock is typically fossil-based. A design feed capacity of 150 MW, corresponding to 560 t/d of dry sorting residue, is considered. This capacity is representative of large waste treatment facilities while maintaining a scale relevant to planned gasification projects. The availability of sufficient waste and renewable electricity is recognized as an important constraint for practical implementation.

Gasification is modelled as a fixed-bed gasifier with a secondary reaction stage. An adiabatic equilibrium approach with a fixed outlet temperature of 1500 °C is applied in all configurations to maintain comparability. Gasification pressure is set to 2 bar, reflecting the technological challenges associated particularly with pressurized plasma operation. In the no-EL and H_2 and configurations, the required gasification temperature is controlled through oxygen input. In PLAS, the corresponding energy is supplied by steam plasma. Additional steam ensures full carbon conversion.

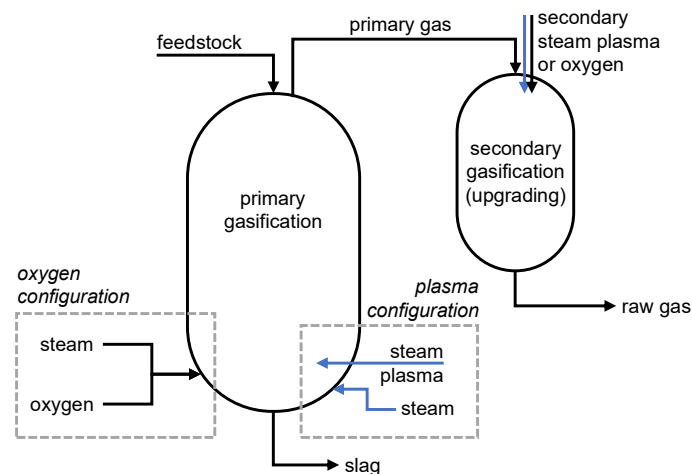


Figure 2: Reactor concept sketch for oxygen-based and plasma-assisted configuration

For the plasma-based configurations, the plasma system is represented as an energy input into the gasifier together with steam as the gasification agent. Both the primary and secondary conversion gasification stage are assumed to be supplied by plasma energy. A plasma system efficiency of 90% is considered. This value represents the upper range of efficiencies reported for thermal plasma systems and is chosen as the base case for the comparative investigation [10]. Electrode erosion and potential catalytic effects are neglected.

Downstream gas processing is represented by a typical syngas treatment chain. A quench and wash unit cools the raw gas and removes particulates and soluble contaminants, followed by a two-stage shift unit with intermediate cooling. A bypass around the shift unit allows the syngas composition to be adjusted. For no-EL and PLAS, the bypass is controlled to obtain

the syngas module required for methanol synthesis. In the hydrogen-integrated configuration, the shift is fully bypassed to maximize carbon recovery.

After shifting, the syngas is compressed and treated by a physical acid gas removal process based on chilled methanol. Sulfur compounds and CO₂ are removed before synthesis. The separated CO₂ is considered a process emission. Methanol synthesis is represented by a Lurgi-type synthesis process based on adjusted thermodynamic equilibrium and recycle [11]. Hydrogen is introduced before synthesis in the electrolysis-based case and adjusted to obtain the required syngas composition. Electrolysis itself is not modelled explicitly; instead, an alkaline electrolysis efficiency of 70% on a higher-heating-value basis is used to determine the corresponding electricity requirement [12]. Oxygen produced as a co-product of electrolysis is utilized for gasification in the H₂ configuration.

Process off-gases are combusted and used for high-pressure steam production and internal heat integration. Remaining steam is expanded for electricity production. Consequently, process-inherent excess heat is internally valorized and no external steam export is assumed.

Carbon Recovery Rate (CRR), defined as the fraction of feedstock carbon retained in the methanol product, and the Energy efficiency, defined as the ratio of chemical energy in the product methanol to the chemical energy of the feedstock and the process power input, are used as the central technological parameter.

$$CRR = \frac{\dot{n}_{C,MeOH}}{\dot{n}_{C,Feed}}$$

CRR – carbon recovery rate in %; $\dot{n}_{C,MeOH}$ – molar flow of carbon in product MeOH in kmol/s; $\dot{n}_{C,Feed}$ – molar flow of carbon in waste feedstock in kmol/s

$$Energy\ efficiency = \frac{\dot{m}_{MeOH} \cdot LHV_{MeOH}}{\dot{m}_{Feed} \cdot LHV_{Feed} + P_{el}}$$

$\dot{m}_{MeOH}$ – mass flow of product MeOH in kg/s; LHV_{MeOH} – lower heating value of MeOH in MJ/kg; $\dot{m}_{Feed}$ – mass flow of waste feed in kg/s; LHV_{Feed} – lower heating value of waste feed in MJ/kg; P_{el} – net electricity demand of the process including electrification power in MW

Environmental and economic assessment

The environmental assessment determines the product fuel GHG intensity according to the methodology defined by the Renewable Energy Directive [13]. A cradle-to-grave system boundary is applied, including emissions associated with feedstock and energy supply, direct process emissions and emissions from final fuel utilization. Waste feedstock entering the process is considered burden-free, while emissions from the combustion of biogenic carbon are considered GHG-neutral. To qualify within the considered RED fuel categories, the produced fuel is required to achieve a minimum GHG emission reduction of 70% relative to the fossil fuel comparator, corresponding to a maximum fuel GHG intensity of approximately 29 g CO₂eq/MJ on a lower-heating-value basis.

Depending on feedstock origin and energy input, the methanol product can comprise different RED fuel categories. Recycled Carbon Fuels (RCF) are produced from eligible fossil waste carbon. For their GHG assessment, the avoided conventional treatment of the waste feedstock is considered; in the present case, incineration with energy recovery represents the reference treatment route. Advanced Biofuels (ABF) are associated with the biogenic fraction of eligible feedstocks listed in Annex IX Part A of the RED and therefore become relevant when the investigated sorting residue contains a biogenic carbon fraction.

Renewable Fuels of Non-Biological Origin (RFNBOs) are subject to additional requirements regarding both the carbon and electricity source. Eligible carbon must originate from defined sources, including biogenic carbon, direct air capture or eligible industrial CO₂ point sources, while renewable electricity used for electrolytic hydrogen production must fulfil the applicable requirements regarding additionality as well as temporal and geographical correlation. Consequently, a feedstock containing both fossil and biogenic carbon in combination with electrolytic hydrogen can result in simultaneous production of RCF, ABF and RFNBO. The respective product fractions are determined by carbon-mass and enthalpy balancing of the gasification feedstock and the electrolytic hydrogen input. Under the currently applied regulatory framework, however, direct process electrification does not result in RFNBO production. Hence, the renewable electricity supplied directly to the plasma gasification process in the PLAS configuration does not generate an RFNBO product fraction.

The techno-economic assessment is based on the generated process inventories. Reference equipment costs are scaled according to unit capacity using cost exponents to account for economy-of-scale effects and are updated to the base year using the Chemical Engineering Plant Cost Index following common process-economic methodology [Peters, 2003]. From the resulting bare erected costs, fixed capital investment and associated capital expenses are estimated. Operating expenditure is calculated based on process material and energy balances together with labour, maintenance and other operational assumptions.

Germany is selected as the geographical framework and 2026 as the base year. Detailed information on process modelling and assessment can be found in [14]. Relevant OPEX base-case assumptions include fossil CO₂ emission cost of 100 €/t, waste gate fees of 100 €/t and a conventional methanol market price of approximately 530 €/t [15]. Beyond that, factors on market methanol prices are assumed for RCF (times 1,5), ABF (times 3,0) and RFNBO (times 6,0) [8,16].

Electricity supply is differentiated between periods in which RED-eligible renewable electricity is available and periods in which the plant is supplied by grid electricity. The annual availability of eligible renewable electricity is therefore introduced as a scenario parameter, representing both the availability of renewable generation and the associated production and storage infrastructure. During periods without eligible renewable electricity, the GHG intensity of grid electricity is considered in the product fuel balance. A renewable-electricity availability of 4500 h/a is used as the base case for the subsequent assessment of feedstock composition, while the annual availability is varied more broadly to determine its influence on RED fuel production and profitability. While cost of electricity from the grid is assumed at 150 €/MWh, green electricity is supplied via a green power-purchase agreement at 80 €/MWh.

Economic performance is assessed primarily using capital expenditure (CAPEX), operating expenditure (OPEX), net present value (NPV) and levelized cost of methanol production (LCOP). NPV accounts for capital expenses, operating expenses, waste revenues and methanol revenues over the considered plant lifetime. LCOP represents the methanol price required to cover production expenses.

A deterministic sensitivity analysis assesses major economic and technological dependencies. Electricity cost is varied between 50 and 250 €/MWh and CO₂ emission cost between 0 and 300 €/t. Plasma and electrolysis efficiencies are varied over technologically plausible ranges and plant availability is reduced to 70% to investigate the impact of reduced operational reliability.

Beyond these conventional techno-economic parameters, the influence of the annual availability of RFNBO-eligible renewable electricity and of the biogenic carbon fraction in the waste feedstock is assessed. Both parameters directly affect the amount and distribution of RED-compliant methanol and, through the assumed market premiums, the resulting economic performance. Two additional scenarios are considered to investigate limitations and flexibility

associated with the current framework. First, the impact of eligibility of direct electrification via plasma for RFNBO production is assessed. Second, the inherent flexibility of the H₂ configuration is investigated by adjusting electrolytic hydrogen production to the actual availability of eligible renewable electricity rather than operating the electrolyzer continuously.

The process model is conceptual and has not been validated against experimental data, as the focus is on comparison between the investigated pathways rather than on exact prediction of individual plants. Heat and carbon losses may consequently be underestimated. Furthermore, an availability of 90% is optimistic for heterogeneous waste feedstocks. Plasma torches and electrolysis systems are assumed to be available at the required scale, although current commercial unit capacities remain substantially smaller than those required in the investigated process chains. Finally, a decreasing gate fee is to be expected for a higher biogenic carbon content, which was not considered.

Results and Discussion

Electrification substantially increases the fraction of feedstock carbon retained in methanol. The non-electrified configuration reaches a carbon recovery of approximately 52%. PLAS increases this value to approximately 82%, corresponding to an increase of 30 percentage points. H₂ reaches approximately 99% carbon recovery, with only unavoidable carbon losses through purge gases remaining. Consequently, both direct and indirect electrification can significantly reduce CO₂ formation, while unrestricted hydrogen addition can approach complete feedstock carbon utilization.

From a thermodynamic perspective, the energy required to achieve a specific increase in carbon recovery is fundamentally similar for the different electrification pathways. Once the conversion efficiencies of the technologies are considered, however, hydrogen integration requires more electricity than plasma integration for the same carbon recovery. Considering energy efficiency, PLAS increases the process energy efficiency compared to baseline case while H₂ decreases it. This results primarily from the assumed 70% electrolysis efficiency compared to 90% efficiency for the plasma system.

Plasma integration also changes the raw syngas composition. Replacement of partial oxidation increases the hydrogen content and the overall gas yield because feedstock carbon is no longer consumed to provide the required gasification heat. These differences are partly equalized in the downstream conditioning processes. In contrast, hydrogen integration acts mainly by reducing the extent of WGS required and supplying the hydrogen necessary for methanol synthesis. Thus, the two approaches achieve increased carbon recovery at different locations within the process chain.

Table 1: Gas compositions at quench outlet, after shift and at synthesis input and gas yield

		raw gas		syngas after shift			synthesis feed		
		O ₂	PLAS	no-EL	PLAS	H ₂	no-EL	PLAS	H ₂
H ₂	mol-%	41.0	60.5	52.1	63.0	41.0	67.2	67.2	68.0
CO		54.5	39.4	25.4	30.7	54.5	32.8	32.8	29.6
CO ₂		4.5	0.1	22.5	6.3	4.5	0.0	0.0	2.4
yield	m ³ (STP)/kg(waf)	1.86	2.78	2.29	2.96	1.86	1.76	2.77	3.32

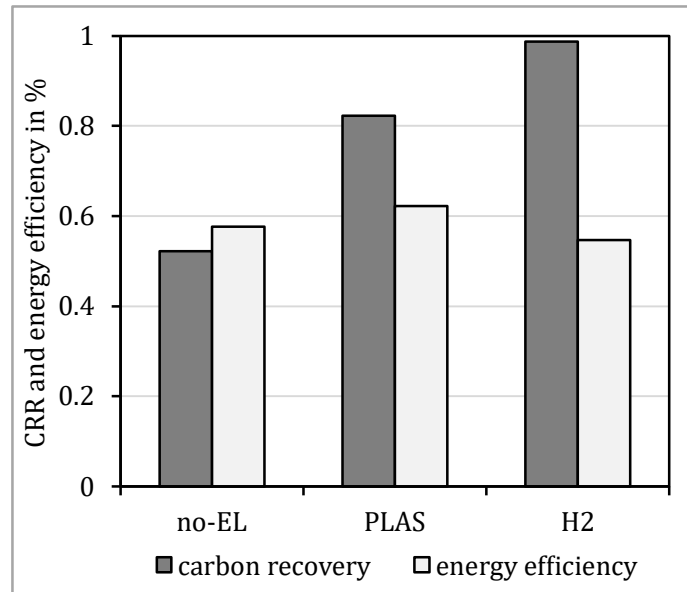


Figure 3: Carbon Recovery Rate CRR and Energy efficiency for different process configurations

The economic assessment shows a significant difference between plasma and electrolysis-based electrification. Total CAPEX of the PLAS case is similar to that of the non-electrified reference. Although the plasma system introduces additional investment and the increased syngas and methanol flow rates require larger downstream equipment, the air separation unit required for oxygen-based gasification is eliminated. These opposing effects largely compensate each other.

Electrolysis introduces substantially higher investment. For example, total CAPEX of H₂ is approximately 1.7 times that of PLAS but only increases the product yield by about 20%. Currently available plasma and electrolysis capacities are significantly below the scale required in the investigated plant, representing an important implementation challenge.

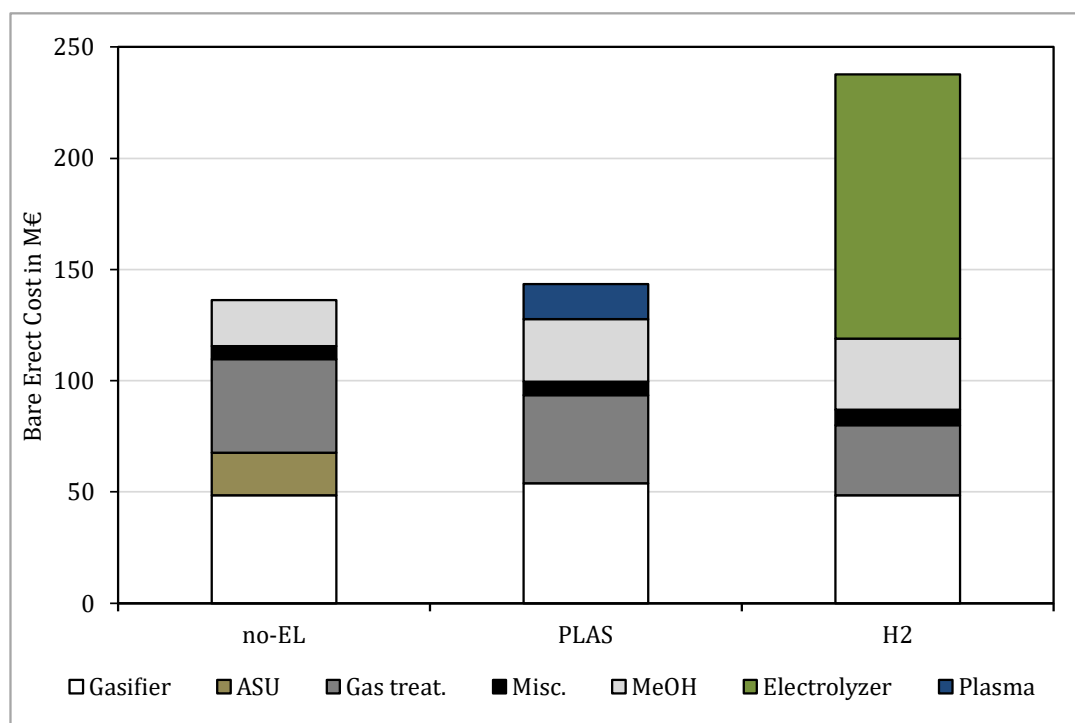


Figure 4: CAPEX distribution for 3 configurations

The annualized NPV analysis is dominated by two opposing effects: increasing methanol revenues with increasing carbon recovery and increasing electricity expenses with the degree of electrification. The no-EL configuration exhibits the most favorable balance of costs and revenues. For H₂, the additional revenues from increased methanol production do not compensate the combination of electrolysis cost and high electricity consumption under base-case conditions.

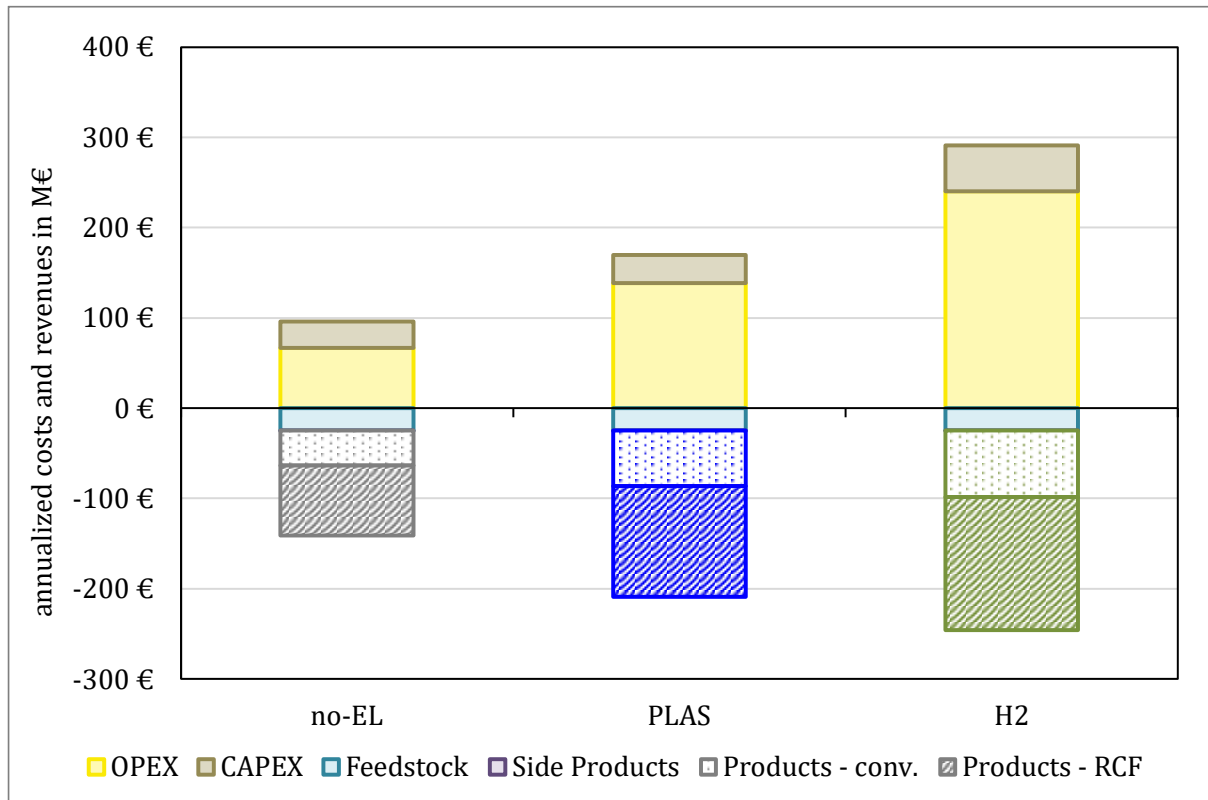


Figure 5: NPV distribution of 3 configurations under baseline conditions

For the LCOP, the non-electrified case remains the least expensive configuration at approximately 527 €/t MeOH, which is within the range of conventional methanol market prices. The PLAS configuration exhibits a higher LCOP than no-EL, but remains below the assumed RCF market benchmark. In contrast, H₂ shows the highest LCOP by a significant margin due to the combined effects of high electrolysis investment and electricity consumption. For the electrified configurations, electricity price and the efficiency of electricity integration have the strongest influence on production cost. The impact increases with the amount of electricity supplied to the process and is therefore particularly pronounced for H₂. The effect of the electrification efficiencies indicates the lever that further technology development has in improving the viability of electrification scenarios. In the non-electrified configuration, the cost of fossil CO₂ emissions becomes the dominant sensitivity parameter, with an LCOP impact range of 477 €/t MeOH, whereas electricity price and plant availability have comparatively limited influence. Overall, the comparison confirms the economic preference for direct electrification also identified for gasification-based methanol production in previous studies [4].

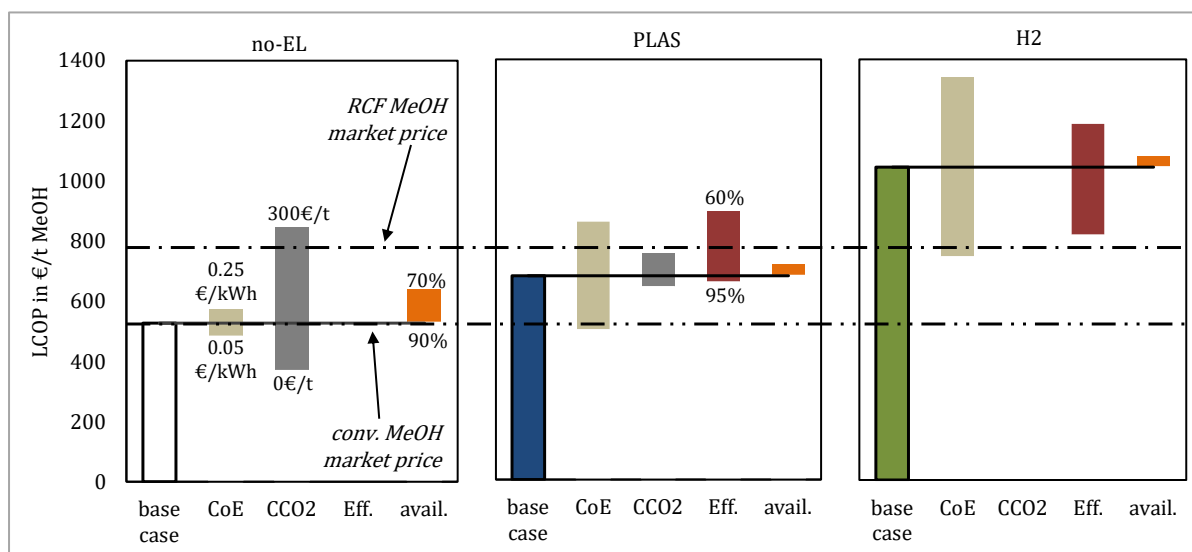


Figure 6: Levelized cost of production LCOP for the 3 configurations, sensitivity for cost of electricity (CoE), cost of CO₂ (CCO₂), efficiency of plasma/electrolyzer and plant availability

GHG calculation impact

The GHG assessment demonstrates that electricity supply is decisive not only for process economics but also for RED fuel eligibility. At the assumed average GHG intensity of grid electricity, none of the three configurations achieves the required 70% GHG emission reduction for RED-compliant fuel production when operating with a fully fossil waste-carbon feedstock. During periods with eligible renewable electricity, however, all configurations exceed the required GHG reduction. For an exclusively fossil feedstock, the share of RCF in total annual methanol production therefore follows the annual availability of eligible renewable electricity.

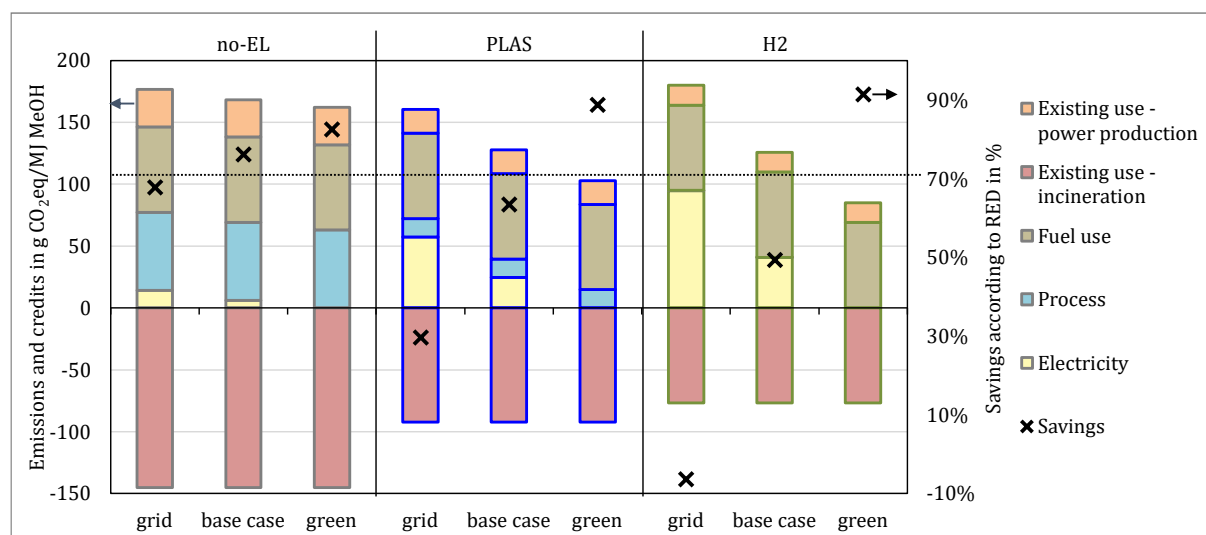


Figure 7: Emissions and emission savings according to RED GHG calculation for grid electricity, base case electricity supply and green electricity supply

Increasing the biogenic carbon fraction of the waste feedstock changes both the overall GHG intensity and the resulting product classification. In the no-EL configuration, the GHG threshold can be met at a greater scope with an increasing biogenic product fraction, ultimately resulting in complete ABF production for a fully biogenic feedstock. In the electrified configurations, operation during periods without eligible renewable electricity continues to be constrained by

the GHG footprint of grid electricity. With increasing biogenic carbon content, however, the RED-compliant product distribution progressively shifts toward ABF in the PLAS configuration and toward a combination of ABF and RFNBO in the H₂ configuration. The latter benefits from the possibility of allocating eligible electrolytic hydrogen to RFNBO production, whereas direct electricity input to the plasma process is not recognized for RFNBO production under the applied framework.

Profitability

The economic impact of renewable-electricity availability differs substantially between the three configurations. For a plastic waste feedstock containing exclusively fossil carbon and operation with high-GHG grid electricity, only the no-EL configuration achieves profitability under the assumed framework. Its comparatively low electricity demand limits the influence of both electricity price and electricity-related GHG emissions, although the relatively small assumed market premium for RCF also limits the economic benefit of RED-compliant operation.

In contrast, the electrified configurations require a minimum annual availability of eligible renewable electricity before the associated product premiums compensate for their additional electricity and capital expenses. Under the investigated assumptions, PLAS requires approximately 2000 h/a of renewable-electricity availability to reach profitability, whereas H₂ requires approximately 6000 h/a. With increasing renewable-electricity availability, however, the economic performance of the electrified configurations improves strongly. At high availability, all three configurations reach comparable annualized economic results in the range of approximately 50–100 M€/a. Consequently, the availability of large quantities of low-cost and low-GHG electricity represents a decisive boundary condition for electrified waste gasification. This observation is consistent with the wider assessment of electrified chemical recycling [2]. As grid GHG emissions reduce due to energy transition efforts, economic viability of electrified routes improves. In a scenario close to net-zero, the PLAS configuration is economically viable without any directly associated renewable electricity installation. This is due to improved revenues as the product methanol qualifies as RCF even when grid electricity is used.

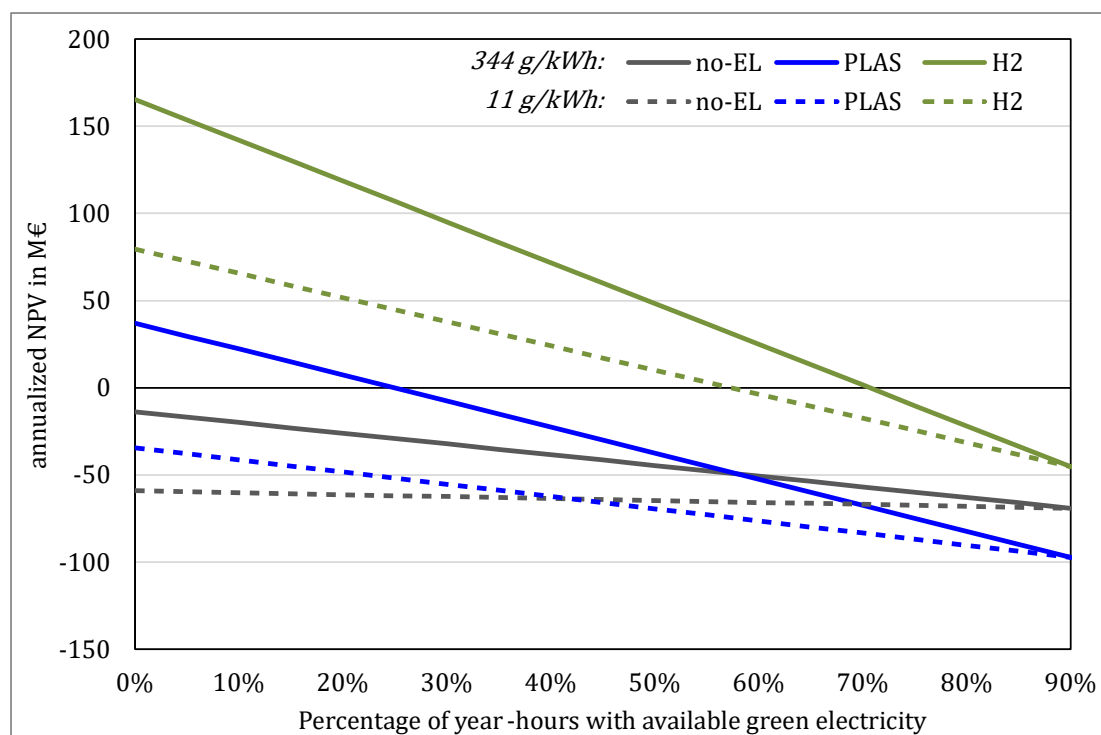


Figure 8: Impact of RE availability on NPV under 100% fossil carbon in feedstock

The influence of feedstock composition becomes increasingly important when a base renewable-electricity availability of 4500 h/a is considered. With increasing biogenic carbon content, both no-EL and H2 exhibit a substantial improvement in profitability. For no-EL, this effect results primarily from the decreasing fraction of conventional methanol and the corresponding increase in higher-value ABF production. H2 additionally benefits from a shift from RCF toward both ABF and RFNBO, which is associated with higher assumed product revenues. In contrast, the economic performance of PLAS improves less strongly because renewable electricity supplied directly to the gasification process does not qualify the corresponding product fraction as RFNBO under the current framework. Hence, the regulatory treatment of direct and indirect electrification has a substantial influence on their relative economic performance.

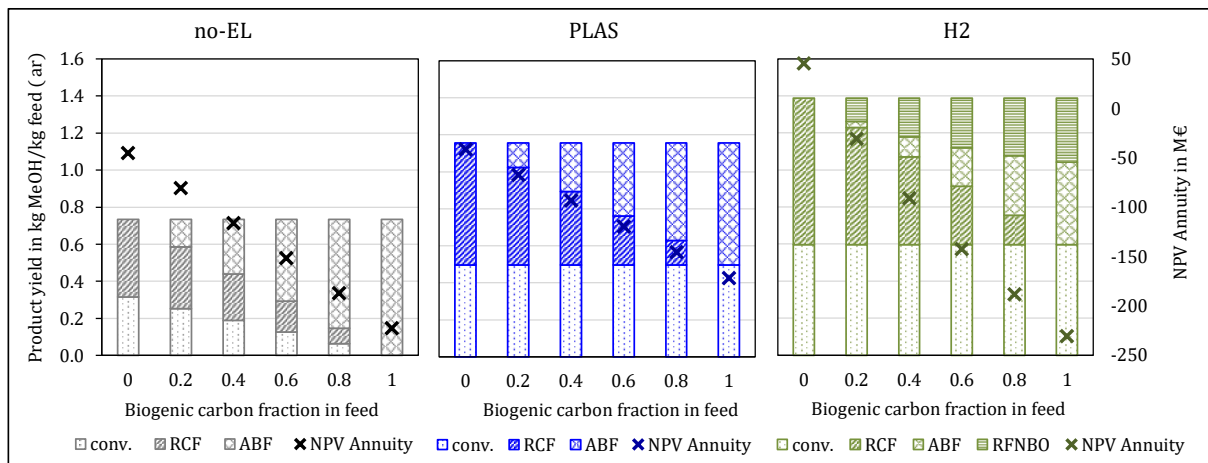


Figure 9: Product yield and distribution and NPV of all configurations with increasing biogenic carbon feed content under 4500 h per year RE availability

To investigate this regulatory effect, a modified PLAS scenario is considered in which the plasma-associated renewable electricity input is treated as an eligible enthalpy contribution to RFNBO production. Under this assumption, PLAS reaches a similar NPV to H2 for feedstocks with a high biogenic carbon fraction, while retaining its comparatively favorable performance for plastic-rich feedstocks. This result indicates that the current differentiation between direct and indirect renewable-electricity integration can materially influence the business case of otherwise comparable electrification pathways.

A second modified scenario exploits the inherent flexibility of hydrogen integration. In the H2 configuration, electrolytic hydrogen production can be adjusted to periods in which eligible renewable electricity is available, as commonly considered for Power-to-X concepts [17]. When hydrogen integration is reduced during periods without renewable electricity, total methanol production decreases and additional equipment required for oxygen-based gasification and syngas conditioning remains necessary. Nevertheless, the modified H2 configuration is substantially more profitable than continuous hydrogen integration and also outperforms PLAS for biogenic carbon fractions above approximately 20% under the investigated assumptions. This advantage results from combining flexible electricity consumption with the higher-value RED fuel fractions enabled by electrolytic hydrogen. Flexible operation of plasma gasification is conceptually possible to a more limited extent, for example through flexible plasma/oxygen operation of a secondary gas polishing stage. Such an operating concept is not considered in the present assessment.

Among the investigated pathways, plasma electrification consequently presents the most favorable compromise between increased carbon recovery and economic performance for plastic-rich feedstock. Hydrogen integration can achieve higher carbon recovery and near-complete utilization of feedstock carbon, but requires substantially more electricity and investment. Hydrogen production at locations with high renewable-energy availability,

intermediate storage and flexible operation during low-price electricity periods may improve the attractiveness of indirect electrification [6].

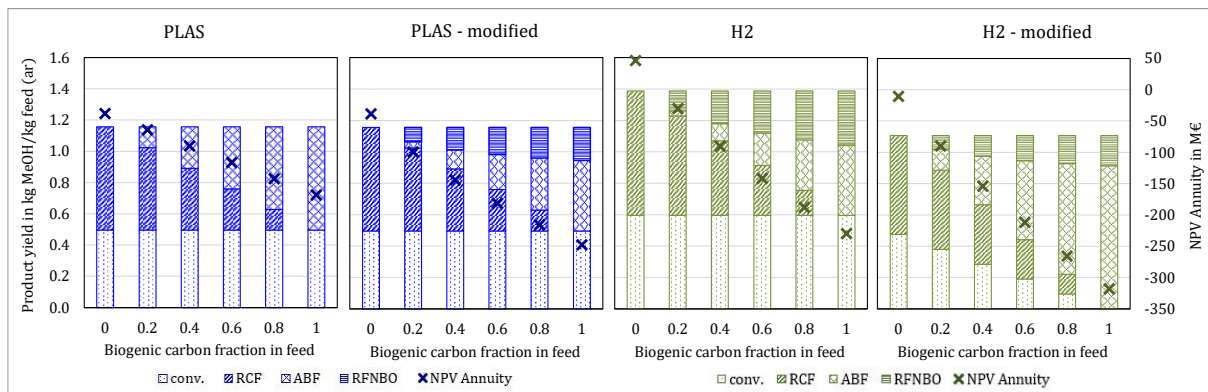


Figure 10: Product yield and distribution and NPV for impact of plasma RFNBO eligibility (PLAS - modified) and flexible hydrogen integration (H2 - modified) with increasing biogenic carbon feed content under 4500 h per year RE availability

Conclusion

A comparative techno-economic and regulatory assessment of three gasification-based methanol production pathways has been conducted, comprising non-electrified oxygen-based gasification, direct electrification via plasma and indirect electrification via electrolytic hydrogen. In addition to process performance and production cost, the assessment considers the GHG requirements and fuel classifications defined by the Renewable Energy Directive. The results demonstrate that the preferred electrification pathway cannot be identified from process performance alone, but depends strongly on renewable-electricity availability, feedstock carbon origin and the regulatory classification of the resulting methanol.

Electrification substantially increases feedstock carbon utilization. Carbon recovery increases from approximately 52% in the non-electrified reference to approximately 82% with plasma-assisted gasification and to approximately 99% with unrestricted hydrogen integration. Plasma electrification also increases the energy efficiency relative to the reference configuration, whereas the lower conversion efficiency associated with electrolysis reduces the corresponding energy performance of the hydrogen pathway. Consequently, plasma provides a more efficient route to increased carbon recovery, while hydrogen integration enables near-complete utilization of feedstock carbon.

This advantage is also reflected in the conventional techno-economic comparison. PLAS requires a similar total CAPEX compared to the non-electrified process, but shows elevated electricity demand. H2 requires substantially higher investment and electricity input. Accordingly, no-EL exhibits the lowest LCOP, while PLAS remains below the assumed RCF market benchmark and H₂ shows the highest production cost. For the electrified configurations, electricity price and electricity-conversion efficiency are the dominant economic parameters.

The RED-based assessment conditions introduce additional dependencies. For a fossil-carbon waste feedstock, operation with average grid electricity does not provide the required 70% GHG emission reduction for any configuration, whereas operation during periods with eligible renewable electricity enables RED-compliant fuel production. The annual availability of renewable electricity therefore determines the fraction of qualifying product and becomes a direct economic parameter through the associated fuel premiums. Under the investigated assumptions, PLAS requires approximately 2000 h/a of eligible renewable-electricity availability to become profitable, compared to approximately 6000 h/a for continuous H₂ integration. At high renewable-electricity availability, however, the profitability of all three

pathways converges.

Feedstock composition introduces a second decisive effect. Increasing biogenic carbon content enables progressively larger shares of ABF and therefore improves the economic performance of no-EL. H₂ benefits additionally from RFNBO production through the integration of eligible electrolytic hydrogen. PLAS does not receive this benefit under the currently applied framework because direct renewable electricity input to the gasification process is not accounted for as an RFNBO contribution. Consequently, increasing biogenic carbon content favors the hydrogen pathway relative to plasma despite the intrinsically higher electricity demand and investment of electrolysis.

The scenario analyses show that this result is not exclusively technology-driven. If renewable electricity supplied to plasma gasification is assumed to contribute to RFNBO production, PLAS reaches economic performance comparable to the H₂ configuration for feedstocks with high biogenic carbon contents while maintaining its advantages for plastic-rich feedstock. Conversely, exploiting the operational flexibility of H₂ production substantially improves the indirect electrification pathway. Restricting electrolytic hydrogen integration to periods of renewable-electricity availability reduces methanol output but avoids unfavorable electricity consumption and improves the production of high-value RED-compliant fuels. Under the investigated assumptions, this flexible H₂ configuration becomes more profitable than PLAS at biogenic carbon fractions above approximately 20%.

The results therefore indicate two different application fields for the investigated electrification concepts. Plasma-assisted gasification represents the more robust pathway for plastic-rich residual waste because it combines substantially increased carbon recovery with comparatively low additional investment and electricity demand. Hydrogen integration becomes increasingly attractive where high shares of biogenic carbon, sufficient eligible renewable-electricity availability and flexible electrolyzer operation coincide. In this case, the ability to generate RFNBO alongside RCF and ABF can compensate for the intrinsically less favorable techno-economic performance of electrolysis.

More generally, the comparison demonstrates that regulatory fuel classification can alter the relative attractiveness of direct and indirect electrification to an extent comparable to the underlying process economics. Future assessments of gasification-based chemical recycling should therefore consider technology development, electricity-system integration and regulatory treatment jointly. In particular, the treatment of direct renewable-electricity input within RFNBO accounting and the practical potential for flexible operation of both plasma and electrolysis systems require further investigation. Application-specific studies should additionally consider realistic temporal renewable-electricity profiles, feedstock composition and availability, and the corresponding development of waste gate fees and product-market premiums.

References

- [1] M. Dossow, D. Klüh, K. Umeki, M. Gaderer, H. Spliethoff, S. Fendt, *Energy Environ. Sci.* **2024**, 17 (3), 925–973. DOI: 10.1039/d3ee02876c.
- [2] S. A. Theofanidis, E. Delikonstantis, V.-L. Yfanti, V. V. Galvita, A. A. Lemonidou, K. Van Geem, *Waste Manag.* **2025**, 193, 155–170. DOI: 10.1016/j.wasman.2024.12.003.
- [3] V. Nagar, R. Kaushal, *Int. J. Hydrog. Energy.* **2024**, 77, 405–419. DOI: 10.1016/j.ijhydene.2024.06.180.
- [4] D. Klüh, E. Anetjärvi, K. Melin, E. Vakkilainen, *Energy Convers. Manag.* **2024**, 314, 118649. DOI: 10.1016/j.enconman.2024.118649.
- [5] K. Prifti, F. Lechtenberg, F. Manenti, A. Espuña, M. Graells, *Resour. Conserv. Recycl.* **2024**, 208, 107653. DOI: 10.1016/j.resconrec.2024.107653.
- [6] A. Poluzzi, G. Guandalini, S. Guffanti, M. Martinelli, S. Moiola, P. Huttenhuis, G. Rexwinkel, J. Palonen, E. Martelli, G. Groppi, et al., *Front. Energy Res.* **2022**, 9. DOI: 10.3389/fenrg.2021.795673.
- [7] Polimerica.it, “Germany opens door to chemical recycling,” available at <https://www.polimericanews.com/articolo.asp?id=568>, **n.d.**
- [8] J. Dierickx, *Economic Value of Methanol for Shipping under FuelEU Maritime and EU ETS*, Methanol Institute **2024**.
- [9] “Decarbonising maritime transport – FuelEU Maritime - Mobility and Transport,” available at https://transport.ec.europa.eu/transport-modes/maritime/decarbonising-maritime-transport-fueleu-maritime_en, **n.d.**
- [10] F. Fabry, C. Rehmet, V. Rohani, L. Fulcheri, *Waste Biomass Valorization.* **2013**, 4 (3), 421–439. DOI: 10.1007/s12649-013-9201-7.
- [11] F. Keller, P. Mamani Soliz, L. G. Seidl, R. P. Lee, B. Meyer, *Data Brief.* **2022**, 41, 107848. DOI: 10.1016/j.dib.2022.107848.
- [12] M. Holst, S. Aschbrenner, T. Smolinka, C. Voglstätter, G. Grimm, *Cost Forecast for Low Temperature Electrolysis*, Fraunhofer ISE **2021**.
- [13] “Renewable Energy Directive,” available at https://energy.ec.europa.eu/topics/renewable-energy/renewable-energy-directive-targets-and-rules/renewable-energy-directive_en, **n.d.**
- [14] A. Helf, F. Keller, M. Gräbner, *Energy Convers. Manag.* **2026**, 353, 121181. DOI: 10.1016/j.enconman.2026.121181.
- [15] *Methanex Pricing*. **n.d.** available at <https://www.methanex.com/our-products/about-methanol/pricing/>.
- [16] *Arg. Biofuels - Mark. Price Comment.* **2025**. available at <https://www.argusmedia.com/en/solutions/products/argus-biofuels>.
- [17] S. Mucci, A. Mitsos, D. Bongartz, *J. Energy Storage.* **2023**, 72, 108614. DOI: 10.1016/j.est.2023.108614.

Circular Carbon for resilient Chemical value chains enabled by Plasma Technology

S. Renninger

Cyclize Gmbh, Stuttgart, Germany

Cyclize introduces an innovative plasma reforming technology to advance the carbon circular economy by converting CO₂ from point sources and non-recyclable waste into syngas, a mixture of carbon monoxide and hydrogen. Syngas serves as a primary building block for the chemical industry. Leveraging their patented plasma reforming technology, Cyclize thus reduces the reliance on natural gas as a feedstock. The technology contributes to resilient and sustainable value chains in a changing geopolitical landscape. It is scalable and requires no green premium at scale.

The plasma dry reforming process can use up to 5 kg of CO₂ as feedstock per kg of waste, ensuring an overall CO₂-negative footprint. A variety of non-recyclable post-consumer and industrial waste streams, such as liquids, automotive waste, refuse derived fuel or composites can be employed. Economic feasibility hinges on robust process design and near-perfect energy efficiency. To achieve this, Cyclize develops key components, such as plasma reactors and power electronics, as well as the overall process application in a growing interdisciplinary team. Following successful demonstration on a lab- and pre-industrial scale, Cyclize is now progressing the first commercial application. The presentation aims to give an overview of the technology, its performance, applicable value chains, and the state of its development.

Production of Fischer-Tropsch Suitable Syngas for Green Jet-fuel Through Dry Reforming of Methane-CO₂-mixtures

M. Bachstädter, A. Jess

Universität Bayreuth, Lehrstuhl für chemische Verfahrenstechnik, Bayreuth, Germany

One of the key challenges of the 21st century is global warming, which is primarily driven by CO₂ emissions. According to current knowledge and status of research, the complete electrification of certain transport sectors, particularly aviation, is not feasible. A promising alternative is the partial substitution of conventional crude oil based fuels by sustainable liquid fuels based on biogas and/or CO₂ and renewable hydrogen. Research into the development of such fuels began in 2023 with the launch of the project *PlasmaFly* [1].

The project is coordinated by the University of Stuttgart and involves several partners, including Overspeed, Infraserb Hoechst, LINDSCHULTE, and the University of Bayreuth (Chair of Chemical Engineering). Together, they aim to develop sustainable jet-fuel derived from biogas. The University of Bayreuth is responsible for the synthesis and characterization of catalysts for the dry reforming of methane.

This endothermic reaction enables the conversion of methane and CO₂ into syngas. Although catalyst deactivation due to carbon deposition remains a major challenge, nickel is considered the most promising active metal, as noble metals are prohibitively expensive for industrial applications [2]. Currently, the University of Bayreuth is working on the development of a nickel-based catalyst with a reduced deactivation rate. The process is carried out at high temperatures of approximately 800 °C and atmospheric pressure. The controlled addition of water is expected to mitigate carbon deposition on the catalyst surface.

So far, a catalyst consisting of 10 wt % nickel supported on aluminium oxide has been selected. Experimental results demonstrate favorable conversion rates, yields, and selectivities. Despite the formation of carbon deposits, if no steam is added to the feed gas, only a minor loss of catalytic activity has been observed. Consequently, current research focuses on further suppressing coking phenomena. It is anticipated that, by the time of the conference, results for a stable, high-performance catalyst will be available.

References:

[1] NOW GmbH, (2023), Nationale Organisation Wasserstoff- und Brennstoffzellentechnologie, PlasmaFly, BMDV, Berlin

[2] Budiman W. A. et al, (2012), Dry Reforming of Methane Over Cobalt Catalysts, Springer, Catal. Surv. Asia, 183-197

Thermal Behavior and Runaway Analysis of Exothermic Reactions in Fixed-Bed Reactors: CO₂ Methanation as a Case Study

C. Bischoff, C. Kern, A. Jess

Universität Bayreuth, Lehrstuhl für Chemische Verfahrenstechnik, Bayreuth, Germany

The catalytic methanation of CO₂ represents a key technology for Power-to-Gas applications and sustainable energy storage. However, the reaction is strongly exothermic, which poses significant challenges for reactor operation, heat management, and process safety, particularly in cooled fixed-bed reactors. Insufficient heat removal can lead to pronounced temperature gradients, hot spot formation, and, in extreme cases, thermal runaway.

This contribution investigates the impact of reactor operation and design parameters on the thermal behavior of CO₂ methanation in a packed-bed reactor. The methanation process serves as a representative case study to generally analyze thermal runaway phenomena in highly exothermic fixed-bed reactions. Special emphasis is placed on the prediction and characterization of temperature profiles within the reactor, as they are critical indicators for safe and stable operation, as well as for an accurate description of reactor performance with respect to conversion behavior.

To this end, one-dimensional (1D) and two-dimensional (2D) reactor models are developed and compared using numerical simulations for generally exothermic reactions in fixed-bed reactors. The models account for reaction kinetics, heat generation, and axial as well as radial heat transport. The one-dimensional model is augmented by an effective heat transfer correlation to enhance its predictive performance. By appropriately adjusting heat removal, the 1D model can closely reproduce the temperature profiles obtained from the 2D model, particularly regarding the onset of thermal runaway.

The results provide insights into the suitability of different modeling approaches for the analysis of exothermic fixed-bed reactors and contribute to the design and safe operation of methanation reactors and related catalytic processes.

EnerFuel – Production of Fuels and Energy Carriers from Biogenic Residues and Plastic Waste for the Development of Regional Value Chains

K. Rimagmos, T. Plessing

Hochschule Hof, Institut für Wasserstoff- und Energietechnik, Hof, Germany

The limited recyclability of heterogeneous waste streams, combined with the increasing demand for low-carbon energy carriers, requires a robust thermochemical conversion pathway capable of handling variable feedstocks. A key challenge is the conversion of mixed biogenic and polymer residues into synthesis gas under conditions that ensure both stable reactor operation and consistent product composition.

The EnerFuel project addresses this challenge through the development of integrated process concepts for waste-to-syngas conversion, followed by upgrading routes toward hydrogen and liquid fuels. The simultaneous achievement of high feedstock flexibility, operational stability and efficient carbon utilisation is central to the approach. The methodology combines experimental investigations at pilot scale with model-based process analysis. Gasification experiments are conducted to characterize reaction behavior, syngas composition, and long-term stability, while process simulations and sensitivity analyses are employed to evaluate system performance and identify key operating parameters. A particular focus is placed on fuel engineering. Tailored pelletization strategies are developed to produce homogeneous composite fuels from mixed plastic and biomass fractions. These engineered fuels are designed to enhance feeding characteristics, mitigate operational instabilities, and improve syngas quality, including the suppression of tar formation.

The project emphasizes technology transfer and industrial applicability through close collaboration with small and medium-sized enterprises. Experimental findings, simulation tools, and optimized fuel formulations are systematically translated into practice to support reactor design and process optimization under industrially relevant conditions. Running from 2025 to 2028 and co-funded by the European Regional Development Fund, the project aims to deliver a validated framework for scalable and reliable waste-to-fuel conversion systems. The expected outcomes contribute to improved resource efficiency, reduced dependence on fossil fuels, and the strengthening of regional value chains.

Investigation of the Electrochemical Ethylene Glycol Oxidation using Ni-based Layered Double Hydroxides

I. Kohlhaas¹, L. Cino², C. Englezos², G. Mul², G. Katsoukis², R. Palkovits³

¹RWTH Aachen University, Institute for Technical and Macromolecular Chemistry, Aachen, Germany,

²University of Twente, Enschede, The Netherlands, ³Forschungszentrum Jülich, Jülich, Germany

Plastic waste has become indispensable in our daily lives and in industry. Post-consumer plastic waste has increased to 260 Mt of waste annually over the last decades, making up approximately 2% of the global CO₂ emission. Polyethylene terephthalate (PET) is one of the most used plastics and accounts for around 13% of annual plastic production. Unfortunately, only 20% of PET waste is recycled, neglecting opportunities given by chemical recycling. PET can easily be recycled by alkaline hydrolysis yielding ethylene glycol (EG) and terephthalic acid (TA) both of which can either be used as monomers for newly produced high-quality PET or transformed into other relevant chemicals for industry. Alkaline electrochemical oxidation of ethylene glycol (EGOR) can convert EG obtained from PET hydrolysate into an industrially relevant formate source.^[1-4]

This work investigates the influence of electrochemical catalyst pretreatment on the EGOR utilizing inexpensive and highly tunable Ni-based layered double hydroxides (LDH) to promote efficient formate production. Results show good catalytic activity for EGOR, showcasing onset potentials of as low as 1.28 V vs. RHE. Electrolysis experiments applying cyclic voltammetry pretreatment result in an increase in yield for NiMn und NiCo LDH reaching yields of 30.7% formate at >80% Faraday efficiency at 1.40 V vs. RHE over 2 h in an unoptimized cell. These results equal an increase in yield of over 10%points compared to experiments without pretreatment. Chronoamperometric pretreatment only showed minor improvement using NiMn LDH and no change or a decrease in performance using Ni, NiCo LDH and NiFe LDH compared to electrolysis without prior catalyst pretreatment. *In situ* infra-red measurements were used to investigate the mechanistic differences between the LDH materials indicating superior C–C bond cleavage activity of NiMn and NiCo LDH compared to the other tested materials.^[5,6]

In conclusion, our study highlights the potential of Ni-based LDH materials for EGOR to reduce PET waste by utilizing chemical recycling. Additionally, the potential of electrochemical pretreatment for industrial application is showcased, increasing productivity and optimizing catalyst performance.

[1]: K. M. AlAqad, M. H. Suliman, M. T. Alhaffar, L. Alhems, *Chem. Phys. Impact* **2026**, 12, 100999.

[2]: Y. Ma, Y. Zhang, W. Yuan, M. Du, S. Kang, B. Qiu, *EES Catal.* **2023**, 892.

[3]: Z. Chen, W. Wei, X. Chen, Y. Liu, Y. Shen, B.-J. Ni, *Renew. Sustain. Energy Rev.* **2024**, 195, 114333.

[4]: H. Zhou, Y. Ren, Z. Li, M. Xu, Y. Wang, R. Ge, X. Kong, L. Zheng, H. Duan, *Nat. Commun.* **2021**, 12, 4679.

[5]: I. Kohlhaas, R. Palkovits, *ChemElectroChem* **2025**, 12, 2500190.

[6]: I. Kohlhaas, L.S. Cino, C. Englezos, G. Mul, G. Katsoukis, R. Palkovits, *in preparation*.

Two-step Glycerol Valorization to 1,2-propanediol as the Basis for the Construction of a SMART-reactor

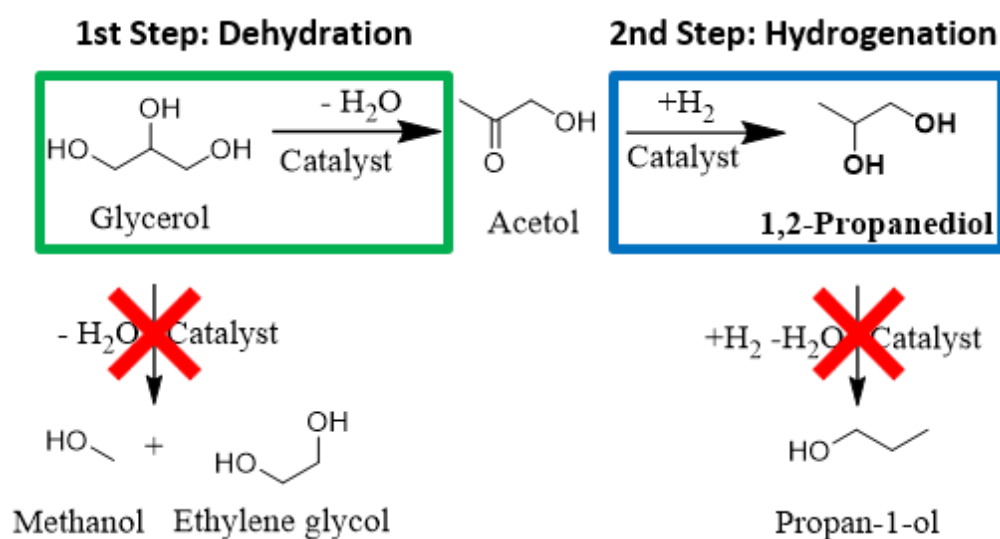
P. Hassenstein, J.-D. Krueger, J. Albert

Universität Hamburg, Institut für Technische und Makromolekulare Chemie, Hamburg, Germany

The conversion of surplus bio-based glycerol (GL), generated as a by-product of biodiesel production, into 1,2-propanediol (1,2-PDO) represents an important opportunity for a circular carbon economy. 1,2-PDO is an important platform chemical used in polymers, food, pharmaceuticals, and cosmetics. Therefore, the selective catalytic hydrogenolysis of GL to 1,2-PDO offers a sustainable alternative to conventional fossil-based production processes. However, side reactions, such as the C-C cleavage of GL to ethylene glycol and subsequent hydrogenolysis of 1,2-PDO, must be suppressed.

Therefore, the primary goal of this study is to optimize the conversion of bio-based crude GL to 1,2-PDO through reaction engineering. To this end, we performed comprehensive kinetic and mechanistic studies of the key sub-reactions to determine optimal reaction conditions that increase selectivity and minimize undesired side reactions. The reaction process is monitored over time using pH measurements, liquid and gas chromatography to determine kinetic parameters, conversion, yield, and selectivity. Based on insights from the study of isolated sub-reactions, a novel two-step process is designed to separate the dehydration and hydrogenation reactions.

In this separated process, shown in Figure 1, GL is first dehydrated under conditions that suppress C-C cleavage, followed by a separate hydrogenation step optimized to prevent product degradation.



Overview of the separated approach for glycerol hydrogenolysis to 1,2-PDO.

Both steps are conducted in the same reactor using the same in-house developed catalyst, using Ru-Cu supported on CNTs, but different reaction conditions. pH measurements have been shown to be a cost-effective, real-time analytical method for monitoring reaction progress during this two-step process. These findings establish the basis for designing an autonomous SMART-reactor (**s**ustainable, **m**ultipurpose, **a**utonomous, **r**esilient, **t**ransferable) with in-situ monitoring (e.g. acetol concentration) to switch automatically between the two process steps. The research advances sustainable GL valorization and supports more resilient, flexible biomass-based chemical production.

In conclusion, glycerol valorization to 1,2-propanediol represents a bio-based alternative to the fossil-based production of 1,2-propanediol. This approach contributes both directly and indirectly to circular economy goals and defossilization: directly, by transforming a renewable waste stream into a valuable

product and thereby reducing dependence on fossil-based feedstocks; and indirectly, by improving the sustainability and economic viability of the underlying biodiesel production process.

Process Scale-Up for Tandem Catalytic Alcohol E-Fuel Production in the E-TANDEM project

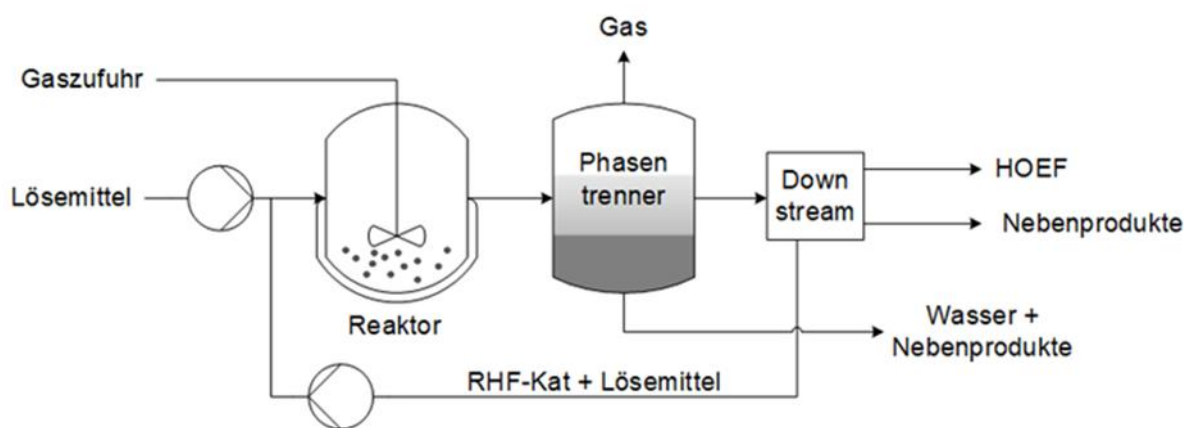
H. Stieber¹, S. Popp¹, W. Leitner^{1,2}, G. Prieto³, A. J. Vorholt¹

¹Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany, ²RWTH Aachen University, Institute of Technical and Macromolecular Chemistry, Aachen, Germany, ³ITQ Instituto de Tecnología Química (CSIC-UPV), Valencia, Spain

With the European Green Deal, the EU has decided to create a climate neutral economy by 2050, i.e. to reduce greenhouse gas emissions to zero. This is essential to stop global warming and its consequences for the climate [1]. At around 25 % (2019), the transport sector accounts for a large share of emissions, so a key aspect of the Green Deal is the substitution of fossil fuels for mobility and transport [2]. For the private transport sector, electrification is the preferred approach, but for other parts of the transport sector this is not considered realistic in the timeframe required. Other concepts are therefore needed for the decarbonisation of transport sectors, such as heavy goods vehicles, long-distance transport, shipping and aviation. One promising approach is the use of e-fuels. These greener, liquid energy sources are artificially produced only from renewable electricity and renewable resources and can also be used in conventional internal combustion engines. Overall, e-fuels can be classified as CO₂-neutral, as the amount of CO₂ emitted during combustion is equal to the amount absorbed from the atmosphere during the production of the fuel [3].

The EU project E-TANDEM aims to realise an efficient and direct production of a new, more oxygenated, diesel-like e-fuel for marine and heavy-duty transport. This involves the use of CO₂ as the only carbon source and renewable electricity as the only energy. The fuel is produced in a hybrid catalytic process that combines three catalytic pathways: High pressure electrocatalytic syngas production from CO₂ and water, coupled with a tandem catalytic e-syngas conversion. In this tandem reaction, the heterogeneously catalysed olefin-selective Fischer-Tropsch reaction is coupled with the homogeneously catalysed olefin-reducing hydroformylation reaction to produce long-chain alcohols, which can either be used directly as fuel or they can be converted into long-chain ethers in a further step [4]. The concept of the E-TANDEM project is shown in the figure below.

Having demonstrated that the tandem reaction of syngas to higher alcohols is feasible in batch mode in the laboratory, the new e-fuel production concept was scaled up in continuous operation in a miniplant as a first step towards industrial implementation [5].



References:

- [1] Europäische Kommission, (2019), Der europäische Grüne Deal
- [2] Eurpäisches Parlament, (2019), CO₂-Emissionen von PkW, <https://www.europarl.europa.eu>
- [3] . Ramirez, M. Sarathy, J. Gascon, (2020), Trends in Chemistry
- [4] E-Tandem Website, (2022), <https://e-tandem.eu/>
- [5] K. Jeske, T. Rösler, M. Belleflamme, T. Rodenas, N. Fischer, M. Claeys, W. Leitner, A.J. Vorholt, G. Prieto, (2022), Angew. Chem. Int. Ed.

Bio-based Polyesters from Itaconic Acid and L-Histidine as Sustainable Alternatives to Fossil-based Polymer Carriers

R. Sebers¹, L. Klug¹, E. Fulajtar², J. L. G. Nava², A. Pich², R. Palkovits^{1,3}

¹ITMC, RWTH Aachen, Aachen, Germany, ²DWI – Leibniz Institute for Interactive Materials, Aachen, Germany, ³Institute for a sustainable Hydrogen Economy (IHE-2), Jülich, Germany

Water-soluble, fossil-based polymers such as poly(vinylpyrrolidone) (PVP) represent an important class of carbon-carrier functional polymers in the chemical and pharmaceutical industries.^[1-3] They are produced exclusively from petrochemical feedstocks and are not biodegradable^[4,5], which means that under tightening sustainability regulations such as RED III, they are increasingly causing problems in the supply chain as well as in end-of-life disposal.^[6] Replacing these materials with biobased, chemically recyclable alternatives requires both new monomers from renewable carbon sources and scalable, resource-efficient catalytic processes.

Within the framework of the catalaix research center, we report on the synthesis of two novel biomass-derived monomers and their polycondensation into functional hydrophilic polyesters as a direct, fossil-free alternative to PVP. Starting from itaconic acid and L-histidine, both of which are accessible from renewable feedstocks, the multifunctional dicarboxylic acid monomer histidine-pyrrolidone-dicarboxylic acid (HPDA) was synthesized under hydrothermal conditions using a Brønsted-acidic zeolite catalyst (HCZM-40) in yields of up to 91%. The complementary diol monomer pyrrolidone-serinol (PS) was obtained from serinol and γ -butyrolactone in yields of up to 84%. Both processes use water as the sole solvent and deliver crystalline products that can be isolated by straightforward procedures.

Melt polycondensation of HPDA and PS yielded a new class of hydrophilic polyesters in high yields (up to 95%). Molecular weights in the range of 2.1 to 4.1 kDa could be tuned systematically by varying catalyst loading, temperature, and reaction time. The amorphous polyesters exhibit acid-catalyzed hydrolytic degradation with approximately 40% mass loss after 30 days — a decisive advantage for disposal and chemical recycling.

Application testing demonstrates that, compared to the established fossil-based PVP, the new HPDA-based polyesters achieve a 27-fold increase in the aqueous solubility of ibuprofen, outperforming PVP (3.9-fold), Soluplus® (19.6-fold), HPMC (3.9-fold), and Lutrol® (4.7-fold). The underlying mechanism is analogous to that of PVP, yet embedded within a degradable, biobased polymer scaffold. Initial cytotoxicity studies further confirm biocompatibility at relevant concentrations.

This work demonstrates an atom-economical chemical transformation of biomass into functional polymer materials that are both high-performing and deliberately designed for end-of-life degradability, thereby contributing to the vision of closed carbon cycles.

Simulation-Driven Validation and Enhancement of Reactor Models for a Technical Fixed-bed Fischer–Tropsch Synthesis

L. Hentschel, C. Kern, A. Jess

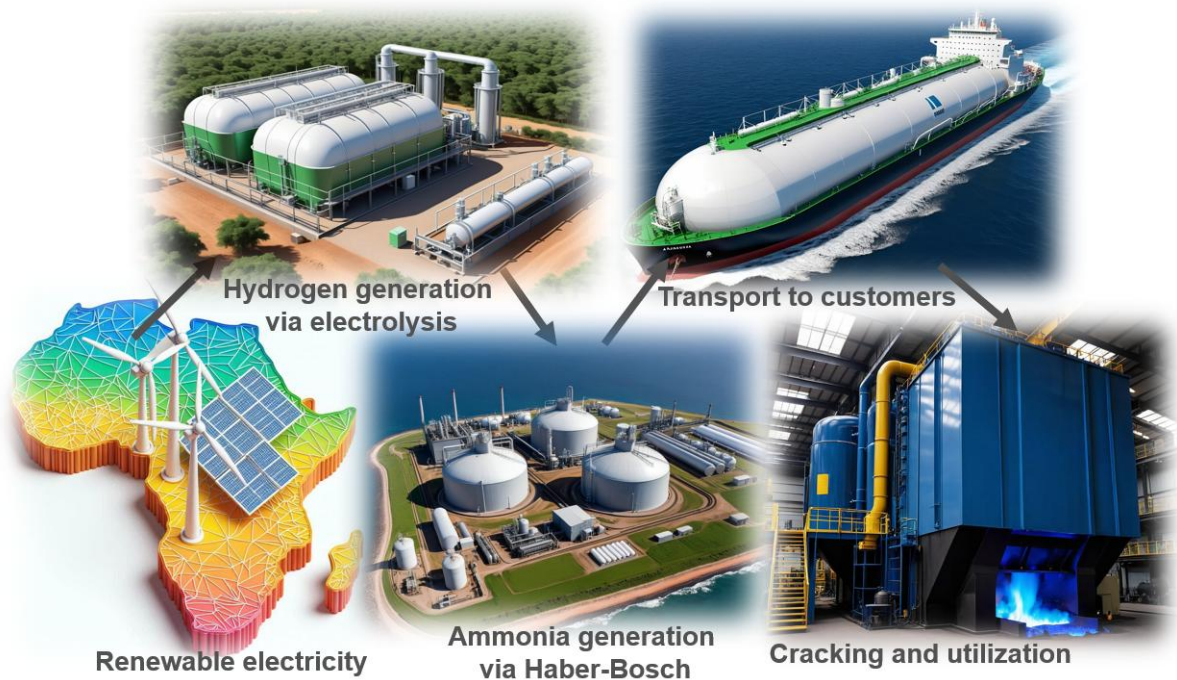
University Bayreuth, Chemical Process Engineering, Bayreuth, Germany

In the context of the energy transition and the pursuit of sustainable carbon cycles, Fischer–Tropsch synthesis (FTS) is increasingly recognized as a key technology for converting CO and CO₂ into valuable hydrocarbons. When combined with renewable hydrogen in Power-to-X concepts, CO₂ can serve as a viable carbon feedstock. Iron-based catalysts, in particular, have shown significant potential for CO and CO₂ hydrogenation due to their lower methane selectivity compared to cobalt-based systems and their promotion of long-chain hydrocarbon formation. This performance arises from their ability to catalyze both the Fischer–Tropsch synthesis and the reverse water–gas shift (RWGS) reaction, thereby enabling a broader and more economically relevant product spectrum [1, 2]. At the University of Bayreuth, a pilot-scale Fischer–Tropsch facility is currently being established, operating under industrially relevant conditions, typically at pressures around 20 bar and temperatures between 200 and 300 °C. The synthesis of the catalyst at relevant scale, along with its experimental evaluation and physicochemical characterization, has already been successfully completed [2]. Results indicate favorable performance in terms of reaction rate, conversion, and selectivity. Of particular interest is the high selectivity toward paraffinic long-chain hydrocarbons (C₂₀⁺), which represent the most economically valuable fraction of the Fischer–Tropsch product spectrum. Within this framework, simulation-based optimization strategies are being developed alongside detailed reactor models. Special attention is given to heat removal and reaction kinetics, as the highly exothermic nature of Fischer–Tropsch synthesis requires advanced thermal management to prevent thermal runaway and ensure stable reactor operation. These simulations are performed using Presto Kinetics and COMSOL Multiphysics, enabling the coupling of computational fluid dynamics (CFD) with detailed chemical reaction engineering models. The primary goal of this optimization is to maximize the conversion of CO₂ within the tubular reactor while maintaining safe operation.

Ammonia Cracking as a Key Enabler for Resilient and Carbon-Free Energy Supply Chains in Industrial High-Temperature Processes

T. Schiek

OWI Science for Fuels gGmbH, Hydrogen Technology, Herzogenrath, Germany



Energy supply chain of imported green ammonia for industrial furnaces

Despite the ongoing expansion of domestic renewable energy capacities, Germany and Europe will remain dependent on imports of physical energy carriers, particularly for hard-to-electrify industrial sectors. While current supply chains are dominated by fossil carbon carriers such as crude oil and its derivatives, the transition towards renewable systems requires carbon-neutral and carbon-free alternatives. Among these, ammonia is a promising hydrogen carrier due to its favorable storage and transport properties compared to compressed or liquefied hydrogen.

Future infrastructures are expected to rely on centralized import hubs, where ammonia is either cracked into hydrogen and fed into hydrogen networks or distributed in liquid form to decentralized industrial users. While ammonia can in principle be directly used as a fuel for industrial furnaces, its low laminar flame speed and the tendency for elevated NO_x emissions pose significant challenges for stable and clean combustion. In addition, direct combustion is energetically disadvantageous, as the enthalpy required for ammonia evaporation and cracking is drawn from the useful heat of the process rather than being supplied by otherwise unused waste heat streams. However, efficient and application-oriented ammonia conversion remains a key challenge. Decentralized cracking concepts for thermoprocess industries are constrained by the limited availability of process waste heat at temperature levels typically between 300 and 600 °C, which is significantly below conventional ammonia cracking conditions.

The project addresses this challenge by combining system-level assessment with experimental investigation. The objective is to evaluate the feasibility of different ammonia supply pathways and to identify suitable catalysts and operating windows for decentralized cracking. A life cycle assessment (LCA) is conducted to compare centralized cracking with hydrogen distribution and decentralized cracking at the point of use.

Experimentally, the project focuses on catalytic ammonia cracking under industrially relevant conditions, with particular emphasis on low-temperature operation and the utilization of available waste heat downstream of recuperation systems. Investigations include ammonia conversion,

temperature-dependent performance, and operational stability.

The expected results provide insights into the technical feasibility and system-level implications of integrating ammonia cracking into thermoprocess industries. By linking experimental data with LCA results, the project aims to identify viable pathways for using ammonia as a carbon-free energy carrier under realistic industrial boundary conditions.

Promotion of Hydrogen Production via the Thermal Decomposition of Piperylene in the Presence of By-Product Light Hydrocarbons

S. Miyamoto¹, Y. Katsuragawa¹, H. Ueda², M. Asahara², T. Watanabe², S. Ohta², T. Miyasaka²

¹Graduate School of Natural Science and Technology, Gifu University, Gifu, Japan;

²Department of Mechanical Engineering, Faculty of Engineering, Gifu University, Gifu, Japan

Abstract

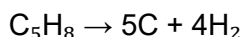
In hydrocarbon co-pyrolysis, the influence of a co-fed component can depend not only on temperature but also on the extent of reaction. In this study, piperylene (1,3-pentadiene), a C₅ diene formed as a by-product in petroleum refining and cracking processes, was investigated using an isothermal plug-flow reactor model to clarify how propane co-feeding alters its pyrolysis behavior. Calculations were performed at 101.325 kPa, 400–1400 °C, nominal residence times of 1–200 s, and piperylene/propane feed compositions of 100/0, 90/10, and 80/20 mol%. At a nominal residence time of 5 s and a temperature of 800 °C, the increments in piperylene conversion relative to pure piperylene were +10.9 and +19.3 percentage points for the 10 and 20 mol% propane conditions, respectively, while the corresponding increments in H₂ yield were +0.7 and +1.5 percentage points; the H₂ yield with 20 mol% propane was approximately 59% higher on a relative basis. At a nominal residence time of 200 s, the largest increments were observed at 700 °C, where the conversion increments were +10.8 and +17.3 percentage points and the H₂-yield increments were +0.7 and +1.4 percentage points. Thus, a comparable enhancement was observed at a temperature approximately 100 °C lower. At a nominal residence time of 5 s and a temperature of 800 °C, the combined outlet mole fraction of H₂ and CH₄ increased by approximately 12 and 21%, while the C₂H₄ mole fraction increased by factors of approximately 2.0 and 3.1. Mapping the conversion and H₂-yield increments over the temperature-nominal-residence-time plane showed that the enhanced-conversion and H₂-yield regions were centered near 800 °C at a nominal residence time of 5 s and near 700 °C at nominal residence times of 20–200 s. These results indicate that propane co-feeding can serve as an operating variable for controlling reaction progress and product selectivity during piperylene pyrolysis within specific temperature-residence-time windows.

1. Introduction

Conventional hydrogen-production routes based on hydrocarbon feedstocks generally convert the carbon contained in the feed into carbon monoxide and carbon dioxide. In contrast, oxygen-free hydrocarbon pyrolysis proceeds through C–H and C–C bond cleavage and produces H₂ together with light hydrocarbons such as CH₄, C₂H₄, and C₂H₂, aromatic compounds, and solid carbon. Therefore, when pyrolysis is considered for hydrogen production, it is important to evaluate not only the amount of H₂ produced but also how carbon and hydrogen are distributed among products during the reaction. In particular, before complete conversion is reached, differences in temperature, residence time, and feed composition are directly reflected in reaction rate and product selectivity.

This study focuses on piperylene, a C₅ component formed as a by-product in petroleum refining and cracking processes. Piperylene is a conjugated diene with the formula C₅H₈ and is treated here as 1,3-pentadiene. In actual pyrolysis, multiple pathways involving light hydrocarbons and aromatic intermediates compete. Zhou et al. [3] reviewed the chemistry of alkenes and alkadienes and showed that molecular features such as the number and position of double bonds and the stability of allylic radicals strongly affect reaction rates and product

distributions. Liu and Farooq [1] measured the thermal decomposition rate of 1,3-pentadiene behind reflected shock waves and reported faster decomposition than that of 1,3-butadiene. Herzler et al. [2] also showed that pentadienes undergo multiple decomposition and isomerization pathways at high temperatures. If complete dehydrogenation and carbonization occurred, the overall stoichiometry would be:



In hydrocarbon mixtures, minor co-fed components can alter the radical pool and thereby change the decomposition rate and H_2 -formation behavior of the major component. Using a homogeneous kinetic model of methane/ethane pyrolysis, Younessi-Sinaki et al. [9] showed that ethane or ethane-containing natural gas produced H_2 faster than methane alone under low-temperature and low-pressure conditions, whereas differences among feed compositions diminished at sufficiently high temperatures and long residence times. Hofberger et al. [10] likewise reported, in liquid-metal bubble-column experiments, increases in methane conversion and H_2 yield in the presence of ethane on the low-temperature side. These studies indicate that the effect of a coexisting hydrocarbon should be evaluated over the temperature–residence-time region in which the reaction is still progressing, rather than at a single temperature.

Propane is a light hydrocarbon that is thermally more stable than piperylene; nevertheless, in a reacting mixture it can participate in the reaction network through the formation and consumption of radical species such as H , CH_3 , C_2H_5 , and C_3H_7 . Co-feeding reactive piperylene with propane may therefore alter not only the progress of piperylene decomposition but also the distribution of products among H_2 , CH_4 , C_2H_4 , C_2H_2 , and other species through changes in the radical pool. Such effects are expected to become most evident in the conditions where the baseline pure-piperylene conversion was approximately 30–80%, where the reaction is neither essentially uninitiated nor complete.

Accordingly, this study uses an isothermal plug-flow reactor model to analyze pyrolysis for three piperylene/propane feed compositions—100/0, 90/10, and 80/20 mol%—and to clarify the effects of propane co-feeding on piperylene decomposition and hydrogen production as functions of both temperature and nominal residence time. Specifically, the increments in piperylene conversion and H_2 yield relative to the pure-piperylene condition are calculated to identify the temperature–nominal-residence-time conditions under which conversion and H_2 formation are enhanced. In addition, the outlet composition, focusing on H_2 , CH_4 , C_2H_4 , and C_2H_2 , is compared to determine how increased conversion is reflected in H_2 formation and in the distribution of hydrogen and carbon among light hydrocarbon products.

2. Numerical Methods

2.1 Reactor Model and Computational Conditions

Calculations were performed using the isothermal plug-flow reactor model in CHEMKIN, with gas-phase and surface reactions coupled [8]. The pressure was fixed at 101.325 kPa, and the temperature was varied from 400 to 1400 °C in 100 °C increments. Eight nominal residence times were considered: 1, 5, 20, 40, 60, 80, 100, and 200 s. The three feed compositions were piperylene/propane = 100/0, 90/10, and 80/20 mol%; the latter two correspond to replacing 10 or 20 mol% of the pure-piperylene feed with propane. The reactor length was 160 mm and the cross-sectional area was 86.6 mm². The NUIG-Polimi kinetic mechanism described by Koshi et al. [11] was employed. For representative comparisons of temperature and residence-time effects, results at 5, 40, and 200 s were used, while the increment maps were constructed from the 1, 5, 20, 40, 60, 80, and 200 s conditions available for all three compositions.

Table 1 Computational and reactor conditions used in this study.

Item	Value
Reactor	Isothermal plug-flow reactor with coupled gas-phase and surface reactions
Pressure	101.325 kPa (1 atm)
Temperature	400–1400 °C, in 100 °C increments
Nominal residence time	1, 5, 20, 40, 60, 80, 100, 200 s; representative comparisons: 5, 40, 200 s
Reactor geometry	Length: 160 mm; cross-sectional area: 86.6 mm ²
Feed condition A	Piperylene/propane = 100/0 mol%
Feed condition B	Piperylene/propane = 90/10 mol%
Feed condition C	Piperylene/propane = 80/20 mol%
Kinetic mechanism	NUIG-Polimi [11]

In this study, the nominal residence time $\tau_{\text{nom}} = V/Q_{\text{in}} = L/u_{\text{in}}$ was defined as the reactor volume V divided by the volumetric flow rate at the inlet condition Q_{in} . Here, L is the reactor length and u_{in} is the inlet axial velocity. The nominal residence time was used as a common basis for setting the inlet flow rate and comparing conditions, and was distinguished from the local residence-time coordinate reported by CHEMKIN, which reflects the evolving local state, composition, and total molar flow along the reactor.

2.2 Definitions of Piperylene Conversion and Hydrogen Yield

Because the total molar flow in the gas phase changes as pyrolysis proceeds, conversion and yield cannot be evaluated correctly by simply comparing inlet and outlet mole fractions. The total molar flow rate F_T at the inlet and outlet was therefore calculated from pressure P , axial velocity u , cross-sectional area A , and temperature T using the ideal-gas relation:

$$F_T = \frac{PuA}{R(T+273.15)}. \quad (1)$$

For species i , let x_i denote the mole fraction and $F_i = x_i F_T$ the corresponding molar flow rate. Piperylene conversion was then defined from the inlet and outlet piperylene molar flow rates as:

$$X_{\text{pip}} = 1 - \frac{x_{\text{pip,out}} F_{T,\text{out}}}{x_{\text{pip,in}} F_{T,\text{in}}}. \quad (2)$$

C_5H_8 and C_3H_8 both contain eight hydrogen atoms per molecule. Thus, if all hydrogen atoms supplied with the feed were recovered as H_2 , each mole of feed molecule could yield at most 4 mol of H_2 . In this study, the H_2 yield was defined as the fraction of the total feed hydrogen leaving the reactor as H_2 :

$$Y_{\text{H}_2} = \frac{F_{\text{H}_2,\text{out}}}{4F_{T,\text{in}}}. \quad (3)$$

This definition uses the total amount of hydrogen supplied to the reactor as the basis, enabling direct comparison among conditions with different propane fractions.

2.3 Comparison on the Temperature–Nominal-Residence-Time Plane

Comparisons among feed compositions were performed at the same temperature and nominal residence time. Relative to pure piperylene, the increments in piperylene conversion, ΔX_{pip} , and H_2 yield, ΔY_{H_2} , under propane co-feeding were defined by Eqs. (4) and (5). Conditions with positive ΔX_{pip} were classified as regions of enhanced piperylene conversion, while those with positive ΔY_{H_2} were classified as regions of enhanced H_2 formation. The H_2

yield and the outlet mole fractions of H_2 , CH_4 , C_2H_4 , and C_2H_2 were also compared to assess how enhanced conversion was reflected in final H_2 production and product selectivity.

$$\Delta X_{\text{pip}}(T, \tau_{\text{nom}}) = X_{\text{pip,mix}}(T, \tau_{\text{nom}}) - X_{\text{pip,pure}}(T, \tau_{\text{nom}}) \quad (4)$$

$$\Delta Y_{\text{H}_2}(T, \tau_{\text{nom}}) = Y_{\text{H}_2,\text{mix}}(T, \tau_{\text{nom}}) - Y_{\text{H}_2,\text{pure}}(T, \tau_{\text{nom}}) \quad (5)$$

3. Results and Discussion

3.1 Baseline Pyrolysis Behavior of Pure Piperylene

Figure 1 shows the temperature dependence of piperylene conversion and H_2 yield for pure piperylene at a nominal residence time of 200 s. Piperylene was essentially unreacted at 400–500 °C and began to decompose at approximately 600 °C. The conversion increased to approximately 80% at 700 °C and reached nearly 100% at 800 °C. By contrast, the H_2 yield was only approximately 4.6% at 700 °C and 23% at 800 °C, increasing more gradually than the piperylene conversion. This difference indicates that, even after piperylene is consumed, a considerable fraction of the feed hydrogen remains in hydrogen-containing products such as CH_4 and C_2H_4 . With further temperature increase, secondary decomposition and dehydrogenation of these hydrocarbons proceed, and the H_2 yield exceeds 95% above 1200 °C.

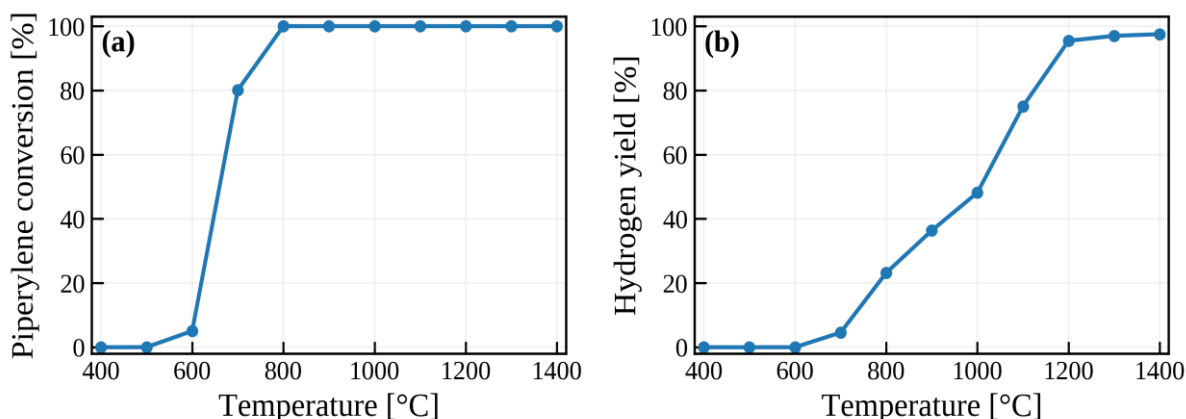


Figure 1 Baseline pure-piperylene condition at a nominal residence time of 200 s: (a) piperylene conversion; (b) H_2 yield based on total hydrogen fed.

3.2 Temperature Dependence of Outlet Product Composition

Figure 2 shows the outlet product composition of pure piperylene at a nominal residence time of 200 s. At 600–700 °C, CH_4 , C_4H_6 , C_2H_4 , and C_5H_6 increase as piperylene decomposes, whereas the H_2 fraction remains small. At 800–1000 °C, piperylene is almost completely consumed, but CH_4 remains a major hydrogen-containing product and H_2 coexists with hydrocarbon products. Above 1100 °C, the fractions of CH_4 and other hydrocarbons decrease rapidly and H_2 becomes the dominant component of the outlet gas. Thus, as temperature increases, the product distribution shifts from a hydrocarbon pool containing C_4 – C_5 species, through a light-hydrocarbon mixture dominated by CH_4 , toward an H_2 -dominated gas.

Figure 3 compares the outlet mole fractions of H_2 , CH_4 , C_2H_4 , and C_2H_2 at a nominal residence time of 5 s for the three feed compositions. At 700–800 °C, the H_2 and C_2H_4 fractions increased with increasing propane content. At 800 °C, the H_2 mole fraction with 20 mol% propane was approximately 43% higher than that for pure piperylene, while the C_2H_4 mole fraction was approximately 3.1 times higher. The CH_4 fraction also increased by approximately 15%, whereas the increase in C_2H_2 was limited to approximately 11%. Propane co-feeding therefore did not increase all products uniformly but selectively shifted the product distribution toward H_2 , CH_4 , and particularly C_2H_4 . At 900 °C, however, CH_4 and C_2H_4 increased by

approximately 5 and 13%, respectively, under the 20 mol% propane condition, whereas H_2 decreased by approximately 8%. This behavior suggests that the effect of propane co-feeding appears as enhanced H_2 formation at 700–800 °C but shifts toward redistribution of hydrogen among light hydrocarbons at 900 °C.

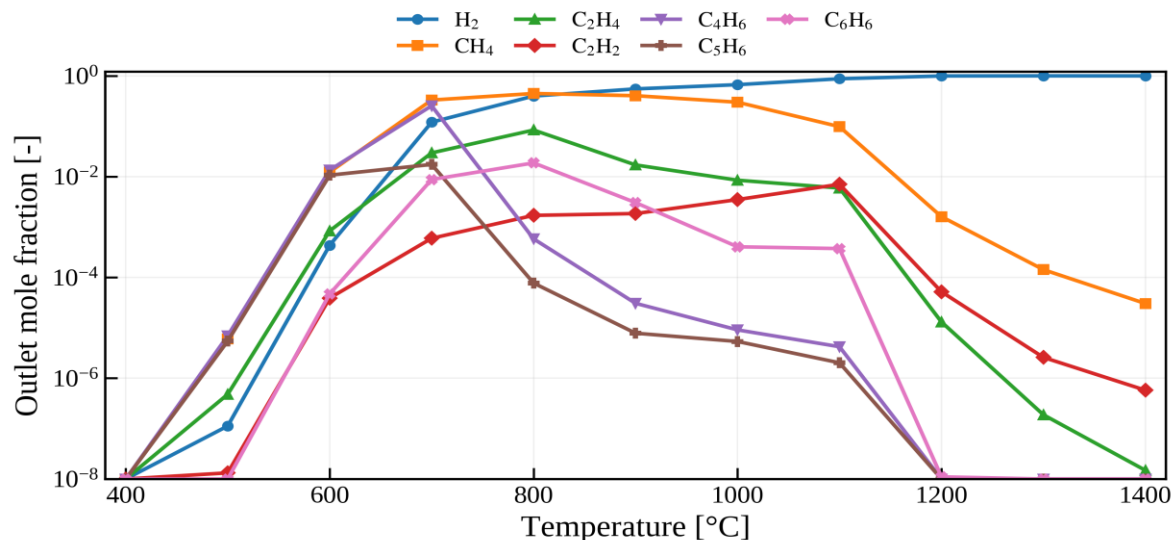


Figure 2 Outlet product composition of pure piperylene at a nominal residence time of 200 s.

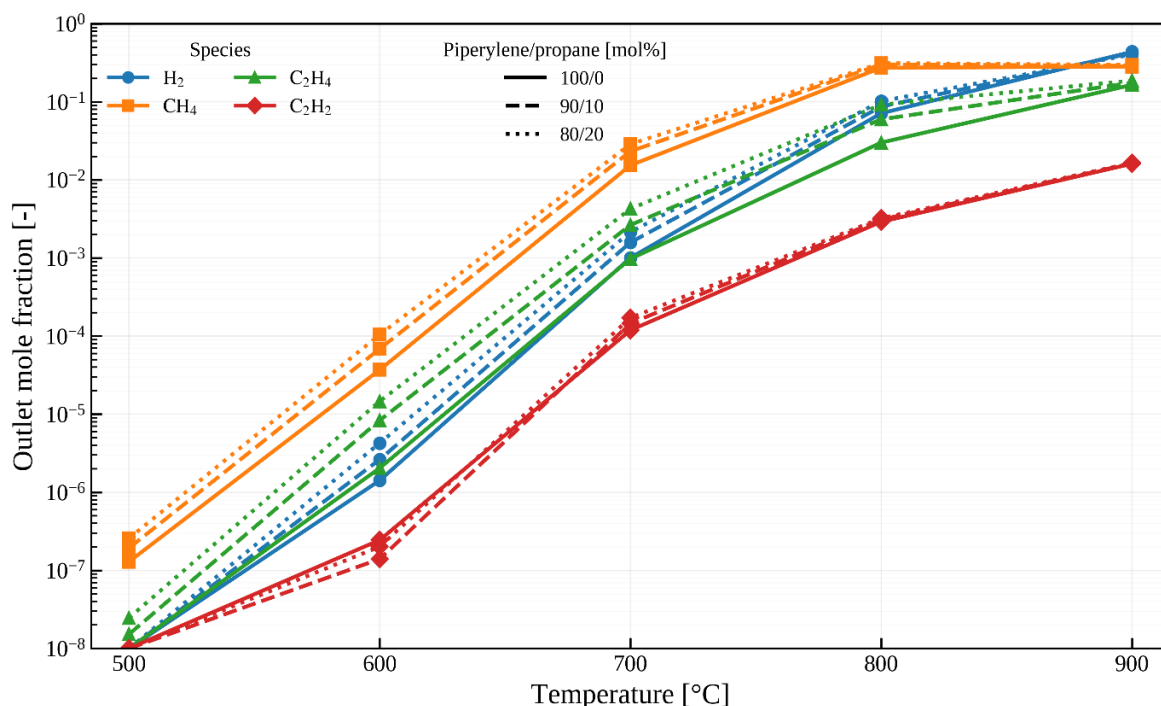


Figure 3 Effect of propane addition on the outlet mole fractions of H_2 , CH_4 , C_2H_4 , and C_2H_2 at a nominal residence time of 5 s. Feed compositions are piperylene/propane = 100/0, 90/10, and 80/20 mol%.

3.3 Temperature–Residence-Time Dependence of the Effect of Propane Co-feeding

Figure 4 shows piperylene conversion as a function of temperature for nominal residence times of 5, 40, and 200 s and for the three feed compositions. Differences caused by propane

co-feeding were small at low temperatures, where little reaction occurred, and at high temperatures, where conversion was already nearly complete, but became pronounced in the conditions where the baseline pure-piperylene conversion was approximately 30–80%. At 5 s and 800 °C, the increments in conversion relative to pure piperylene were +10.9 percentage points with 10 mol% propane and +19.3 percentage points with 20 mol% propane. At 40 s, the conditions showing the largest differences shifted to 700 °C, where the corresponding increments were +6.1 and +12.0 percentage points. At 200 s and 700 °C, the increments were +10.8 and +17.3 percentage points, respectively. Thus, a comparable enhancement was observed at a temperature 100 °C lower when the nominal residence time was increased to 200 s.

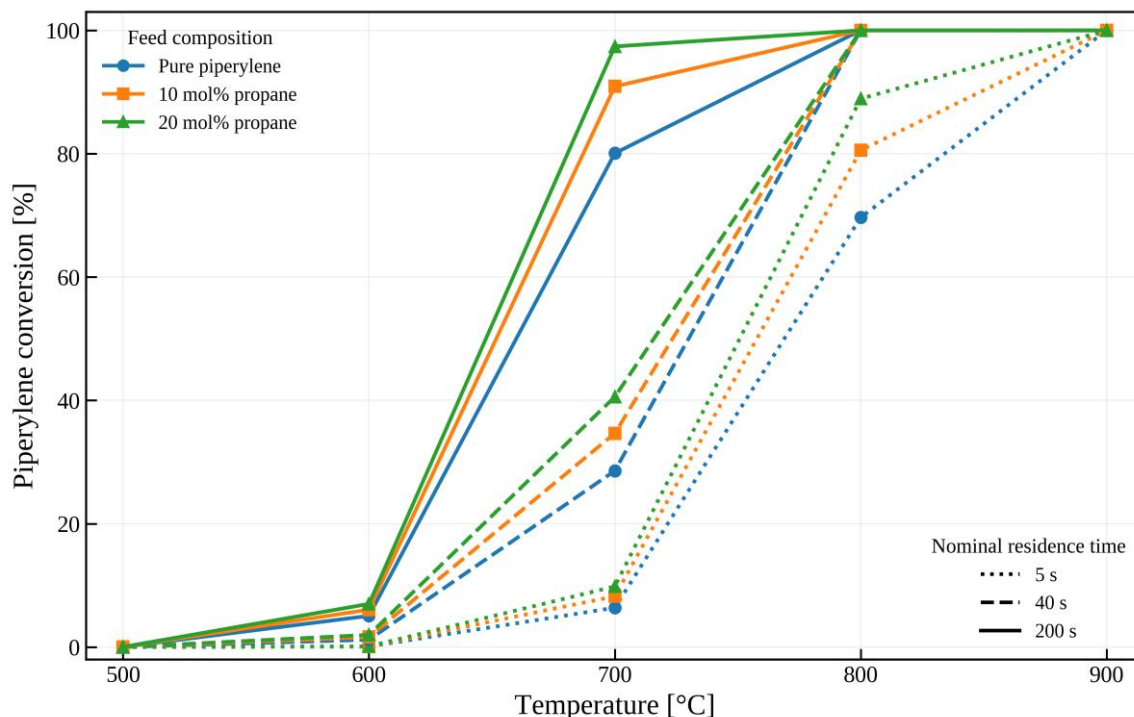


Figure 4 Temperature dependence of piperylene conversion at nominal residence times of 5, 40, and 200 s. Colors and markers denote feed composition, and line styles denote nominal residence time.

This trend is not limited to a single condition such as 200 s and 700 °C. At short residence times, a higher temperature is required for the reaction to reach an intermediate extent, and the largest increases in conversion caused by propane co-feeding therefore appear on the higher-temperature side, around 800 °C. As the residence time increases, the temperature at which intermediate conversion is reached decreases, and the region of strongest enhancement shifts toward 700 °C. Hence, the increase in piperylene conversion is associated with the extent of reaction determined jointly by temperature and residence time rather than with a single fixed temperature.

Table 2 Representative conditions showing pronounced enhancement with propane co-feeding. Column headings indicate piperylene/propane feed composition (mol%); values in parentheses are increments or ratios relative to pure piperylene.

Condition / metric	100/0	90/10	80/20
5 s, 800 °C: Piperylene conversion (%)	69.7	80.5 (+10.9 pp)	88.9 (+19.3 pp)
5 s, 800 °C: H ₂ yield (%)	2.5	3.2 (+0.7 pp)	3.9 (+1.5 pp)
5 s, 800 °C: Outlet H ₂ +CH ₄ mole fraction	0.345	0.388 (+12%)	0.416 (+21%)
5 s, 800 °C: Outlet C ₂ H ₄ mole fraction	0.030	0.060 (2.0×)	0.092 (3.1×)
200 s, 700 °C: Piperylene conversion (%)	80.1	90.9 (+10.8 pp)	97.4 (+17.3 pp)
200 s, 700 °C: H ₂ yield (%)	4.6	5.3 (+0.7 pp)	5.9 (+1.4 pp)

3.4 Region of Enhanced H₂ Yield

Figure 5 compares H₂ yield at nominal residence times of 5 and 200 s. At 5 s and 800 °C, the increments in H₂ yield relative to pure piperylene were +0.7 percentage points with 10 mol% propane and +1.5 percentage points with 20 mol% propane; the H₂ yield for the 20 mol% condition was approximately 59% higher on a relative basis. At 5 s and 900 °C, however, the increment for 20 mol% propane was –2.2 percentage points, indicating a reversal in the composition effect. At 200 s, the conditions of enhanced H₂ yield shifted to 700 °C, where the increments were +0.7 percentage points for 10 mol% propane and +1.4 percentage points for 20 mol% propane. These values are nearly the same as those at 5 s and 800 °C, indicating that a comparable enhancement in H₂ production was observed at a temperature approximately 100 °C lower when the residence time was increased. In contrast, at 200 s and 800 °C, the increment for the 20 mol% propane condition was –2.4 percentage points. Thus, the effect of propane co-feeding on H₂ production depends on reaction progress: H₂ formation is enhanced in the conditions where the baseline pure-piperylene conversion was approximately 30–80%, whereas the effect decreases and can reverse as the reaction proceeds further.

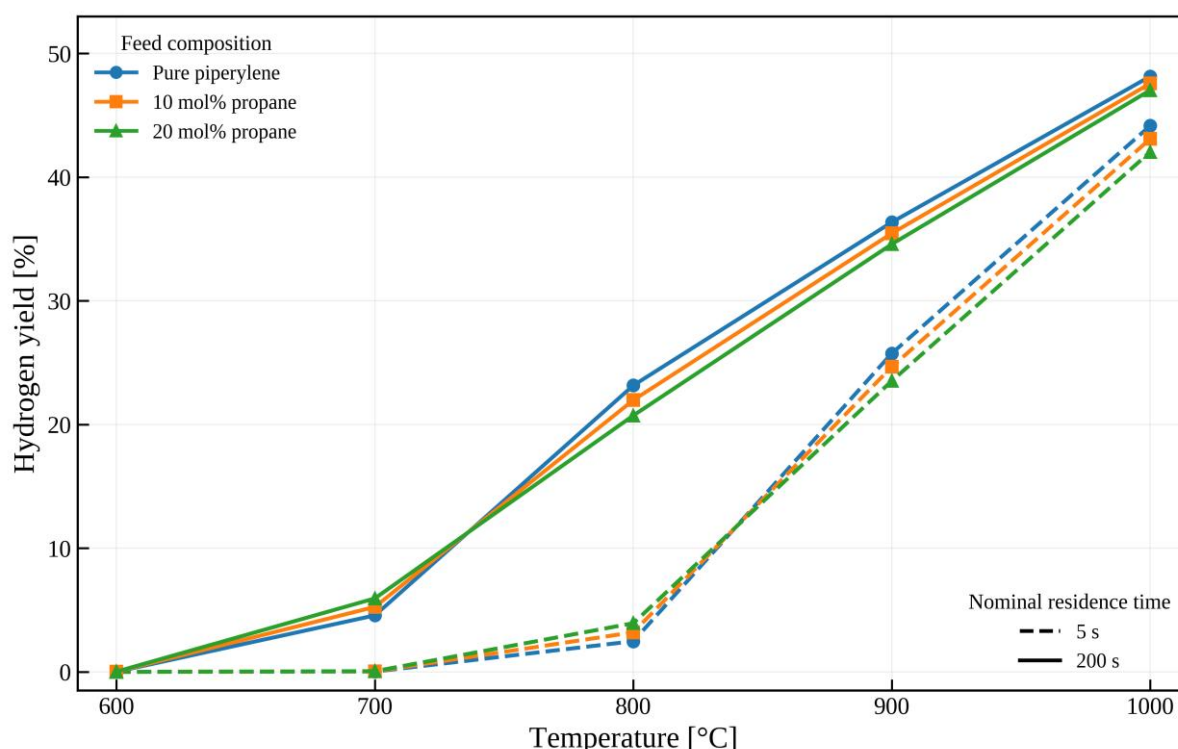


Figure 5 H₂ yield based on total hydrogen fed at nominal residence times of 5 and 200 s. Dashed lines indicate 5 s and solid lines indicate 200 s.

3.5 Visualization of Regions of Enhanced Piperylene Conversion and H₂ Yield with Propane Co-feeding

Figure 6 maps the increments in piperylene conversion, ΔX_{pip} , and H₂ yield, ΔY_{H_2} , relative to the pure-piperylene condition over the temperature–nominal-residence-time plane. In Fig. 6(a), ΔX_{pip} was +10.9 percentage points at 5 s and 800 °C and +10.8 percentage points at 200 s and 700 °C for 10 mol% propane; the corresponding values for 20 mol% propane were +19.3 and +17.3 percentage points. The maximum increments were therefore of similar magnitude at 5 and 200 s, while the temperature at which they occurred shifted by approximately 100 °C toward lower values as residence time increased. At 600 °C, the amount of reaction was small,

whereas at 900 °C piperylene was nearly completely converted; accordingly, ΔX_{pip} was close to zero under these conditions.

For ΔY_{H_2} in Fig. 6(b), the region with positive values was narrower than that for ΔX_{pip} . With 20 mol% propane, ΔY_{H_2} was +1.5 percentage points at 5 s and 800 °C and +1.4 percentage points at 200 s and 700 °C, showing that a similar enhancement in H₂ yield occurred at different temperatures depending on residence time. In contrast, ΔY_{H_2} was –2.2 percentage points at 5 s and 900 °C and –2.4 percentage points at 200 s and 800 °C. Thus, the conditions associated with enhanced H₂ production also shifted from higher temperatures at short residence time toward lower temperatures at long residence time, but occupied a narrower range than the conditions associated with enhanced piperylene conversion.

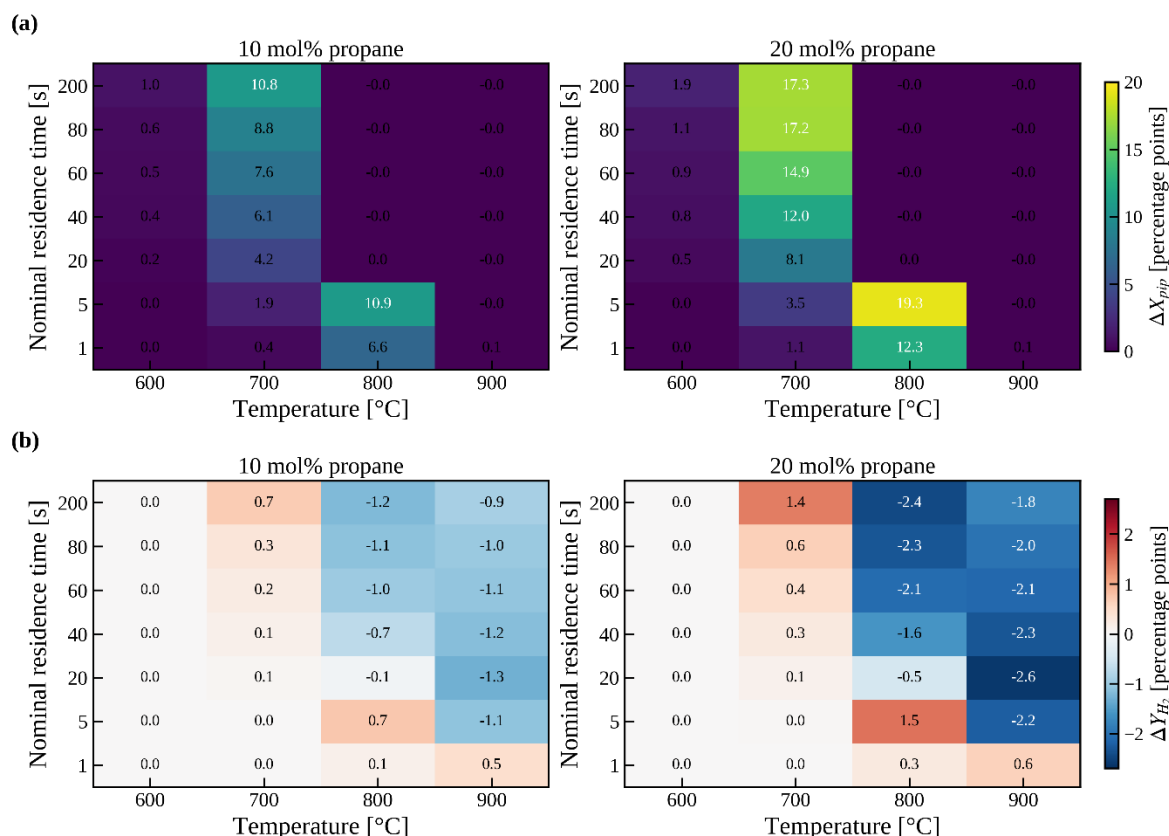


Figure 6 Temperature–nominal-residence-time maps of increments relative to pure piperylene: (a) piperylene-conversion increment, ΔX_{pip} ; (b) H₂-yield increment, ΔY_{H_2} . In each row, the left panel corresponds to 10 mol% propane and the right panel to 20 mol% propane. Positive values indicate enhancement relative to pure piperylene, whereas negative values indicate suppression.

Comparison of the two maps shows that enhancement of feed conversion and enhancement of H₂ production by propane co-feeding are not equivalent. In the conditions where the baseline pure-piperylene conversion was approximately 30–80%, ΔX_{pip} first becomes positive, while ΔY_{H_2} is positive only for a subset of those conditions. As the reaction proceeds further, the additional carbon and hydrogen converted from the feed are distributed among hydrogen-containing intermediates such as CH₄, C₂H₄, and C₃H₆, causing ΔY_{H_2} to approach zero or become negative. Accordingly, the conditions associated with enhanced conversion should be distinguished from the narrower set of conditions in which both ΔX_{pip} and ΔY_{H_2} are positive and H₂ production is enhanced. These results do not imply that propane enhances H₂ production under all conditions; rather, they demonstrate the need to select temperature and residence time according to the desired objective.

4. Implications of Propane Co-feeding for Reaction-Condition Design

The regions of enhanced reaction identified in this analysis indicate that reaction conditions should not simply be set to the highest temperature and longest residence time; instead, temperature and residence time should be combined according to the desired extent of reaction. For example, pronounced composition effects appeared around 700 °C at 200 s, whereas differences of comparable or greater magnitude appeared around 800 °C at 5 s. Therefore, if a short reactor residence time is prioritized, the increase in conversion may be exploited on the higher-temperature side, whereas a longer residence time may allow a similar enhancement to be achieved at a lower temperature.

At 5 s and 800 °C, propane co-feeding simultaneously increased H₂, CH₄, and C₂H₄, and the combined H₂+CH₄ mole fraction with 20 mol% propane was approximately 21% higher than that for pure piperylene. At 900 °C, H₂ and CH₄ together accounted for approximately 70% of the outlet gas. These results suggest a staged operating concept in which, rather than decomposing piperylene completely to H₂ in a single stage, an H₂–CH₄-rich gas is first formed at intermediate temperature and short residence time, followed by further decomposition of CH₄ and C₂ species in a subsequent higher-temperature stage. Combining the temperature–residence-time maps with the product-composition analysis enables reaction conditions to be selected while considering both H₂ production and the composition of the product gas.

Previous studies have reported that co-fed hydrocarbons such as ethane can enhance methane pyrolysis on the low-temperature side [9,10]. Extending the present evaluation framework to mixtures in which methane, ethane, or propane is the major component could provide a basis for using by-product hydrocarbons not merely as impurities but as co-components that tune reactivity and product distribution. To identify the reaction mechanism responsible for the enhanced-reaction regions observed here, future analysis should track the concentrations of radicals such as H, CH₃, C₂H₅, and C₃H₇ together with the rates of elementary reactions and clarify the dominant reaction pathways.

5. Conclusions

(1) Pure piperylene began to decompose at approximately 600 °C and was nearly completely converted at 800 °C at a nominal residence time of 200 s. The increase in H₂ yield was more gradual than the increase in piperylene conversion because, during the intermediate stages of reaction, hydrogen remained distributed among hydrogen-containing products such as CH₄ and C₂H₄.

(2) The increase in piperylene conversion caused by propane co-feeding was most pronounced in the conditions where the baseline pure-piperylene conversion was approximately 30–80%. Relative to pure piperylene, the conversion increments were +10.9 and +19.3 percentage points for the 10 and 20 mol% propane conditions at 5 s and 800 °C, and +10.8 and +17.3 percentage points, respectively, at 200 s and 700 °C. Thus, a similar degree of enhancement was observed at different temperatures depending on residence time.

(3) H₂ yield was also enhanced under specific conditions. The H₂-yield increments at 5 s and 800 °C were +0.7 and +1.5 percentage points for the 10 and 20 mol% propane conditions, while the corresponding values at 200 s and 700 °C were +0.7 and +1.4 percentage points. In contrast, the H₂-yield increment for 20 mol% propane became negative at 5 s and 900 °C and at 200 s and 800 °C, indicating that the effect of propane co-feeding reverses as the reaction proceeds.

(4) At 5 s and 800 °C, the combined outlet mole fraction of H₂ and CH₄ increased by approximately 12% with 10 mol% propane and 21% with 20 mol% propane relative to pure piperylene, while the C₂H₄ mole fraction increased by factors of approximately 2.0 and 3.1, respectively. Propane co-feeding therefore altered not only piperylene conversion but also product selectivity.

(5) When the piperylene conversion increment, ΔX_{pip} , and the H₂ yield increment, ΔY_{H_2} , each defined relative to pure piperylene, were organized over the temperature–nominal-residence-time plane, distinct regions of enhanced reaction shifted toward higher temperatures at short

residence times and toward lower temperatures at long residence times. The range of conditions associated with enhanced H₂ production was narrower than that associated with enhanced conversion, indicating that the two should be distinguished when selecting reaction conditions.

(6) Overall, propane co-feeding did not enhance hydrogen production under all conditions. Instead, it showed potential as an operating variable for modifying reaction progress and the distribution of light products within the conditions where the baseline pure-piperylene conversion was approximately 30–80%.

References

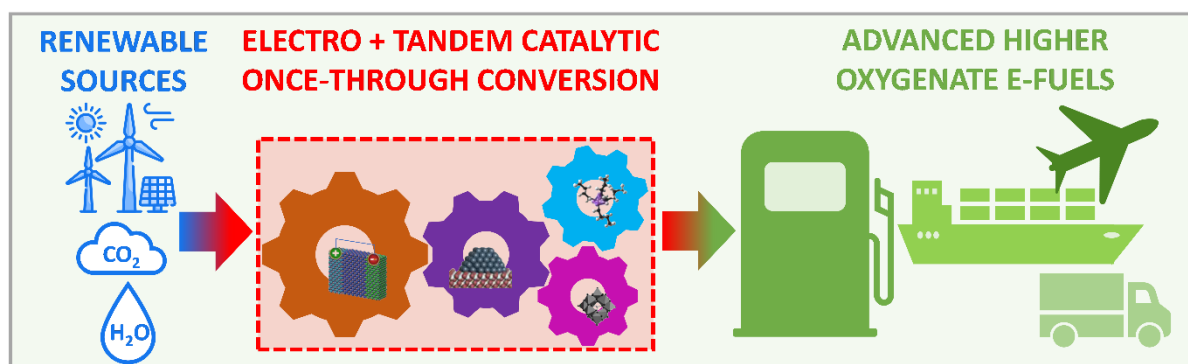
- [1] D. Liu, A. Farooq, Fuel 387, 134301 (2025).
- [2] J. Herzler, J. A. Manion, W. Tsang, International Journal of Chemical Kinetics 33, 755 (2001).
- [3] C.-W. Zhou, A. Farooq, L. Yang, A. M. Mebel, Progress in Energy and Combustion Science 90, 100983 (2022).
- [4] N. Hansen, J. A. Miller, T. Kasper, K. Kohse-Höinghaus, P. R. Westmoreland, J. Wang, T. A. Cool, Proceedings of the Combustion Institute 32, 623 (2009).
- [5] H. Richter, J. B. Howard, Progress in Energy and Combustion Science 26, 565 (2000).
- [6] M. Frenklach, Physical Chemistry Chemical Physics 4, 2028 (2002).
- [7] H. Wang, Z. Liu, S. Gong, Y. Liu, L. Wang, X. Zhang, G. Liu, Combustion and Flame 212, 189 (2020).
- [8] Ansys, Chemkin Theory Manual, Plug Flow Reactor Theory, Release 2024 R2, Chapter 11 (2024).
- [9] M. Younessi-Sinaki, E. A. Matida, F. Hamdullahpur, International Journal of Hydrogen Energy 34, 3710 (2009).
- [10] C. M. Hofberger, B. Dietrich, I. Durán Vera, R. Krumholz, L. Stoppel, N. Uhlenbruck, T. Wetzol, Hydrogen 4, 357 (2023).
- [11] M. Koshi, T. Uehara, M. Asahara, International Journal of Hydrogen Energy 72, 850 (2024).

Higher Oxygenate E-Fuel Synthesis by Tandem Fischer-Tropsch Synthesis and Reductive Hydroformylation

S. Popp^{1,2}, H. Stieber¹, W. Leitner^{1,2}, G. Prieto³, A. Vorholt¹

¹Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany, ²Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany, ³Institute for Chemical Technology (CSIC-UPV), Valencia, Spain

The EU project E-TANDEM aims to unlock an efficient and direct production of a new higher-oxygenate diesel-like e-fuel for the marine and heavy-duty transport sector in a once-through hybrid catalytic conversion process.[1],[2] Using renewable electricity and resources, the production of e-fuels offers a CO₂-neutral option for the energy-intensive transport sector. The process combines syngas production via co-electrolysis using CO₂ and water with a tandem catalytic e-syngas conversion coupling the Fischer-Tropsch reaction and the reductive hydroformylation reaction to produce long-chain alcohols.[3],[4] These alcohols can be used directly as fuel or further processed into ethers.[5] The concept of the E-TANDEM project is shown in the figure below.



Schematic illustration of integrated higher oxygenate e-fuel production aimed for by E-TANDEM

While the heterogeneous catalyzed Fischer–Tropsch and the homogeneous catalyzed hydroformylation were already successfully integrated in a batch tandem reaction, both the scale and the reaction conditions are not feasible for technical implementation yet. Therefore, our research is focused on operating a continuous miniplant to demonstrate the aimed reaction and the downstream processes including product separation and catalyst recycling on a larger scale. Catalyst engineering and optimization of the reaction conditions are crucial approaches to address challenges related to the technical feasibility of high pressures and undesired side product formation. Furthermore, interferences of the reaction components present and catalyst deactivation mechanisms are investigated. This supports the potential for a synergistic interaction of homogeneous and heterogeneous metal catalysts, ensuring efficient and selective tandem reactions.

References:

- [1] A. Ramirez, S. M. Sarathy, J. Gascon, (2020), Trends Chem., 785–795, 2
- [2] E-TANDEM Website, (2025), <https://e-tandem.eu/>
- [3] K. Jeske, T. Rösler, M. Belleflamme, T. Rodenas, N. Fischer, M. Claeys, W. Leitner, A.J. Vorholt, G. Prieto, (2022), Angew. Chem. Int. Ed., e202201004, 61
- [4] R. Caldogno, I. Giaccardo, X. Sun, A. Hagen, (2025), J. Power Sources, 237825, 654
- [5] J. Rorrer, A. T. Bell, F. D. Toste, (2019), ChemSusChem, 2835 – 2858, 12

Decentralized Methanol Production at Wastewater Treatment Plants: Synergies and Regulatory Challenges in the E-BO₂t Project

B. Bender¹, C. Ait Tarint¹, F. Voit², T. Lind³

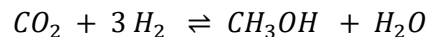
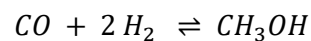
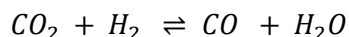
¹OWI Science for Fuels gGmbH, Herzogenrath, Germany,

²Research Institute for Water Management and Climate Future at RWTH Aachen University, Aachen, Germany

³EMSCHERGENOSSENSCHAFT / LIPPEVERBAND, Essen, Germany

Introduction and motivation

The production of green Methanol is an appropriate step to defossilize the methanol generation itself and make usage of a platform chemical, which can be used downstream for a wide variety of products. An essential role is the substitution of fossil fuels for aviation and maritime usage, where electrification and other hydrogen carriers like hydrogen are not possible due to their characteristics like a high mass for batteries and low volumetric energy density for hydrogen. Due to these disadvantages, it is not senseful possible to use them for high sea maritime and middle- to long distance aviation usage. Therefore, it is necessary to find alternative energy carriers to subsidize fossil fuels. Methanol as platform chemical can be used to produce maritime diesel and kerosine, which makes it a versatile intermediate for green energy carriers in those fields. In the project E-BO₂t the methanol production out of sewage gas at a wastewater treatment plant (WWTP) is investigated and the potential synergies, which comes with the methanol synthesis and the facilities. In this project the carbon dioxide is separated from the methane of the sewage gas and is a green point source for carbon dioxide. Together with green hydrogen of an electrolysis, it goes into a methanol synthesis. The following chemical equations describe the reaction of the methanol synthesis for carbon dioxide and hydrogen. The carbon dioxide reacts with hydrogen to carbon monoxide and water. The carbon monoxide reacts with 2 hydrogen molecules to methanol. The third equation shows the overall reaction for the methanol synthesis of carbon dioxide and hydrogen to methanol and water as byproduct.



The methane after the carbon dioxide removal with a much lower amount of carbon dioxide can be still used at combined heat and power plants (CHP) for onsite electricity and heat production, which is needed at the WWTP. The project is carried out at the WWTP in Bottrop. Figure 1 shows the Power-to-Methanol (P2MeOH)-plant and its connections to the WWTP.

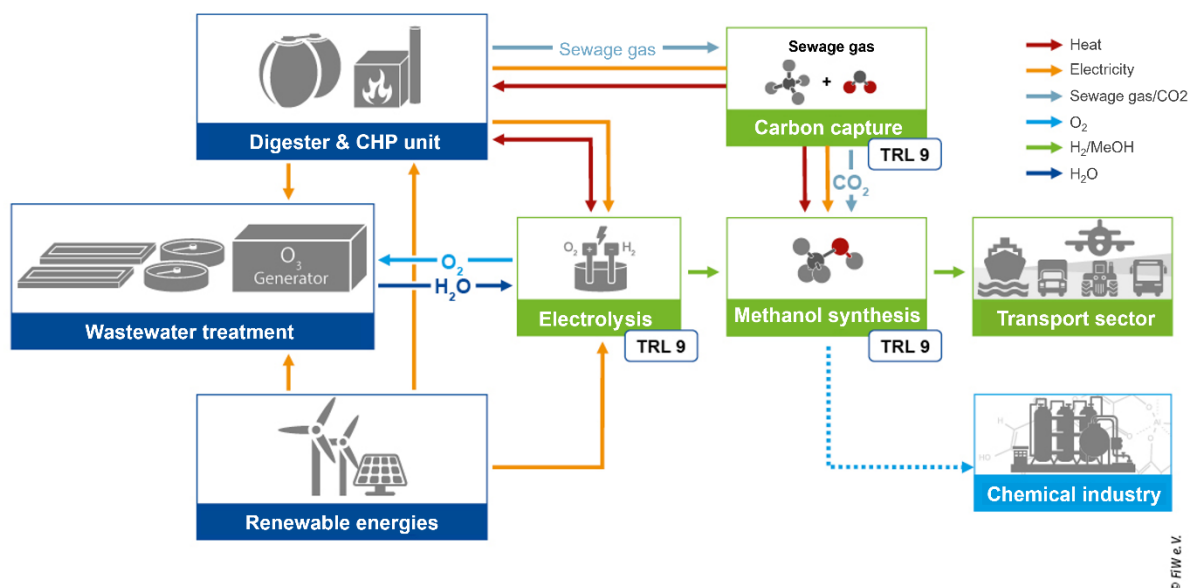


Figure 1: Overview of the project and the link between the WWTP and Power-to-Methanol-Plant Adapted from [1].

Process concept: Power-to-Methanol at wastewater treatment plants

Municipal wastewater treatment plants are increasingly considered as technical interfaces between the water, wastewater, energy and mobility sectors [2]. In conventional operation, sewage sludge digestion produces sewage gas that is mainly used in combined heat and power units to provide electricity and heat for the WWTP. Often WWTP have also high amount of renewable energy production like PV or wind turbines to produce electricity. In general, they have a high demand on electricity to operate pumps and other devices like agitators to treat wastewater. Therefore, the production of electricity is fluctuating and WWTP has often surplus and deficit in electricity, which is balanced with the grid. With this fluctuating amount of electricity, it is possible with a P2X-Storage to enhance flexibility by decoupling production and consumption of electrical energy.

Sewage gas typically contains around 60 vol.-% methane as energetic component and carbon dioxide approx. 35 vol.-% as an unused by-product and often goes as to the atmosphere during the firing of methane in the CHP-plant. The E-BO₂t approach makes use of this existing carbon source and combines it with renewable hydrogen from electrolysis to synthesize methanol. In this way, an established WWTP infrastructure is extended by a Power-to-Methanol process without replacing the core task of wastewater treatment. Therefore, it is possible to use oxygen as byproduct of the electrolysis onsite for different operations like aeration of the activated sludge basin. Another option for coupling is further usage of waste heat of the P2MeOH-plant, which can be used for heating the digester or in the sewage sludge drying. Especially sewage sludge drying gives the opportunity to reduce natural gas consumption, because during lack of solar thermal energy and other heating options a CHP with natural gas is used to fulfill the heat demand of sewage sludge drying.

The process chain starts with the separation of carbon dioxide from sewage gas. The remaining methane-rich stream can still be used in existing CHP units or, depending on gas quality and site-specific boundary conditions, be upgraded for biomethane applications. The separated carbon dioxide is fed to methanol synthesis together with hydrogen. For the hydrogen supply, water electrolysis is the central conversion step. The overall concept therefore, links three streams that are already present or relevant at a wastewater treatment plant: biogenic carbon, water and electricity. The main product is methanol, while oxygen and waste heat occur as valuable co-products.

A decisive advantage of decentralized methanol production is the possibility to integrate the

process into existing infrastructure. Wastewater treatment plants already operate gas handling systems, heat networks, water treatment units and electrical infrastructure. These installations reduce the need for completely new peripheral systems. At the same time, the integration must be carefully designed because the methanol process introduces additional requirements regarding gas purity, hydrogen safety, pressure levels, heat recovery and operational control. The plant therefore must be regarded as an integrated energy system rather than as a stand-alone fuel production unit.

For the Bottrop case study, the system boundaries include sewage gas treatment, carbon dioxide capture, electrolysis, methanol synthesis, product conditioning and the use of by-products.

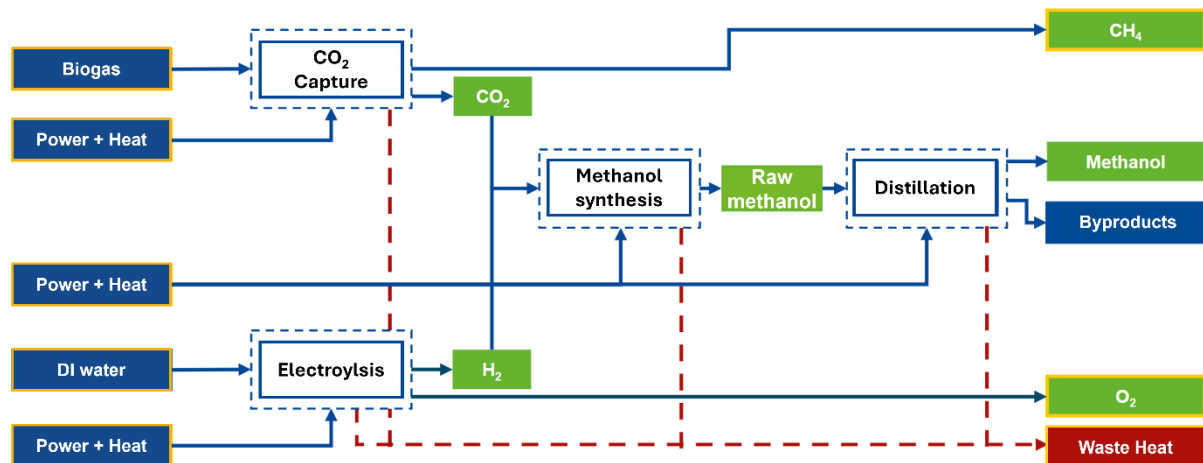


Figure 2: System boundaries, yellow marked are the interfaces, between WWTP and P2MeOH-plant with material and energy flow for the implementation of the P2MeOH-Plant. Adapted from [3].

This allows a site-specific evaluation of the technical and economic potential. The concept is not limited to one single plant size. Instead, it represents a modular approach that can be adapted to wastewater treatment plants with sufficient sewage gas production, available space and access to renewable electricity. The modularity is important because wastewater treatment plants differ substantially in load profile, sludge digestion capacity, energy demand and local infrastructure. During the project also the minimum size of WWTP will be examined to build Power-to-Methanol efficient and produce an additional value for WWTPs.

Power-to-Methanol-process

Carbon dioxide supply from sewage gas

The carbon source is a key element for the classification and environmental performance of the produced methanol. Sewage gas from anaerobic digestion contains about 35 % carbon dioxide that originates from the biological degradation of organic matter. Instead of being emitted directly or passing through conventional combustion processes, this carbon dioxide can be captured and converted into a liquid energy carrier and platform chemical. This creates a circular use of carbon on the plant site and supports the transition from linear waste treatment to resource-oriented operation with respect to the surrounding conditions.

The material flow and components of the P2MeOH-plant and WWTP are shown in Figure 1. However, the quality of the separated carbon dioxide is decisive for stable methanol synthesis. Trace components such as hydrogen sulphide, siloxanes, water vapour and oxygen have to be removed or limited because they may poison catalysts, cause corrosion or disturb downstream compression and synthesis. Consequently, gas cleaning is not only a preliminary step but a central process unit. The selected separation technology must provide sufficient purity while maintaining acceptable energy demand and operational robustness under varying sewage gas compositions.

Compared with direct air capture, the effort for separation is significantly reduced, because air contains about 400 ppm carbon dioxide, which is orders of magnitude smaller compared to the 35 % of carbon dioxide in sewage gas. Compared with large industrial point sources, wastewater treatment plants are scale-limited and geographically distributed. This leads to lower individual production capacities but offers the advantage of local implementation and reduced transport demand. Decentralized concepts can therefore be attractive where several medium-sized plants are located near fuel users, logistics hubs or chemical value chains. There is also the opportunity to use carbon dioxide sources of nearby emitters like steel and chemical industries, refineries and power plants. Regarding compliance with the Renewable Fuels of Non-Biological Origin (RFNBO) requirements not all carbon dioxide sources are legit and the acceptance of some carbon dioxide sources is changed in the future.

Hydrogen production and oxygen utilization

Hydrogen represents the chemical energy input for the methanol in the Power-to-Methanol pathway. In the E-BO₂t concept, hydrogen is produced by water electrolysis using renewable electricity. The hydrogen reacts with captured carbon dioxide to form methanol and water, as shown in the chemical equations in chapter “Introduction and motivation”. From a technical perspective, the electrolyzer must be sized in relation to the expected carbon dioxide availability, the desired methanol output and the electricity supply concept. The Demonstrator P2MeOH-plant in E-BO₂t will have an electrolyzer of nearly 1 MW electricity input and can produce 700 – 800 t/a Methanol. From an economic perspective, the electrolyzer is usually one of the most cost-intensive components and strongly influences the levelized cost of methanol. Another challenge is the fluctuating availability of enough renewable energy to operate the electrolyzer at its planned operating point. It is necessary to change the loading point regarding the availability of renewable energy to fulfil the RFNBO requirements in respect of the greenhouse gas emission reduction to certificate the produced methanol. The oxygen stream from electrolysis is often treated as a by-product without major value. At wastewater treatment plants, however, oxygen has direct potential use. Biological treatment requires large amounts of oxygen for aerobic degradation processes, and advanced treatment steps such as ozonation can also benefit from an on-site oxygen supply. If the oxygen can be integrated into aeration or oxidation processes, the overall system efficiency improves and part of the electricity demand for conventional air compression may be avoided. The actual benefit depends on oxygen purity, pressure level, transfer efficiency and the operating strategy of the wastewater treatment process. This synergy is particularly relevant because the economic pressure on renewable fuels is high. Any additional use of co-products reduces the burden on the main product. Nevertheless, the integration of oxygen must be evaluated carefully. Biological treatment processes are sensitive to changes in oxygen concentration and mixing conditions. In addition, operational safety, metering and control have to be adapted to the use of concentrated oxygen. The value of the oxygen stream is therefore not automatic but depends on suitable process integration.

Methanol synthesis and heat integration

Methanol synthesis converts carbon dioxide and hydrogen into methanol in the presence of a catalyst. The reaction is exothermic and typically requires elevated pressure and temperature. The design of the synthesis loop has to balance conversion, recycle flow, catalyst performance and heat management. For decentralized applications, compact and robust system designs are particularly important because the plants are operated in an environment where fuel production is not the primary task of the site operator. Heat integration is one of the central advantages of installing the process at a wastewater treatment plant. Both electrolysis and methanol synthesis generate heat at different temperature levels. Depending on the process design, this heat can be used for building heating, digester temperature control, sludge drying or other thermal consumers on site.

Sludge drying is especially relevant because it can reduce disposal mass and improve the energetic or material use of sewage sludge, which is especially for the WWTP in Bottrop interesting, because the sewage sludge of nearby WWTP is carried to Bottrop for further processing and energetic usage in the sewage sludge furnace. The combined use of electricity, heat, oxygen and carbon streams increases the effective utilization of renewable electricity beyond the methanol product alone.

A challenge is the temporal mismatch between heat generation and heat demand. Methanol synthesis may operate depending on hydrogen availability and electricity sourcing rules, whereas wastewater treatment has its own seasonal and daily load patterns. Therefore, thermal storage, flexible operation and prioritization of heat consumers are required. Without such measures, a relevant part of the available heat may remain unused, reducing the practical efficiency of the concept.

Regulatory framework and RFNBO compliance

The regulatory classification of the produced methanol is a decisive factor for market access and economic feasibility. Under the European Renewable Energy Directive and the related delegated regulation for renewable fuels of non-biological origin (RFNBO), synthetic fuels based on renewable hydrogen must fulfil strict criteria for the electricity used in electrolysis and in further downstream processes during the methanol production. These criteria include additionality, temporal correlation and geographical correlation. Their purpose is to ensure that hydrogen production does not merely divert existing renewable electricity from other consumers but stimulates additional renewable energy plants. These criteria do not meet for plants until 1. January 2038, if the liquid fuel plant is in operation before 1. January 2028. To meet the criteria for RFNBO a greenhouse gas reduction of 70 % compared to fossil is required. The fossil comparator has a greenhouse gas emission of 94 g_{CO₂-Äq}/MJ. Therefore, the produced Methanol is allowed to emit 28,2 g_{CO₂-Äq}/MJ_{MeOH}. The emissions of methanol are summed up of the emissions of the input material, direct process emissions, logistics, fuel burning, and potential negative emissions through carbon capture and geological storage.

For decentralized methanol production, these rules create a direct link between plant operation and electricity procurement. If the electrolyzer may only operate during periods that meet the required correlation with renewable electricity generation, the achievable full-load hours can decrease. This increases the specific capital cost contribution of the electrolyzer, the synthesis unit and all related infrastructure. As a result, compliance with RFNBO requirements is not only an administrative issue it is a process design parameter for the economic perspective. Analysing the current situation at the WWTP Bottrop there is the opportunity to produce 4400 – 5300 hours per year of certifiable RFNBO methanol without any changes and optimization in the energy and electricity system of the WWTP. The other times, the greenhouse gas emission reduction cannot be fulfilled for RFNBO regulations but e.g. optimizing the production of electricity out of biogas and shifting electricity demand of consumers, these hours can be increased.

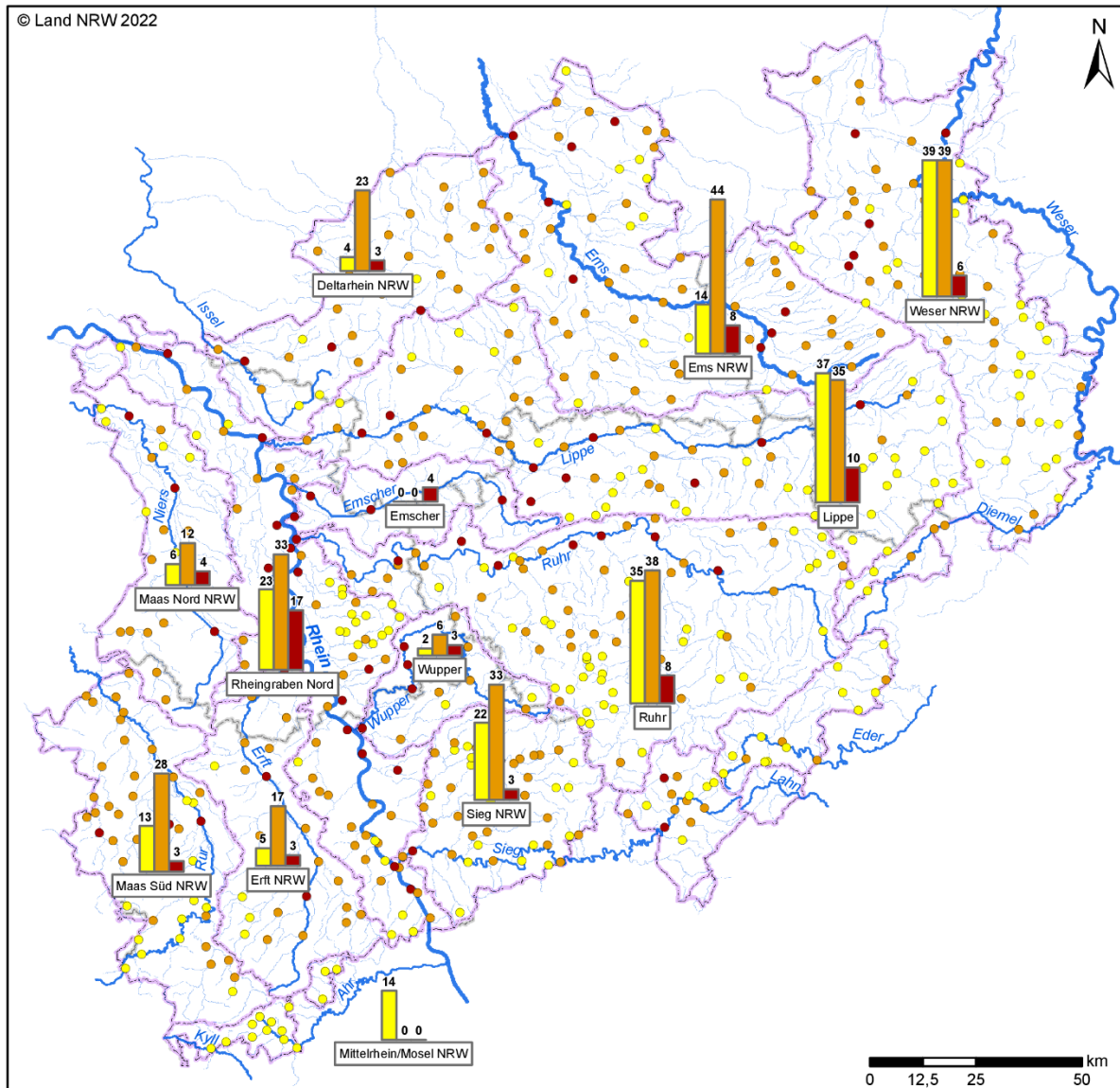
The certification effort also affects project implementation. Producers must document electricity origin, carbon source, production quantities and greenhouse gas savings. For small and medium-sized decentralized plants, the relative burden of monitoring, reporting and verification can be higher than for large industrial installations. The E-BO₂t project therefore assesses not only technical feasibility but also the practical consequences of the regulatory framework for wastewater treatment plant operators.

For the future different aspects can be relevant regarding the used electricity. Power purchase agreements are a valid source for RFNBO conform electricity and due to the expansion of renewable energy in the grid, it might also meet the criteria for green electricity also.

Economic assessment and sensitivity factors

The levelized cost of methanol depends on investment costs, electricity price, full-load hours, carbon dioxide availability, hydrogen efficiency, heat utilization, oxygen valorisation and certification costs. Among these factors, electricity-related parameters usually dominate because electrolysis is energy-intensive. Low-cost renewable electricity and high electrolyzer utilization are therefore essential for a competitive product. At the same time, strict temporal correlation may reduce utilization and increase cost, creating a tension between environmental integrity and economic feasibility.

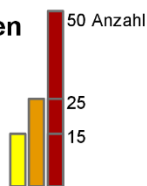
The wastewater treatment plant environment provides several options to improve the business case. On-site use of oxygen can reduce operational expenses in aeration or advanced oxidation. Heat recovery can replace external heat generation or increase sludge treatment efficiency. Continued use of the methane-rich gas stream preserves an established energy source in CHP with a higher efficiency compared to raw sewage gas. In addition, local production can reduce logistics requirements if methanol is consumed regionally. These benefits must be quantified for each site because they depend on existing equipment, energy prices and the local demand structure.



Legende

Kläranlagen nach Größenklassen

- ≤ 10.000 EW (GK 1-3)
- 10.001 bis 100.000 EW (GK 4)
- > 100.000 EW (GK 5)



- Größere Fließgewässer
- Weitere Fließgewässer

- Teileinzugsgebiet
- Regierungsbezirk

Anzahl der Kläranlagen nach Größenklassen

● ≤ 10.000 EW	214
● 10.001 bis 100.000 EW	308
● > 100.000 EW	72
NRW gesamt	594

Der Einwohnerwert setzt sich zusammen aus der Einwohnerzahl und den Einwohnerequivalenten aus gewerblichem und industriellem Abwasser.

Stand: 2022

Figure 3: Shows an overview of WWTP in North Rhine Westphalia and their size [4] .

An overview of the location of WWTP in North Rhine Westphalia and their size is shown in Figure 3. Despite the fact, that there are many WWTP most of them are not suitable for a P2MeOH-plant because they are mostly too small to produce methanol economically.

In Figure 4 the nearby WWTP in a distance to 100 km of Bottrop are shown and their responding processing size in population equivalents (Data [4]). The WWTPs are clustered along their size and potential for sewage gas production. Due to the specific investment costs, which lowers with bigger plants, there is threshold, when a P2MeOH-plant becomes

economically. In some cases, a clustering of WWTP is suitable with e.g. sewage sludge transport, carbon dioxide transport, or sewage gas transport, which is feasible and offers the opportunity to have centralized P2MeOH, if WWTPs are too small for an own plant, but located near enough to transport materials. This also goes into account for the greenhouse gas emissions of the produced methanol but can be feasible in some cases.

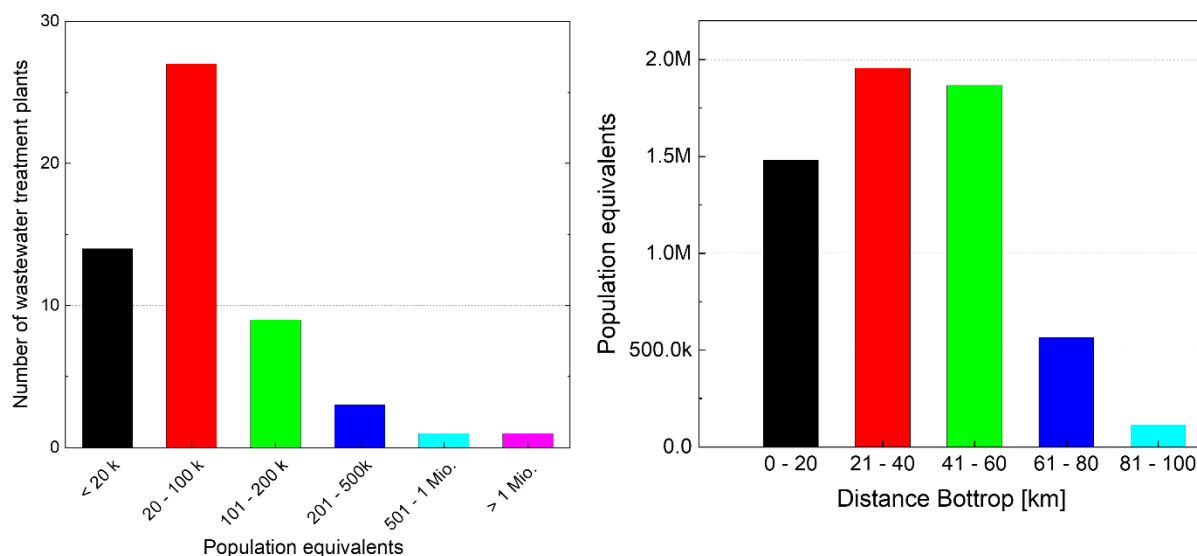


Figure 4: Overview of nearby WWTP and its size regarding their population.

The Levelized costs for the Methanol production (LCMeOH) depending on different parameters, like the P2MeOH-plantsize, boundary conditions for used electricity, source of carbon dioxide etc. are in different studies at a high span. The LCMeOH for an upscaled plant, using the whole carbon dioxide of the biogas, is at a span of 1400 - 1800 €/t_{MeOH}. The market price for fossil methanol is between 525 - 915, with a high increase in the last months due to the conflict between Iran and USA, leading to issues and uncertainties in the supply chain. Compared to other studies there is a wide span depending on the carbon dioxide source and the plant scale. Direct air capture has in general the highest LCMeOH, because the effort for carbon dioxide removal is the highest. Using biogas as educt flow for carbon, there are two pathways. On the one hand, the complete biogas is used in a reformer to produce synthesis gas for the methanol synthesis. There is still additional hydrogen necessary, because the stoichiometric ratio of the synthesis gas out of biogas is not suitable for methanol synthesis. On the other hand, the path of carbon dioxide removal from biogas, as shown in E-BO₂t, is a way to use green carbon dioxide. The other carbon dioxide point sources are e.g. energy plants, cement-plants or industrial plants with combustion. They all have a higher fraction of carbon dioxide than air, about 12 – 30 %, but usually lower than sewage gas. Also, there is sometimes an additional air filtration step necessary to remove poisonous components from the exhaust gas, which has often critical components for the carbon dioxide removal processes. Overall the studies show a wide range of expected methanol prices between 310 – 2300 €/t_{MeOH} [5], [6], [7].

Downstream utilization of renewable methanol

Methanol is a versatile platform chemical and energy carrier. It can be used directly as a chemical feedstock, as a marine fuel, as a component in biodiesel production or as an intermediate for further synthesis routes like Jetfuel. For hard-to-electrify transport sectors, especially maritime applications and aviation, renewable methanol can contribute to greenhouse gas reduction where direct battery-electric solutions are difficult because of energy density, range and infrastructure limitations.

In maritime transport, methanol has practical advantages because it is liquid at ambient

conditions and can be stored and handled more easily than cryogenic or highly compressed fuels. However, engine adaptation, fuel standards, safety concepts and bunkering infrastructure are necessary for broad implementation. In aviation, methanol can serve as an intermediate for synthetic kerosene via Methanol-to-Jet pathways. This route adds conversion steps and energy losses but may be relevant where drop-in fuels compatible with existing aircraft and infrastructure are required.

The meaningfulness of each pathway depends on the balance between technical complexity, market value and regulatory incentives. Direct use of methanol can be advantageous because it avoids additional conversion losses. Further conversion to hydrocarbons may be justified if a high-value market requires specific fuel properties. The E-BO₂t project therefore evaluates methanol not only as an isolated product but as part of a broader renewable fuel value chain.

Operational challenges and safety aspects

The integration of hydrogen, oxygen, carbon dioxide and methanol handling introduces additional safety requirements at wastewater treatment plants. Hydrogen has a wide flammability range and requires appropriate ventilation, leak detection, explosion protection and separation distances. Methanol is toxic and flammable, which makes storage, transfer and spill management essential topics, but is comparable to common fossil fuels. Oxygen-enriched atmospheres can increase fire risk and have to be avoided in technical rooms and process areas.

Operational reliability is also important because wastewater treatment plants must fulfil legal discharge requirements continuously. The methanol production units must therefore not compromise wastewater treatment performance. A practical control strategy should allow the Power-to-Methanol plant to reduce load or shut down without disturbing essential plant operation. Interfaces between the methanol process and the wastewater plant must be designed with clear priorities, fail-safe modes and maintenance concepts.

Scalability, transferability and implementation challenges

The transferability of the E-BO₂t concept depends on site size, sewage gas production, availability of renewable electricity, existing heat demand and local methanol markets. Large wastewater treatment plants offer higher and more stable carbon dioxide flows, while smaller plants may benefit from modular standardized units, but have the disadvantage of higher production costs per tonne Methanol. Regional clusters could combine several plants with shared logistics or centralized product upgrading. Such concepts may improve economy of scale without losing the advantages of using distributed carbon sources.

A systematic screening of wastewater treatment plants should include annual sewage gas volume, carbon dioxide content, existing gas utilization, electricity grid connection, potential renewable power purchase options, space availability and environmental permitting constraints. In addition, the willingness and capability of operators to manage a methanol production process are relevant. Cooperation with technology providers, municipalities and methanol off takers can reduce implementation barriers and distribute responsibilities across the value chain.

Conclusion and outlook

Decentralized methanol production at wastewater treatment plants can transform existing environmental infrastructure into regional energy hubs. The E-BO₂t project demonstrates how captured carbon dioxide from sewage gas, renewable hydrogen, oxygen utilization, heat integration and continued methane use can be combined in one site-specific concept. The approach creates technical synergies that are not available in isolated methanol or fuel production plants and can improve overall resource efficiency.

At the same time, the concept faces significant challenges. The RFNBO framework requires strict proof of renewable electricity use and greenhouse gas performance. These requirements

influence full-load hours, investment utilization and certification effort. In addition, the integration of hydrogen, oxygen and methanol handling requires careful safety and operational concepts. The success of such projects therefore depends on the combined optimization of process engineering, regulation, economics and site operation.

Future work should focus on detailed mass and energy balances, dynamic operation under renewable electricity constraints, validated cost models and practical certification procedures. Demonstration projects are essential to show whether the theoretical synergies can be realized reliably under real wastewater treatment plant conditions, which is part of E-BO₂t. If these challenges are addressed, wastewater treatment plants can become important, decentralized sources of renewable methanol for chemical and transport applications.

FUNDING ACKNOWLEDGMENTS

Project E-BO(2)t is funded with a total of 12.4 million euros by the Federal Ministry for Transport as part of the Funding Programme Renewable Fuels. The funding guideline for the development of renewable fuels is coordinated by NOW GmbH and supported by the project management agencies VDI/VDE Innovation + Technik GmbH and Fachagentur Nachwachsende Rohstoffe e. V. «



With funding from the



by decision of the
German Bundestag

Coordinated by



Project management agency



References:

- [1] K. Ooms, F. Voit, J. Blankenstein, C. Fritsch, D. Blöhse, und I. Nafo, „Enhanced Sector Coupling of Wastewater, Energy and Transportation through Power-to-Methanol - A Case Study for the WWTP Bottrop“, gehalten auf der 19th IWA Leading Edge Conference on Water and Wastewater Technologies, Essen, Juni 2024.
- [2] M. Schäfer, O. Gretzschel, und H. Steinmetz, „The Possible Roles of Wastewater Treatment Plants in Sector Coupling“, *Energies*, Bd. 13, Nr. 8, S. 2088, Apr. 2020, doi: 10.3390/en13082088.
- [3] F. Voit u. a., „Sektorenkopplung – Elektrolysebasierte Methanolkraftstoffe und wasserwirtschaftliche Sauerstoffnutzung auf Kläranlagen“, gehalten auf der 57. Essener Tagung für Wasserwirtschaft – Wege zur nachhaltigen Wasserwirtschaft und Gesellschaft, Aachen: Gesellschaft zur Förderung des Instituts für Siedlungswasserwirtschaft an der RWTH Aachen e.V., März 2024, S. 9/1-9/13. [Online]. Verfügbar unter: <https://www.fiw.rwth-aachen.de/>
- [4] Ministerium für Umwelt, Naturschutz und Verkehr des Landes Nordrhein-Westfalen und Landesamt für Natur, Umwelt und Verbraucherschutz – LANUV NRW Fachbereich 57, „Entwicklung und Stand der Abwasserbeseitigung in Nordrhein-Westfalen“, Nr. 20., Juli 2024.
- [5] K. Harris, R. G. Grim, Z. Huang, und L. Tao, „A comparative techno-economic analysis of renewable methanol synthesis from biomass and CO₂: Opportunities and barriers to commercialization“, *Applied Energy*, Bd. 303, S. 117637, Dez. 2021, doi: 10.1016/j.apenergy.2021.117637.
- [6] J. Van Antwerpen u. a., „A model for assessing pathways to integrate intermittent renewable energy for e-methanol production“, *International Journal of Hydrogen Energy*, Bd. 48, Nr. 78, S. 30221–30237, Sep. 2023, doi: 10.1016/j.ijhydene.2023.04.177.
- [7] G. J. Fulham, P. V. Mendoza-Moreno, und E. J. Marek, „Managing intermittency of renewable power in sustainable production of methanol, coupled with direct air capture“, *Energy Environ. Sci.*, Bd. 17, Nr. 13, S. 4594–4621, 2024, doi: 10.1039/D4EE00933A.

Closing the Carbon Loop: CO₂-to-Fuel via Hybrid Catalysis

S.Feldhoff¹

¹OWI Science for Fuels gGmbH, Herzogenrath, Germany

Abstract

The decarbonization of maritime transport requires renewable fuels that combine low-carbon production pathways with favorable combustion characteristics and compatibility with existing fuel infrastructures. Within the Horizon Europe project E-TANDEM, a novel Higher Oxygenate E-Fuel (HOEF) has been developed from carbon dioxide, water, and renewable electricity through a hybrid catalytic conversion pathway involving co-electrolysis, tandem Fischer–Tropsch/reductive hydroformylation, and subsequent etherification. The resulting fuel consists predominantly of long-chain aliphatic ethers in the middle-distillate range and has been designed for application as a blend component for Marine Gas Oil (MGO). This work evaluates the performance of the final Ether-HOEF formulation with particular emphasis on fuel properties, ignition quality, auto-ignition behaviour, soot formation characteristics, and deployment potential. The final Ether-HOEF exhibited a cetane number of 113, while blends containing 10%, 20%, and 50% Ether-HOEF increased the cetane number of MGO from 54 to 59, 62, and 73, respectively. Ignition-delay measurements further demonstrated substantially improved auto-ignition behaviour compared with conventional marine fuel. The soot-forming tendency of the fuel was assessed using the Yield Sooting Index (YSI) methodology. The final Ether-HOEF achieved a YSI value of 38 compared with 170 for conventional MGO, corresponding to a reduction of approximately 78% in intrinsic soot-forming tendency. Significant soot reductions were already observed for blend ratios of 10% and 20%, indicating the potential for meaningful emissions improvements through gradual fuel substitution. The investigated blends maintained physicochemical properties compatible with marine-fuel applications and support a phased implementation strategy based on increasing renewable-fuel content within existing fuel infrastructures. Combined with the successful TRL4 demonstration of the underlying production pathway, the results indicate that Ether-HOEF represents a promising renewable blend component capable of simultaneously enhancing ignition quality, reducing soot formation, and supporting the progressive decarbonization of maritime transport.

1. Introduction

The decarbonization of the transport sector represents one of the major challenges in achieving the climate neutrality objectives defined by the European Green Deal. While significant progress is being made in the electrification of passenger vehicles, several transport segments remain difficult to electrify due to their demanding energy-density requirements, long operating ranges, and limited refueling opportunities. Maritime transport is among the most challenging of these sectors. Large commercial vessels require energy-dense fuels that can be stored onboard without excessive volume penalties while ensuring reliable operation under a wide range of environmental and operational conditions. As a result, liquid fuels are expected to remain a key energy carrier for shipping for the foreseeable future.

Synthetic fuels produced from renewable electricity, water, and captured carbon dioxide have therefore attracted considerable interest as potential pathways toward low-carbon maritime transport. Such power-to-liquid (PtL) fuels can reduce dependence on fossil resources while utilizing existing fuel distribution infrastructure and propulsion systems. Among the fuels currently discussed for marine applications, methanol has emerged as one of the leading candidates due to its relative simplicity of production and handling. However, methanol suffers from a significantly lower volumetric energy density than conventional marine gas oil (MGO), requiring larger fuel storage volumes and modifications to onboard fuel systems. Other options, including hydrogen and ammonia, face challenges associated with storage, infrastructure requirements, safety considerations, and engine adaptation. Fischer-Tropsch-derived

synthetic diesel fuels provide excellent compatibility with existing engines but do not inherently address local pollutant emissions such as particulate matter and soot.

Oxygenated fuels have been proposed as an alternative approach to improve combustion quality and reduce pollutant formation. The presence of chemically bound oxygen within the fuel molecule can promote more complete oxidation during combustion and suppress the formation of soot precursors. In recent years, considerable research efforts have focused on oxygenated compounds such as dimethyl ether (DME), oxymethylene ethers (OME), alcohols, and oxygen-containing fuel additives. While these fuels have demonstrated significant potential for reducing particulate emissions, many suffer from limitations related to fuel handling, storage stability, material compatibility, or insufficient compatibility with existing diesel infrastructure. Consequently, there remains a need for oxygenated fuel concepts that simultaneously provide favorable combustion characteristics, high energy density, and compatibility with current transportation systems.

Within this context, the Horizon Europe project E-TANDEM has developed a novel class of Higher Oxygenate E-Fuels (HOEF) derived exclusively from renewable electricity, water, and carbon dioxide. The project focuses on the production of long-chain oxygenated molecules in the middle-distillate range through a hybrid catalytic conversion pathway combining high-temperature co-electrolysis, tandem Fischer-Tropsch synthesis and reductive hydroformylation, followed by catalytic conversion into long-chain ethers. These ether-based HOEF formulations have been specifically designed to combine diesel-like fuel properties with the combustion advantages associated with oxygenated fuels. In contrast to highly oxygenated compounds such as methanol or DME, the long-chain ether molecules retain physicochemical characteristics closer to conventional diesel fuels, thereby offering the potential for gradual implementation through blending with existing marine fuels.

The practical deployment of novel marine fuels requires more than low-carbon production pathways alone. In addition to favorable lifecycle greenhouse-gas performance, candidate fuels must provide suitable ignition characteristics, low soot formation tendencies, and compatibility with existing fuel-system components. Furthermore, pathways that allow incremental introduction through blending with conventional fuels are particularly attractive, as they minimize both economic risk and infrastructure requirements during market uptake. For this reason, the present study focuses on the application of ether-based HOEF as a blend component for marine gas oil rather than as a standalone fuel.

The objective of this work is therefore to evaluate the suitability of long-chain ether-based HOEF for maritime applications from a fuel-performance perspective. Particular emphasis is placed on ignition quality, auto-ignition behavior, soot formation characteristics, and fuel-system compatibility. In addition, the implications for large-scale deployment and future market introduction are discussed. The central hypothesis of this work is that ether-based HOEF can simultaneously function as a cetane-enhancing component, a soot-reducing oxygenated fuel, and a drop-in blend component for existing marine fuel systems, thereby providing a practical transition pathway toward the decarbonization of maritime transport.

2. Background and Related Work

The maritime transport sector is currently evaluating a broad range of alternative fuel pathways to reduce greenhouse-gas emissions while maintaining operational reliability and competitiveness. Unlike road transport, where battery-electric solutions have achieved considerable market penetration, shipping applications remain strongly dependent on energy-dense liquid fuels due to the long operational ranges and high energy demands associated with commercial vessels. Consequently, a variety of renewable and synthetic fuel concepts are being investigated for future marine propulsion systems.

Among the most widely discussed options are hydrogen and ammonia. Both fuels offer the potential for near-zero carbon emissions during operation and have therefore attracted significant attention within international decarbonization strategies. However, their deployment

faces substantial challenges. Hydrogen requires either cryogenic storage or high-pressure containment systems and exhibits a very low volumetric energy density. Ammonia benefits from a higher volumetric energy density than hydrogen but introduces concerns related to toxicity, fuel handling, and combustion stability. In both cases, large-scale implementation requires extensive modifications to fuel infrastructure, storage systems, and propulsion technology.

Methanol has emerged as one of the most mature alternative marine fuel candidates and is already being introduced in commercial shipping applications. Compared with hydrogen and ammonia, methanol benefits from easier storage, well-established industrial production routes, and increasing regulatory acceptance. Nevertheless, its relatively low volumetric energy density requires larger onboard fuel tanks and reduces vessel range compared with conventional marine gas oil. In addition, methanol exhibits fundamentally different combustion characteristics and generally requires dedicated fuel-system adaptations.

Synthetic hydrocarbon fuels produced through Fischer-Tropsch synthesis represent another important pathway for maritime decarbonization. Fischer-Tropsch diesel exhibits physicochemical properties very similar to conventional diesel fuels and can therefore be utilized in existing engines with minimal modifications. Furthermore, the technology benefits from extensive industrial experience acquired through coal-to-liquid, gas-to-liquid, and biomass-to-liquid processes. Despite these advantages, paraffinic Fischer-Tropsch fuels lack oxygen within their molecular structure and therefore provide limited intrinsic benefits regarding soot reduction. As a result, particulate emissions remain largely dependent on engine calibration and aftertreatment technologies rather than fuel composition.

In response to these limitations, increasing attention has been directed toward oxygenated fuels and fuel additives. Oxygenated compounds introduce chemically bound oxygen directly into the fuel molecule, thereby influencing combustion chemistry and promoting more complete oxidation of intermediate hydrocarbon species. Previous studies have demonstrated that oxygenated fuels can substantially reduce particulate matter formation and soot emissions compared with conventional hydrocarbon fuels. Dimethyl ether (DME), oxymethylene ethers (OME), alcohols, and other oxygen-containing compounds have therefore been investigated extensively in compression-ignition engines.

Dimethyl ether is particularly notable for its exceptionally high cetane number and excellent ignition behavior. However, its gas-like properties under ambient conditions require pressurized storage systems and dedicated fuel infrastructure. Similarly, oxymethylene ethers have demonstrated significant potential for near-soot-free combustion but remain associated with challenges related to production complexity, fuel cost, material compatibility, and large-scale commercialization. Furthermore, both DME and OME differ substantially from conventional diesel fuels in terms of handling and infrastructure requirements, thereby limiting their potential as drop-in solutions.

Higher alcohols have also been considered as promising renewable fuel candidates due to their renewable production potential and oxygen content. Nevertheless, alcohol-based fuels typically exhibit relatively poor ignition quality compared with diesel fuels. Lower cetane numbers and longer ignition delays often restrict their applicability in compression-ignition engines without additional fuel modifications or blending strategies. Similar trends were observed within the E-TANDEM project, where higher-alcohol HOEF formulations displayed significantly lower cetane numbers than corresponding ether-based formulations.

Long-chain ether molecules represent a comparatively less explored class of renewable transportation fuels. Unlike short-chain ethers or highly oxygenated compounds, long-chain ethers combine moderate oxygen content with molecular structures resembling conventional middle-distillate fuels. Consequently, they offer the potential to retain favorable diesel-like physical properties while simultaneously introducing combustion benefits associated with oxygenated fuels. Previous research has suggested that ether functionalities can improve ignition behavior and reduce soot formation; however, the majority of available studies focus either on low-molecular-weight ethers or on oxygenated additives developed primarily for road

transport applications.

A further challenge associated with the introduction of alternative marine fuels concerns compatibility with existing infrastructure. Many proposed decarbonization pathways require substantial investments in storage, distribution, bunkering, and propulsion systems. Such requirements increase deployment costs and slow market penetration. For this reason, fuels capable of being introduced progressively through blending with conventional marine fuels are particularly attractive. A blend-based implementation strategy permits gradual reduction of fossil-fuel consumption while minimizing technical risk and capital expenditure.

Within this context, the ether-based Higher Oxygenate E-Fuels (HOEF) developed in the E-TANDEM project occupy a unique position. The fuel concept combines several characteristics that are rarely addressed simultaneously in the literature. First, the fuels are produced entirely from renewable electricity, water, and captured carbon dioxide. Second, the resulting long-chain ether molecules exhibit combustion properties that differ fundamentally from paraffinic Fischer-Tropsch products. Third, the fuel has been specifically designed to operate as a blend component for marine gas oil, thereby enabling gradual implementation without requiring fundamental modifications to existing vessels and fuel infrastructures. Finally, the project not only addresses fuel synthesis but also includes comprehensive assessments of ignition performance, soot formation behavior, material compatibility, system interactions, and scale-up potential.

Despite the growing interest in oxygenated marine fuels, there remains limited experimental evidence regarding the suitability of long-chain ether mixtures as marine fuel blend components. In particular, little information is available concerning the combined evaluation of ignition quality, soot reduction potential, fuel-system compatibility, and practical deployment pathways. The present study addresses this gap by investigating ether-based HOEF blends with marine gas oil and assessing their potential to support maritime decarbonization through a drop-in transition strategy

3. Fuel Concept and Experimental Methodology

3.1. Ether-HOEF Fuel Concept

The Higher Oxygenate E-Fuel (HOEF) investigated in this work was developed within the Horizon Europe E-TANDEM project and represents a novel class of renewable middle-distillate fuels produced exclusively from carbon dioxide, water, and renewable electricity. Unlike conventional synthetic diesel fuels, which predominantly consist of paraffinic hydrocarbons, the E-TANDEM fuel concept deliberately incorporates oxygen-containing ether functionalities into the molecular structure of the final product. This approach aims to combine the favorable storage, handling, and energy-density characteristics of diesel fuels with the combustion advantages typically associated with oxygenated fuel compounds.

The E-TANDEM production pathway integrates three major conversion steps. In the first step, syngas is generated through co-electrolysis of carbon dioxide and water. The resulting syngas is subsequently converted through a tandem catalytic process combining Fischer-Tropsch synthesis and reductive hydroformylation, producing a mixture of higher alcohols. In the final conversion stage, these alcohols are dehydrated to form higher aliphatic ethers in the middle-distillate boiling range. Experimental investigations performed during the project demonstrated that a staged process configuration consisting of tandem Fischer-Tropsch/reductive hydroformylation followed by a separate dehydration step provides superior performance compared with a fully integrated one-pot process.

From a fuel-design perspective, the resulting ether molecules differ fundamentally from both paraffinic Fischer-Tropsch products and highly oxygenated fuels such as methanol or dimethyl ether. The long hydrocarbon chains preserve diesel-like fuel properties, while the incorporated oxygen atoms are expected to improve combustion behavior by enhancing fuel oxidation and reducing soot precursor formation. This combination of characteristics makes ether-HOEF

particularly attractive for maritime applications, where both high energy density and reduced pollutant emissions are important requirements.

3.2. Investigated Fuel Samples

Several fuel-development iterations were produced during the E-TANDEM project to optimize the physicochemical and combustion characteristics of the targeted ether-based Higher Oxygenate E-Fuel (HOEF). The present study focuses exclusively on the final optimized Ether-HOEF formulation (hereafter referred to as *Ether-HOEF*), which was specifically developed to improve fuel quality and compliance with marine-fuel requirements while preserving the favorable combustion characteristics of long-chain oxygenated ethers. The final Ether-HOEF consists predominantly of long-chain aliphatic ether compounds in the C10–C18 range and was designed to minimize the concentration of low-flash-point species while maintaining high ignition quality and reduced soot-forming tendency. The resulting formulation serves as the basis for all investigations presented in this work.

To evaluate practical applicability in maritime transport, Ether-HOEF was blended with commercially available Marine Gas Oil (MGO). The selected fuel matrix was designed to represent realistic implementation scenarios for gradual introduction into existing marine-fuel supply chains. Blend ratios of 10% and 20% were selected as representative near-term deployment scenarios, while a 50% blend was included to evaluate the effects of substantial renewable-fuel substitution. Neat MGO served as the reference fuel throughout the study.

Table 1: Investigated Fuel Samples

Fuel Sample	Composition (v/v)
Marine Gas Oil (MGO)	100% Marine Gas Oil
10% Ether-HOEF Blend	10% Ether-HOEF + 90% MGO
20% Ether-HOEF Blend	20% Ether-HOEF + 80% MGO
50% Ether-HOEF Blend	50% Ether-HOEF + 50% MGO
Ether-HOEF	100% final Ether-HOEF formulation

Particular emphasis was placed on blend concentrations that can realistically be implemented without requiring major modifications to existing maritime fuel infrastructures or propulsion systems. The investigated blends therefore provide a practical framework for evaluating Ether-HOEF as a drop-in component for future low-carbon marine-fuel applications.

3.3. Fuel Characterization

A comprehensive fuel-characterization program was conducted to evaluate the suitability of Ether-HOEF and its blends with Marine Gas Oil for maritime applications. The investigations focused on the physicochemical properties that are most relevant for fuel handling, storage, safety, and combustion performance, while simultaneously providing the basis for the ignition and soot assessments discussed in subsequent sections. The characterization campaign included measurements of density, kinematic viscosity, flash point, oxidation stability, lubricity, and distillation behavior.

The resulting dataset provides the physicochemical basis for evaluating Ether-HOEF as a blend component for Marine Gas Oil and establishes the framework for interpreting the ignition-quality and soot-formation results presented in the following sections. By combining fuel-property characterization with combustion-related investigations, the present methodology enables a comprehensive assessment of the suitability of Ether-HOEF for future maritime

deployment.

3.4. Ignition Quality Assessment

The ignition behavior of all fuel samples was assessed using an Advanced Fuel Ignition Delay Analyzer (AFIDA), a constant-volume combustion chamber apparatus designed for the characterization of compression-ignition fuels. The method allows the determination of ignition delay times and derived cetane numbers under highly controlled conditions while requiring comparatively small fuel quantities. Standard cetane number measurements were performed under reference conditions defined by DIN EN 17155. In addition, a matrix of experiments was conducted using different combustion chamber temperatures and pressures to investigate the sensitivity of the fuels to varying operating conditions. Besides standard cetane number determination, complete pressure traces were analyzed to obtain a more detailed understanding of the auto-ignition process. This approach allowed investigation of ignition delay, pressure-rise characteristics, combustion phasing, and overall ignition stability. The combined analysis of cetane number and ignition delay provides a robust basis for evaluating the suitability of ether-HOEF as a marine fuel blend component.

3.5. Soot Formation Characterization

The soot-forming tendency of the investigated fuels was evaluated using the Yield Sooting Index (YSI) methodology. This approach was selected because it provides a quantitative measure of the intrinsic soot-forming behavior of a fuel while requiring only very small sample volumes. Such low fuel requirements were particularly advantageous within the E-TANDEM project, where the availability of HOEF surrogate fuels was limited. Moreover, the YSI methodology allows direct comparison between conventional marine fuels and novel oxygenated fuel formulations under highly controlled combustion conditions.

The YSI methodology is based on the addition of a small amount of test fuel, commonly referred to as a dopant, into a standardized methane-air diffusion flame. The resulting increase in soot concentration is subsequently quantified and normalized against reference compounds with predefined YSI values. This procedure minimizes the influence of burner geometry, operating conditions, and fuel concentration effects, thereby enabling comparison of fuels possessing substantially different chemical compositions. Experiments were conducted using a Yale co-flow diffusion burner operating under laminar, non-premixed combustion conditions. The burner generated an axisymmetric methane-air flame into which the investigated fuel samples were introduced in highly diluted concentrations. To ensure reproducibility and complete vaporization, the fuel delivery system and associated fuel lines were heated during operation. After establishing stable flame conditions, soot formation characteristics were measured by means of optical diagnostics based on color-ratio pyrometry. Flame images were acquired using a high-resolution digital imaging system equipped with optical filters to eliminate unwanted radiation outside the visible spectrum. The resulting images were subsequently processed using established image-analysis procedures. Two-dimensional soot volume-fraction distributions were reconstructed from the recorded flame images following Abel transformation methods, allowing determination of characteristic soot concentrations within the flame structure. The maximum soot volume fraction was then used to calculate the corresponding Yield Sooting Index of each investigated fuel sample.

The soot characterization campaign covered both neat ether-HOEF surrogates and their blends with Marine Gas Oil to assess whether measurable emissions benefits could already be achieved at practically relevant blending levels. This aspect is particularly important from a deployment perspective, since early market introduction will likely occur through low-to-moderate blending ratios rather than immediate substitution of conventional marine fuels.

From a shipping perspective, soot formation is of growing importance because particulate matter and black-carbon emissions are increasingly being addressed by environmental regulations and local air-quality initiatives. Consequently, quantifying the soot-reduction potential of ether-HOEF blends represents a critical element in assessing their suitability for

future maritime deployment. The YSI methodology therefore provides a scientifically robust basis for evaluating the contribution of ether-HOEF to cleaner marine combustion systems.

4. Fuel Properties and Blend Quality

The practical implementation of alternative marine fuels requires compliance with a range of physicochemical properties that govern fuel handling, storage, transportation, and engine operation. Consequently, the final Ether-HOEF formulation was evaluated with respect to key fuel parameters relevant for maritime applications, including density, viscosity, flash point, oxidation stability, lubricity, and distillation behavior. The obtained properties were assessed against the requirements of ISO 8217 for marine fuels and EN 590 for diesel fuels in order to evaluate the suitability of Ether-HOEF as a blend component for Marine Gas Oil (MGO).

Density and Viscosity

The final Ether-HOEF formulation exhibited a density of approximately 796 kg/m³, which is somewhat lower than conventional Marine Gas Oil but remains within the range typically associated with middle-distillate transportation fuels. Blending with MGO progressively increased density towards values characteristic of commercial marine fuels. The 50% Ether-HOEF blend exhibited a density of approximately 825 kg/m³, while the 20% and 10% blends reached densities of approximately 840 and 847 kg/m³, respectively. These results indicate that the incorporation of Ether-HOEF does not fundamentally alter fuel handling characteristics and remains compatible with existing marine fuel logistics systems.

A similar trend was observed for kinematic viscosity. The neat Ether-HOEF exhibited a viscosity of approximately 1.5 mm²/s at 40 °C, reflecting the influence of the oxygenated molecular structure. Upon blending with MGO, viscosity increased into the range typically required for practical fuel-system operation. The 50% blend exhibited a viscosity of approximately 2.3 mm²/s, while the 20% and 10% blends reached approximately 2.9 and 3.4 mm²/s, respectively. Consequently, all investigated blends fulfilled viscosity requirements relevant for compression-ignition marine fuels and suggest good compatibility with existing fuel-delivery systems.

Flash Point

Flash point is one of the most important safety-related fuel properties for maritime applications because it directly influences onboard fuel storage and handling procedures. The final Ether-HOEF formulation exhibited a flash point of approximately 52 °C. Although this value remains slightly below the ISO 8217 limit of 60 °C for marine fuels, it represents a substantial improvement over earlier development-stage formulations and demonstrates the effectiveness of the final fuel optimization strategy. Blending with MGO effectively mitigated this limitation. The 50% Ether-HOEF blend achieved a flash point of approximately 62 °C and therefore fulfilled the ISO 8217 marine-fuel requirement while simultaneously maintaining a substantial renewable-fuel fraction. The results demonstrate that practical implementation of Ether-HOEF through blending strategies is fully compatible with marine fuel-safety requirements.

Oxidation Stability

Long-term storage stability is of particular importance in maritime applications due to extended fuel residence times and the large fuel inventories typically carried aboard commercial vessels. Oxidation-stability investigations showed favorable performance for both the final Ether-HOEF and the corresponding MGO blends. Measured oxidation-stability values remained comfortably within specification limits and no significant peroxide formation was detected during testing. These findings indicate that the oxygenated nature of the fuel does not lead to unusual degradation behavior during storage. In contrast to concerns frequently associated with oxygenated fuels, the long-chain ether-based formulation demonstrated stability characteristics comparable to conventional middle-distillate fuels and is therefore unlikely to create operational challenges related to fuel ageing.

Lubricity and Distillation Behaviour

Lubricity measurements confirmed that all investigated blends remained within acceptable operational limits. Although a slight increase in wear-scar diameter was observed with increasing Ether-HOEF concentration in the fuel blends, all measured values remained well below specification limits applicable to marine and diesel fuels. The results therefore suggest that the introduction of Ether-HOEF does not introduce significant risks for fuel pumps, injectors, or other lubrication-sensitive fuel-system components. The distillation characteristics of the investigated blends remained consistent with those expected for diesel-like middle-distillate fuels. While the introduction of Ether-HOEF slightly shifted the boiling distribution toward lighter fractions, the overall distillation behavior remained compatible with conventional MGO. The investigated blend compositions therefore retained the essential fuel-property characteristics required for marine applications.

Summary of Key Fuel Properties

Table 2 summarizes the most relevant fuel properties of the final Ether-HOEF formulation and the corresponding 50% blend with Marine Gas Oil.

Table 2: Selected fuel properties of final Ether-HOEF and 50% MGO Blend

Property	Ether-HOEF	50% Ether-HOEF Blend
Density @ 15 °C (kg/m ³)	796	825
Kinematic viscosity @ 40 °C (mm ² /s)	1.5	2.3
Flash point (°C)	52	62
Oxidation stability	Within specification limits	Within specification limits
Lubricity	Acceptable	Acceptable

Implications for Marine Fuel Applications

Overall, the physicochemical characterization demonstrates that the final Ether-HOEF formulation possesses a combination of properties suitable for maritime blending applications. While the neat fuel remains marginally below the marine flash-point requirement, blending with conventional Marine Gas Oil enables full compliance with relevant marine-fuel standards while preserving the combustion and emissions-related advantages of the oxygenated fuel. From a deployment perspective, the investigated 10-20% blends appear particularly attractive because they satisfy the majority of fuel-quality requirements while simultaneously providing the basis for the substantial ignition-quality enhancement and soot-reduction benefits discussed in the following sections. Consequently, the final Ether-HOEF formulation can be considered a technically viable blend component for future low-carbon marine-fuel strategies.

Cetane Enhancement

One of the most significant findings of this study is the exceptionally high ignition quality exhibited by the final Ether-HOEF formulation. While conventional Marine Gas Oil showed a cetane number of approximately 54, the final Ether-HOEF reached a cetane number of 113, more than doubling the ignition quality of the reference fuel. These values are substantially higher than those typically observed for conventional diesel fuels and place Ether-HOEF among the most ignition-reactive liquid fuels investigated for compression-ignition applications. The beneficial influence of Ether-HOEF was not limited to the neat fuel. A consistent increase in cetane number was observed with increasing blend ratio, demonstrating that the fuel can act as an effective cetane-enhancing component within conventional marine fuels. The measured values are summarized in Table 3.

Table 3: Cetane Number development with increasing Ether-HOEF content

Fuel Sample	Cetane Number
Marine Gas Oil (MGO)	54
10% Ether-HOEF Blend	59
20% Ether-HOEF Blend	62
50% Ether-HOEF Blend	73
Final Ether-HOEF	113

Even a relatively modest addition of 10 vol.% Ether-HOEF increased the cetane number by approximately 9% relative to neat MGO. Increasing the blend ratio to 20 vol.% further increased the cetane number to 62, while a 50 vol.% blend reached a value of 73. These results demonstrate that increasing renewable fuel content is accompanied by improved, rather than deteriorated, ignition quality. This behavior differentiates Ether-HOEF from several alternative renewable fuels that either exhibit ignition characteristics comparable to conventional diesel fuels or require additional fuel-conditioning measures to compensate for reduced ignition quality. Ether-HOEF therefore performs a dual role as both a renewable fuel component and a cetane improver.

4.1. Auto-Ignition Behaviour

To further investigate combustion reactivity beyond the standardized cetane-number measurement, ignition-delay experiments were performed under a range of temperature and pressure conditions representative of compression-ignition combustion. Ignition delay is a particularly important parameter because it directly affects combustion timing and governs the amount of fuel accumulated prior to ignition. Consequently, ignition delay strongly influences heat-release behaviour, pressure development, combustion stability, and pollutant formation.

Across all investigated fuels, ignition delay decreased with increasing temperature and pressure, consistent with established auto-ignition kinetics. However, significant differences were observed between conventional Marine Gas Oil and Ether-HOEF. Under low-temperature and low-pressure conditions of 480 °C and 17.5 bar initial pressure, conventional MGO exhibited an ignition delay of approximately 4.8 ms. Under identical conditions, the final Ether-HOEF ignited after approximately 2.4 ms, corresponding to a reduction of roughly 50%. The shorter ignition delays observed for Ether-HOEF were maintained across the complete test matrix. Furthermore, blends containing Ether-HOEF consistently exhibited reduced ignition delays relative to neat MGO, confirming that the ignition benefits observed through cetane-number measurements translate directly into improved auto-ignition behavior. The particularly strong ignition performance under low-temperature conditions is noteworthy because ignition-related challenges are typically most pronounced during these operating regimes. The data therefore indicate that Ether-HOEF possesses highly favorable intrinsic reactivity characteristics that can improve the robustness of diesel combustion under demanding operating conditions.

Pressure-Trace Analysis and Implications for Marine Engine Operation

Representative pressure traces obtained during AFIDA testing provided additional insight into the combustion behaviour of the investigated fuels. Following fuel injection, all fuels exhibited an initial pressure decrease associated with fuel evaporation, followed by a rapid pressure increase indicating ignition and subsequent combustion. The overall shape of the pressure traces remained remarkably similar for MGO and Ether-HOEF, suggesting that the oxygenated fuel maintains combustion characteristics generally consistent with conventional diesel-type fuels. However, the onset of the pressure rise occurred noticeably earlier for Ether-HOEF,

reflecting the shorter ignition delays and higher cetane numbers discussed above. Despite the accelerated ignition behaviour, no evidence of unstable combustion or excessively aggressive pressure-rise characteristics was observed. Instead, the fuel exhibited highly reproducible ignition and combustion behavior throughout the investigated operating range.

Perhaps the most important implication of these findings is that increasing the renewable-fuel content does not compromise ignition performance. In many alternative-fuel pathways, improved sustainability is achieved at the expense of combustion quality. In contrast, Ether-HOEF simultaneously increases renewable fuel content and improves ignition characteristics. This combination may constitute a significant advantage for future market adoption because operators can obtain environmental benefits without sacrificing engine operability or combustion performance. Overall, the combination of exceptionally high cetane numbers, substantially reduced ignition delays, and stable pressure-trace behaviour demonstrates that the final Ether-HOEF formulation exhibits highly favorable ignition characteristics for marine compression-ignition applications. These findings also establish the basis for the subsequent analysis of soot-formation characteristics, where the oxygenated molecular structure of Ether-HOEF provides additional environmental benefits

4.2. Soot Formation Characteristics

Among all investigated performance parameters, soot formation represents one of the most significant environmental advantages of Ether-HOEF. While greenhouse-gas emissions are commonly used as the primary metric for evaluating alternative fuels, local pollutant emissions remain an equally important consideration for maritime transport. Particulate matter and black-carbon emissions generated by marine diesel engines contribute to air-quality degradation in coastal regions and ports, while also exerting adverse impacts on human health and climate. Consequently, fuels capable of reducing soot formation without requiring extensive engine modifications are of particular interest for near-term maritime decarbonization strategies.

Yield Sooting Index Results

The soot-forming tendency of the investigated fuels was quantified using the Yield Sooting Index (YSI) methodology. The measured values demonstrate substantial differences between conventional Marine Gas Oil and Ether-HOEF-containing blends. Table 3 summarizes the obtained results.

Table 3. Yield Sooting Index values of Ether-HOEF and MGO Blends

Fuel Sample	YSI
Marine Gas Oil (MGO)	170
10% Ether-HOEF Blend	110
20% Ether-HOEF Blend	100
50% Ether-HOEF Blend	88
Final Ether-HOEF	38

The results demonstrate a pronounced decrease in intrinsic soot-forming tendency with increasing Ether-HOEF content. Whereas conventional MGO exhibited a YSI value of approximately 170, the final Ether-HOEF formulation achieved a value of only 38. This corresponds to a reduction of approximately 78% in soot-forming tendency compared with the fossil reference fuel. Even relatively low blending ratios produced substantial improvements. The 10% blend reduced the YSI value from 170 to approximately 110, corresponding to a reduction of roughly 35%. Increasing the blend ratio to 20% further lowered the YSI value to approximately 100, while the 50% blend achieved a value of 88. These findings indicate that

meaningful emissions benefits can already be realized at blending levels that are fully compatible with existing fuel infrastructures. The approximately monotonic decrease in YSI with increasing Ether-HOEF concentration suggests predictable blending behaviour and indicates that the soot-reduction potential scales consistently with renewable-fuel content. This characteristic is advantageous for practical implementation because operators can estimate expected emissions benefits directly from the selected blend ratio. An important observation is that these improvements are achieved intrinsically through fuel composition rather than through hardware modifications. Consequently, the soot-reduction potential remains available across a wide range of engine platforms and operating conditions, making Ether-HOEF attractive as a broad deployment option for existing marine fleets.

Implications for Maritime Applications

The observed reduction in soot-forming tendency has several implications for maritime transportation. First, lower soot formation may contribute to reductions in particulate-matter emissions and black-carbon release, particularly in coastal regions and heavily trafficked port areas. Such reductions are becoming increasingly relevant as environmental regulations continue to evolve toward stricter emissions requirements. Second, the ability to achieve substantial soot reductions through blending offers a practical pathway for environmental improvement without requiring extensive modifications to engines or fuel infrastructure. Even the 10% Ether-HOEF blend produced a large reduction in YSI while maintaining compatibility with conventional fuel systems. This finding supports the concept of a phased implementation strategy in which increasing renewable-fuel content is accompanied by progressively cleaner combustion behaviour. Finally, the simultaneous improvement in ignition quality and soot-forming behaviour is particularly noteworthy. Many alternative fuels improve one aspect of combustion performance while compromising another. Ether-HOEF, by contrast, combines exceptionally high ignition quality with substantially reduced soot propensity. This combination is rarely achieved within a single fuel concept and represents one of the most important outcomes of the present study. Overall, the YSI investigations demonstrate that Ether-HOEF possesses a strong inherent capability for reducing soot formation while maintaining diesel-like fuel characteristics. The results therefore establish soot reduction as a second major performance advantage of Ether-HOEF alongside the ignition-quality improvements discussed in the previous section.

4.3. Assessment of Drop-In Potential

A key requirement for the successful introduction of alternative marine fuels is the ability to integrate them into existing fuel infrastructures and vessel fleets with minimal technical disruption. While many proposed low-carbon fuels require substantial modifications to storage systems, fuel logistics, bunkering infrastructure, or propulsion technologies, the concept investigated in this work is based on the gradual introduction of Ether-HOEF through blending with conventional Marine Gas Oil (MGO). The practical feasibility of such an approach depends on whether the fuel can provide meaningful environmental and performance benefits while maintaining the operational characteristics expected from established marine fuels.

The physicochemical properties of the final Ether-HOEF formulation indicate a high degree of compatibility with conventional middle-distillate fuels. Although the neat fuel exhibits a flash point slightly below the ISO 8217 marine-fuel requirement, blending with MGO effectively resolves this limitation. Furthermore, density, viscosity, oxidation stability, and lubricity remain within ranges consistent with marine-fuel applications. These observations suggest that Ether-HOEF can be incorporated into existing fuel supply chains without creating fundamental challenges related to fuel handling or storage.

From a combustion perspective, Ether-HOEF provides several characteristics that are highly favorable for gradual implementation. The addition of Ether-HOEF increases cetane number, shortens ignition delay, and significantly reduces soot-forming tendency. Importantly, these improvements are observed even at relatively low blending ratios. The 10% and 20% blends already exhibit measurable benefits in ignition quality and soot reduction while remaining

closely aligned with conventional MGO in terms of their overall fuel characteristics. The ability to achieve performance improvements at modest blending levels represents a significant advantage when compared with several alternative maritime fuel pathways. Unlike fuels such as ammonia, hydrogen, or methanol, which generally require dedicated infrastructure and substantial vessel modifications, Ether-HOEF can be introduced incrementally within existing fuel systems. This enables a phased transition strategy in which renewable-fuel content can gradually increase as production capacity expands and operational experience accumulates.

A further advantage of the blend-based approach is its flexibility. Fuel suppliers and ship operators can adapt blending ratios to local fuel availability, regulatory requirements, and economic considerations without fundamentally changing engine operation or fuel-supply infrastructure. Such flexibility is particularly valuable during the transition period toward low-carbon shipping, where multiple fuel pathways are expected to coexist for an extended period. The results of the present investigation indicate that blends containing 10–20% Ether-HOEF represent particularly attractive candidates for near-term implementation. These blends provide substantial improvements in ignition quality and soot reduction while maintaining fuel properties compatible with existing marine-fuel specifications. Higher blending ratios offer additional environmental benefits and may become increasingly attractive as production volumes increase and fuel costs decrease.

Overall, the combination of favorable fuel properties, exceptional ignition quality, and substantial soot-reduction potential supports the classification of Ether-HOEF as a promising drop-in blend component for Marine Gas Oil. Rather than requiring a disruptive transition toward entirely new fuel infrastructures, Ether-HOEF enables a progressive approach to maritime decarbonization that can be implemented within existing supply chains and vessel fleets. This characteristic distinguishes the fuel concept from many competing alternative-fuel pathways and represents one of its most significant strengths from a deployment perspective.

5. Discussion

The results presented in this work demonstrate that the final Ether-HOEF formulation occupies a distinctive position within the current portfolio of alternative marine fuels. While most proposed low-carbon fuels require trade-offs between sustainability, combustion performance, and infrastructure compatibility, Ether-HOEF combines several advantageous characteristics within a single fuel concept. The fuel simultaneously provides exceptionally high ignition quality, substantially reduced soot-forming tendency, and the possibility of gradual introduction through blending with conventional Marine Gas Oil (MGO). Taken together, these properties suggest that Ether-HOEF may represent a particularly attractive transition fuel for the maritime sector.

5.1. Ether-HOEF within the alternative marine fuel landscape

Current maritime decarbonization pathways are dominated by discussions surrounding hydrogen, ammonia, methanol, and synthetic hydrocarbon fuels. Each option offers specific benefits but also introduces significant technical and economic challenges.

Hydrogen and ammonia possess considerable long-term decarbonization potential but require major modifications to storage systems, bunkering infrastructure, and propulsion technologies. Methanol benefits from increasing industrial adoption and growing operational experience but suffers from a comparatively low volumetric energy density, requiring increased fuel-storage capacity aboard vessels. Fischer-Tropsch diesel offers excellent compatibility with existing infrastructure but behaves largely as a conventional hydrocarbon fuel and therefore provides limited intrinsic benefits regarding particulate-emission reduction.

The Ether-HOEF investigated in this study occupies an intermediate position between these approaches. Similar to Fischer-Tropsch fuels, it retains diesel-like handling characteristics and compatibility with existing fuel infrastructures. At the same time, the incorporation of oxygen into the molecular structure provides combustion advantages that are more commonly associated with oxygenated fuels. Consequently, Ether-HOEF combines infrastructure

compatibility with improved local-emissions performance and represents a complementary pathway alongside other emerging marine-fuel concepts.

5.2. Soot reduction as a key environmental benefit

While greenhouse-gas emissions remain the primary driver of maritime decarbonization strategies, local pollutant emissions continue to represent an important challenge for the shipping sector. Soot and particulate matter are particularly relevant because of their impact on both air quality and climate. Emissions generated in ports, coastal regions, and heavily trafficked shipping routes directly affect densely populated areas and are increasingly becoming the subject of environmental regulation. Against this background, the observed Yield Sooting Index reductions constitute one of the most significant findings of this study. The reduction from approximately 170 for conventional MGO to 38 for the final Ether-HOEF formulation represents a dramatic decrease in intrinsic soot-forming tendency. Importantly, substantial reductions were already observed at blending ratios of 10% and 20%, which are also the concentrations considered most realistic for near-term market introduction. An important aspect of these results is that the soot reduction originates directly from the fuel composition rather than from additional emissions-control technologies. The oxygen incorporated within the ether molecules alters combustion chemistry and suppresses soot formation during the combustion process itself. Consequently, the emissions benefit is fundamentally linked to fuel composition and remains largely independent of engine-specific optimization measures.

This characteristic may be particularly valuable for existing vessel fleets, where large-scale engine replacement is economically challenging. Under such conditions, fuel-based emissions-reduction strategies provide a practical pathway toward cleaner combustion without requiring extensive modifications to onboard systems. Ether-HOEF therefore offers the potential to simultaneously contribute to greenhouse-gas reduction objectives and local air-quality improvements.

5.3. Drop-in deployment and scale-up perspective

The successful deployment of alternative maritime fuels depends not only on fuel performance but also on compatibility with existing infrastructures. In contrast to fuels that require dedicated storage, bunkering, or propulsion systems, Ether-HOEF can be introduced gradually through blending with conventional Marine Gas Oil. The investigated 10% and 20% blends maintained fuel properties suitable for marine applications while simultaneously improving ignition quality and reducing soot-forming tendency. This enables a phased transition strategy, allowing renewable-fuel content to increase progressively as production capacity expands. The successful TRL4 demonstration of the E-TANDEM production pathway further supports the industrial scalability of the concept. Although challenges related to production costs and large-scale validation remain, these are primarily associated with technology maturation rather than fundamental limitations of the fuel itself. Overall, Ether-HOEF combines renewable production, favorable combustion properties, and practical deployability, strengthening its potential as a maritime decarbonization fuel.

6. Conclusions and Outlook

The decarbonization of maritime transport requires renewable fuels that can be integrated into existing fuel infrastructures while simultaneously delivering favorable combustion performance. In this work, the suitability of a long-chain ether-based Higher Oxygenate E-Fuel (Ether-HOEF) as a blend component for Marine Gas Oil (MGO) was evaluated with particular emphasis on fuel properties, ignition behavior, soot formation characteristics, and deployment potential.

The results demonstrate that Ether-HOEF exhibits exceptionally favorable ignition characteristics. The final fuel formulation achieved a cetane number of 113, while blends

containing 10%, 20%, and 50% Ether-HOEF increased the cetane number of MGO from 54 to 59, 62, and 73, respectively. Ignition-delay measurements confirmed significantly faster auto-ignition compared with conventional marine fuel across a broad range of operating conditions. These findings establish Ether-HOEF not only as a renewable fuel component but also as a highly effective cetane improver for compression-ignition applications.

A second major finding concerns the soot-forming tendency of the fuel. Yield Sooting Index measurements demonstrated a substantial reduction in intrinsic soot propensity, decreasing from approximately 170 for conventional MGO to 38 for neat Ether-HOEF. Meaningful reductions were already observed at blend ratios of 10% and 20%, indicating that significant emissions benefits can be achieved through gradual implementation strategies. The results confirm that the oxygenated molecular structure of long-chain ethers can promote cleaner combustion while maintaining diesel-like fuel characteristics.

The investigated blends furthermore maintained physicochemical properties compatible with marine-fuel applications. In particular, the 10% and 20% blends combined favorable fuel properties with improved ignition quality and reduced soot formation, supporting their suitability for near-term implementation within existing marine fuel supply chains. These characteristics distinguish Ether-HOEF from many alternative fuel concepts that require dedicated storage, bunkering, or propulsion technologies.

Overall, the present study demonstrates that long-chain ether-based HOEF represents a promising renewable blend component for Marine Gas Oil. By simultaneously enhancing ignition quality, reducing soot formation, and enabling gradual integration into existing fuel infrastructures, Ether-HOEF offers a practical pathway toward the decarbonization of maritime transport.

Future work should focus on large-scale marine-engine validation and detailed emissions analysis under realistic operating conditions. Such studies will be essential to further quantify the benefits of Ether-HOEF and support its transition from bench-scale fuel demonstration to practical maritime deployment.

7. Acknowledgement

This work has been funded by the European Union under grant number 101083700 (E-TANDEM). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

8. References

- [1] Europäische Kommission: Der europäische Grüne Deal, 2019.
- [2] A. Ramirez, M. Sarathy, J. Gascon, Trends in Chemistry, 2020.
- [3] E-Tandem Website, <https://e-tandem.eu/>, 2022.
- [4] ISO 8217 Petroleum products-fuels (class F) – Specification of marine fuels. 6th edition. 2017-03. reference number ISO 8217-2017(E).
- [5] EN 590 Automotive fuels – Diesel – requirements and test methods. German version EN 90:2013+A1:2017.
- [6] A. Dmitry. What are MGO and MDO fuels? Fuels Explained. October 25. 2024. www.maritimpage.com/what-are-mgo-and-mdo-fuels-marine-fuels-explained/
- [7] DIN EN 14214 Flüssige Mineralölzeugnisse - Fettsäure-Methylester (FAME) zur Verwendung in Dieselmotoren und als Heizöl - Anforderungen und Prüfverfahren; Deutsche Fassung EN 14214:2012

- [8] M. Perčić et al. "Environmental Footprint of Diesel Fuel in the Shipping Sector." WIT Transactions on Ecology and the Environment (eISSN: 1743-3541), Vol. 262, 2024
- [9] R. Caldogno et al. "Green Syngas Production with Metal-Supported Solid Oxide Cells." Journal of Power Sources, Vol. 654, 2025
- [10] I. Jovanovic et al. "The potential of e-fuels in the reduction of environmental footprint of a ferry." Ships and Offshore Structures, ISSN: 1744-5302, 2026
- [11] R. Caldogno et al. "Assessing co-electrolysis stability with metal-supported solid oxide cells under dynamic current conditions. Journal of Power Sources, Vol. 677, 2026

Studying Deactivation phenomena using Pd/1,2-DTBPMB in the Tandem Isomerization- Methoxycarbonylation Reaction

N. Kumari¹, R. Franke^{2,3}, A. J. Vorholt¹

¹Max Planck Institute for chemical and Energy Conversion, Mülheim an der Ruhr, Germany

²Evonik Oxeno GmbH, Marl

³Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum

Homogenous palladium catalysts are widely used for the methoxycarbonylation of unsaturated compounds. However, catalyst deactivation primarily through the formation of Palladium black and ligand degradation, remains a key limitation for practical application. We report a systematic study to find optimal reaction conditions for a stable catalytic system which was scaled-up to study the recyclability. The catalyst was successfully recycled at larger scale without loss of catalytic activity or selectivity with no observable Pd black. Consequently, to determine the minimum effective catalyst loading, the catalyst concentration was further reduced, it could be recycled for up to four consecutive runs, a decrease in reactivity was observed in the fifth run. This loss in activity was attributed to extensive ligand oxidation, as confirmed by NMR spectroscopy. Based on these findings, the optimized catalytic system was subsequently scaled up, achieving sustained catalytic performance over six consecutive recycling cycles with a total turnover number (TON) of 10342.

Plasma-assisted entrained flow gasification as a key technology for Net Zero - a review

L. Kufferath-Sieberin¹, S. Fleck¹, U. Santo¹, D. Becker², M. Vogelbacher², J. Matthes², F. Scheiff^{1,3}

¹Karlsruhe Institute of Technology (KIT), Institute for Technical Chemistry, Gasification Technology (ITC vgt), Eggenstein-Leopoldshafen, Germany,

²Karlsruhe Institute of Technology (KIT), Institute for Automation and Applied Informatics (IAI), Eggenstein-Leopoldshafen, Germany,

³Karlsruhe Institute of Technology (KIT), Engler-Bunte-Institute, Fuel Technology (EBI ceb), Karlsruhe, Germany

Gasification is a well-known thermochemical process for converting carbon-based feedstocks into high-value syngas. Oxygen-based gasification is a high-temperature, autothermal process based on partial oxidation. Especially at higher H₂/CO ratios, significant quantities of CO₂ are generated, which limits the overall carbon efficiency (CE). A promising alternative is plasma-assisted gasification, which uses electrical generated heat and steam as the gasification medium, substantially reducing CO₂ production. The plasma flame serves as an independent and flexible heat source that can be powered by renewable electricity. Bastek et al. [1] and Dossow et al. [2] published Aspen-based simulations of biomass-to-liquid processes, demonstrating the potential for upgrading low-quality biogenic feedstocks via plasma-assisted entrained flow gasification (PEFG). Kuznetsov et al. [3] reviewed various reactor designs, covering both existing installations and their future potential.

At ITC, the conversion of biogenic and plastic waste-based pyrolysis oils has been examined in the last years [4], [5], [6]. An Aspen Plus model for entrained flow gasification (EFG) was developed, validated by experimental data derived from the high-pressure EFG operated at Carbon Cycle Lab at KIT. This model is used for scale-up of to a 100 MW gasifier-scale case study.

To quantify the benefits and identify challenges of steam-plasma-assisted entrained flow gasification (PEFG), the Aspen Plus model has been extended to account for plasma integration. The model integrates (i) gas and fuel supply, (ii) plasma-assisted gasifier and (iv) downstream syngas clean-up. In the presented work, plasma-assisted entrained flow gasification is compared against oxygen-based biogenic and plastic waste-based pyrolysis oil gasification simulation.

Parametric studies shed a light on the influence of gasification media (O₂, steam, CO₂) and the thermal efficiency of plasma-derived heat. Performance is evaluated applying characteristic parameters, e.g., Carbon Efficiency (CE) and Cold gas efficiency (CGE). An outlook on the flexibilization of chemical processes with the focus on grid stability is given.

The findings suggest, that plasma-assisted gasification is a promising route toward a circular carbon economy for the chemical industry, acting both as a high efficiency syngas producer and as a functional CO₂ sink. Leveraging this potential will require further development in reactor design, stable-to-operate plasma sources, long-term testing and upscaling approaches.

References:

- [1] Bastek S, Dossow D, Tamošiūnas A, Umeki K, Spliethoff H, Fendt S, (2025), Technical evaluation of plasma-assisted entrained flow gasification for hydrogen-rich syngas production from waste and biomass, Elsevier, International Journal of Hydrogen Energy, 150184, 157, 2025-08-13
- [2] Dossow M, Bastek S, Spliethoff H, Fendt S, (2025), Electrifying biomass-to-liquid processes using plasma-assisted entrained flow gasification, Elsevier, Energy Conversion and Management, 120049, 341, <https://linkinghub.elsevier.com/retrieve/pii/S0196890425005734>, 2025-09-09
- [3] Kuznetsov VA, Gräbner M, Schimpke R, Uhrandt D, Richter A, (2026), Systematic evaluation of

- gasifiers driven by the high-enthalpy plasma supply, Elsevier, Fuel, 138538, 417, <https://linkinghub.elsevier.com/retrieve/pii/S0016236126002917>, 2026-03-04
- [4] Eberhard M, Santo U, Michelfelder B, Günther A, Weigand P, Matthes J, Waibel P, Hagenmeyer V, Kolb T, (2020), The bioliq® Entrained-Flow Gasifier – A Model for the German Energiewende, Wiley, ChemBioEng Reviews, 106-118, <https://onlinelibrary.wiley.com/doi/abs/10.1002/cben.202000006>, 2025-09-04
- [5] Dammann M, (2024), Numerical modelling and simulation of atmospheric entrained flow gasification of surrogate fuels, Karlsruhe, <https://publikationen.bibliothek.kit.edu/1000172116>, 2026-02-20, Karlsruhe Institute of Technology (KIT)
- [6] Dammann M, Santo U, Böning D, Knoch H, Eberhard M, Kolb T, (2025), Entrained flow gasification: Pilot-scale experimental, balancing and equilibrium data for model validation, Elsevier, Fuel, 132809, <https://linkinghub.elsevier.com/retrieve/pii/S0016236124019586>, 2025-08-25

Turning Emission to Feedstock: Mapping Europe's CO₂ Market for Fuels and Chemicals

I. Akhmetova, N. Fuchs, C. Gruber, H. Basche, S. Bernhardt, H. Lehmann
PtX Lab Lausitz | ZUG gGmbH, Cottbus, Germany

The defossilisation of the European industry requires alternative, sustainable carbon sources to ensure a resilient supply for fuels and chemicals. In this context, CO₂ is increasingly discussed as a valuable carbon carrier that can be transformed into chemicals and fuels, contributing to a circular carbon economy. While CCU technologies are advancing, a systemic understanding of how CO₂ can be integrated into reliable and scalable value chains – such as CCU or PtX – is lacking.

Turning CO₂ into a marketable raw material requires addressing several issues simultaneously: the geographic distribution of CO₂ sources and potential users, the need for purification and suitable transport infrastructure, cost structures along the entire value chain, and regulatory framework across Europe.

This project tackles these questions by developing a data-driven framework to analyse potential CO₂ flows across Europe. The approach combines:

- spatially resolved data on industrial CO₂ point sources and activity data from industry and mobility (aviation and shipping) as possible consumers of CO₂-based chemicals and fuels,
- assessment of transport options, infrastructure needs, and location choice for potential carbon hubs,
- evaluation of policy instruments such as ETS, CBAM, quotas, funding programmes, and of cost pathways for CO₂-based products.

A key focus lies on identifying regions where CO₂ supply, demand, and infrastructure coincide, potentially enabling integrated value chains.

By integrating the above elements, the project seeks to clarify the conditions under which CO₂-based fuels and chemicals can become part of a European carbon economy. Based on this framework, the project will provide a science-based foundation for policy decisions on the development of a European CO₂ market. The results are intended to support policy makers in designing infrastructure strategies and regulatory frameworks for CO₂-based value chains. In support, the project will deliver an interactive online map displaying European CO₂ flows and highlighting emerging carbon hubs. This tool will support infrastructure planning and provide evidence-based policy insights for decision makers.

Therefore, the work directly connects to the key themes of this conference:

How can CO₂ contribute to a resilient supply of carbon for fuels and chemicals? What infrastructure and market structures are required? What conditions are required to enable large-scale deployment?

High Temperature Workflows in High Throughput Experimentation: From NH₃ Cracking and CO₂-to-CO to Methane Pyrolysis

M. Moll, Ch. Hauber¹, B. Mutz¹

¹hte GmbH, Heidelberg, Germany

Abstract

High-temperature hydrogen and carbon carrier technologies require catalyst testing workflows that combine rapid screening with process-relevant validation under demanding thermal, pressure, and feed conditions. This work demonstrates complementary hte workflows based on a 16-fold high throughput fixed-bed reactor platform and a 4-fold high-temperature bench-scale tubular reactor platform. The combined approach enables automated catalyst and parameter screening, operation at elevated temperature and pressure, advanced inert reactor concepts with minimal blank activity, robust online analytics, and scale-relevant validation with commercial catalyst geometries.

The 16-fold platform was applied to pressurized ammonia cracking as a demonstration case for hydrogen release from a chemical carrier. The workflow enabled controlled NH₃ and H₂O dosing, hydrogen balance closure, kinetic data generation, stability assessment, and reliable conversion resolution in kinetically controlled regimes. The 4-fold bench-scale platform was applied to CO₂-to-CO conversion via dry reforming and reverse water-gas shift chemistry. Here, the combination of advanced inert reactor design and axial temperature profiling enabled catalyst performance to be interpreted together with thermal gradients, cold spot formation, and heat-management effects under high-temperature and elevated-pressure conditions.

Together, these workflows bridge the gap between early-stage catalyst screening and scale-relevant process assessment. Beyond ammonia cracking and CO₂-to-CO conversion, the methodology is transferable to further high-temperature processes in which reactor inertness, heat management, deactivation, product analytics, pressure-drop evolution, and long-term stability are decisive. Methane pyrolysis is a particularly relevant next application, as hydrogen formation, solid-carbon accumulation, catalyst deactivation, pressure-drop development, and regeneration behavior must be assessed simultaneously. The resulting workflow concept supports faster development and de-risking of catalyst and reactor technologies for future hydrogen, syngas, fuel, and chemical value chains.

1. Introduction

The transformation of energy and chemical value chains requires resilient routes for the production, storage, transport, and conversion of hydrogen and carbon carriers. Hydrogen is widely considered a key molecule for defossilized energy systems and chemical production, but its low volumetric energy density and demanding storage and transport requirements remain major barriers for large-scale deployment. Chemical hydrogen carriers such as ammonia have therefore attracted significant attention, as ammonia combines high hydrogen density with established production and logistics infrastructure and can release hydrogen by catalytic decomposition. [1–4] In parallel, carbon carrier technologies are becoming increasingly important for circular fuel and chemical value chains. High-temperature enabling steps such as CO₂-to-CO conversion, methane pyrolysis, hydrocarbon or plastic-waste pyrolysis, gasification, and related syngas-generation routes can provide key intermediates for downstream processes such as methanol synthesis, Fischer–Tropsch products, e-fuels, sustainable aviation fuel, and other carbon-based chemicals. Although these value chains differ strongly in chemistry, operating window, and application, the high-temperature steps addressed in this work share common experimental challenges: elevated temperature and pressure, heat-transfer sensitivity, catalyst deactivation and the need to distinguish intrinsic catalyst performance from reactor-induced artefacts. [5–12]

Ammonia cracking is a representative example of hydrogen carrier conversion. High hydrogen recovery requires elevated temperatures, while operation at increased pressure, although attractive for downstream hydrogen utilization, shifts the equilibrium unfavorably. Catalyst activity, stability, water tolerance, and performance under industrially relevant pressure and space velocity conditions are therefore critical development targets. Recent literature on ammonia cracking technologies highlights the need for catalyst development, suitable reactor concepts, and scalable process implementation. [3,4,13]

CO₂-to-CO conversion provides a complementary example for high-temperature carbon carrier conversion. Reverse water-gas shift converts CO₂ and H₂ into CO and H₂O, while dry reforming of methane converts CH₄ and CO₂ into synthesis gas. Both routes provide access to CO-rich syngas, but their interpretation is strongly affected by temperature gradients, side reactions, coking, and reactor-wall effects. Meaningful catalyst evaluation therefore requires not only conversion and selectivity data, but also inert reactor concepts, representative catalyst geometries, robust product analytics, and spatially resolved temperature information. Reviews on rWGS, dry reforming, and CO₂-to-CO conversion emphasize the importance of catalyst design, thermodynamic interpretation, kinetics, and testing under realistic process conditions. [10–12]

Methane pyrolysis represents a further high-temperature technology at the interface of hydrogen and carbon carrier chemistry. In contrast to steam methane reforming, methane pyrolysis decomposes methane into hydrogen and solid carbon without direct CO₂ formation in the main reaction. The route is therefore discussed as a pathway toward turquoise hydrogen, particularly if the required heat is supplied from low-carbon or electrified energy sources. Industrial implementation remains challenging because the process requires very high temperatures, efficient heat transfer, control of carbon formation, mitigation of catalyst deactivation, and reactor concepts capable of handling solid carbon products. Recent reviews identify reactor design, catalyst performance, carbon-product quality, process economics, greenhouse gas emissions, and scale-up as key topics for future methane pyrolysis development. [8,9,14]

A central gap across these technologies is the limited transferability of early-stage laboratory data to industrially relevant operation. Conventional single-reactor testing can provide high-quality data but is time-consuming and limited in throughput. Small-scale screening can accelerate catalyst ranking, but may not adequately represent commercial catalyst shapes,

thermal profiles, pressure effects, or long-term time-on-stream behavior. This gap is particularly critical for endothermic high-temperature reactions, where cold spots, axial temperature gradients, and background activity of reactor materials can distort apparent kinetics and lead to misinterpretation of catalyst performance.

hte addresses this challenge by developing complementary high throughput and high-temperature bench-scale workflows for catalyst and process development. The present work illustrates this approach using ammonia cracking and CO₂-to-CO conversion as demonstration cases. Ammonia cracking shows how automated parallel testing can generate catalyst performance, kinetic, and stability information under pressurized high-temperature conditions. CO₂-to-CO conversion demonstrates how inert reactor design, commercial catalyst geometries, online analytics, and axial temperature profiling enable scale-relevant interpretation of strongly temperature-sensitive gas-phase reactions. Together, these workflows provide a basis for transferring the methodology to further high-temperature processes such as methane pyrolysis, where hydrogen formation, carbon accumulation, pressure-drop evolution, regeneration behavior, and catalyst robustness must be evaluated simultaneously.

2. Ammonia Cracking as Demonstration Case for Pressurized High-Temperature Testing

Ammonia cracking was selected as a first demonstration case for hte's high-temperature high throughput technology because it combines several experimental challenges that are representative for future hydrogen and carbon carrier processes. The reaction is strongly endothermic, requires elevated temperatures to achieve high hydrogen recovery, and becomes thermodynamically less favorable at increased pressure. Nevertheless, pressurized operation is highly relevant for industrial applications, since hydrogen is often required at elevated pressure for downstream use or further conversion. [15, 16] Meaningful catalyst evaluation therefore requires testing under conditions that combine high temperature, elevated pressure, inert reactor concept, reliable ammonia handling, and sufficiently sensitive analytics. [17]

For this purpose, a flexible 16-fold parallel fixed-bed reactor unit was tuned for NH₃ cracking. The system is designed for automated high throughput operation and enables parallel testing of catalysts under different temperatures, pressures, space velocities, feed compositions, and time-on-stream protocols. The reactor section is based on high-temperature metal alloy reactors equipped with inert ceramic inlays. This reactor concept is essential for NH₃ cracking because metallic surfaces contributes to undesired background conversion at > 550°C (Figure 1). By minimizing reactor-induced blank activity, the setup allows isolating the activity of the catalyst from the blank conversion of the reactor material. Blank experiments showed less than 1% NH₃ conversion up to 700 °C and only approximately 2% at 750 °C (see Figure 1),

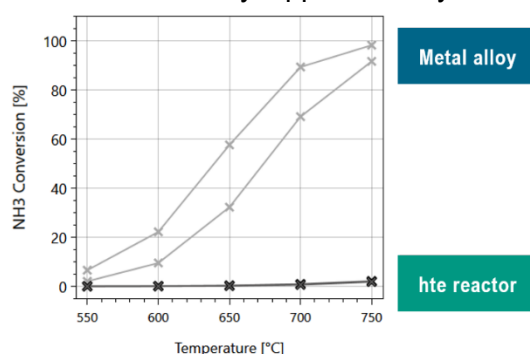


Figure 1. Blank activity of high-temperature metal alloy reactors compared to hte's inert high-temperature reactor design at 15 and 40 barg.

demonstrating the inert behavior of the reactor concept under severe high-temperature conditions.

The 16-fold configuration also enables efficient experimental design. Individual catalyst beds can be loaded with different bed lengths, allowing gas hourly space velocity to be varied in parallel within one experiment. In addition, individual reactor heating allows temperature programs and stability investigations to be combined in the same campaign. This makes it possible to generate activity, stability, and kinetic information within significantly shorter development times compared with conventional single-reactor testing.

The feed and analytics concept was adapted to the specific requirements of NH_3 cracking. Gaseous components such as H_2 , N_2 , and Ar were supplied via mass flow controllers, while NH_3 and H_2O were introduced as liquids using high-precision syringe pumps followed by vaporization and mixing. Water was intentionally co-fed at trace level to represent commercial-grade ammonia and to validate the ability of the workflow to dose and recover water reliably. [18] The product gas was analyzed by an in-house configured online gas chromatograph equipped with thermal conductivity detectors for permanent gases, ammonia, and water enabling closed feed recovery, even on trace component levels. Automated process control and data evaluation allowed continuous operation and efficient handling of the large datasets generated by the parallel testing setup. A scheme of the unit is shown in Ref [NH3 3].

The unit was validated using an in-house prepared Fe-based catalyst. The validation campaign covered temperatures from 550 to 750 °C, pressures of 15 and 40 barg, and gas hourly space velocities between 11,000 and 100,000 h^{-1} . Additional scouting experiments extended the covered parameter space up to 50 barg and up to 200,000 h^{-1} . During the full campaign, 5,000 ppm H_2O were co-fed and recovered by the analytical system, confirming the robustness of the dosing and analytics workflow. [17]

The catalytic data, depicted in Figure 2, showed the expected temperature, pressure, and space-velocity dependencies. At 550 °C, NH_3 conversion was low but still resolved reliably, including conversion levels below 2% at high space velocity. Increasing temperature resulted in a pronounced increase in conversion, reaching nearly complete NH_3 conversion at 750 °C and the lowest space velocity investigated. Higher pressure and higher GHSV both reduced conversion, in line with the thermodynamic and kinetic constraints of NH_3 decomposition. More details see Ref [17].

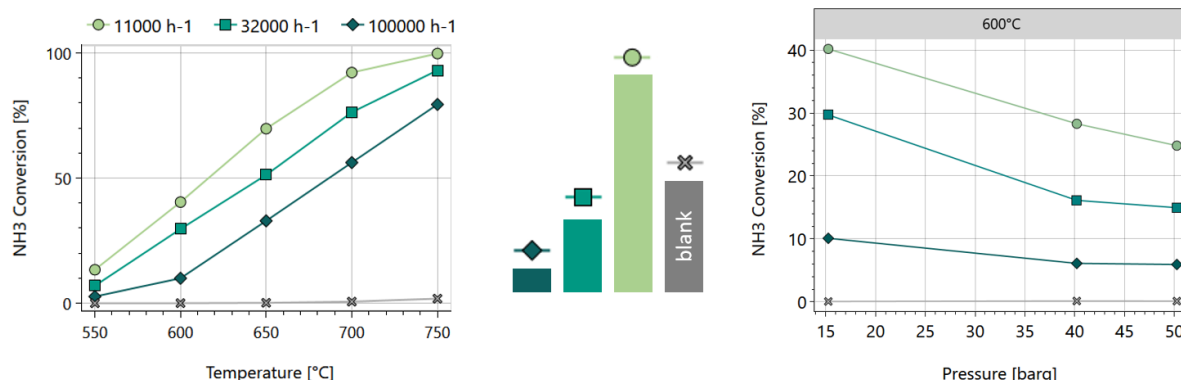


Figure 2. NH_3 cracking using an Fe-based catalyst and hte's advanced high throughput technology (95 % NH_3 , 5 000 ppm H_2O , 4.5 % Ar, 550-750 °C, 15 & 40 barg, 11 000-100 000 h^{-1}). [17]

In a custom R&D project for commercial catalyst benchmarking, four commercial catalysts were tested over broad parameter windows, with each material loaded in different bed lengths to enable parallel GHSV variation. This swift catalyst ranking approach enabled screening 27-36 parameters per catalyst in only 13 days including variations in temperature, space velocity,

and ammonia feed concentration. Some materials already showed measurable NH_3 conversion at comparatively low temperature, while the best-performing catalyst reached near-equilibrium conversion at approximately 650-750 °C depending on catalyst type and space velocity. The variation of NH_3 feed concentration provided additional insight into catalyst behavior under conditions relevant to bed-zone utilization, dilution effects, and potential recycle operation (Results see Ref [17])

The industrial relevance of the workflow is reflected in publicly reported ammonia cracking collaborations with JGC and Heraeus Precious Metals. In the JGC project, hte's 16-fold high-throughput unit enabled catalyst testing under high temperature and pressure, parallel investigation of catalysts and process parameters, and catalyst evaluation in the kinetically controlled conversion range enabled by hte's inert reactor concept. JGC highlighted that the approach significantly accelerated catalyst testing and provided comprehensive and accurate data for catalyst evaluation. [19] In a separate collaboration with Heraeus Precious Metals, hte screened precious-metal-based catalyst materials for catalytic ammonia cracking at temperatures above 700 °C and pressures in the mid-two-digit bar range. Heraeus emphasized the importance of testing under industrially relevant pressure, temperature, and feed-composition conditions and reported that the data supported the development of a high-performing and stable ruthenium catalyst. [20] Together, these examples demonstrate that the NH_3 cracking workflow has already been applied to real industrial catalyst screening questions and provides a robust basis for rapid catalyst ranking, kinetic studies, and stability assessment under demanding conditions.

Overall, the NH_3 cracking study demonstrates the value of hte's 16-fold high-temperature high throughput technology for pressurized gas-phase reactions. The workflow combines parallelized catalyst screening, low blank activity, reliable NH_3 and trace water recovery, sensitive online analytics, stability assessment, and kinetic data generation. In the context of this publication, NH_3 cracking therefore serves as a first example showing how hte's high-temperature platform can generate robust and process-relevant datasets. The same methodological principles such as controlled high-temperature operation, inert reactor design, defined time-on-stream protocols, and comprehensive analytics are directly relevant for the subsequent CO-from- CO_2 and methane pyrolysis workflows discussed in the following sections.

3. CO_2 -to-CO as Bench Scale Demonstration of High-Temperature Catalyst Validation

The second workflow demonstrates how hte's high-temperature technology can be extended from rapid catalyst screening toward more process-relevant bench scale validation. While the NH_3 cracking example highlights parallel screening under demanding high-temperature and high-pressure conditions, CO_2 -to-CO conversion adds a complementary requirement: the realistic evaluation of commercial catalyst shapes under conditions where heat management and reactor inertness directly influence the interpretation of catalytic performance.

CO_2 conversion to CO is an important enabling step for syngas production from carbon-containing feedstocks. In this context, both the reverse water-gas shift reaction (rWGS) and dry reforming of methane (DRM) are relevant routes. rWGS converts CO_2 and H_2 into CO and H_2O , while DRM converts CH_4 and CO_2 into H_2 and CO. Both reactions require elevated temperatures to achieve relevant conversion and CO selectivity, and both are highly sensitive to the actual thermal environment inside the catalyst bed. In addition, realistic catalyst validation often requires operation at elevated pressure and with commercial catalyst geometries such as extrudates or tablets. [21-24]

These requirements make CO_2 -to-CO an excellent second demonstration case for hte's high-temperature platform. Compared with NH_3 cracking, the main experimental risk is not only background conversion, but also unwanted carbon formation or secondary reactions at

exposed metallic reactor surfaces. This is particularly relevant for reforming chemistry, where coking, hydrogenation, methanation, and wall-induced side reactions can distort conversion and selectivity data. The advanced inert reactor concept introduced in the previous section is therefore critical here as well, because it enables the combination of high temperature and elevated pressure while minimizing interference from the reactor material. In blank experiments under representative reforming conditions at 900 °C and 20 bar, methane conversion in the empty reactor was only 0.6%, confirming negligible background activity under these severe conditions. [25] The absence of visible downstream coking during the catalytic tests further confirms the relevance of the inert reactor concept for CO₂-to-CO testing, where reactor-wall-induced carbon formation would distort catalyst performance data. During system stress tests with S/C up to 2.5 at 38 bar steam partial pressure stable, pulse-free bench scale operation was achieved enabling to cover broad S/C ratios during parameter optimization.

For this workflow, hte developed a 4-fold high-temperature bench scale platform designed for catalyst validation after the screening stage. The system operates at up to 940 °C and 30 bar and allows representative catalyst loadings of approximately 25-30 mL in reactors with 10 mm inner diameter. This enables the testing of full-size commercial extrudates and tablets rather than only powders or crushed fractions. The unit therefore bridges the gap between high-throughput microreactor screening and more industrially relevant catalyst evaluation. [25]

A key feature of the CO₂-to-CO workflow is the integration of movable thermowells for axial temperature profiling along the catalyst bed. This is especially important because DRM and rWGS can show very different thermal signatures depending on reaction regime and operating conditions. In DRM, strong endothermicity can lead to pronounced cold spots at the bed inlet. In rWGS, the system can shift from a lower-temperature, methanation-dominated regime with local hot spots to a high-temperature CO-forming regime where endothermic behavior and cold spot formation become dominant. Therefore, conversion and selectivity data are only meaningful when interpreted together with the local temperature profile. [25]

3.1. Dry Reforming of Methane (DRM)

DRM was used to demonstrate the importance of temperature profiling for interpreting catalytic performance. Commercial catalyst material was tested under reforming conditions, and the measured conversion trends correlated directly with the temperature profiles inside the catalyst bed. As depicted in Figure 4, cold spots of up to approximately 155-167 K were observed at the catalyst bed inlet, caused by the high endothermic heat demand of the reaction. Longer catalyst beds and lower gas hourly space velocity allowed stronger temperature recovery toward the reactor outlet and resulted in higher methane conversion, whereas shorter beds and higher space velocity showed lower outlet temperatures and reduced conversion. These results show that catalyst ranking in DRM can be misleading if the actual catalyst-bed temperature is not known. [25]

Dilution of the catalyst bed with inert material reduced the intensity of the cold spot to approximately 30 K and improved thermal homogeneity. During extended DRM operation with commercial 3 mm extrudates, temperature profiling provided additional diagnostic value: the cold spot gradually weakened and shifted along the bed during time-on-stream, indicating changes in the activity distribution before conversion loss became clearly visible (Figure 4). This makes axial temperature profiling a useful tool not only for heat-management studies, but also for detecting early-stage catalyst aging and reaction-zone migration. [25]

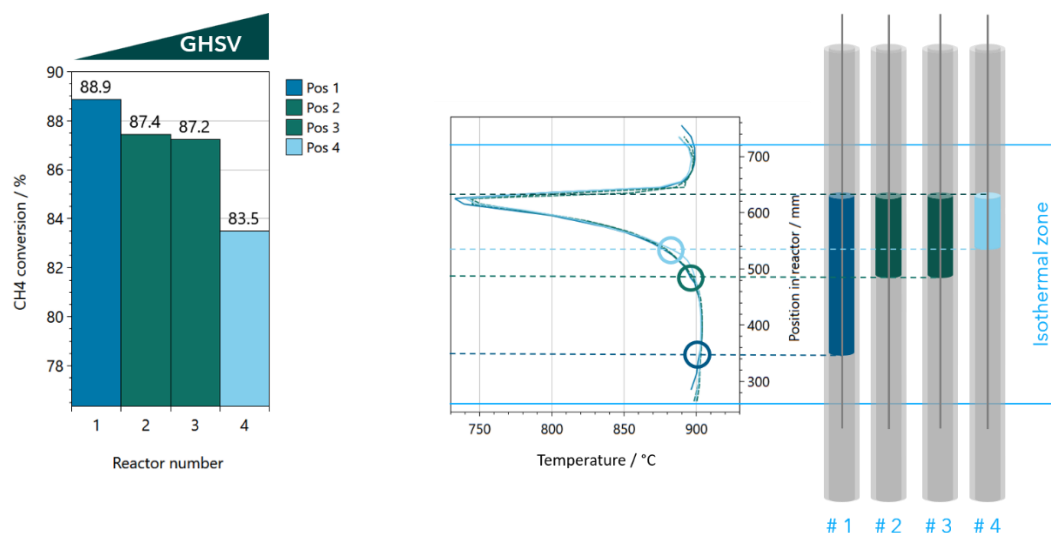


Figure 3. Conversion of CH₄ at different GHSVs (left) and respective temperature profiles and catalyst bed lengths (right). Conditions: 900 °C, 20 bar, S/C = 1.5, CO₂/C = 1. [25]

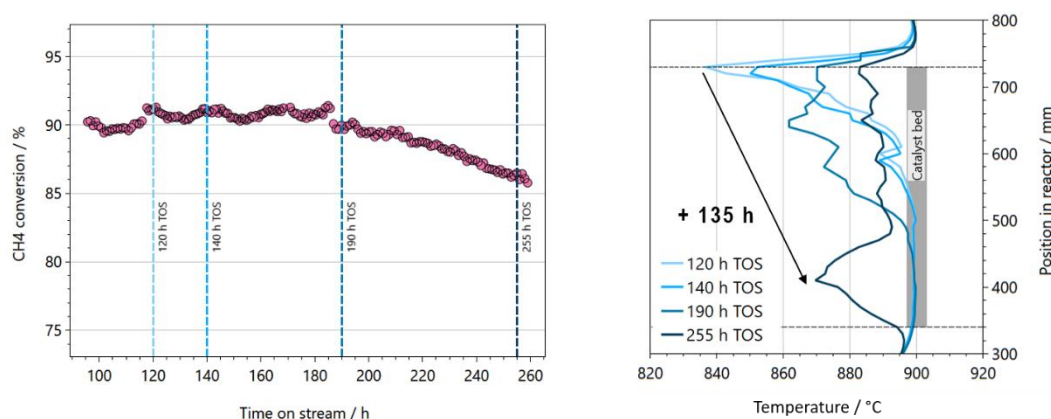


Figure 4. Temperature profiles after certain times-on-stream (left) and the respective CH₄ conversion during that time period (right). Conditions: 900°C, 20 bar, S/C = 1.5, CO₂/C = 1.[25]

3.2. Reverse Water-Gas Shift (rWGS)

The rWGS validation provided a complementary example within the same CO-from-CO₂ workflow. A commercial catalyst was tested between 700 and 900 °C at 10-30 barg. With increasing temperature, CO₂ conversion increased and the product spectrum shifted from methane formation at lower temperature toward CO as the dominant carbon-containing product at higher temperature. The temperature profiles shown in Figure 5 directly reflected this transition: lower-temperature operation showed hot spot behavior associated with exothermic methanation, while higher-temperature operation showed cold spot formation as endothermic rWGS became dominant. [25]

Long-term operation further confirmed the suitability of the unit for process-relevant validation. rWGS testing with commercial catalyst tablets was demonstrated over several hundred hours, and single-reactor operation at high feed rate confirmed the operational flexibility of the platform. Under optimized high-temperature conditions, methane formation was suppressed to very low levels, reaching 0.18 mol% CH₄ at 940 °C, 10 bar, H₂/CO₂ = 2, and 5 vol% steam. [25]

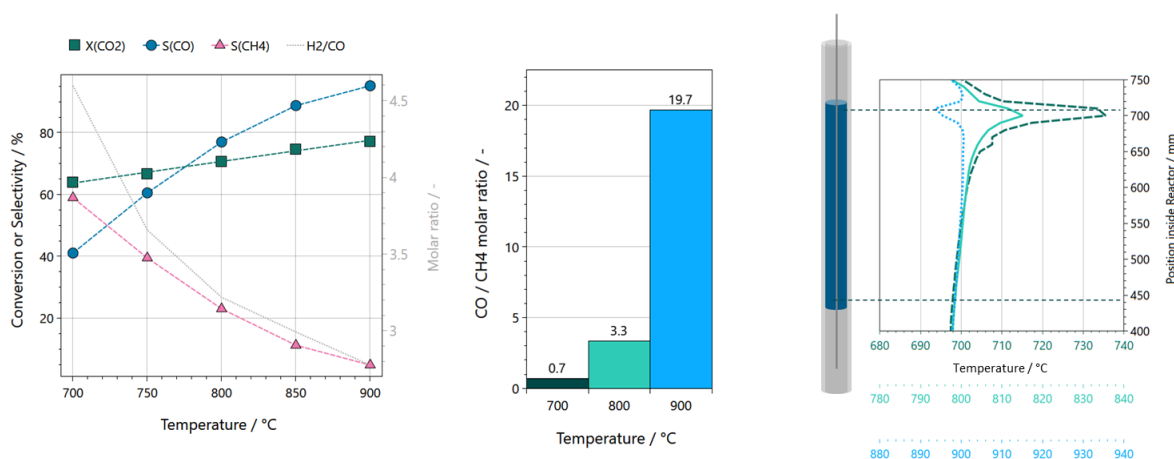


Figure 5. Effect of temperature on conversion and carbon-based selectivity during rWGS at 10 bar, $H_2/CO_2 = 3$ (left) and the resulting cold or hot spot in the temperature profile (right). [CO 5]

A publicly reported collaboration with Stanford University further demonstrates the applicability of hte's CO_2 -to-CO workflow to externally driven catalyst-development programs. During a custom R&D project, hte supported the evaluation of novel transition-metal-free rWGS catalysts under process-relevant high-temperature and elevated-pressure conditions. [26] dispersed alkali carbonate catalysts on commercial $\gamma-Al_2O_3$ supports reached equilibrium-limited CO_2 conversion at 550 °C and 10 bar, maintained essentially complete CO selectivity up to 700 °C, and remained stable over several hundred hours on stream in extended testing at hte. [27] This example highlights the value of the platform for accelerating catalyst screening and validation for sustainable syngas production from CO_2 .

Together, the DRM and rWGS examples demonstrate the role of the 4-fold bench scale unit within hte's high-temperature technology platform. The value of the workflow lies in combining high temperature, elevated pressure, advanced inert reactor design, realistic catalyst geometries, flexible feed handling, robust online analytics, and spatially resolved temperature diagnostics. In CO-from- CO_2 conversion, these features are essential because reactor-wall-induced side reactions, carbon formation, or downstream coking would distort the interpretation of catalyst performance. The absence of visible downstream coking behind the catalyst zone therefore further supports the reliability of the inert reactor concept for strongly temperature-sensitive CO_2 conversion chemistry. In the context of this publication, CO_2 -to-CO serves as an intermediate technology example between NH_3 cracking and methane pyrolysis: it shows how hte's technology can move from parallel screening to bench scale validation of high-temperature gas-phase reactions where heat management, reactor inertness, and reliable balances are critical. This directly links to the methane pyrolysis workflow discussed in the following section. While carbon formation is an unwanted artefact in CO_2 -to-CO conversion, solid carbon becomes the target product and central performance descriptor in methane pyrolysis, together with hydrogen formation, pressure-drop evolution, catalyst deactivation, and regeneration behavior.

4. Application for Pyrolysis of Methane

4.1. Chemical and Technical Overview

Methane pyrolysis is increasingly discussed as a promising route for low-carbon hydrogen production. In contrast to steam methane reforming, methane is decomposed in the absence of oxygen or steam according to $CH_4 \rightarrow C + 2H_2$, producing hydrogen and solid carbon without direct CO_2 formation in the main reaction. If the required heat is supplied from low-carbon or electrified energy sources, the process can provide a pathway toward so-called turquoise hydrogen. The attractiveness of methane pyrolysis lies in its potential to combine existing

natural gas infrastructure with reduced process-related CO₂ emissions and the formation of a solid carbon co-product. Depending on quality and morphology, this carbon may either be stored or valorized, for example as carbon black, graphite-like material, carbon nanotubes, or other carbon products, which can significantly influence the economic viability of the process. However, the overall climate benefit must be assessed in the context of the carbon intensity of the heat supply, methane leakage in the upstream gas chain, and the final use or storage of the carbon product. [8, 9, 14]

From a technical perspective, methane pyrolysis remains challenging. The reaction is strongly endothermic and typically requires very high temperatures to achieve relevant methane conversion. Catalytic methane decomposition can reduce the required temperature window, but catalyst deactivation by carbon accumulation remains one of the main obstacles. Current research therefore focuses on catalyst development, heat management, carbon formation mechanisms, and suitable reactor concepts such as fixed beds, fluidized beds, plasma reactors, molten media systems, and electrified reactor technologies. [8, 9]

A central difficulty is that solid carbon is both the desired co-product and a potential source of operational problems. In catalytic fixed-bed reactors, carbon may block pores, cover active sites, change heat transfer, and increase pressure drop. In molten media or plasma-based processes, the challenges shift toward carbon separation, product purity, and continuous solids handling. Reliable testing methods are therefore required to distinguish intrinsic catalyst behavior from thermal conversion, reactor-wall effects, heat-transfer limitations, and carbon-induced deactivation. This requires workflows that combine hydrogen formation analysis, carbon balance, pressure-drop monitoring, and regeneration studies under well-defined high-temperature conditions. [9, 14]

4.2. Transfer of hte's Workflows to Methane Pyrolysis Testing

Methane pyrolysis imposes specific requirements on both reactor technology and experimental workflow design. In contrast to the NH₃ cracking, DRM, and rWGS case studies discussed above, methane pyrolysis involves the continuous formation of solid carbon, which directly affects catalyst performance, pressure-drop development, reactor operability, carbon removal, and regeneration strategy. Consequently, the established high-temperature workflows cannot be transferred without modification. Their application to methane pyrolysis requires dedicated adaptations in reactor operation, automated consecutive on-stream switching, pressure-drop monitoring, product analytics, coke burn-off and quantification, and carbon balance evaluation. These requirements are consistent with the broader literature on methane pyrolysis, which identifies carbon formation, catalyst deactivation, reactor stability, heat management, and carbon handling as central challenges for process development. [8, 9, 14]

4.2.1. Testing Unit

Fixed-bed methane pyrolysis evolves dynamically during time on stream. Catalyst testing therefore requires an experimental workflow that can handle strongly varying deactivation and carbon build-up behavior without relying only on predefined experiment durations. For this purpose, hte's 16-fold high-temperature screening unit was adapted for automated consecutive methane pyrolysis testing. Up to 15 catalyst-filled reactors can be evaluated consecutively under identical and reproducible conditions, while one reactor position is reserved as bypass, safety, or reference channel. Instead of exposing all catalyst positions simultaneously for long periods, individual catalyst beds are switched on stream one after another. This enables catalyst-specific monitoring of time on stream, pressure-drop evolution, hydrogen formation, and carbon deposition behavior. For this purpose, hte's 16-fold high-temperature screening unit was adapted for methane pyrolysis testing. A scheme of the unit is depicted in Figure 6.

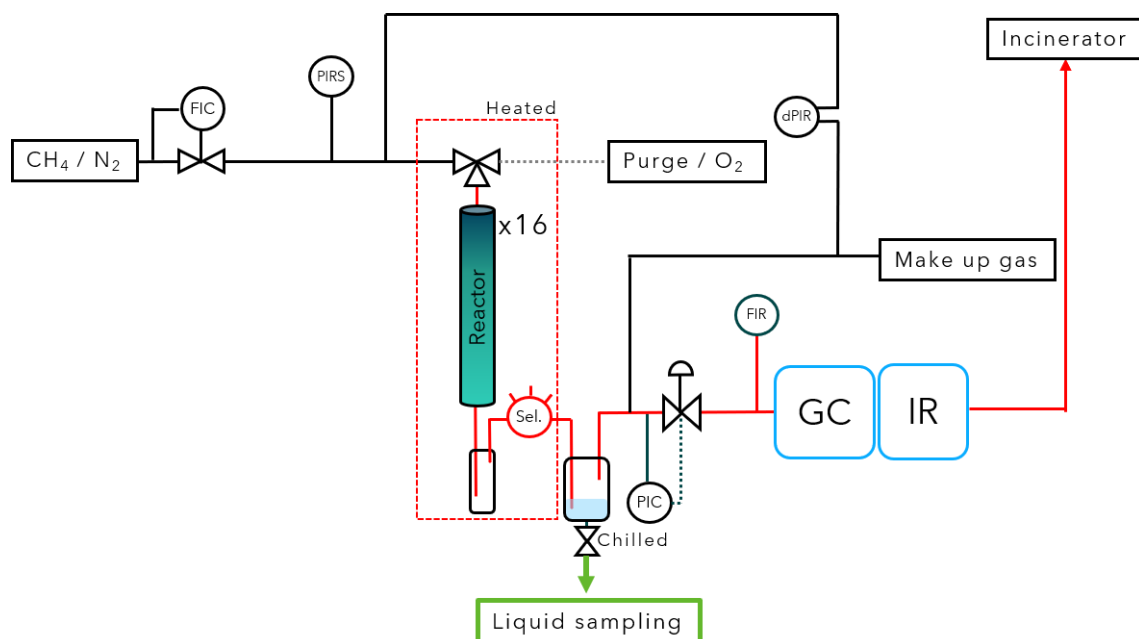


Figure 6. Schematic unit design for rapid methane pyrolysis catalyst screening.

The unit comprises 16 fixed-bed reactor positions and is designed for operation at temperatures up to 1100 °C and pressures up to 7 bar. Each reactor has an inner diameter of 6 mm and can be loaded with approximately 0.5–4 mL of catalyst, allowing rapid comparison of catalyst formulations, supports, pretreatments, bed configurations, and operating conditions. Total gas flows between 10 and 600 NL h⁻¹ can be applied, enabling systematic variation of residence time, methane feed concentration, hydrogen co-feed, nitrogen dilution, and natural-gas-type feed mixtures. Importantly, the reactor positions are not operated simultaneously under methane pyrolysis conditions. Instead, the catalyst-filled reactors are switched on stream consecutively within an automated sequence, while the remaining positions remain isolated or bypassed. This sequential operation enables individual monitoring of time on stream, pressure-drop evolution, hydrogen formation, and carbon deposition behavior.

The unit is equipped with mass-flow-controlled gas dosing for CH₄, H₂, and N₂, a high-temperature reaction zone, hot-gas flow measurement, online gas chromatography, and downstream condensation for heavy products. This analytical concept is important because methane pyrolysis requires simultaneous quantification of permanent gases, light hydrocarbons, condensable products, and deposited carbon to close hydrogen and carbon balances. Beyond permanent gases and light hydrocarbons, methane pyrolysis may form condensable aromatic by-products. Public literature describes polycyclic aromatic hydrocarbon (PAH) growth during methane pyrolysis via acetylene intermediates and subsequent aromatic growth reactions; PAH denotes polycyclic aromatic hydrocarbons, i.e., fused aromatic ring systems that can act as precursors to larger carbonaceous species. Therefore, the downstream section includes a chilled, solvent-filled condensation trap to collect condensable heavy products, prevent accumulation of aromatic deposits in the analytical section, and, if required, enable offline analysis of condensable PAH-type species. [28, 29]

To achieve reaction temperatures above 1000 °C, the high-temperature screening unit was equipped with a newly developed radiation heater system. This heating concept provides improved thermal homogeneity along the reactor axis and minimizes local temperature gradients that could otherwise affect catalyst performance and data interpretation. Temperature profiling confirmed a nearly isothermal reaction zone of approximately 160 mm, as illustrated in Figure 7.

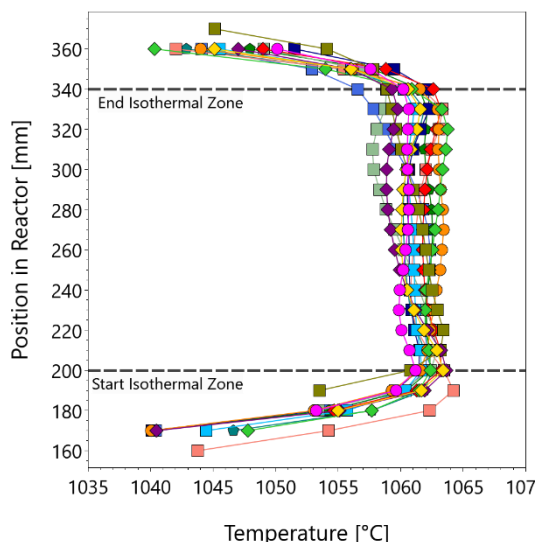


Figure 7. Internal reactor thermoprofiles at 1060°C of newly developed high-throughput radiation heater system.

4.2.2. Pyrolysis Workflow

A central element of the methane pyrolysis workflow is its standardized automated test sequence. At the start of each cycle, the selected process conditions are first established in bypass mode. This allows the feed composition, total flow, and analytical response to reach stationary conditions before the respective catalyst bed is exposed to methane. The inlet baseline and mass balance are determined under these stable bypass conditions. Subsequently, one catalyst-filled reactor is switched from bypass to on-stream operation for a precisely defined time on stream or until a predefined termination criterion is reached. At the end of the individual reactor experiment, data acquisition is stopped automatically, the reactor is isolated from the methane feed, and the system is switched to N₂ purge. After purging, the setup returns to bypass operation, and the next catalyst-filled reactor is selected for the subsequent test cycle.

This consecutive reactor-to-bypass workflow provides a high degree of reactor-to-reactor comparability. Identical feed stabilization, defined switching events, reproducible time-on-stream definitions, automated start/stop procedures, and standardized N₂ purging minimize the influence of different start-up or stabilization times. As a result, hydrogen formation rates, methane conversion, pressure-drop development, and carbon deposition behavior can be directly compared across all tested catalysts.

This is particularly important for methane pyrolysis because catalyst activity and deactivation can evolve dynamically during time on stream. The dynamic nature of fixed-bed methane pyrolysis makes automated pressure-drop monitoring particularly important. Depending on catalyst formulation and operating conditions, methane pyrolysis catalysts may show an initial increase in activity, followed by carbon growth, increasing pressure drop, and eventually partial or complete bed blockage. Since the breakthrough time cannot be predicted reliably for different catalyst systems, a differential-pressure sensor is used to monitor each on-stream reactor individually, as shown in Figure 8. Once a predefined pressure threshold is reached, the active reactor is automatically isolated from the methane feed and purged with nitrogen. The system can then either proceed to the next catalyst position or initiate an oxidizing coke

burn-off step for the previously tested reactor.

This workflow enables experiments to be terminated at a comparable operability limit rather than after an arbitrary fixed reaction time. Consequently, the pressure-drop signal becomes a process-relevant deactivation descriptor. In addition to activity-based metrics, catalysts can be ranked by carbon tolerance, including time on stream until pressure-drop increase, time to plugging, pressure-drop increase per hour, cumulative hydrogen production before reaching

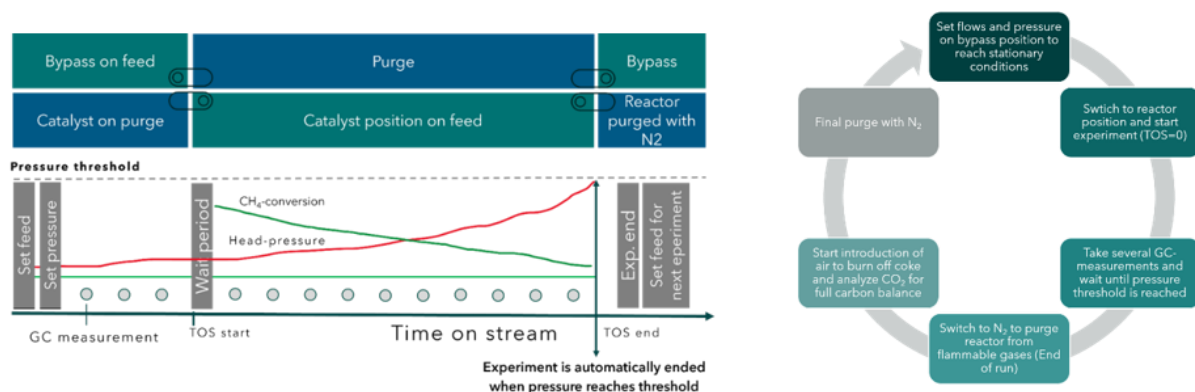


Figure 8. Automated workflow for consecutive experiments including measurements of CH_4 conversion and the observed increase in pressure drop, indicated by increasing head-pressure.

the pressure limit, and estimated carbon deposition rate. These parameters are highly relevant for reactor design because they link catalytic activity with bed stability and the ability of the reactor configuration to accommodate solid carbon formation.

Hydrogen formation is treated as the primary performance indicator. H_2 yield, H_2 formation rate, and cumulative H_2 production are more application-relevant than methane conversion alone, because the target product is hydrogen and the practical value of a catalyst depends on how much hydrogen can be produced before deactivation or plugging occurs. Online GC analysis with thermal conductivity detection, supported by hot-gas flow measurement, enables determination of instantaneous H_2 formation rate and cumulative H_2 production as a function of time on stream. These values can be correlated directly with methane conversion, catalyst deactivation, pressure-drop evolution, and carbon accumulation. Literature on methane pyrolysis emphasizes that methane conversion, hydrogen yield, carbon productivity, and hydrogen and carbon balances are key descriptors for meaningful catalyst evaluation. [9]

Carbon accumulation is calculated from the carbon balance over the defined time on stream. In the general case, accumulated carbon is estimated from the difference between carbon entering the reactor as methane and carbon leaving the system as detected carbon-containing gas-phase and condensable products. If regeneration is applied, the subsequent oxidizing step provides an additional carbon descriptor: the CO_2 formation profile during burn-off reflects the amount and removability of deposited carbon. Integration of this signal can be used to estimate removable carbon, while repeated pyrolysis/regeneration cycles provide information on regenerability, activity recovery, and long-term robustness.

5. Summary and Outlook

5.1. Summary

This work demonstrates how complementary high throughput and high-temperature bench-scale workflows can accelerate the development of hydrogen and carbon carrier technologies under industrially relevant conditions. The central value of the approach is not limited to individual reaction examples, but lies in the combination of automated experimentation, high-

temperature and elevated-pressure operation, advanced inert reactor design, robust feed and product analytics, and process-relevant validation at increasing catalyst scale.

The 16-fold high throughput platform enables rapid catalyst and parameter screening under demanding gas-phase conditions. Key capabilities include flexible feed dosing, automated 24/7 operation, high-resolution online analytics, reliable handling of reactive feeds, defined time-on-stream protocols, and the possibility to resolve low conversion levels in kinetically controlled regimes. The advanced inert reactor concept minimizes reactor-induced background activity and allows catalytic performance to be isolated from artefacts caused by reactor materials. These features are particularly relevant for high-temperature reactions where metallic surfaces can otherwise contribute to undesired conversion, side reactions, or carbon formation.

The 4-fold high-temperature bench-scale platform complements this screening capability by enabling validation with larger catalyst volumes and commercial catalyst geometries. Its value lies in combining high temperature, elevated pressure, minimal blank activity, realistic catalyst shapes, flexible feed handling, robust online analytics, and spatially resolved axial temperature profiling. This allows strongly endothermic or temperature-sensitive reactions to be interpreted beyond conversion and selectivity data alone. Local cold spots, hot spots, reaction-zone movement, and heat-management limitations can be identified and linked to catalyst performance, bed configuration, and process conditions.

Together, both platforms bridge the gap between early-stage catalyst screening and scale-relevant process assessment. The workflows generate comparable datasets on activity, selectivity, stability, pressure effects, thermal behavior, product distribution, and elemental balances. They also provide a methodological basis for evaluating strongly deactivating systems, where performance must be assessed as a function of time on stream rather than by initial activity alone. This integrated strategy supports faster identification of promising materials, more reliable interpretation of kinetic and thermal data, and better de-risking of catalyst and reactor concepts before transfer toward industrial application.

5.2. Outlook

The transferability of the demonstrated workflows originates from a common experimental challenge shared by many high-temperature processes: catalyst or material performance is often governed not only by intrinsic activity, but also by heat management, reactor inertness, deactivation, carbon or coke formation, pressure-drop evolution, regeneration behavior, and by-product handling. The workflow developed in this study is therefore relevant beyond the specific NH_3 cracking and CO_2 -to- CO examples. It provides a platform concept for processes in which rapid screening must be combined with realistic validation under demanding thermal, chemical, and mechanical boundary conditions.

Methane pyrolysis represents the most relevant next application for this methodology. The technology combines low-carbon hydrogen production with continuous solid-carbon formation, but remains limited by catalyst deactivation, heat management, carbon extraction, reactor stability, and long-term operability. Current research covers catalytic fixed-bed and fluidized-bed systems, molten metal and salt concepts, plasma processes, and other electrified reactor technologies. Despite their differences, all these concepts require reliable experimental data to separate intrinsic material performance from reactor, heat-transfer, and carbon-handling effects. [8, 9, 14]

For methane pyrolysis, the hte workflow expands the established high-temperature methodology toward carbon-forming operation. The 16-fold unit enables rapid screening of catalyst composition, temperature, pressure, residence time, feed composition, and regeneration strategy. Its standardized bypass-to-reactor sequence enables comparable time-

on-stream conditions, while continuous hydrogen analysis and differential-pressure monitoring connect hydrogen productivity with carbon-induced deactivation and reactor operability. Automated reactor isolation, coke burn-off, and regeneration allow materials to be ranked not only by methane conversion, but also by cumulative hydrogen production, carbon tolerance, regeneration efficiency, activity recovery, and cyclic stability.

Selected materials can subsequently be validated in the 4-fold bench-scale platform (design conditions 1100 °C at 15 bar) using larger catalyst quantities and shaped materials. Axial temperature measurements, long-term operation, and scale-relevant pressure-drop development can then be used to evaluate heat management, reaction-zone movement, carbon distribution, and mechanical stability. Together, the two platforms connect rapid material screening with process-oriented validation and can provide the kinetic, thermal, analytical, and durability data required to de-risk methane-pyrolysis catalyst and reactor concepts.

Further development of the methane pyrolysis workflow should focus on four areas. First, hydrogen and carbon balances should be validated by combining gas-phase analysis, carbon accumulation calculations, regeneration-derived carbon quantification, and post-test solid characterization. Second, cyclic pyrolysis-regeneration experiments can be used systematically to determine whether activity and bed operability are restored over repeated cycles and how regeneration affects catalyst structure and carbon-handling behavior. Third, feed studies should establish the robustness of promising materials toward realistic natural-gas compositions and impurities. Fourth, the analytical workflow should be expanded toward carbon-product quality, including morphology, structure, purity, and potential application value. The commercialization potential of methane pyrolysis depends not only on hydrogen productivity, but also on the consistent production, separation, and utilization or storage of the solid carbon coproduct.

Beyond methane pyrolysis, the same workflow logic is transferable to other high-temperature processes in which deactivation, coke formation, regeneration, heat management, or material transformation determine process performance. Carbon-forming applications include hydrocarbon cracking and plastic-waste pyrolysis, where gas, condensate, solid-carbon, and coke balances must be closed. Recent literature on catalytic plastic-waste pyrolysis highlights the importance of catalytic materials, reactor concepts, and the distribution of gas, liquid, and solid products, making this process family a relevant example for such workflows. [30]

Carbon-removal applications include oxidative or steam-assisted regeneration and cyclic coking-decoking studies. Catalyst deactivation by coking, poisoning, thermal degradation, and mechanical damage, as well as regeneration strategies such as oxidation, gasification, and hydrogenation, are widely recognized as central challenges in heterogeneous catalysis. [31] Fast-deactivating catalyst systems, such as methanol-to-hydrocarbons, can also benefit from standardized time-on-stream protocols and high-resolution analytics to capture rapid changes in activity and product distribution. Public hte-related work on methanol-to-hydrocarbons demonstrates the need for time-resolved analytics in systems where deactivation occurs on short time scales under commercially relevant severities. [33]

Endothermic gas-conversion applications include DRM, rWGS, steam reforming, electrified reforming, and other syngas routes, where temperature gradients and local reaction-zone shifts can strongly affect apparent performance. The combination of online gas analysis, condensate trapping, pressure-drop monitoring, regeneration, and catalyst characterization is also relevant to biomass-gasification tar reforming, where coke formation, catalyst poisoning, particle clogging, thermal stress, and regenerability remain major challenges. [32]

The platform can also support controlled-atmosphere high-temperature material treatment. In this case, the reactor system would not necessarily be used for catalyst testing, but as a defined thermal environment for oxidative or oxygen-free treatment of carbonaceous materials.

Such treatments can be used to tune material properties such as surface chemistry, pore structure, porosity, adsorption behavior, electrochemical behavior, electrical conductivity, or corrosion stability, depending on material and atmosphere. This is relevant because mesoporous and activated carbon materials derive important application properties from pore structure, surface chemistry, stability, conductivity, and adsorption behavior, and thermal treatment has been shown to influence adsorption, electrochemical, corrosion, morphology, and porosity characteristics of activated carbon materials. [34,35]

The broader value of the hte approach lies in combining high experimental throughput with validation at increasing process relevance. Instead of evaluating catalysts solely by initial activity, the workflow generates comparable datasets on hydrogen productivity, material stability, carbon accumulation, pressure-drop evolution, regeneration efficiency, thermal behavior, and by-product formation. This integrated methodology can shorten development cycles and support evidence-based decisions when transferring methane-pyrolysis catalysts and other high-temperature technologies from laboratory screening toward industrial application.

Literature

- [1] M. Yang, R. Hunger, S. Berrettoni, B. Sprecher, B. Wang, *Clean Energy*, 2023, 7, 190–216.
- [2] Z. Xie, Q. Jin, G. Su, W. Lu, *Energies*, 2024, 17, 4070.
- [3] V. Negro, M. Noussan, D. Chiaramonti, *Energies*, 2023, 16, 6192.
- [4] M. Aziz, A. T. Wijayanta, A. B. D. Nandiyanto, *Energies*, 2020, 13, 3062.
- [5] S. Dell'Aversano, C. Villante, K. Gallucci, G. Vanga, A. Di Giuliano, *Energies*, 2024, 17, 3995.
- [6] E. V. Ramos-Fernandez, J. L. Santos, D. K. Alsaadi, A. Bavykina, J. M. R. Gallo, J. Gascon, *Chemical Science*, 2025, 16, 530–551.
- [7] A. Keunecke, M. Dossow, V. D. Dieterich, H. Spliethoff, S. Fendt, *Frontiers in Energy Research*, 2024, 12, 1344179.
- [8] H. Rohani, G. Sudiarova, S. M. Lyth, A. Badakhsh, *Energies*, 2025, 18, 2393.
- [9] T. I. Korányi, M. Németh, A. Beck, A. Horváth, *Energies*, 2022, 15, 6342.
- [10] K. Kang, H. Sampei, Y. Sekine, *RSC Sustainability*, 2025, 3, 1598–1628.
- [11] M. González-Castaño, B. Dorneanu, H. Arellano-García, *Reaction Chemistry & Engineering*, 2021, 6, 954–976.
- [12] C. Zhou, J. Zhang, Y. Fu, H. Dai, *Molecules*, 2023, 28, 7657.
- [13] K. Trangwachirachai, K. Rouwenhorst, L. Lefferts, J. A. Faria Albanese, *Current Opinion in Green and Sustainable Chemistry*, 2024, 100945.
- [14] A. Lotfollahzade Moghaddam, S. Hejazi, M. Fattahi, M. G. Kibria, M. J. Thomson, R. AlEisa, M. A. Khan, *Energy & Environmental Science*, 2025, 18, 2747–2790.
- [15] A. Klerke, C.H. Christensen, J.K. Nørskov, T. Vegge, *J. Mater. Chem.*, 2008, 18, 2304–2310.
- [16] S. Ristig, M. Poschmann, J. Folke, O. Gómez-Cápiro, Z. Chen, N. Sanchez-Bastardo, R. Schlögl, S. Heumann, H. Ruland, *Chemie Ingenieur Technik* 2022, 94 (10), 1413–1425.
- [17] B. Mutz, R. Baumgarten, *Decarbonisation Technology* 2024, Q1 (Feb), 79–83. <https://ptqmagazines.digitalrefining.com/view/528948587>.
- [18] J. Ashcroft, H. Goddin, *Johnson Matthey Technol. Rev.* 2022, 66 (4), 375–385.
- [19] hte GmbH and JGC Holdings Corporation, “hte conducts research for JGC on low-emission hydrogen production,” press release, June 26, 2025. Available online: <https://www.hte-company.com/en/press/hte-conducts-research-for-jgc-on-low-emission-hydrogen-production/> (accessed July 29, 2026).
- [20] hte GmbH and Heraeus Precious Metals, “hte and Heraeus Precious Metals collaborate

- on catalytic ammonia cracking,” press release, May 20, 2025. Available online: <https://www.hte-company.com/en/press/hte-and-heraeus-precious-metals-collaborate-on-catalytic-ammonia-cracking/> (accessed July 29, 2026).
- [21] K. Wittich, M. Krämer, N. Bottke, S.A. Schunk, *ChemCatChem* 2020, 12, 1-19.
 - [22] B. Mutz, C. Hauber, P. Kolb, M. Weber, *DGMK Conference Proceedings* 2022, 70-79.
 - [23] P. Kaiser, R.B. Unde, C. Kern, A. Jess, *Chemie Ingenieur Technik* 2013, 85 (4), 489-499.
 - [24] F.V. Vázquez, P. Pfeifer, J. Lehtonen, P. Piermartini, P. Simell, V. Alopaeus, *Industrial & Engineering Chemistry Research* 2017, 56, 13262-13272.
 - [25] B. Mutz, R. Baumgarten, C. Hauber, *Hydrocarbon Engineering* 2025, Q4 (Nov.), 25-30.
 - [26] hte GmbH, “hte supports research on metal-free catalysts to produce CO from CO₂,” press release, October 17, 2023. Available online: <https://www.hte-company.com/en/press/hte-supports-research-on-metal-free-catalysts-to-produce-co-from-co2/> (accessed July 29, 2026).
 - [27] K.N. Tamakuwala, R.P. Kennedy, C.S. Li, B. Mutz, P. Boller, S.R. Bare, M.W. Kanan, *JACS Au* 2025, 5, 1083-1089.
 - [28] A. Khrabry, I. D. Kaganovich, Y. Barsukov, S. Raman, E. Turkoz, D. Graves, *International Journal of Hydrogen Energy*, 2024, 56, 1340–1360.
 - [29] M. Altarawneh, L. Ali, *Energy & Fuels*, 2024.
 - [30] S. Tasleem, A. Soliman, E. H. Alsharaeh, *RSC Advances*, 2025, 15, 20881–20907.
 - [31] I. M. S. Anekwe, Y. M. Isa, *Energy Advances*, 2025, 4, 1075–1113.
 - [32] T. Liu, X. Lian, D. Liang, S. Wang, R. Shan, H. Yuan, Y. Chen, *Green Energy & Environment*, 2025.
 - [33] A. Haas, C. Hauber, M. Kirchmann, *ACS Catalysis*, 2019, 9, 5679–5691.
 - [34] W. Zhou, Y. Zhi, J. Wang, *Frontiers in Materials*, 2025, 12, 1548671.
 - [35] A. Świątkowski, E. Kuśmierk, K. Kuśmierk, S. Błażewicz, *Molecules*, 2024, 29, 4930.

Catalyst-modulated Discharge Chemistry: Tailoring Electron-surface Interactions in the total Oxidation of n-butane to CO₂ over a MnO₂/CaO-coated Surface Dielectric Barrier Discharge

J. Hiepel¹, T. Oppotsch¹, G. Hübner², P. Awakowicz², I. Korolov², M. Muhler¹

¹Ruhr University Bochum, Chair of Industrial Chemistry, Bochum, Germany, ²Ruhr University Bochum, Chair of Applied Electrodynamics and Plasma Technology, Bochum, Germany

Industrial exhaust streams often contain volatile organic compounds (VOCs) that pose risks to both the environment and human health. Conventional thermal oxidation achieves high conversion but requires substantial energy input at elevated temperatures. Non-thermal plasma (NTP) provides an alternative by generating reactive species for VOC decomposition at low gas temperatures. Surface dielectric barrier discharges (SDBDs) offer scalability, low flow resistance, and efficient operation in complex gas mixtures. However, NTP oxidation typically shows limited CO₂ selectivity and significant CO formation. Catalytic coatings improve selectivity towards CO₂, but pure MnO₂ coatings inhibit discharge, requiring scaffold materials such as BaTiO₃ or CaO.^[1]

Here, we investigate a MnO₂/CuO/CaO (3:1) dual-component coating in a twin-SDBD reactor. Ultrasonic spray-coating applies uniform 3 mg/cm² loadings, characterized by laser scanning microscopy (15-25 µm coating thickness). The system operates in different N₂/O₂/n-butane mixtures at 2.5 and 10 standard liters per minute (slm) and 35-115 W dissipated power, examining plasma-catalyst interactions without external heating.

Results show distinct performance characteristics: at 2.5 slm/115 W, a MnO₂/CaO coated electrode configuration reaches 87.5% n-butane conversion and 95.0% CO₂ selectivity (compared to 82.0%/83.4% for a MnO₂/BaTiO₃ coated electrode configuration and 87.5%/56.5% for uncoated electrode configurations); at 10 slm/115 W, CO₂ selectivity is 76.1%. Carbon balances approach up to 100%, indicating complete carbon accounting. ICCD streamer imaging further reveals brighter streamers for MnO₂/CaO coatings compared to an uncoated electrode configuration.

These observations relate to CaO's material properties: low permittivity ($\epsilon_r \approx 11.8$) could enhance microdischarges within pores through elevated electric fields, while the low work function (1.7 eV) promotes secondary electron emission.^[2] This increases local electron density, ionization rates, and local plasma heating, facilitating MnO₂ activation for CO → CO₂ conversion via O radicals. Diluted O₂ conditions favor O-radical pathways over O₃/NO_x formation, with residence time and energy density influencing reaction selectivity.

These findings demonstrate how scaffold material selection influences plasma-catalyst interplay in SDBD systems. This approach enables efficient VOC conversion through localized discharge heating, avoiding external thermal inputs, with potential for scalable exhaust treatment applications.

Acknowledgement: This work was supported by the German Research Foundation in the frame of the collaborative research center SFB 1316 (DFG327886311), project A7.

[1] T. Oppotsch, C. Oberste-Beulmann, A. Böddecker, G. Hübner, I. Korolov, P. Awakowicz and M. Muhler, *Plasma Processes and Polymers*, **2025**, 22

[2] S. Yu, L. Chauvet and A. v. Keudell, *Plasma Sources Science and Technology*, **2024**, 33

Influences on the Selective Catalytic Oxidation of Residual Ammonia in Ammonia Cracking Gas

A. Sack^{1,2,3}, H.-P. Schmid⁴, J. A. Wünnig⁴, T. Plessing¹, A. Jess^{2,3}

¹University of Applied Sciences Hof, Institute for hydrogen and energy technology, Hof, Germany,

²University Bayreuth, Chair of Chemical Engineering, Bayreuth, Germany, ³University Bayreuth, Center of Energy Technology, Bayreuth, Germany, ⁴WS GmbH, Renningen, Germany

The Federal Government of Germany assigns hydrogen in its national hydrogen strategy a “[...] central role in the further development and completion of the energy transition” [1] while acknowledging that “[...] the greater part of demand will have to be covered permanently by imports of hydrogen and its derivatives.” [2] Green ammonia as a hydrogen carrier will play a significant role and the Federal Ministry for Economic Affairs and Climate Action recently signed the first delivery contract for green ammonia starting 2027. [3]

To use hydrogen after importing, the ammonia must be cracked. Due to the thermodynamic equilibrium of the reaction, the resulting product gas contains a residual amount of ammonia that must be removed for further gas separation and usage, especially in decentralized ammonia cracking plants. One possible technology for the purification of the product gas could be selective catalytic oxidation of the residual ammonia in a second reactor after the cracker, which shall be experimentally proven in this project. The pilot plant ammonia cracker for this project works between 750 °C and 950 °C and between atmospheric pressure and 10 bar. In a past catalyst study, different catalysts were examined for their performance at different reaction temperatures and residence times to determine one preferable catalyst for future experiments and process trials.

In this study the best performing catalyst from the previous one was used in further ammonia oxidation experiments to determine its usability and performance for the proposed process. A set of experiments varying GHSV, reaction temperature, pressure, oxygen and ammonia content were performed in a laboratory reactor. At low pressures and corresponding low ammonia contents, a full conversion of residual ammonia from the cracking gas was possible. Further experiments show promising results for the technical feasibility of the SCO-process. The results of this study will be used to scale up the laboratory reactor to pilot plant scope.

References:

[1] Bundesministerium für Wirtschaft und Klimaschutz (BMWK), (2020), „Die Nationale Wasserstoffstrategie“, BMWi, Berlin

[2] Bundesministerium für Wirtschaft und Klimaschutz (BMWK), (2023), „Fortschreibung der Nationalen Wasserstoffstrategie“, BMWK, Berlin

[3] Bundesministerium für Wirtschaft und Klimaschutz (BMWK), (2024), „Wichtiger Schritt für globalen Wasserstoffhochlauf – Deutschland importiert ab 2027 mit H2Global grüne Wasserstoffprodukte im großen Umfang“, BMWK, <https://www.bundeswirtschaftsministerium.de/Redaktion/DE/Pressemitteilungen/2024/07/20240711-h2global.html>, 2026-05-08

Comparative Simulation Study of Fuel Production Pathways from Biomass-derived Syngas

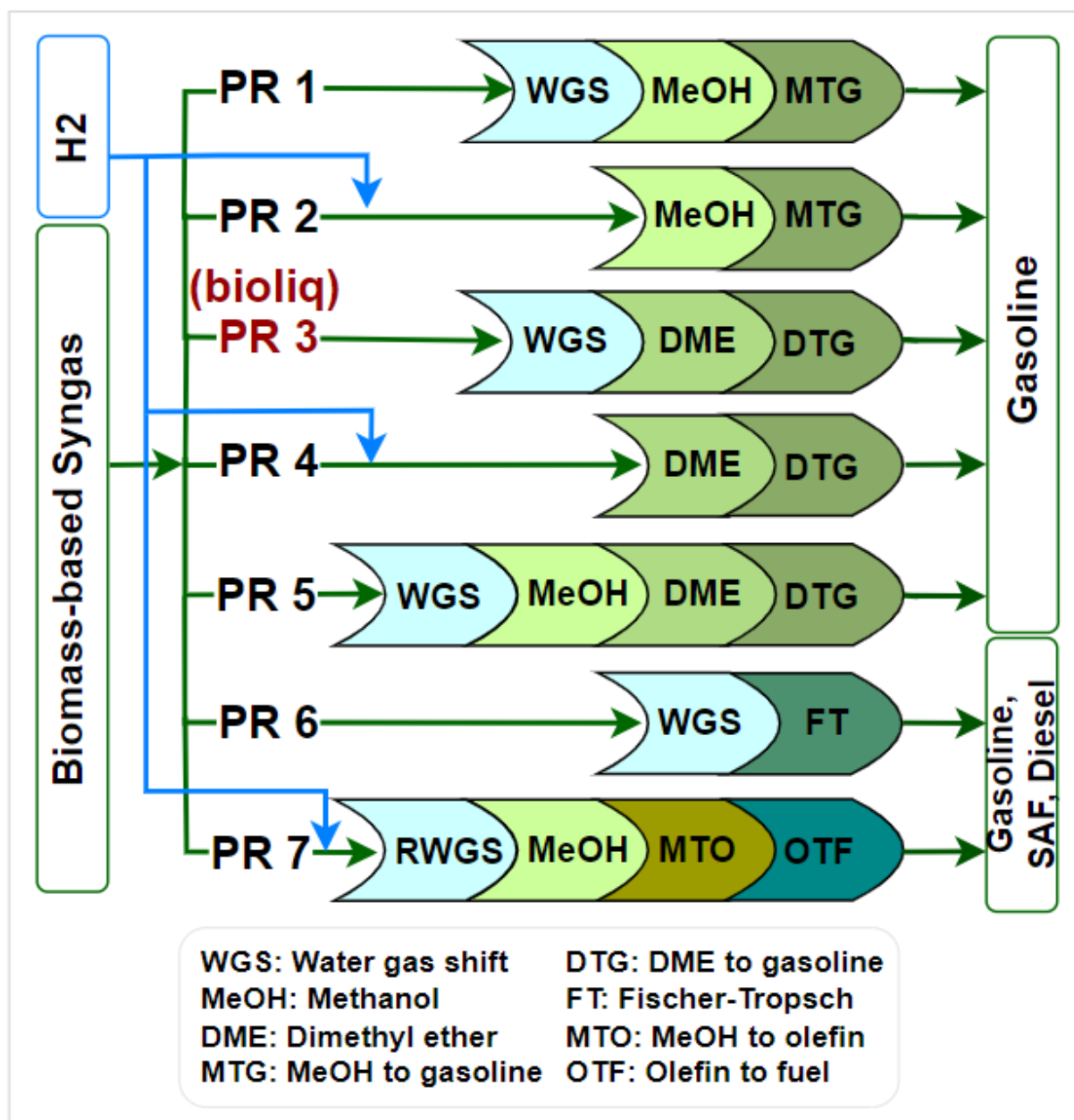
M. E-Moghaddam, N. Dahmen

Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT),
Karlsruhe, Germany

The bioliq® pilot plant located at the KIT in Germany is a successful example of conversion of lignocellulosic biomass into gasoline. The process includes four steps: fast pyrolysis, entrained flow gasification, syngas cleaning, and fuel synthesis, where biomass-derived syngas is converted into gasoline via dimethyl ether (DME) synthesis.[1] During the bioliq project, several tons of fuel were produced over the last years operational campaigns; the produced gasoline fraction was blended with fossil-based fuels and successfully applied to test engines and cars. The focus of the present work is on the “fuel synthesis unit” of this pilot plant for converting biomass-derived syngas into fuels. The optimization of the current plant configuration is conducted first, followed by the investigation of alternative process pathways for production of gasoline [2], sustainable aviation fuel (SAF), and diesel fractions.

This study is performed by developing reliable simulations in Aspen Plus® to evaluate different processes beyond experimental investigation. For this purpose, process pathways of DME synthesis followed by DME to gasoline (DTG), MeOH synthesis followed by MeOH-to-gasoline (MTG) and MeOH-to-olefin (MTO) to fuels, as well as Fischer-Tropsch (FT) synthesis to fuels are selected, as represented by Figure 1. The precision of simulations is ensured through detailed technical considerations by employing kinetic models, experimental data from lab or industrial plants, and validation with real plant data when available. The process pathways are compared based on feed conversion rate, fuel mass and energetic efficiencies and also hydrogen and carbon balances. Technical studies comparing these process pathways for biofuel synthesis from biomass-derived syngas are limited in existing literature, and most of the recent works focus on fuel synthesis via power-to-liquid technology using renewable CO₂ and H₂ as feedstock. This work follows the bioliq process concept and uses a biobased syngas-feed derived from an operational test.

The process pathways are compared in terms of feed conversion rate, fuel mass and chemical energetic efficiencies, as well as H₂ consumption and CO₂ formation. The simulation results indicate that for gasoline production the current bioliq process constellation, i.e. direct conversion of biomass-derived syngas to DME followed by DTG process, is more advantageous than other process routes. For SAF production the MTO-to-fuels pathway is promising, for which data obtained from an innovatively developed laboratory-scale reactor at the KIT have been used in modeling. The findings of this detailed technical study provide insights for approximating achievable fuels efficiency, and facilitate the identification of the most optimal process configurations concerning different optimization objectives. Besides, this technical work will support the basis for subsequent TEA and LCA studies.



Comparison of process routes (PR) for fuel synthesis from biomass-derived syngas

References:

- [1] Dahmen, N. et al., (2017), The Bioliq Process for Producing Synthetic Transportation Fuels, WIREs Energy & Environment, <https://wires.onlinelibrary.wiley.com/doi/10.1002/wene.236>
- [2] E-Moghaddam, M. et al., (2024), Gasoline Synthesis from Biomass-Derived Syngas Comparing Different Methanol and Dimethyl Ether Pathways by Process Simulation, Based on the Bioliq Process, Energy Fuels, <https://pubs.acs.org/doi/10.1021/acs.energyfuels.3c04524>

Modeling and Prediction of Phase Equilibria in Systems Containing Bio-Oil Compounds

A. Jalalinejad, A. Funke, N. Dahmen

Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research & Technology (IKFT),
Eggenstein-Leopoldshafen, Germany

Accurate prediction of phase equilibria is essential for the design, simulation, and optimization of separation and upgrading processes for pyrolysis-derived condensate fractions. Fast pyrolysis bio-oil is a complex renewable carbon carrier containing water and a wide range of polar oxygenated compounds, including acids, aldehydes, ketones, alcohols, phenols, furans, and carbohydrate-derived molecules. This chemical complexity leads to strong non-ideal behavior and makes the prediction of vapor-liquid and liquid-liquid equilibria challenging, especially for novel pyrolysis products with limited experimental data. The objective of this study is to evaluate and improve predictive thermodynamic models for bio-oil-derived mixtures, with emphasis on their application to fractionation, distillation, and extraction. COSMO-SAC, UNIFAC, UNIFAC-DMD, and NIST-modified UNIFAC are assessed using critically selected phase equilibrium data for representative bio-oil compounds and surrogate mixtures. The performance of each model is analyzed for binary and ternary systems containing water and oxygenated compounds commonly found in fast pyrolysis bio-oil. The evaluation indicates that general predictive models have important limitations for bio-oil-related systems. These limitations are mainly related to the insufficient representation of strong molecular interactions, the limited availability of reliable experimental phase equilibrium data, and inadequate group interaction parameters for complex oxygen-rich mixtures. In particular, group contribution models are highly sensitive to the quality of the data used during parameter estimation, while purely predictive approaches may not fully capture the separation behavior of highly polar bio-oil fractions. To overcome these limitations, selected interaction parameters are re-optimized using reliable vapor-liquid and liquid-liquid equilibrium data, and additional functional group descriptions are introduced for key bio-oil compounds, especially furan-based molecules. The refined thermodynamic framework is validated using phase equilibrium data and advanced distillation curve information. Its applicability is further demonstrated through the analysis of distillation and extraction processes relevant to bio-oil refining. This work shows that a bio-oil-oriented UNIFAC-type model can improve the prediction of phase behavior in fast pyrolysis bio-oil mixtures and provide a practical tool for process design. By improving thermodynamic predictions for pyrolysis-derived liquids, this study supports more efficient bio-oil upgrading and the sustainable utilization of renewable carbon resources for fuels and chemical production.

Minimum Achievable Cost of Methanol-to-Jet Sustainable Aviation Fuel: A Bottom-Up Decomposition by Optimization Measures

A. Elwalily, V. Erfurt, M. Wenzel, L. Tafur, S. Günthner, H. Lehmann

PtX Lab Lausitz, Zukunft - Umwelt - Gesellschaft (ZUG) gGmbH, Cottbus, Germany

Abstract

This study derives an independent minimum-cost prediction for methanol-to-jet (MTJ) production pathway of sustainable aviation fuel (SAF), decomposed by individual optimization measures. It sets out the modelling framework, reports the cost structure and decomposition obtained from the completed model, and identifies which optimization axes dominate the achievable cost reduction.

The methodology of the study has been implemented in three stages. Stage 1 establishes a benchmarked baseline levelized cost of production (LCOP), anchored to a published techno-economic assessment and reproduced in a steady-state process model of a commercial-scale plant under German conditions. Stage 2 applies the six optimization measures cumulatively (hydrogen production, methanol synthesis, MTJ conversion, geographic siting, spatial configuration, and CO₂ sourcing) and quantifies the marginal contribution of each, with each improvement assumption anchored to a published trajectory and characterized as near-term feasible or longer-term aspirational. Stage 3 compares the derived minimum against existing techno-economic studies and circulating industry and policy projections.

The principal finding is that MTJ-SAF economics are dominated by purchased feedstocks rather than by the conversion plant: hydrogen and captured carbon together account for approximately nine-tenths of the LCOP, while the capital charge accounts for under five per cent. The decomposition consequently shows that the dominant cost-reduction axes are procurement and siting decisions rather than process optimization. A component-specific learning-curve analysis reinforces this conclusion, indicating that almost all deployment-driven cost reduction originates outside the plant boundary, in the hydrogen and carbon-capture supply chains rather than in the conversion plant itself. Stage 3 confirms that a residual gap remains between the bottom-up derived minimum and the most optimistic figures currently in circulation.

Keywords: methanol-to-jet; e-SAF; RFNBO; power-to-liquid; techno-economic assessment; cost decomposition; minimum-cost prediction

1. Introduction

Methanol-to-jet is among the most technically advanced sustainable aviation fuel pathways and a leading candidate for meeting the renewable fuels of non-biological (RFNBO) origin sub-mandate under ReFuelEU Aviation, and the route received ASTM qualification in 2026, methanol having been incorporated as an approved feedstock within the D7566 Annex A5 alcohol-to-jet pathway (ASTM International, 2026; European Union, 2023). The pathway proceeds through methanol as an intermediate: captured CO₂ is hydrogenated to methanol, the methanol is dehydrated to light olefins, the olefins are oligomerized to jet-range chain lengths, and the product is hydrogenated and fractionated to a finished fuel. A recent technical review of the complete chain identifies the route as advantageous relative to alternatives principally in terms of yield and low by-product formation (Elwalily et al., 2025). Its appeal rests on three properties: methanol is a stable, storable liquid that decouples intermittent hydrogen production from downstream synthesis; the constituent unit operations rest on commercially mature technology; and recent harmonized assessments indicate that direct CO₂-hydrogenation configurations achieve lower production costs than competing routes (Sendlhofer et al., 2026).

Peer-reviewed techno-economic assessments place current MTJ-SAF production cost in the range of approximately €4.2-9.45 per kilogram, while various industry and policy projections imply substantially lower achievable costs over longer horizons (Eyberg et al., 2024; Bube et al., 2025; Sin et al., 2025; International Council on Clean Transportation, 2022; Fasihi & Breyer, 2022). This dispersion reflects differences in baseline assumptions, optimization horizons, and the treatment of geographic, technical and supply-chain levers.

The analytical difficulty is not that estimates differ, which is expected, but that they differ opaquely. When a study reports a single levelized cost derived from a bundle of assumptions applied together, a reader cannot determine how much of the divergence from another study is attributable to any one assumption. Nor can a policymaker determine whether an optimistic projection is reachable through identifiable actions or depends on conditions that have not been demonstrated. What the field lacks is not further point estimates but a decomposition: an account of how much each driver contributes to the LCOP, and how much each available lever can remove.

The study therefore pursues both methodological and numerical objectives:

- To derive a minimum-cost prediction for MTJ-SAF from a bottom-up model in which cost component parameters and intermediate results are analysed.
- To decompose the achievable cost reduction across six discrete optimization measures, quantifying each separately rather than reporting an aggregate improvement.
- To establish which optimization axes dominate the cost-reduction potential.
- To distinguish reductions attributable to the conversion plant from those attributable to upstream commodity supply, since the two imply entirely different intervention strategies.
- To characterize the residual gap between the bottom-up derived minimum and the most optimistic estimates in current circulation.

2. Methodology

2.1 Design principles

Because the objective is to attribute cost reduction to individual measures rather than to report a single production cost, the model is structured to make the propagation from input assumption to result explicit and reproducible. Each reported quantity can be traced to the parameters and formulae that generate it, which allows the sensitivity of any result to a given assumption to be examined directly. Three implementation choices follow from this requirement.

First, process and financial parameters are taken from peer-reviewed techno-economic assessments and design handbooks, while feedstock, utility and labour costs are taken from institutional and statistical sources representing the German and wider European market.

Second, capital cost is estimated by three independent methods rather than one. Capital estimates at this stage of definition carry substantial uncertainty and are difficult to verify externally, so the four results are reported as a range, and any divergence between them is retained in the reporting rather than resolved to a single figure.

Third, the measures that act on purchased commodities are implemented mechanistically, propagating through the model's own cost structure, rather than being applied as external reduction factors. Their computed effect therefore depends on the cost shares generated by the model rather than on a reduction fraction specified in advance.

2.2 System boundary and process configuration

The process modelled is the direct CO₂-hydrogenation route to jet fuel, in which carbon dioxide and renewable hydrogen are the only carbon and hydrogen feedstocks. The chain comprises four reaction blocks. In the first, CO₂ and H₂ are converted to methanol over a copper-based catalyst at elevated pressure, the reaction being equilibrium-limited so that unconverted gas is recycled, and a purge stream is taken to prevent inert accumulation. Water is co-produced in stoichiometric proportion and separated from the crude methanol.

In the second block the methanol is dehydrated over a zeolitic catalyst to a mixture of light olefins, releasing a further mole of water per mole of carbon converted. In the third block the light olefins are oligomerized to longer chains spanning the jet range. In the fourth, the oligomerate is hydrogenated to saturate residual olefins and fractionated into a jet cut together with naphtha and liquefied petroleum gas, which are treated as saleable co-products.

The plant boundary encloses the four reaction blocks together with CO₂ conditioning, hydrogen handling, product fractionation and storage, and the associated utilities. Water electrolysis and CO₂ capture lie outside the boundary and enter as purchased commodities at a specified price. This separation isolates the conversion plant from upstream hydrogen and carbon markets, allowing the same configuration to be evaluated against alternative feedstock price scenarios without re-simulation. Electricity is required for compression, separation, and utilities within the conversion plant, and is distinct from the far larger electrical demand of hydrogen production upstream. It also means that the electricity appearing in the plant energy balance covers only conversion duties, the far larger electrolysis demand being embedded in the hydrogen price.

The model is licensor-agnostic. Commercial MTJ offerings differ in which blocks they supply (some licensors provide the complete chain, others only methanol synthesis or only downstream conversion) but all follow the same topology. The model represents this generic chain and is parameterised by yields and operating costs, so that licensor-specific data can be substituted without structural change as vendor performance data become available following qualification. Technology licence fees are correspondingly excluded from the cost estimate, since they are licensor-specific and would tie the result to a particular provider. Because purchased feedstocks account for approximately nine-tenths of the levelized cost, a licence charge of the magnitude conventionally encountered would not alter the attribution reported in Section 3.

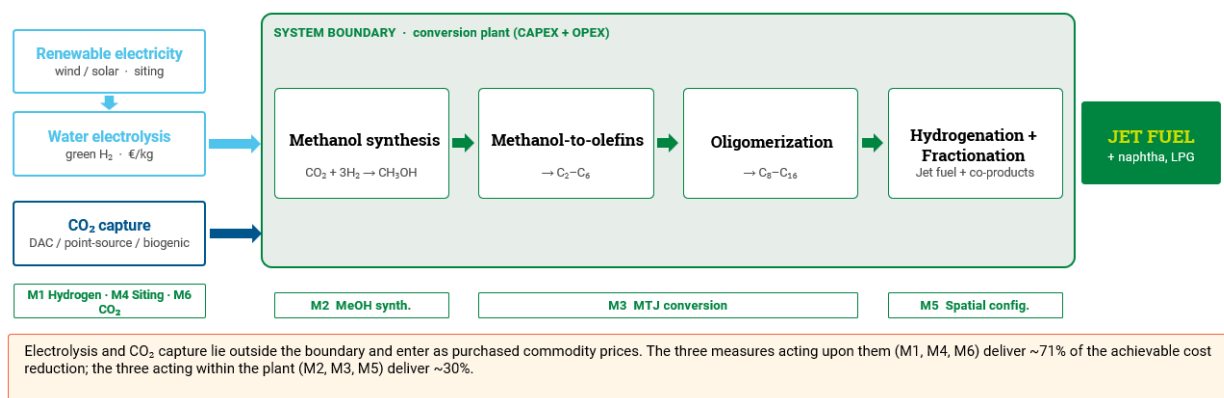


Figure 1 Process chain, system boundary and the allocation of optimization measures. Electrolysis and CO₂ capture lie outside the boundary and enter as purchased commodity prices.

2.3 Stage 1

2.3.1 Validated baseline

The first stage establishes the baseline LCOP against which all subsequent reductions are measured. A steady-state process model is constructed from a design basis of 100 kt a⁻¹ of jet fuel at an operating regime consistent with capacity factors adopted in comparable power-to-X assessments (Frontiers in Energy Research, 2021). Three yield ratios, methanol-to-jet, CO₂-to-methanol and hydrogen-to-methanol, propagate this basis to the full feed and product slate, with stoichiometric limits imposed as hard constraints so that no configuration can exceed the theoretical carbon yield of the dehydration step (Asif et al., 2024).

The process model is reproduced against a published techno-economic assessment to confirm that it returns a comparable LCOP under comparable assumptions, and the reproduced baseline then serves as the anchor for the decomposition. Anchoring the decomposition to the reproduced baseline maintains internal consistency, since the marginal effect of each measure is computed from the cost structure of the same model that generates the baseline.

The water balance of the pathway warrants explicit treatment. Both principal reaction steps generate water: methanol synthesis produces one mole of water per mole of methanol, and methanol dehydration produces a further mole per mole of carbon converted. The conversion plant is therefore a net producer of process water, and the resulting stream is treated in the model as a discharge duty rather than a purchased utility. The upstream electrolyzer separately requires demineralized feed water in quantities exceeding the process production; this lies outside the cost boundary but is relevant to siting and permitting.

2.3.2 Capital and operating cost estimation

Several independent capital cost methods are applied to the same plant definition: a top-down factored estimate in which installed costs are assigned to process areas and escalated by offsite and engineering percentages (Towler & Sinnott, 2013); the Turton module method, in which each equipment item is sized, costed from a published correlation, and multiplied by a bare-module factor incorporating material and pressure effects explicitly, a significant correction for a plant operating in high-pressure hydrogen service (Turton et al., 2018); a literature-anchored per-block estimate scaled from published capital intensities (Verleysen et al., 2023); and the Peters factorial method, adopted as the study basis, in which every element of fixed capital is expressed as a defined factors of delivered equipment cost, producing an auditable line-item breakdown (Peters, Timmerhaus & West, 2003). Costs are escalated to the current year using the Chemical Engineering Plant Cost Index (Chemical Engineering, 2024). The four estimates agree within a

factor of approximately 1.5, which at this stage of definition constitutes reasonable price uncertainty.

Operating cost is separated into variable components, computed as mass-balance quantities multiplied by unit prices, and fixed components comprising maintenance and insurance as percentages of fixed capital investment, operating labour, and general plant overhead. Maintenance and insurance are applied to fixed capital rather than to total capital investment, the latter including working capital that is recovered at end of life and therefore not subject to these charges. The process water stream enters as a discharge cost rather than a purchased utility, and cooling and boiler makeup are carried separately. German market conditions are applied throughout for feedstock, electricity, water and labour (EWI, 2025; Öko-Institut, 2025; Destatis, 2025). The LCOP is reported as a pre-tax levelized cost, the convention dominant in the power-to-liquid literature because it renders results location-agnostic and comparable across jurisdictions.

2.4 Stage 2: cumulative measure decomposition

The second stage applies the six optimization measures sequentially to the first stage baseline and records the marginal reduction attributable to each. The measures, in the order applied, address hydrogen production, methanol synthesis, MTJ conversion, geographic siting, spatial configuration, and CO₂ sourcing. Each improvement assumption is anchored to a published trajectory and specified in two parameterizations, characterized as near-term feasible or longer-term aspirational, so that the derived minimum is reported as a range rather than a point.

The hydrogen and CO₂ sourcing measures are implemented mechanistically. The hydrogen measure re-prices the hydrogen stream through the model at a revised unit cost and propagates the effect through the hydrogen share of the baseline, which the model computes from its own cost structure. The CO₂ sourcing measure is computed from the model's own carbon cost share and the actual price differential between capture routes. The remaining measures are applied as fractional reductions anchored to published improvement trajectories, each with its source trajectory identified.

Sensitivity analysis is performed on both measure ordering and the underlying improvement assumptions. Because the fractional measures are multiplicative, the derived minimum is mathematically independent of the order in which they are applied, although the saving attributed to each individually is not; this property is verified numerically within the model. Marginal attributions are consequently reported as indicative of relative magnitude under a stated sequence rather than as unique decompositions, a caveat inherent to sequential decomposition analyses. Sensitivity on the improvement assumptions is performed by repeating the decomposition across the published baseline range, which tests whether the structure of the result is robust to baseline choice.

2.5 Stage 3: critical comparison

The third stage benchmarks the derived minimum against peer-reviewed techno-economic assessments, official reference prices, and modelled industry and policy projections. Each external figure is classified according to whether it lies within the range reachable by the bottom-up model under its near-term or longer-term aspirational parameterization. Figures falling below the aspirational case are identified as requiring assumptions the present framework does not support, and the magnitude of that residual gap is quantified.

The comparison is restricted to assessments reporting a levelized production cost on a consistent basis. Figures reported after subsidy, after blending with conventional jet fuel, or on a delivered rather than production basis are excluded, since these are not comparable to a pre-tax production cost at the plant gate.

2.6 Supporting analyses

Two further analyses extend the framework, both bearing directly on the question of which optimization axes dominate.

The first applies experience curves to assess how the LCOP evolves with cumulative deployment. Learning rates are applied separately by component (electrolytic hydrogen, carbon capture, and conversion-plant capital) rather than as a single plant-level rate, because these components differ substantially in both learning rate and cost share (IRENA, 2020; International Journal of Hydrogen Energy, 2025).

The second examines spatial configuration in greater depth than a single fractional measure permits, comparing one large facility against many small modular units of identical aggregate capacity, with capital scaled and labour charged per site at a fraction of a full crew. Because the two governing assumptions are not precisely known, results are reported across a grid rather than as a point estimate.

3. Findings

3.1 The LCOP is dominated by purchased feedstocks

The Stage 1 cost structure is reported in Table 1. Under current German conditions with direct air capture as the carbon source, purchased feedstocks account for approximately nine-tenths of the LCOP, while the capital charge accounts for under five per cent.

Table 1 Approximate contribution of each component to the levelized cost of production.

Cost component	Share of LCOP	Character
Hydrogen	~54%	Purchased feedstock
Captured CO ₂ (direct air capture)	~37%	Purchased feedstock
Capital charge	~5%	Plant capital
Fixed operations, labour, overhead	~4%	Plant operating
Electricity, water, catalyst (conversion)	~2%	Plant operating
Co-product credit	~ -1%	Revenue offset

The share attributable to plant capital and conversion operating cost is low relative to that typical of process plants, where capital charges commonly exceed twenty per cent of production cost. Optimization of the conversion process therefore acts on approximately one-tenth of the cost stack, which bounds the reduction attainable from improvements to reactor performance, separation efficiency or heat integration.

The share attributable to carbon supply depends on the capture route assumed. Assessments adopting industrial point-source CO₂ report carbon as a minor cost component, whereas the direct air capture basis used here places it second only to hydrogen. The base case adopts direct air capture on the grounds that point-source supply from fossil installations is not a durable carbon source at the deployment scale implied by the ReFuelEU trajectory. Sustainability criteria governing which carbon sources and production routes may count towards RFNBO targets, including the criteria under review for the forthcoming revision of the EU rules, are examined in PtX Lab Lausitz (2025) and in the earlier standards work of PtX Lab Lausitz (2022).

The co-products credited in Table 1 are the non-jet fractions of the same hydrocarbon pool of naphtha and liquefied petroleum gas, valued at prevailing European market prices. Their

combined revenue offsets slightly under one per cent of the jet cost, and they are credited against that cost rather than allocated across products. Because naphtha and LPG prices are crude-linked, this treatment introduces a sensitivity that is independent of the process economics; at the volumes involved, however, it does not materially affect the cost structure reported here.

3.2 Procurement and siting dominate the cost-reduction potential

Applying the six optimization measures cumulatively reduces the LCOP by approximately three-quarters under the near-term parameterization. The distribution of that reduction across the six measures is given in Table 2.

Table 2 Approximate contribution of each optimization measure to the total achievable reduction.

Optimization measure	Share of total reduction	Acts on
Hydrogen production	~33%	Upstream commodity
Geographic siting	~24%	Location decision
CO₂ sourcing	~14%	Upstream commodity
MTJ conversion	~14%	Process design
Methanol synthesis	~10%	Process design
Spatial configuration	~6%	Plant configuration

Three measures (hydrogen production, geographic siting and CO₂ sourcing) together account for roughly seventy per cent of achievable reduction. The three measures internal to the conversion process contribute the remaining thirty per cent.

The siting measure acts principally through the renewable electricity price, which propagates into the delivered hydrogen cost. Siting and hydrogen production are therefore not independent levers but two channels acting on the same underlying variable; taken together they account for approximately fifty-seven per cent of the total reduction. Transport costs are not included in the model. The boundary is drawn at the plant gate, and feedstock delivery and product distribution are excluded throughout, Germany being retained as the reference location. This should be borne in mind when reading the siting measure: relocating production to a site with cheaper renewable electricity would in practice incur the cost of delivering the finished fuel to the point of demand, which is not netted against the saving reported here.

The elevation of CO₂ sourcing to the third-largest measure is a direct consequence of the carbon source assumed in the base case. In decompositions anchored to a baseline built on inexpensive point-source carbon, this measure appears marginal; here it contributes more than either of the process-design measures. The ranking of a measure is therefore conditional on the baseline against which it is assessed, which is relevant when comparing decompositions that adopt different carbon-supply assumptions.

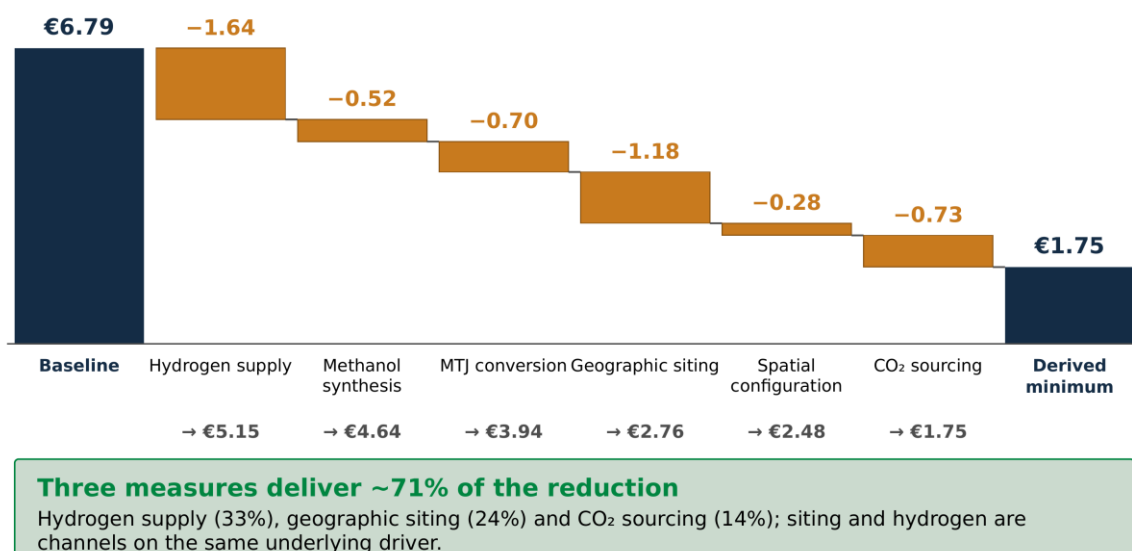


Figure 2 Cumulative cost-reduction decomposition. Each floating bar shows the reduction attributable to one measure; the running levelized cost is given beneath each step.

3.3 Deployment-driven reduction originates outside the plant

The decomposition describes reductions available through deliberate choices. The learning analysis addresses a separate question: how the LCOP evolves as the technology is deployed at scale. Component-specific experience curves applied over successive capacity doublings yield the cost decline and attribution given in Table 3.

Table 3 Approximate origin of the deployment-driven cost reduction.

Component	Share of learning-driven reduction	Learning driven by
Hydrogen	~60%	Global electrolyser deployment
Captured CO ₂	~37%	Global carbon-capture deployment
Conversion-plant capital	~3%	MTJ plant deployment

Approximately ninety-seven per cent of the deployment-driven reduction originates in the hydrogen and carbon-capture supply chains, and only about three per cent in conversion-plant capital. Deployment-driven cost reduction for this pathway is therefore governed by the learning trajectories of the electrolysis and carbon-capture industries, which are driven by their aggregate deployment across all applications, rather than by the installed capacity of MTJ plants specifically. A corollary is that a cost floor exists: fixed operations, labour, insurance and other items that do not learn are unaffected by deployment, and at high cumulative capacity these become the binding constraint. Expressed differently, the projected decline in the levelized cost of production is contingent on sustained learning and development in electrolytic hydrogen production and in carbon capture. Absent progress in those two supply chains, improvement in the conversion plant alone cannot deliver a reduction of comparable magnitude.

3.4 Spatial configuration & modularity

Replacing one large plant with many small ones of identical aggregate capacity raises specific capital intensity substantially, by roughly a factor of three per annual tonne, yet increases the LCOP by only around twenty per cent, and between roughly thirteen and thirty per cent across

plausible parameterizations of the scaling exponent and per-site staffing. This follows from the cost structure: because capital constitutes approximately five per cent of the LCOP, a threefold increase in specific capital intensity propagates to a proportionally much smaller increase in fuel cost.

This is a pure production-cost premium. It does not value the benefits of decentralization (siting flexibility near carbon or hydrogen sources, shorter lead times, staged capital commitment, reduced single-point-of-failure risk), nor does it capture duplicated permitting and grid connections or more complex product logistics. The comparison therefore provides an estimate of the production-cost penalty of modular deployment without addressing whether the associated benefits justify it.

3.5 Capital cost

The four capital estimates were constructed independently: two are size-driven, resting on equipment sizing and unit cost correlations, and two are benchmark-driven, resting on published capital intensities and process-area allowances.

The four converge within a factor of approximately 1.5, which for an estimate at this stage of definition constitutes reasonable price uncertainty and is considerably tighter than the spread across published assessments of comparable plants. A single capital estimate provides no internal test of its own consistency. Estimating by multiple independent methods allows a persistent evaluation of the price uncertainties.

The equipment sizing underlying the size-driven methods rests on preliminary values extracted from the conceptual process simulation model, and selected package units are scoping estimates rather than vendor quotations. The bracketed range should therefore be read as a Class 4 estimate, appropriate for comparative and screening purposes but not for investment decisions.

3.6 Stage 3: the residual gap

The Stage 3 comparison indicates that the near-term derived minimum is consistent with the lower bound of recent harmonized peer-reviewed estimates and lies below the cost implied by official 2030 policy projections. The most optimistic long-horizon figures currently in circulation, however, fall below even the longer-term aspirational parameterization derived here. These figures are not thereby shown to be wrong, but they cannot be reproduced from the improvement trajectories used in this study. Reaching them would require some combination of assumptions beyond those adopted: hydrogen at costs below the range presently projected for favorable sites, capital intensity substantially below current benchmarks, financing at a cost of capital below that typical for first-of-a-kind industrial assets, or co-product revenues materially above recent market levels. Assessment of such projections therefore requires the specific assumption set on which they rest to be stated. The harmonized peer-reviewed estimates referred to are those of Eyberg et al. (2024), Bube et al. (2025) and Sendlhofer et al. (2026), which together define the published baseline range against which the Stage 1 cost is positioned; the official 2030 projection is that implied by the ReFuelEU impact assessment (European Union, 2023) and the reference prices published by EASA (2025). The most optimistic long-horizon figures are the 2050 projections of the International Council on Clean Transportation (2022) and of Fasihi and Breyer (2022), the latter derived for favourable production sites.

4. Discussion

The cost structure, the measure decomposition and the learning analysis are methodologically independent of one another yet converge on the same conclusion. The cost structure shows feedstocks at roughly ninety per cent of the LCOP. The decomposition shows procurement and siting delivering roughly seventy per cent of achievable reduction. The learning analysis shows

nearly all deployment-driven reduction originating outside the plant boundary. The three analyses are methodologically independent, and their agreement indicates that the attribution is not an artefact of any single analytical route.

The internal measures nonetheless contribute approximately thirty per cent of the achievable reduction, of which the conversion-route measure accounts for roughly half. The result concerns the relative magnitude of the available levers rather than the absence of process-side potential.

Instruments that reduce the delivered cost of renewable hydrogen act on the dominant cost component, whereas support directed at conversion capacity addresses approximately one-tenth of the cost stack. The siting result further implies that restricting production to jurisdictions with high electricity prices forgoes a substantial share of the achievable reduction, which is relevant to policy frameworks that couple e-SAF mandates to domestic production. This does not, however, constitute an argument against the European framework, under which production is mandated within the Union. While production in a country with high electricity prices is more expensive, it strengthens resilience: domestic capacity reduces exposure to import dependence and to the geopolitical and supply-chain risks that accompany it. The cost difference identified here is therefore better read as the price of that resilience than as an inefficiency to be removed. At present capture costs the choice of carbon source is an economic determinant of comparable order to hydrogen procurement, rather than a secondary consideration. The scale premium reported indicates that distributed configurations incur a limited production-cost penalty, a consequence of the low capital share.

Whether the reported feedstock dominance is specific to methanol-to-jet or common to SAF more generally can be assessed on structural grounds. Any pathway converting renewable hydrogen and captured carbon into liquid hydrocarbons must purchase both feedstocks at prices set by markets external to the fuel plant, and the thermodynamic minimum quantities of each are fixed by stoichiometry rather than by process design. Fischer-Tropsch configurations differ in conversion efficiency and product slate but face the same two purchased inputs in comparable quantities. The proportions reported here would therefore be expected to hold approximately across the e-fuel family, with the split between hydrogen and carbon shifting according to the carbon source assumed.

Three conditions would alter this result, and each bounds its applicability. First, if carbon were available at negligible cost, from a waste stream carrying a disposal credit, for instance, then the carbon term would collapse and hydrogen would dominate still more completely. This condition requires immediate qualification. Carbon drawn from fossil waste streams is not a sustainable basis for e-fuel production, and its eligibility under the RFNBO framework is in any case time-limited. More fundamentally, as industrial emitters decarbonise, concentrated CO₂ streams will become scarcer rather than more abundant, so that the long-run direction of travel is towards atmospheric and biogenic sources rather than away from them. Second, if capital intensity were substantially higher than estimated here, for a first-of-a-kind plant with significant contingency, the capital share would rise and the scale conclusion would weaken correspondingly. Third, if hydrogen were produced on site rather than purchased, the boundary would shift and electrolyser capital would enter the plant capital rather than the feedstock price, changing the apparent structure without changing the underlying economics. The last of these is a presentational difference rather than a substantive one, and it may explain part of the dispersion among published assessments: studies that internalize electrolysis report a capital-heavy cost structure, while those that purchase hydrogen report a feedstock-heavy one, for physically identical systems.

Comparison between e-fuel cost assessments therefore requires the treatment of the electrolyser to be stated explicitly, since it determines whether a reported cost structure is capital- or feedstock-dominated independently of any subsequent modelling choice.

4.1 Limitations

- Only two of the six measures are implemented mechanistically the remainder are anchored fractional reductions that inherit the uncertainty of their source trajectories.
- Equipment sizing in the bottom-up capital estimates rests on preliminary values based on conceptual process simulation, and selected package units remain scoping estimates rather than vendor quotations.
- Learning rates, particularly for direct air capture, are uncertain by a significantly large factor.
- Co-product revenue is credited against jet cost rather than allocated across products, introducing a sensitivity to petrochemical prices separate from the process economics. More generally, the framework values production cost alone: benefits such as security of supply and the resilience conferred by domestic production, discussed in Section 4, are not monetised and therefore do not appear in the reported figures.
- Yield and selectivity parameters rest partly on licensor disclosures that have not been independently verified, while published operating data from qualified commercial plants remain limited.

5. Conclusions and outlook

This study derived an independent minimum-cost prediction for MTJ-SAF from a bottom-up process and cost model and decomposed the achievable reduction across six optimization measures. Five findings follow.

First, purchased hydrogen and captured carbon together constitute approximately ninety percent of the LCOP, while plant capital constitutes under five percent. The cost structure is therefore governed by feedstock procurement rather than by plant economics.

Second, the dominant cost reduction axes are hydrogen procurement, geographic siting and carbon sourcing, which together account for approximately seventy percent of the achievable reduction. Measures internal to the conversion process account for the remainder.

Third, the contribution of the carbon sourcing measure is conditional on the capture route assumed in the baseline, ranking third under a direct air capture basis and substantially lower under point source supply.

Fourth, approximately ninety seven percent of the deployment driven cost reduction is attributable to learning in the hydrogen and carbon capture supply chains rather than in conversion plant capital.

Fifth, the derived minimum lies below the lowest harmonized peer reviewed estimate for this pathway, and published current cost assessments and official reference prices are reproducible within the framework. The most optimistic long horizon projections in current circulation nonetheless fall below the aspirational parameterization and cannot be reconstructed from the improvement trajectories adopted here.

Taken together, these findings indicate that the levelized cost of MTJ-SAF is determined principally by the delivered price of renewable hydrogen and captured carbon, and only secondarily by the design and operation of the conversion plant. The three analyses supporting this conclusion, the cost structure, the measure decomposition and the learning attribution, are methodologically independent, and their agreement indicates that the result is not an artefact of a single analytical route.

Three directions for further analysis follow from these findings. The first is to apply the same decomposition framework to the Fischer-Tropsch pathway under identical boundary and parameter conventions, which would establish whether the attribution reported here is specific to the methanol route or common to SAF generally.

The second is to couple the cost model to an hourly renewable supply profile, permitting the interaction between intermittent hydrogen availability, methanol buffering and plant utilization to be represented explicitly rather than through an assumed capacity factor.

The third is to carry a carbon-accounting dimension alongside the cost dimension. The present analysis treats the CO₂ source as a cost parameter alone, whereas capture routes differ in the durability of their climate benefit and in their standing under the RFNBO criteria. Since the cost ranking of the available sources is inverse to their regulatory robustness, and since carbon sourcing is among the three dominant levers identified here, the trade-off between cost and compliance durability warrants explicit representation. Should the RFNBO criteria be met and consistently enforced over the long term, however, such an extension would become largely unnecessary: compliance would itself ensure that only carbon sources of durable climate benefit are used, and the cost dimension would again be sufficient.

For assessments of this class more generally, two methodological recommendations follow. Capital cost should be estimated by more than one independent method, since a single estimate admits no internal test of its own consistency. The treatment of the electrolyser should be stated explicitly, since whether hydrogen is purchased or produced within the boundary determines whether a reported cost structure appears capital- or feedstock-dominated independently of any subsequent modelling choice.

References

- Asif, M., et al. (2024). Kinetic modelling and techno-economic assessment of CO₂ hydrogenation to methanol. *Energy & Fuels*, 38(5).
<https://pubs.acs.org/doi/10.1021/acs.energyfuels.3c04147>
- ASTM International. (2026). D7566 Standard specification for aviation turbine fuel containing synthesized hydrocarbons (Annex A5, alcohol-to-jet, methanol feedstock). ASTM International. <https://store.astm.org/d7566-26.html>
- Bube, S., et al. (2025). Power-to-liquid kerosene cost. *Fuel*, 384, 133901.
<https://www.sciencedirect.com/science/article/pii/S0016236124030308>
- Chemical Engineering. (2024). Chemical Engineering Plant Cost Index (CEPCI). *Chemical Engineering Magazine*. <https://www.chemengonline.com/site/plant-cost-index/>
- Destatis - Federal Statistical Office of Germany. (2025). Water management statistics and labour cost statistics. https://www.destatis.de/EN/Themes/Society-Environment/Environment/Water-Management/_node.html
- Elwalily, A., Verkama, E., Mantei, F., Kaliyeva, A., Pounder, A., Sauer, J., & Nestler, F. (2025). Sustainable aviation fuel production via the methanol pathway: A technical review. *Sustainable Energy & Fuels*, 9(19), 5151-5180. <https://doi.org/10.1039/D5SE00231A>
- European Aviation Safety Agency. (2025). 2024 aviation fuels reference prices (Briefing note). EASA. <https://www.easa.europa.eu/en/downloads/141675/en>
- European Union. (2023). Regulation (EU) 2023/2405 of the European Parliament and of the Council on ensuring a level playing field for sustainable air transport (ReFuelEU Aviation). Official Journal of the European Union.
<https://www.easa.europa.eu/en/domains/environment/eaer/sustainable-aviation-fuels/saf-policy-actions>
- EWI - Institute of Energy Economics, University of Cologne. (2025). Global PtX cost tool V2.1. <https://www.ewi.uni-koeln.de/en/news/hydrogen-production-in-the-eu-is-cheaper-than-imports-by-ship/>
- Eyberg, V., et al. (2024). Techno-economic assessment and comparison of Fischer-Tropsch and methanol-to-jet processes to produce sustainable aviation fuel via power-to-liquid. *Energy Conversion and Management*.
<https://www.sciencedirect.com/science/article/pii/S0196890424006691>
- Fasihi, M., & Breyer, C. (2022). E-kerosene for commercial aviation from green hydrogen and direct air capture. LUT University. <https://www.researchgate.net/publication/363417593>
- Frontiers in Energy Research. (2021). Techno-economic assessment of power-and-biomass-to-X processes, 9, 795673. <https://www.frontiersin.org/journals/energy-research/articles/10.3389/fenrg.2021.795673/full>
- International Council on Clean Transportation. (2022). Current and future cost of e-kerosene in the United States and Europe. ICCT. <https://theicct.org/publication/fuels-us-eu-cost-ekerosene-mar22/>
- International Journal of Hydrogen Energy. (2025). European electrolyser learning rates and deployment dataset.
<https://www.sciencedirect.com/science/article/pii/S0360319925027661>
- IRENA. (2020). Green hydrogen cost reduction: Scaling up electrolyzers to meet the 1.5°C climate goal. International Renewable Energy Agency.
<https://www.irena.org/publications/2020/Dec/Green-hydrogen-cost-reduction>

- Johnson Matthey & Honeywell UOP. (2024). eMERALD CO₂-to-methanol and methanol-to-jet technology. <https://matthey.com/products-and-markets/energy/sustainable-aviation-fuels/methanol-to-jet>
- Methanol Institute & Argus Media. (2026). Methanol to jet: A SAF pathway for aviation decarbonisation. <https://www.argusmedia.com/en/news-and-insights/market-opinion-and-analysis-blog/methanol-to-jet-saf-pathway-a>
- Öko-Institut (Matthes, F. C., & Brauer, W.). (2025). Hydrogen production costs: Determinants, status and perspectives. https://www.oeko.de/fileadmin/oekodoc/Matthes_Brauer-Hydrogen-production-costs.pdf
- Peters, M. S., Timmerhaus, K. D., & West, R. E. (2003). Plant design and economics for chemical engineers (5th ed.). McGraw-Hill.
- PtX Lab Lausitz. (2022). Development of PtX sustainability standards and indicators (with LBST and ifeu). PtX Lab Lausitz, Cottbus. <https://ptxlablausitz.de/en/publications/>
- PtX Lab Lausitz. (2024). Fit for Zero - Climate-neutral European aviation by 2050 (PtX Lab Briefing 09/2024). PtX Lab Lausitz, Cottbus. <https://ptxlablausitz.de/en/publications/>
- PtX Lab Lausitz. (2025). Sustainability criteria for green fuels and basic materials from renewable energy: A comprehensive approach for a rapid and secure market ramp-up. PtX Lab Lausitz, Cottbus. <https://ptxlablausitz.de/en/publications/>
- Royal Society of Chemistry. (2023). Economic analysis of hydrogen production in Germany. Sustainable Energy & Fuels. <https://pubs.rsc.org/en/Content/ArticleLanding/2023/SE/D3SE00073G>
- Sendlhofer, A., et al. (2026). Comparative techno-economic assessment of CO₂-based sustainable aviation fuels: Fischer-Tropsch, methanol-to-jet and ethanol-to-jet across the EU, USA and Middle East. Fuel, 402, 139021. <https://www.sciencedirect.com/science/article/pii/S001623612600774X>
- Sin, G., et al. (2025). Production of sustainable aviation fuel: Influence of feedstock and plant capacity on fuel price. International Journal of Hydrogen Energy. <https://www.sciencedirect.com/science/article/pii/S0360319925034937>
- Towler, G., & Sinnott, R. (2013). Chemical engineering design: Principles, practice and economics of plant and process design (2nd ed.). Butterworth-Heinemann. <https://www.sciencedirect.com/book/9780080966595/chemical-engineering-design>
- Transport & Environment. (2025). Spotlight on e-SAF. T&E. <https://www.transportenvironment.org/topics/planes/saf-observatory/spotlight-on-e-kerosene>
- Turton, R., Bailie, R. C., Whiting, W. B., & Shaeiwitz, J. A. (2018). Analysis, synthesis and design of chemical processes (5th ed.). Pearson.
- Verleysen, K., et al. (2023). Cost-optimal power-to-methanol: Bare-module capital costing by the Biegler method (arXiv:2305.18338). <https://arxiv.org/pdf/2305.18338>

Comparative Assessment of Fischer–Tropsch and Methanol Synthesis Pathways for Resilient Fuel Production from Sustainable CO₂ Sources

V. Erfurt, L. Tafur, A. Elwalily, M. Wenzel, S. Günthner, H. Lehmann

Zukunft – Umwelt – Gesellschaft (ZUG) gGmbH, PtX Lab Lausitz, Cottbus, Germany

The Fischer–Tropsch synthesis and methanol-to-jet (MtJ) pathways are of strategic importance for resilient energy systems because they enable the production of liquid fuels from a wide range of alternative carbon sources, including biomass, waste streams, captured CO₂, and renewable hydrogen. Unlike conventional fossil-based refining, these technologies reduce dependence on crude oil imports and diversify fuel supply chains, thereby increasing energy security in times of geopolitical instability and market disruptions. In particular, they support the domestic production of sustainable aviation fuels and chemical feedstocks, helping to establish more flexible, decentralized, and climate-compatible energy infrastructures.

Both routes, Fischer–Tropsch synthesis and methanol-to-jet synthesis represent key technologies for transforming synthesis gas into liquid energy carriers and chemical intermediates. This study presents a comparative assessment of both pathways in terms of process efficiency, carbon utilization, and flexibility in handling fluctuations in renewable-energy supply and upstream operation. Process simulation models are developed to evaluate system performance under fluctuating operating conditions and different integration scenarios, including DAC-based CO₂ supply.

The analysis focuses on identifying key performance indicators such as carbon efficiency, energy demand, and process robustness. Particular attention is given to the integration of renewable hydrogen. Results will be presented and discussed with regard to the suitability of Fischer–Tropsch and methanol to jet synthesis for resilient and sustainable fuel production systems. The findings are expected to provide insights into optimal process configurations and their role in future circular carbon economies.

Compliance of Synthetic Fuels with European Standards: The German Regulatory Perspective

M. J. Alhnidi, N. Dahmen, M. Glaser

Karlsruher Institut für Technologie, Institut für Katalyseforschung und -technologie, Eggenstein-Leopoldshafen, Germany

Synthetic fuels are considered key elements for reducing greenhouse gas emissions in the transport sector while maintaining compatibility with existing engines and fuel infrastructure. However, their market introduction depends strongly on compliance with European fuel quality standards and national regulatory frameworks. This work presents an overview of compliance pathways for synthetic fuels within the European standardization system, with particular focus on the German implementation. The study explores different production pathways for synthetic fuels, including Fischer–Tropsch fuels and methanol-derived fuels, and evaluates their compliance with relevant European fuel standards such as DIN EN 15940 and DIN EN 228. Particular attention is given to physicochemical fuel properties, fuel quality requirements, and regulatory approval procedures.

A comparative analysis of mainly literature-derived fuel property datasets was conducted to assess the compliance of different synthetic fuel pathways with European fuel quality specifications. The study further includes a comparative assessment of key physicochemical properties of fuels produced via the considered production pathway.

The outcomes of the study provide guidance for fuel producers and policymakers to support the broader implementation of synthetic fuels. The study demonstrates that successful market integration of synthetic fuels requires not only greenhouse gas reduction potential, but also strict compliance with physicochemical fuel specifications and regulatory approval pathways.

The presented overview contributes to a better understanding of current regulatory challenges and future opportunities for integrating synthetic fuels into the European fuel market.

Revealing Resonances in Technical Dehydration of Ethanol

M. Seifert, L.A. Lorenz, L.A. Haufe

Technische Universität Dresden, Dresden, Germany

Introduction

The description and understanding of chemical processes based on balances (mass, heat, momentum, finance) is inevitably coupled with proper quantification of process dynamics to enable process control. For the showcase of continuous conversion of ethanol over a solid-acid catalyst different dependencies between process parameters (T, p), steady-state flows (heat, carrier, feed) and chemical conversion parameters (conversion, selectivity, heat formation) are analyzed to show quantitative interconnections. Control of test units by design for specialized purposes provides/enables opportunities to control T, p and flow profiles, as well as to limit measurement and control errors from actuators and sensors. [1,2]

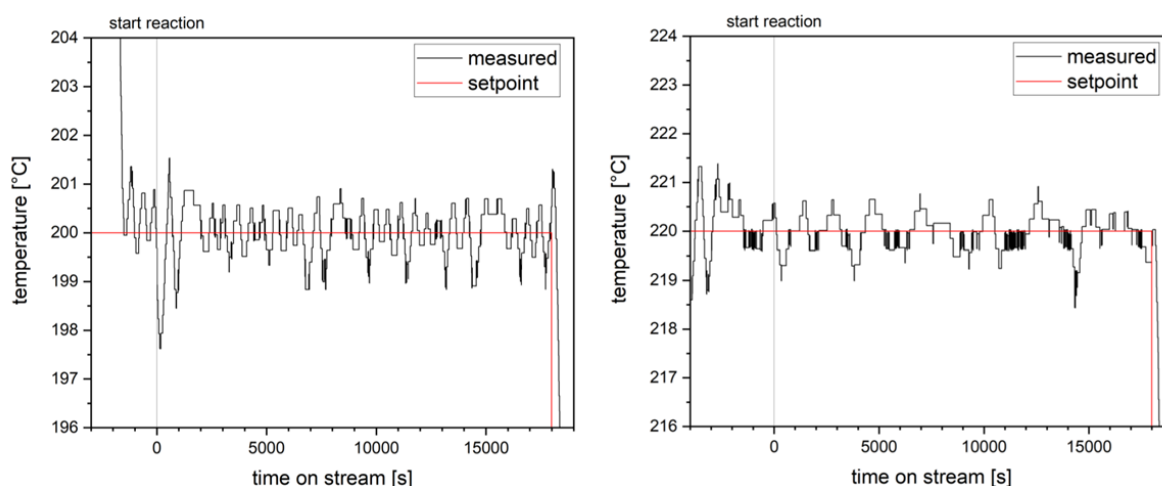


Figure 1. Steady-state temperature with time on stream: (left) 200°C, (right) 220°C.

Beyond limits of process automation errors, this work reveals options to observe and quantify a complex interplay between setpoint and parameter oscillation (see **Figure 1**) using different types of phase analysis. While classic routines for quantifying process dynamics often simplify dependencies between steady-state chemistry and reaction engineering (e.g. heat flows), phase analysis circumvents many simplifications.

Much underrated, but fruitful in its power to support understanding of non-equilibrium continuous processes are thermodynamic variables such as Gibbs free energy, enthalpy or different kinds of entropy. Their trends reveal different types of uncertainty which overlay with the measurable oscillations. [3] The use of thermodynamic variables helps to estimate ranges of reasonable discussion, to quantify and separate the different effects such as parameter quantization in engineering (see **Figure 1**), and model restrictions from the physical parameter independencies such as temperature, pressure, flow and chemical reaction interference.

- [1] L.A. Haufe, F. Bismark, J. Tippner, M. Seifert, J.J. Weigand; *Results in Engineering* (2025), 28, 107302.
- [2] Forschen mit System: Automatisierung als Brücke zwischen Labor und Industrie; J. Tippner, M. Seifert, L.A. Haufe, J.J. Weigand; *INDUSTRIELLE AUTOMATION* (2026), 02, 12-15.
- [3] J. Dutschke, S.J. Geiger, L.A. Haufe, S. Kaiser, M. Seifert, *Chemie-Ingenieur-Technik* (2026).

Kinetic Modelling of the Sabatier Reaction over Ni/CeO₂–ZrO₂ for Synthetic Natural Gas Production

G. Ramis^{1*}, W. Da Silva Cardoso², S. Romegialli², M. Tommasi², A. Gramegna², I. Rossetti²

¹DICCA, Università degli Studi di Genova, Genoa, Italy; ²Department of Chemistry, Università degli Studi di Milano, Milan, Italy

Abstract

CO₂ methanation provides a route for storing renewable hydrogen as synthetic natural gas, but reactor design and process optimization require kinetic expressions that remain predictive over wide operating windows. This work develops an Aspen-ready kinetic framework for CO₂ hydrogenation over a Ni/CeO₂–ZrO₂ catalyst using approximately 40 experimental conditions selected by a central composite design. Temperature, pressure, gas hourly space velocity, H₂/CO₂ ratio and inert dilution were varied to span CO₂ conversions from approximately 10 to 90%, including kinetic and equilibrium-influenced regimes. The reaction network explicitly represents reverse water-gas shift (RWGS) and CO methanation, whose combination gives the global Sabatier reaction. Several Python implementations were compared: constrained baseline models, an Aspen-parity generalized Langmuir–Hinshelwood–Hougen–Watson formulation with independent Arrhenius parameters (SM5), and a structural screening extension that varies adsorption-denominator exponents (SM6). Packed-bed balances were integrated along catalyst mass, parameters were estimated through bounded global/local optimization, and candidate solutions were screened for numerical stability before conversion to Aspen Plus format. On a literature reference dataset, SM5 recovered an RWGS activation energy of 106.02 kJ mol^{–1} versus 106.15 kJ mol^{–1} for the reference and a CO-methanation activation energy of 4.3 versus 4.4 kJ mol^{–1}. For the here developed dataset, SM5 returned 106.16 and 3.51 kJ mol^{–1}, respectively, while reproducing the observed temperature, pressure and space-time trends more consistently than the constrained models. Removing two influential pressure points at 20 and 25 bar changed the high-pressure response but left the principal SM5 kinetic parameters comparatively stable. The gain of SM6 over SM5 was moderate and did not justify replacing the more transparent baseline without further external and Aspen validation. The results identify independent RWGS and CO-methanation kinetics, bounded multistart fitting and explicit structural discrimination as key requirements for a robust reactor model.

1. Introduction

Renewable electricity can be converted into hydrogen by water electrolysis, but long-duration storage and distribution of hydrogen remain technically and economically demanding. Conversion of H₂ and captured CO₂ into synthetic methane provides a complementary power-to-gas route because methane is compatible with established transmission, distribution and storage assets [1-4]. The core chemistry is the Sabatier reaction, $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$. Its large exothermicity favours methane at low temperature and elevated pressure, but also creates strong thermal gradients in industrial catalyst beds. Reliable reactor design therefore depends on kinetic models that separate intrinsic chemistry from equilibrium, heat-transfer and transport effects.

Nickel catalysts are widely investigated for CO₂ methanation because they offer high methane selectivity at substantially lower cost than noble metals. Activity depends on Ni dispersion, support basicity, reducibility and metal-support interactions. Ceria-zirconia is especially attractive because its oxygen storage capacity and oxygen-vacancy chemistry can facilitate CO₂ activation and mitigate carbon accumulation [5-9]. Nevertheless, reported kinetic parameters vary widely because catalyst formulation, pretreatment, pressure, dilution, reactor configuration and regression strategy differ. A model calibrated only near one operating point may fit that dataset while extrapolating poorly.

The reaction network is more informative than a single global rate. CO₂ may first form CO through reverse water-gas shift (RWGS), $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$, followed by CO methanation, $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$. The sum yields the global Sabatier reaction. Depending on surface coverage and operating conditions, CO can be an intermediate, a parallel product or an inhibitor. Power-law equations provide computational convenience, whereas Langmuir–Hinshelwood–Hougen–Watson (LHHW) models incorporate adsorption and competitive surface coverage. The latter can improve physical interpretation but introduce correlated parameters and multiple local optima [10-13].

Parameter estimation is consequently an inverse problem rather than a simple curve fit. Pre-exponential factors and activation energies are strongly correlated; adsorption terms can compensate for kinetic terms; and numerical integration can fail for unphysical candidate vectors. Bounds that are too narrow force a predetermined answer, whereas bounds that are too broad permit abrupt or unstable reactivity. Multistart global/local search strategies, parameter transformations, residual diagnostics and independent validation are therefore essential [14-17]. A further practical requirement is parity between the regression code and the equation form implemented in a commercial process simulator.

This work develops a Python-to-Aspen kinetic workflow for CO₂ methanation over Ni/CeO₂–ZrO₂ catalyst. The starting point was a generalized Langmuir-Hinshelwood-Hougen-Watson (LHHW) formulation, validated against a literature dataset and applied to kinetic data newly collected within the project. Approximately 40 internal experimental conditions were designed to explore temperature, pressure, gas hourly space velocity (GHSV), H₂/CO₂ ratio and dilution. Conversion ranged from about 10 to 90%, ensuring that parameter estimation encountered both strongly kinetic and increasingly equilibrium-influenced regions.

The objective was not merely to minimize an aggregate residual. Five code families were compared to determine which formulation was numerically stable, mechanistically defensible, reproducible in Aspen Plus and predictive across operating variables. The main model structure preserves the driving-force and adsorption terms structure but estimates RWGS and CO-methanation Arrhenius parameters independently. An updated version then screens discrete adsorption exponents without altering the driving forces. This paper evaluates parameter recovery on the reference dataset, prediction on new measurements, influential pressure points and the incremental value of adsorption-structure screening.

2. Experimental and computational methods

2.1 Catalyst, experimental domain and design of experiments

The kinetic dataset was obtained for a Ni/CeO₂–ZrO₂ methanation catalyst under conditions representative of power-to-gas operation. A central composite design was used to distribute experiments across temperature, pressure, GHSV and H₂/CO₂ ratio, with replicated central points to assess repeatability. The overall dataset contained approximately 40 conditions and covered CO₂ conversion from roughly 10 to 90%. Additional one-factor series were used to visualize temperature, pressure, space-time, reactant-ratio and inert-dilution effects. The literature dataset used to validate the kinetic modelling tool, included atmospheric-pressure temperature series, GHSV series at 250 and 290 °C, H₂/CO₂-ratio series and inert fractions from 2 to 40%.

The internal series included temperature variation at 6 bar and $Q_t/W = 45,000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$; pressure variation at 285 °C and the same Q_t/W ; and Q_t/W variation at 285 °C and 6 bar. The pressure sequence included 2, 4, 6, 8, 10, 15, 20, 25 and 30 bar. Measurements at 20 and 25 bar were treated as potentially influential because they departed from the otherwise smooth pressure trend. They were retained in the principal fit and excluded only in a labelled sensitivity case, SM5_filtered.

2.2 Reaction network and generalized LHHW form

RWGS and CO methanation were implemented explicitly. For reaction j , the rate was

represented generically as $r_j = k_j(T) \cdot DF_j(p,T)/D(p,T)^n$, where $k_j = k_{j,0} \exp(-E_j/RT)$, DF_j is a reversible driving-force term containing forward partial-pressure products and an equilibrium correction, and D is a competitive adsorption denominator. The overall component source terms follow the stoichiometry of the two reactions; the apparent Sabatier rate emerges from their combination. In Aspen-parity models, the driving-force exponents and coefficients multiplying inverse equilibrium terms were kept fixed. Free variables were the Arrhenius parameters for RWGS and CO methanation and the temperature-dependent coefficients for adsorption constants.

The reference denominator contains fractional hydrogen dependencies characteristic of the kinetic scheme. The simplified v22 model instead uses $[1 + K_2p_{H_2} + K_3p_{H_2O} + K_4p_{CO}]^2$. SM1 restores the reference denominator but constrains CO-methanation parameters through a speed-up factor and activation-energy difference relative to RWGS. SM5 preserves the reference driving forces and denominator while estimating the two Arrhenius pairs independently. This removes an artificial coupling that can cause one reaction to compensate for the other.

2.3 Packed-bed calculation and observables

The reactor was simulated by integrating molar-flow balances along catalyst mass W . At each integration point, partial pressures were computed from total flow, pressure and gas composition; temperature was treated according to the experimental condition used for fitting. Outlet CO_2 conversion was calculated as $X_{CO_2} = (F_{CO_2,in} - F_{CO_2,out})/F_{CO_2,in}$. CO selectivity was included where sufficiently reliable, but the internal fitting objective was primarily based on CO_2 conversion because CO data were not available for most tests due to high selectivity towards methane. Catalyst mass and feed-flow units were harmonized before fitting so that rate parameters could be transferred without hidden scaling factors.

Candidate parameter sets that generated integration failure, non-finite rates, negative flows or excessively abrupt response across neighbouring conditions were rejected or penalized. This stability layer was important because a low residual at isolated points can coexist with unusable interpolation. After regression, parameters were converted to the units and sign conventions required by the Aspen Plus generalized LHHW reaction form. Aspen parity means that the same driving forces, adsorption structure, units and fixed exponents are represented in both environments, it does not imply that the Python solver and Aspen numerical algorithms are identical.

2.4 Optimization strategies and model hierarchy

Table 1. Model hierarchy and role in discrimination.

Model	Kinetic structure	Optimization	Role
v16e	Aspen-parity GLHHW; single step methanation	LHS + pattern search	Initial baseline
v22	Simplified squared denominator; single step methanation	LHS + pattern search	Numerical diagnostic
SM1	Reference denominator; single step methanation	LHS + pattern search	Intermediate Aspen-parity model
SM5	Reference form; independent RWGS/CO-methanation Arrhenius pairs	Multistart L-BFGS-B + least_squares	Principal model
SM6	SM5 driving forces; discrete adsorption-exponent screening	Fit repeated for each candidate structure	Structural sensitivity

Early implementations used Latin hypercube sampling (LHS) followed by local pattern search (Table 1). SM5 used bounded multistart L-BFGS-B and a final nonlinear least-squares refinement. Wide but finite bounds were combined with timeouts and runout checks. Reference kinetic parameters from the literature could initialize a start but were not imposed as constraints. Model screening considered parameter plausibility, stability, recovery of the reference parameterization and response across each experimental series in addition to the

objective value.

2.5 SM6 adsorption-structure screening

SM6 retained the SM5 driving forces and independently fitted Arrhenius parameters, while screening discrete exponents in the adsorption denominator at increments of 0.5. Candidate K terms could also be disabled from optimisation. Every candidate structure underwent the same bounded optimization and numerical checks. The approach separates structural selection from unrestricted exponent regression, which would otherwise increase parameter correlation and create poorly identifiable continuous exponents.

3. Results and discussion

3.1 Recovery of the reference kinetic parameterization

The dataset reported in the literature by Vidotto & Raco [18] was first used as a control problem. The critical test was whether the implementation could recover Aspen-ready kinetic and adsorption parameters close to the supplied reference. SM5 recovered $E_{RWGS} = 106.02 \text{ kJ mol}^{-1}$ compared with $106.15 \text{ kJ mol}^{-1}$ and $E_{meth} = 4.3$ compared with 4.4 kJ mol^{-1} . Its pre-exponential factors were 1.395×10^8 versus $1.100 \times 10^8 \text{ kmol kg}^{-1} \text{ s}^{-1}$ for RWGS and 3.39 versus $2.34 \text{ kmol kg}^{-1} \text{ s}^{-1}$ for CO methanation (Table 2).

Table 2. Selected parameters fitted to the Vidotto–Raco reference dataset.

Parameter	Reference	SM1	SM5
$k_{RWGS} / \text{kmol kg}^{-1} \text{ s}^{-1}$	1.100×10^8	7.374×10^3	1.395×10^8
$E_{RWGS} / \text{kJ mol}^{-1}$	106.15	75.2	106.02
$k_{0,meth} / \text{kmol kg}^{-1} \text{ s}^{-1}$	2.34	306.37	3.39
$E_{meth} / \text{kJ mol}^{-1}$	4.4	38.4	4.3
A Kterm3	-7.14	-6.85	-7.26
B Kterm3	4762.0	61	4833.5
A Kterm4	-4.69	-6.76	-4.34
B Kterm4	6426.0	110.9	6486.2

SM1 produced acceptable curves in portions of the domain but did not recover the parameter structure: E_{RWGS} decreased to 75.2 kJ mol^{-1} and E_{meth} increased to 38.4 kJ mol^{-1} . Several adsorption temperature coefficients also moved by orders of magnitude. The coupled speed-up/difference parameterization therefore allowed compensating effects that obscured the reference kinetics. Independent Arrhenius estimation in SM5 materially improved identifiability under the imposed structure. The most representative results of kinetic model validation are reported in Figure 1.

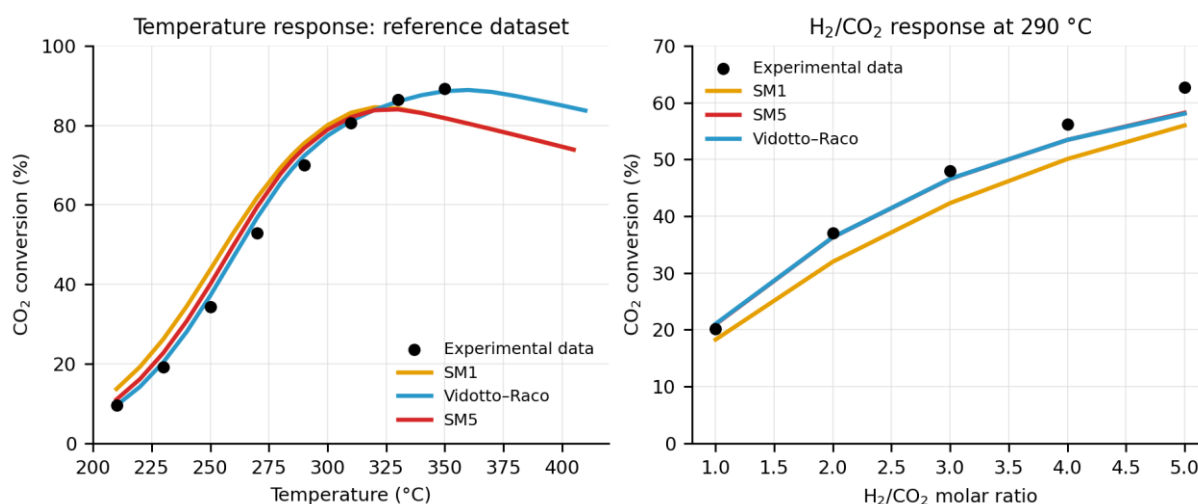


Figure 1. Left: temperature response at GHSV = 20,000 Ncc h⁻¹ g_{cat}⁻¹ and 1 atm. Right: H₂/CO₂ response at 290 °C, 1 atm, fixed p_{CO2} = 0.17 atm and GHSV = 50,000 Ncc h⁻¹ g_{cat}⁻¹.

The reference temperature curve shows the transition from kinetically limited conversion at low temperature to an equilibrium-influenced maximum. All models reproduce the increasing branch; differences become more visible above 330 °C. The H₂/CO₂ series shows monotonic conversion enhancement with hydrogen availability. SM5 and the reference model are nearly superimposed, while SM1 underpredicts conversion at high ratio. Agreement across different manipulated variables is more informative than agreement along a single temperature series.

3.2 New kinetic dataset and transfer of kinetic structure

Applying the model hierarchy to the newly collected dataset tested over a new Ni/CeO₂-ZrO₂ catalyst allowed to assess kinetic model consistency when transferred to the new measurements. SM5 gave $E_{RWGS} = 106.16$ kJ mol⁻¹, essentially unchanged from the reference model, and $E_{meth} = 3.51$ kJ mol⁻¹. SM6_0021 gave 108.41 and 4.38 kJ mol⁻¹, respectively. By contrast, v16e and SM1 returned much lower RWGS activation energies (84.5 and 87.7 kJ mol⁻¹, respectively) and much higher CO-methanation activation energies (52.4 and 83.8 kJ mol⁻¹). The latter pairs reflect the constrained parameterization rather than a credible transfer of the reference structure. The most relevant parameters are reported in Table 3.

Table 3. Kinetic parameters fitted to the internal dataset.

Parameter	v16e	SM1	SM5	SM5 filtered	SM6_0021
$k_{RWGS} / \text{kmol kg}^{-1} \text{s}^{-1}$	2.335×10^4	3.513×10^4	9.163×10^7	7.736×10^7	2.65×10^7
$E_{RWGS} / \text{kJ mol}^{-1}$	84.5	87.7	106.16	105.84	108.41
$k_{meth} / \text{kmol kg}^{-1} \text{s}^{-1}$	5875	7.037×10^5	11.3	11.39	5.55
$E_{meth} / \text{kJ mol}^{-1}$	52.4	83.8	3.51	3.70	4.38
A Kterm3	-1.74	1.29	-7.33	-6.47	-5.9588
B Kterm3	832.4	-759.9	5607.1	5121.5	4778.91
A Kterm4	5.25	1.86	-4.74	-5.60	-6.3803
B Kterm4	571.2	1498.9	7156.8	7546.3	6097.84

The numerical similarity of the SM5 activation parameters across reference and internal datasets is encouraging, but it should not be interpreted as proof that every fitted constant is uniquely identified. Adsorption coefficients changed more substantially, and the objective function was dominated by conversion. Confidence intervals, profile likelihoods and parameter-correlation matrices are required before mechanistic interpretation. Nevertheless, the transfer supports SM5 as a practical model for process calculations because its response is not produced by extreme compensation between the two reaction rates.

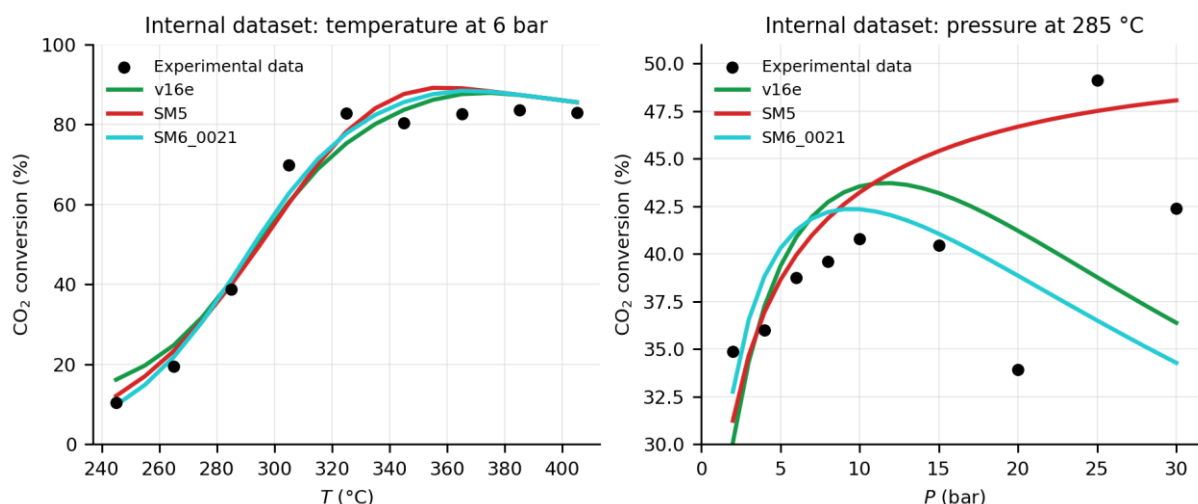


Figure 2. Newly developed experimental dataset and fitted responses. Left: temperature variation at $P = 6$ bar and $Q_i/W = 45,000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$. Right: pressure variation at 285 °C and the same Q_i/W .

At 6 bar, conversion rises steeply from approximately 10% at 245 °C to above 80% at 325 °C and then approaches a plateau (Figure 2). SM5 and SM6 follow the sigmoidal rise and high-temperature plateau, while v16e overpredicts the lowest-temperature region. The pressure series is more problematic. Measurements increase gradually to 15 bar, fall at 20 bar, rise strongly at 25 bar and return near 42% at 30 bar. No smooth intrinsic model should be expected to interpolate these alternating excursions exactly. Their origin may include experimental scatter, run order, catalyst state, analytical uncertainty or unrepresented heat/mass-transfer effects.

3.3 Influence of pressure points and robust fitting

To quantify the leverage of the anomalous pressure observations, SM5_filtered omitted the 20 and 25 bar points but retained the remaining dataset. E_{RWGS} changed only from 106.16 to 105.84 kJ mol^{-1} , k_{meth} from 11.3 to 11.39 $\text{kmol kg}^{-1} \text{ s}^{-1}$ and E_{meth} from 3.51 to 3.70 kJ mol^{-1} . This stability suggests that the principal Arrhenius parameters are not controlled exclusively by those two points. The high-pressure curve, however, became more strongly increasing because the local decrease at 20 bar was no longer penalized.

The filtered fit is a sensitivity experiment, not the preferred model. Removing observations after inspecting residuals can artificially improve apparent performance and understate uncertainty.

Residual analysis should therefore be stratified by experimental series. A global sum of squares can be dominated by dense temperature curves, leaving pressure or ratio response weakly constrained. Recommended diagnostics include parity plots for training and validation subsets, standardized residuals against each factor, leverage/Cook-type measures, bootstrap parameter distributions and prediction intervals. The report dataset did not yet provide a completely independent external validation subset, so predictive claims should remain conditional. Yet, it captures with sufficiently good approximation the variable dependence in order to be implemented in Aspen Plus for basic process design.

3.4 Space-time, reactant-ratio and dilution behaviour

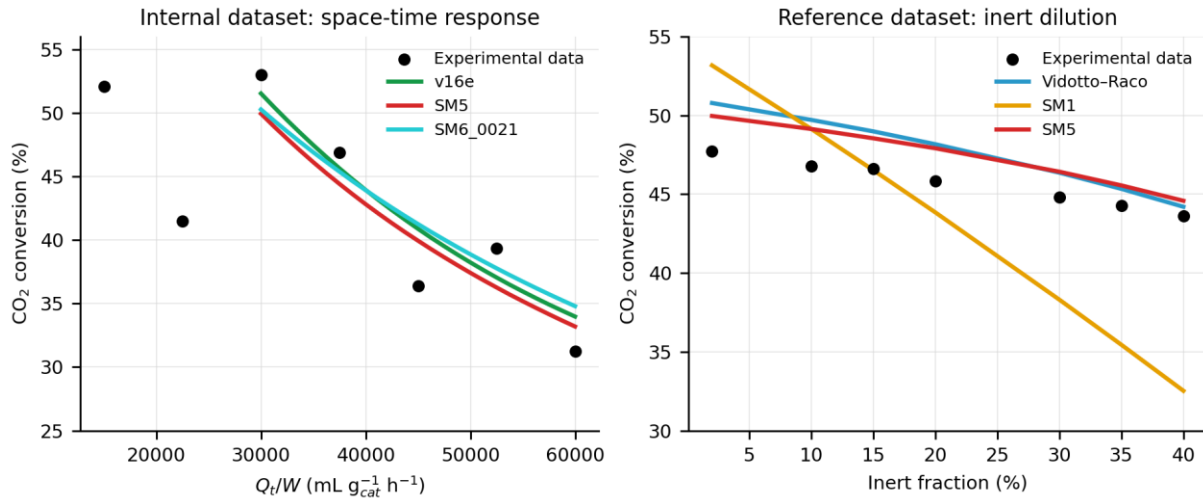


Figure 3. Effects of space time and dilution. Left: data at 285 °C and 6 bar as a function of Q_t/W . Right: reference data at 290 °C and 1 atm as a function of inert fraction.

All models predict decreasing conversion as Q_t/W increases, consistent with shorter residence time per catalyst mass. The measurements are scattered: conversion at 30,000 mL g_{cat}⁻¹ h⁻¹ exceeds that at 22,500, and the point at 52,500 exceeds the point at 45,000. The smooth SM5 curve captures the overall decline but not these local variations. Because Q_t/W combines total flow and catalyst mass, an error in either quantity directly shifts the independent variable; careful unit harmonization and mass-basis documentation are therefore essential.

Inert dilution at 290 °C produces a modest experimental decline from 47.7% conversion at 2% inert to 43.6% at 40%. SM5 and the Vidotto–Raco reference model reproduce the shallow decrease. SM1 predicts an excessive fall to approximately 32.5%, showing that its coupled parameterization exaggerates coverage or partial-pressure effects. The dilution series is thus a useful discriminator even though it spans a smaller conversion range than the temperature-related data.

The reactant-ratio series further reveals whether the model distinguishes hydrogen availability from simple dilution. At 290 °C with p_{CO_2} fixed, measured conversion rises from 20.1% at $\text{H}_2/\text{CO}_2 = 1$ to 62.7% at 5; SM5 predicts 20.9–58.2%, respectively. With p_{H_2} fixed and CO_2 varied, the measured increase of conversion is 16.4–74.4%, while SM5 predicts 15.9–65.7%. At 250 °C the absolute conversion is lower and SM1 shows pronounced saturation when p_{H_2} is fixed. These cross-series differences justify retaining explicit adsorption terms rather than using a single apparent reaction order.

3.5 Adsorption-denominator screening with SM6

SM6 examined whether the reference adsorption denominator was unnecessarily restrictive (Table 4). The best candidate, SM6_0021, used $D = 1 + K_2 p_{\text{H}_2} + K_3 p_{\text{H}_2\text{O}} p_{\text{H}_2}^{-1} + K_4 p_{\text{CO}} p_{\text{H}_2}$. Its final objective function value was 0.1263. The next structures gave 0.1283 and 0.1288, a small variation. The improvement originated from adsorption structure rather than altered driving forces or added Arrhenius coupling.

Table 4. Highest-ranked SM6 adsorption structures.

ID	Adsorption denominator	Final objective function value
SM6_0021	$1 + K_2 p_{\text{H}_2} + K_3 p_{\text{H}_2\text{O}} p_{\text{H}_2}^{-1} + K_4 p_{\text{CO}} p_{\text{H}_2}$	0.1263
SM6_0020	$1 + K_2 p_{\text{H}_2} + K_3 p_{\text{H}_2\text{O}} p_{\text{H}_2}^{-1} + K_4 p_{\text{CO}} p_{\text{H}_2}^{0.5}$	0.1283
SM6_0018	$1 + K_2 p_{\text{H}_2}^{0.5} + K_3 p_{\text{H}_2\text{O}} + K_4 p_{\text{CO}} p_{\text{H}_2}$	0.1288

SM6_0021 improved the temperature onset estimate at low conversion and modified the

curvature of the pressure response, but the gain was moderate. Selecting it solely because it has the lowest value of objective function would overstate the evidence. A more complex structural search must be penalized for the number of candidates evaluated and verified on withheld experiments. Information criteria are useful only if residual assumptions and effective parameter counts are credible; cross-validation by entire operating series is preferable.

SM5 was therefore retained as the principal model because it has a transparent connection to the Aspen Plus standard kinetic formulation, independent reaction kinetics and stable parameter recovery. This would avoid implementing user models that would limit the computational agility of the process simulator. SM6_0021 is a promising secondary candidate for future discrimination.

3.6 Aspen Plus implementation and use in reactor design

The parameter vector was converted to Aspen Plus units and mapped to generalized LHHW reactions. Successful transfer requires explicit documentation of pressure units in every power term, catalyst-mass basis, rate basis, equilibrium-constant convention, Arrhenius sign convention and denominator exponent. A unit mismatch can be absorbed during Python regression yet produce orders-of-magnitude error in Aspen. Parity should be demonstrated condition-by-condition by comparing outlet conversion and, where available, CO selectivity from both platforms with an identical feed and reactor discretization.

Once parity is established, the model can support packed-bed sizing, staged or cooled reactor design, recycle optimization and integration within power-to-gas flowsheets. The broad conversion window here achieved is advantageous because it contains both kinetic and equilibrium-sensitive observations. However, isothermal laboratory fitting is not sufficient to predict industrial hot spots. The kinetic submodel must be combined with energy balances, heat-transfer coefficients and effectiveness factors, and intrinsic validity should be checked by criteria for external and internal transport limitation [19, 20].

For process optimization, the model should not be extrapolated beyond the calibrated temperature, pressure and composition domain without uncertainty bounds. The current pressure response is particularly uncertain above 15 bar. Recommended deliverables for the next implementation stage are: a frozen equation specification; a machine-readable dataset with replicates and uncertainties; Python/Aspen Plus parity tables; parameter covariance or bootstrap intervals; and validation experiments targeted where SM5 and SM6 predictions diverge most.

3.7 Comparison with literature kinetic datasets and models.

In comparison with kinetic datasets commonly reported for CO₂ methanation, the present experimental campaign can be considered particularly broad in terms of operating-domain coverage, although not exceptionally large in terms of the absolute number of experiments. The approximately 40 runs span temperature, total pressure, space velocity, H₂/CO₂ ratio and inert dilution, covering CO₂ conversions from about 10 to 90%. This combination is important because it includes both kinetically controlled and equilibrium-affected conditions and, unlike datasets developed exclusively under differential conversion, provides information directly relevant to integral packed-bed reactor design. Early investigations by Weatherbee and Bartholomew [21] were fundamental in establishing the effects of reactant partial pressures and the inadequacy of simple power-law expressions, but were conducted at essentially atmospheric pressure and over a more restricted set of operating variables. More recent benchmark studies are numerically larger: Koschany et al. [22] collected more than 200 data points for NiAl(O)_x catalysts over different temperatures, pressures and gas compositions, whereas Onrubia-Calvo et al. reported 124 experiments for Ni/CeO₂, systematically varying temperature, pressure, GHSV and reactant and product partial pressures. Nevertheless, the present dataset reaches pressures up to 30 bar—higher than the 15 bar explored by Koschany et al. [22], the 20 bar investigated by Yang et al. [23] and the 6 bar considered in the Ni/CeO₂

study—and therefore provides valuable information for process-relevant high-pressure extrapolation. The quality of the proposed SM5 model is supported by its ability to reproduce, with a single physically interpretable LHHW formulation, the temperature, space-time, dilution and reactant-ratio trends over a wide conversion window. Moreover, the almost exact recovery of the reference activation energies for RWGS and CO methanation indicates that the parameter-estimation procedure is internally consistent. Its performance is therefore comparable in scope to literature LHHW models capable of describing both differential and integral regimes.

4. Conclusions

A transferable kinetic-modelling workflow was developed for CO₂ methanation over Ni/CeO₂–ZrO₂. The reaction network explicitly represents RWGS and CO methanation, while reversible driving forces and competitive adsorption are retained in a generalized LHHW form. Approximately 40 experiments across temperature, pressure, GHSV, H₂/CO₂ ratio and dilution supplied a broad 10–90% conversion window.

The main SM5 formulation, which estimates RWGS and CO-methanation Arrhenius parameters independently, recovered the Vidotto–Raco reference activation energies with high fidelity. On the newly developed dataset, the corresponding values were 106.16 and 3.51 kJ mol⁻¹. Constrained models produced strongly compensating parameters and inferior responses to reactant-ratio and inert-dilution changes.

Temperature and GHSV trends were reproduced satisfactorily, whereas the 20 and 25 bar measurements created a non-monotonic pressure series that no smooth model represented completely. Excluding those points had limited effect on principal SM5 Arrhenius parameters but changed high-pressure curvature. They should therefore be replicated and investigated rather than automatically discarded.

Discrete adsorption screening identified SM6_0021 with an objective function value of 0.1263, only moderately better than the next structures. The gain was insufficient to displace the more transparent SM5 model before independent validation. SM6 is best viewed as a structured model-discrimination tool that identifies experiments capable of distinguishing alternative coverage descriptions.

The immediate outcome is an Aspen-ready kinetic framework suitable for reactor and flowsheet studies. Final certification requires complete CO-selectivity data, a frozen and fully documented equation set, Python–Aspen Plus parity tests, uncertainty analysis and external validation. These steps will convert a competitive regression model into a defensible design model for synthetic-methane production.

Finally, the discussion deliberately distinguishes verified numerical results from limitations of the present dataset. CO selectivity was not available with comparable completeness for every internal experiment, due to the extremely high selectivity to methane of the developed catalyst, so the current objective function is dominated by CO₂ conversion. This restricts identifiability of the two-reaction network and prevents a definitive mechanistic claim. Yet, the separate reactions model was more affordable than the single step CO₂ methanation one. The resulting model was therefore translated as Aspen-ready and suitable for reactor simulation, but it does not yet represent a validated intrinsic kinetic law.

Acknowledgements

The authors gratefully acknowledge the Italian Ministry of Environment and Energy Sustainability (MASE, formerly MITE) for funding the project “RSH2A_000018 - Stoccaggio e distribuzione di idrogeno attraverso una strategia power-to-gas/gas-to-power con cattura ed utilizzo completi del carbonio - Hydrogen storage and distribution through power-to-gas strategy, with full carbon capture and utilization-CUP: F57G25000180006” in the frame the European Union Next-GenerationEU, Piano Nazionale di Ripresa e Resilienza (PNRR) –

Missione 2 “Rivoluzione verde e transizione ecologica”, Componente 2 “Energia rinnovabile, idrogeno, rete e mobilità sostenibile”, Investimento 3.5 “Ricerca e sviluppo sull'idrogeno” (bando A).

References

- [1] M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, Renewable Power-to-Gas: A technological and economic review, *Renewable Energy*, 85 (2016) 1371–1390.
- [2] S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz, J. Lefebvre, P. Prabhakaran, S. Bajohr, Review on methanation – From fundamentals to current projects, *Fuel*, 166 (2016) 276–296.
- [3] M. Thema, F. Bauer, M. Sterner, Power-to-Gas: Electrolysis and methanation status review, *Renew Sust Energ Rev*, 112 (2019) 775–787.
- [4] A. Shahsavar, S. Khanmohammadi, M. Khaki, M. Salmanzadeh, Performance assessment of an innovative exhaust air energy recovery system based on the PV/T-assisted thermal wheel, *Energy*, 162 (2018) 682–696.
- [5] J.J. Gao, Q. Liu, F.N. Gu, B. Liu, Z.Y. Zhong, F.B. Su, Recent advances in methanation catalysts for the production of synthetic natural gas, *Rsc Advances*, 5 (2015) 22759–22776.
- [6] K. Stangeland, D. Kalai, H.L. Li, Z.X. Yu, CO methanation: the effect of catalysts and reaction conditions, *Enrgy Proced*, 105 (2017) 2022–2027.
- [7] M.A.A. Aziz, A.A. Jalil, S. Triwahyono, A. Ahmad, CO methanation over heterogeneous catalysts: recent progress and future prospects, *Green Chemistry*, 17 (2015) 2647–2663.
- [8] G. Garbarino, P. Riani, L. Magistri, G. Busca, A study of the methanation of carbon dioxide on Ni/AlO catalysts at atmospheric pressure, *International Journal of Hydrogen Energy*, 39 (2014) 11557–11565.
- [9] M. Tommasi, L. Rotasperti, A. Gramegna, A. Di Michele, M. Galloni, E. Falletta, F. Galli, C. Hammond, G. Ramis, I. Rossetti, Ni/Al₂O₃ and Ni/TiO₂ catalysts for CO₂ methanation: structure-performance relationship and optimization, *Appl. Catal. A*, submitted.
- [10] G.A. Mills, F.W. Steffgen, Catalytic Methanation, *Catalysis Reviews*, 8 (2006) 159–210.
- [11] G.F. Froment, K.B. Bischoff, J. De Wilde, *Chemical Reactor Analysis and Design*, Wiley 2011.
- [12] K.M.V. Bussche, G.F. Froment, A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al₂O₃ Catalyst, *Journal of Catalysis*, 161 (1996) 1–10.
- [13] J. Xu, G.F. Froment, Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics, *AIChE Journal*, 35 (2004) 88–96.
- [14] P. Virtanen, R. Gommers, T.E. Oliphant, M. Haberland, T. Reddy, D. Cournapeau, E. Burovski, P. Peterson, W. Weckesser, J. Bright, S.J. van der Walt, M. Brett, J. Wilson, K.J. Millman, N. Mayorov, A.R.J. Nelson, E. Jones, R. Kern, E. Larson, C.J. Carey, I. Polat, Y. Feng, E.W. Moore, J. VanderPlas, D. Laxalde, J. Perktold, R. Cimrman, I. Henriksen, E.A. Quintero, C.R. Harris, A.M. Archibald, A.H. Ribeiro, F. Pedregosa, P. van Mulbregt, C. SciPy, SciPy 1.0: fundamental algorithms for scientific computing in Python, *Nat Methods*, 17 (2020) 261–272.
- [15] R.H. Byrd, P.H. Lu, J. Nocedal, C.Y. Zhu, A Limited Memory Algorithm for Bound Constrained Optimization, *Siam Journal on Scientific Computing*, 16 (1995) 1190–1208.
- [16] M.D. McKay, R.J. Beckman, W.J. Conover, A Comparison of Three Methods for Selecting Values of Input Variables in the Analysis of Output from a Computer Code, *Technometrics*, 21 (1979) 239–245.
- [17] D.M. Bates, D.G. Watts, *Nonlinear Regression Analysis and Its Applications*, Wiley 1988.
- [18] D. Vidotto, G. Raco, *Kinetic Modeling of CO₂ Methanation over a Ni–Al Coprecipitated Catalyst*, Politecnico di Milano, Milan, Italy, 2021.
- [19] C.N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, MIT Press 1970.

- [20] E.W. Thiele, Relation between Catalytic Activity and Size of Particle, *Industrial & Engineering Chemistry*, 31 (2002) 916–920.
- [21] G. Weatherbee, Hydrogenation of CO₂ on group VIII metals II. Kinetics and mechanism of CO₂ hydrogenation on nickel, *Journal of Catalysis*, 77 (1982) 460–472.
- [22] F. Koschany, D. Schlereth, O. Hinrichsen, On the kinetics of the methanation of carbon dioxide on coprecipitated NiAl(O), *Appl Catal B-Environ*, 181 (2016) 504–516.
- [23] J. Yang Lim, J. McGregor, A.J. Sederman, J.S. Dennis, Kinetic studies of CO₂ methanation over a Ni/γ-Al₂O₃ catalyst using a batch reactor, *Chemical Engineering Science*, 141 (2016) 28–45.

Three-pipeline Gas Grid for Renewable Hydrogen Storage and Distribution: Integrated Power-to-gas/gas-to-power Conversion with Closed-loop Carbon Utilization

I. Rossetti^{1*}, M. Tommasi¹, S. Romegialli¹, W. Da Silva Cardoso¹, A. Gramegna¹, G. Ramis²

¹Department of Chemistry, Università degli Studi di Milano, Milan, Italy; ²DICCA, Università degli Studi di Genova, Genoa, Italy

Abstract

Renewable hydrogen can decarbonize energy conversion, but its large-scale deployment remains constrained by storage, transport and infrastructure requirements. This work develops and validates an integrated power-to-gas/gas-to-power (P2G/G2P) route in which electrolytic H₂ is converted with recovered CO₂ into synthetic methane and subsequently reconverted into electricity and heat. A novel three-pipeline gas-grid (3PGG) architecture couples the existing methane network with dedicated O₂ and CO₂ lines, enabling valorization of the oxygen co-produced by electrolysis and closed-loop carbon circulation. The concept was investigated from functional materials to integrated energy systems. Reversible solid-oxide-cell electrodes were screened for H₂/CH₄ operation; Ni-based methanation catalysts were synthesized and tested; CO₂-diluted oxy-fuel combustion was analysed experimentally and by computational fluid dynamics; and steady-state process, energy-management, techno-economic and life-cycle models were developed. A 36 wt% Ni/CeO₂ catalyst prepared by ultrasound-assisted coprecipitation exceeded 87% CO₂ conversion with 100% CH₄ selectivity at 325 °C. In the integrated electrolyser-methanator-SOFC demonstration, electrolytic H₂ gave approximately 89% steady-state conversion for 3 h, near-complete CH₄ selectivity, a carbon-balance deviation below 3% and a CO selectivity of approximately 0.2%. Scale-up simulations predicted 99.69% H₂/CO₂ conversion, 99.94% CH₄ selectivity and a dry product containing 98.67 mol% CH₄. The SOFC-based cycle achieved 41.4% electrical efficiency, compared with 22.2% for the oxy-fuel configuration. A 15 min energy-management system reduced representative seasonal operating costs by 30-66% with SOFC and 36-69% with an Allam/oxy-combustion route relative to the non-integrated case. Multi-objective optimization showed that P2G and inter-node CO₂/O₂ exchange become valuable as renewable penetration and decarbonization constraints increase. Life-cycle greenhouse-gas emissions for synthetic methane were 9.9 and 34.8 g CO_{2-eq} MJ⁻¹ (HHV, GWP100) when hydrogen was produced from wind and photovoltaic electricity, respectively. Wind-based methane met a direct 70% reduction threshold relative to the 94 g CO_{2-eq} MJ⁻¹ fossil comparator, whereas the photovoltaic case requires reconciliation with the regulatory accounting methodology adopted in the project. The results demonstrate technical and environmental feasibility while identifying electricity supply, electrolyser capital cost, round-trip efficiency and component durability as the principal levers for commercial deployment.

1. Introduction

The deep decarbonization of electricity, industry, buildings and transport requires energy carriers that connect variable renewable generation with long-duration storage and geographically distributed demand. Hydrogen produced by water electrolysis is attractive because it can couple the electricity system to fuels and chemical production. Nevertheless, direct hydrogen storage and delivery are limited by its low volumetric energy density, compression or liquefaction penalties, materials compatibility, safety constraints and the slow development of dedicated transport infrastructure [1-4]. These barriers are particularly important when hydrogen must be stored seasonally or supplied to users that already rely on gaseous fuels.

Power-to-methane offers a complementary route. Renewable electricity is first converted into H₂, which reacts with captured CO₂ through the Sabatier reaction ($\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$).

Synthetic methane can be stored and transported using mature natural-gas assets, while its carbon intensity depends primarily on the origin of electricity and CO₂ and on the recovery of process heat [5-8]. Methanation is thermodynamically favoured at low temperature and elevated pressure, but kinetics, heat removal and suppression of the reverse water-gas-shift reaction must be addressed. Nickel catalysts are widely considered because they combine high activity and methane selectivity with markedly lower cost than noble metals; support chemistry, Ni dispersion and oxygen-vacancy mobility strongly affect low-temperature performance and resistance to coking or sintering [6-9].

Conventional power-to-gas studies commonly stop at methane synthesis or assume open-loop combustion. Here, the central hypothesis is that hydrogen-derived methane can serve as a transitional storage vector without releasing the recycled carbon to the atmosphere. The proposed three-pipeline gas grid (3PGG) retains the existing CH₄ line and adds two lower-capacity lines for CO₂ and O₂. CO₂ collected from gas-to-power units or point sources is returned to methanation, while O₂ co-produced by electrolysis supports oxy-fuel conversion. After combustion, the exhaust mainly contains CO₂ and H₂O; water condensation yields a concentrated CO₂ stream suitable for recycling. Alternatively, methane is electrochemically oxidized in an intermediate-temperature solid oxide fuel cell (SOFC), again enabling CO₂ recovery after water removal. The architecture therefore links electricity, methane and industrial carbon flows rather than treating them as independent networks.

The concept presents several scientific and engineering questions. Reversible solid oxide cells require electrodes and electrolytes that remain active under alternating oxidizing and reducing environments and tolerate methane without severe carbon deposition. The highly exothermic methanator must combine high conversion, near-quantitative methane selectivity and stable temperature control. Oxy-fuel flames diluted with recycled CO₂ require operating windows that avoid both blowout and flashback. Finally, a technically viable chain may still be economically unattractive if renewable electricity, electrolyser capacity, storage or conversion equipment are poorly dispatched. These interactions demand experimental validation, process simulation, optimal energy management and life-cycle assessment within a common boundary.

The present work reports the principal outcomes of the a project, which integrated laboratory experiments below 1 kW with models for pilot systems (10-100 kW) and commercially relevant islanded systems up to approximately 16 MW. The work spans eight coordinated research objectives: materials and reversible cells; methanation; oxy-fuel combustion; steady-state modelling; multi-carrier energy management; multi-objective system optimization; and techno-economic and environmental assessment. Rather than presenting these activities independently, this paper examines how evidence propagates through the full P2G/G2P chain.

The contribution is threefold. First, it provides experimental evidence for low-temperature Ni/CeO₂ methanation and for an integrated electrolyser-methanator-SOFC laboratory chain. Second, it quantifies alternative G2P routes and the operational value of coordinating electricity, methane, oxygen and carbon dioxide through a 15 min energy-management system. Third, it combines process scale-up, economic analysis and LCA to identify where the 3PGG concept is already robust and where further development is required. This integrated perspective is relevant to resilient carbon-carrier supply because it uses existing gas infrastructure, converts curtailed renewable electricity into a storable molecule and treats captured CO₂ as a circulating resource rather than a terminal waste stream.

A critical distinction is made between carbon circularity at plant level and climate neutrality over the life cycle. Recycling CO₂ within an islanded network can nearly eliminate direct process emissions, but upstream emissions from renewable-power equipment, electrolyser manufacture, catalyst and infrastructure production remain. For this reason, the environmental assessment reports GWP over 20, 100 and 500 years and compares wind- and photovoltaic-powered hydrogen. The system is benchmarked against the European requirement of a 70% life-cycle greenhouse-gas reduction for renewable fuels of non-biological origin relative to a fossil comparator of 94 g CO_{2-eq} MJ⁻¹ [10, 11].

The analysis also recognizes that round-trip electrical efficiency is not the only system

objective. Molecule-based storage can provide duration, capacity and compatibility that electrochemical batteries may not provide economically at seasonal scale. Likewise, a configuration with lower conversion efficiency can sometimes reduce operating cost if it exploits price differences, minimum-load constraints, heat demand, storage state and renewable surplus more effectively. Consequently, efficiency, cost, emissions and broader environmental damage are treated as distinct metrics rather than collapsed into a single indicator.

The sections below describe the multiscale experimental and modelling methodology, followed by a discussion organized around materials-to-device validation, methane synthesis and integration, oxy-fuel conversion, system operation, scale-up economics and environmental performance. Numerical values are reported using the common bases adopted in the project, economic results should therefore be interpreted as comparative design indicators rather than firm quotations for a commercial plant.

2. Experimental and modelling methods

2.1 Reversible solid oxide materials and cell testing

Electrolytes and fuel electrodes were designed for reversible SOFC/SOEC operation at intermediate temperature. Rare-earth-doped (RE) ceria solid solutions, $\text{Ce}_{1-x}\text{RE}_x\text{O}_{2-x/2}$, were investigated together with $\text{RE}_2\text{Zr}_2\text{O}_7$ pyrochlores. $\text{Gd}_2\text{Zr}_2\text{O}_7$ was synthesized by sol-gel processing and sintered at 900 or 1500 °C. Ionic transport was measured by impedance spectroscopy from 0.1 Hz to 1 MHz. Fuel-electrode families included $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC), Pd/CuO-GDC nanocomposites containing 0.5-3 wt% Pd, titanate and ferrite perovskites, and double perovskites tested between 500 and 850 °C. Compatibility was assessed by mixing candidate electrodes with LSGM, YSZ or GDC electrolytes (50:50), calcining at 1200 °C and examining phase retention and electrochemical response.

Button cells were produced from 2.5 g powder pellets, 25 mm in diameter, pressed at 4 t for LSGM or 3.5 t for GDC and sintered at 1500 °C for 8 h; electrodes were deposited by tape casting. Laboratory cells had an active order of area of 300 mm². Open-circuit potential, polarization, power and area-specific resistance (ASR) were recorded in H₂, CH₄ and their mixtures. Carbon formation and redox behaviour were studied by in-situ Raman spectroscopy. Synchrotron experiments followed the Ni oxidation state in Ni/YSZ and Ni/GDC|GDC under Ar, H₂ and H₂O+CO₂ co-electrolysis conditions.

2.2 Catalyst synthesis, characterization and methanation tests

A library of Ni catalysts was prepared on Al₂O₃, TiO₂, SiO₂, CeO₂, ZrO₂ and zeolite ZSM-5 using wet impregnation, sol-gel and conventional or ultrasound-assisted coprecipitation. Metal loading ranged from 6 to 94 wt%. Fresh and spent samples were characterized by N₂ physisorption, FT-IR, UV-Vis diffuse-reflectance spectroscopy, Raman spectroscopy, SEM-EDX, powder X-ray diffraction, XPS and temperature-programmed reduction. These methods were combined to relate NiO crystallite size, surface area, metal-support interaction, reducibility and ceria oxygen vacancies to catalytic performance.

Fixed-bed continuous testing quantified CO₂ conversion and CH₄/CO selectivity as functions of temperature, pressure up to 10 bar, space velocity (Qt/W) and H₂/CO₂ ratio. The stoichiometric ratio H₂/CO₂ = 4 was selected as the reference to minimize hydrogen excess. Stability tests used 200 mg catalyst, a concentrated undiluted feed, Qt/W = 60,000 mL g⁻¹ h⁻¹ and atmospheric pressure. The selected 36 wt% Ni-CeO₂ catalyst was subjected to thermal excursions and prolonged time-on-stream testing; steam co-feeding was evaluated as an approach to limit hot spots.

2.3 Integrated EC-MET-SOFC laboratory demonstrator

The laboratory P2G/G2P demonstrator connected a Titan EZ-300 PEM water-electrolysis stack to the methanator and to a bench-scale SOFC. The single electrolysis cell had a total

diameter of 138 mm, an 80 mm active-area dimension, approximately 2 V direct-current supply, a maximum current of 40 A and a maximum H₂ flow near 300 mL min⁻¹. Tests were conducted at atmospheric pressure. Methanation at 325 °C was compared using hydrogen produced in situ. Reactor temperatures, gas composition, carbon balance and CO formation were monitored. The methanator product then fed the SOFC in replicated tests between 650 and 850 °C.

2.4 Oxy-fuel combustion experiments and CFD

Two oxy-fuel configurations were studied. A hot-coflow diffusion flame used a 4.25 mm central nozzle supplied with 50 vol% CH₄/50 vol% H₂ and an 82 mm inner-diameter annular coflow at 3.2 m s⁻¹. Oxygen mass fractions of 3, 6 and 9% were considered in CO₂-rich coflow. Mesh independence was evaluated with approximately 50,000, 100,000 and 150,000 cells and local refinements of 0.005, 0.0028 and 0.002 m. DRM19 (19 species, 84 reactions) and GRI-Mech (53 species, 325 reactions) were compared.

A swirl-stabilized premixed CH₄/O₂/CO₂ flame was modelled using a 55° vane swirler, a converging-diverging duct with 30°/45° angles, a 2 cm throat, a 28° axial cone and 5.2 m s⁻¹ bulk throat velocity. Chemical mechanisms, P1 radiation, k- ω BSL and calibrated k- ϵ turbulence closures were tested. Equivalence ratio Φ and oxygen fraction OF were varied to identify blowout and flashback limits. Experiments employed tangentially fed cyclone-type swirlers and controlled CH₄/O₂/CO₂ flows. Planar OH laser-induced fluorescence used a 1064 nm Nd:YAG laser (about 850 mJ pulse⁻¹, up to 10 Hz), frequency doubling to 532 nm, a Rhodamine-590 dye laser and approximately 283 nm ultraviolet excitation.

2.5 Steady-state process modelling, EMS and optimization

Mass and energy balance models for alkaline electrolysis (AEC), Sabatier methanation and SOFC conversion were implemented in MATLAB. The AEC block was validated against 80 °C voltage-current curves for a 0.5 kW high-pressure alkaline electrolyser. The reference P2G case used 1 MW renewable input, 30 bar, 80 °C and 100 m² total AEC active area, corresponding to two modules of 25 cells with 2 m² per cell. Reactor temperature and pressure were varied to locate the integrated efficiency optimum.

At system level, an energy-management system represented component input-output relations and coordinated the electric grid, P2G, G2P, methane storage and the CH₄/O₂/CO₂ network. A daily horizon with 15 min intervals was solved as a constrained mixed-integer nonlinear programming problem. The objective included grid-electricity purchases, natural-gas purchases, electricity-sale revenue and, for the Allam/oxy-combustion route, start-up and shutdown penalties. Minimum load, ramping and minimum up/down-time constraints were applied where appropriate. Three arrangements were compared for a hospital-scale case: a non-integrated baseline, configuration A with SOFC G2P, and configuration B with an Allam/oxy-combustion G2P block.

Multi-objective models were applied at district, city and national scales. Four representative seasonal days were derived from multi-year hourly data. Sensitivity analyses varied battery capital cost and self-discharge, natural-gas price and CO₂ constraints. Objectives included annualized cost, direct greenhouse-gas emissions and total environmental damage calculated with ReCiPe. This distinction allowed the optimization to reveal whether a pathway that minimizes operational CO₂ also reduces life-cycle damage.

2.6 Techno-economic analysis and life-cycle assessment

Integrated process cases were scaled to approximately 16 MW net electricity. A 25 year project life and 8,000 h year⁻¹ operation were adopted for economic indicators. Capital and operating expenditures were estimated by process block, and levelized costs were calculated for hydrogen (LCOH), methane (LCOM) and electricity. LCA was performed in SimaPro using Ecoinvent 3.0 consequential datasets, the adapted EF 3.0 method and Italian wind and photovoltaic electricity cases. GWP20, GWP100 and GWP500 were calculated for hydrogen

and synthetic methane. Methane intensities were reported on higher- and lower-heating-value bases; Rankine-cycle heat valorization was excluded from the conservative fuel-production comparison.

3. Results and discussion

3.1 From functional materials to reversible solid oxide cells

The materials campaign confirmed that electrolyte densification and electrode-electrolyte compatibility were as important as nominal composition. $\text{Gd}_2\text{Zr}_2\text{O}_7$ sintered at 900 °C remained too resistive for the available instrument range because of insufficient densification. Replicate pellets sintered at 1500 °C exhibited thermally activated ionic transport with a constant activation energy of 1.12 eV (108 kJ mol⁻¹), within the 0.85-1.52 eV interval reported for GZO pyrochlores. This result validates the conduction mechanism but also shows that high-temperature processing remains necessary for dense pyrochlore electrolytes.

Among the fuel-electrode candidates, $\text{La}_{0.8}\text{Sr}_{0.1}\text{Fe}_{0.5-x}\text{Cr}_{0.5}\text{M}_{0.1}\text{O}_3$ (M = Ni or Cu) delivered the most promising overall response and operated in both SOFC and SOEC modes. Compatibility tests gave a clear materials-selection rule. GDC retained compatibility and was selected as the preferred electrolyte. Synchrotron measurements further showed that Ni in Ni/YSZ re-oxidized under $\text{H}_2\text{O}+\text{CO}_2$ co-electrolysis, whereas Ni in Ni/GDC|GDC did not. The redox-buffering capacity of GDC therefore appears decisive for maintaining metallic active sites during reversible operation.

The most representative results are summarised in Table 1. Pd loading produced a measurable improvement in methane-fed button cells. At 650 °C and 50% CH_4 , the 1% Pd electrode had $\text{ASR} = 16.5 \text{ } \Omega \text{ cm}^2$ without useful power or open-circuit potential, whereas 2% Pd lowered ASR to $11.1 \text{ } \Omega \text{ cm}^2$ and to $9.9 \text{ } \Omega \text{ cm}^2$ after one day, while producing 38 mW at OCP = 0.83 V. In H_2 , the 2 wt% Pd/Cu@GDC-GDC-LSCF cell yielded reproducible OCP/power pairs of 0.980 V/14 mW at 500 °C and 0.960 V/26 mW at 550 °C; repeats gave 0.978 V/14 mW and 0.956 V/27 mW. Raman spectra showed loss of CuO and PdO bands upon exposure to methane, consistent with in-situ reduction. Absolute performance was limited by the thick, electrolyte-supported button-cell architecture, but the composition trend and repeatability provide a reliable basis for thinner supported designs.

Table 1. Representative reversible-cell results.

Condition	OCP / V	Power / mW	ASR / $\Omega \text{ cm}^2$
1% Pd, 50% CH_4 , 650 °C	not useful	0	16.5
2% Pd, 50% CH_4 , 650 °C	0.83	38	11.1 → 9.9
2% Pd, H_2 , 500 °C	0.980	14	-
2% Pd, H_2 , 550 °C	0.960	26	-

The device results should be interpreted as proof of materials compatibility rather than a claim of commercial power density. This work nevertheless established a complete experimental chain from phase screening and operando redox analysis to functioning cells.

3.2 Low-temperature CO₂ methanation and integrated laboratory validation

Catalyst screening (Table 2) demonstrated that the ceria-supported formulations shifted high methane yield to lower temperature. Reference 36 wt% Ni/Al₂O₃ and Ni/TiO₂ catalysts reached 81% conversion/99% CH₄ selectivity at 403 °C and 80%/97% at 408 °C, respectively. A 36 wt% Ni-CeO₂ sol-gel catalyst reached 86% conversion with approximately 100% CH₄ selectivity at only 345 °C. Ultrasound-assisted coprecipitation improved this result further: 36 wt% Ni/CeO₂ (US) exceeded 87% conversion with 100% selectivity at 325 °C. The trend is consistent with improved Ni dispersion and the ability of ceria oxygen vacancies to activate CO₂ and remove carbonaceous intermediates [9].

Table 2. Performance of selected Ni methanation catalysts.

Catalyst	Temperature / °C	CO ₂ conversion / %	CH ₄ selectivity / %
36 wt% Ni/Al ₂ O ₃ CN	403	81	99
36 wt% Ni/TiO ₂ P25	408	80	97
36 wt% Ni-CeO ₂ SG	345	86	≈100
36 wt% Ni/CeO ₂ US	325	>87	100

Under the more demanding undiluted stability conditions, the selected catalyst maintained approximately 57% conversion at 350 °C without a progressive decline. Activity recovered after overheating cycles, and spent-sample characterization did not indicate substantial irreversible structural change. The lower conversion relative to diluted screening is expected from the larger heat and mass-transfer burden and does not contradict the intrinsic ranking. Steam addition reduced thermal severity and was therefore retained as a practical hot-spot-control option, although excessive steam would impose condensation and recycle penalties.

The integrated EC-MET-SOFC experiment was the most direct validation of the proposed P2G/G2P logic. With electrolyser-produced hydrogen, the 325 °C methanator showed only an approximately 5 °C hot spot and maintained about 89% conversion for 3 h. Methane selectivity was close to 100%, CO selectivity was about 0.2% and the carbon-balance deviation remained below 3%. The methane-rich effluent directly supplied the SOFC. At 850 °C and an H₂ flow of 72 mL min⁻¹, the cell reached a maximum power density of 36 mW cm⁻². The experiment achieved TRL 4 by demonstrating that the individual blocks can operate with real inter-stage streams, not merely with bottled surrogate mixtures.

The remaining scale-up challenge is thermal management. Because the Sabatier reaction is highly exothermic, increasing diameter or catalyst inventory can create temperature gradients that promote CO formation, Ni sintering and equilibrium loss. The system model addressed this through pressure, reactor geometry, steam dilution and heat recovery. In the 0.2 m diameter, 5 m long reactor case (50 kmol h⁻¹, 20% CO₂/80% H₂, GHSV 7,130 h⁻¹), conversion rose from 88.7% at 20 bar/320 °C to 96.1% at 20 bar/370 °C and 96.6% at 30 bar/370 °C. Pressure improved conversion, but benefits beyond 15-30 bar were limited relative to the influence of temperature.

3.3 Oxy-fuel operating window and G2P configuration

The diffusion-flame CFD study identified a reduced chemistry model suitable for engineering calculations. A mesh of approximately 100,000 elements reproduced the solution obtained with 150,000 cells at lower computational cost. DRM19 provided a more favourable accuracy-cost balance than the larger GRI-Mech mechanism. Increasing CO₂ dilution broadened the reactive zone and lowered peak temperature, while a stable diffusion flame was predicted even with up to 92 wt% CO₂ in the coflow. This tolerance is central to the 3PGG concept because recycled CO₂ is both the carbon carrier and the thermal diluent.

For the premixed swirl flame, the Hu mechanism combined with P1 radiation and k- ω BSL turbulence gave the best agreement. At 60% O₂, Φ was varied from 0.2 to 0.6; the flame remained stable at $\Phi = 0.2$ and extinguished below $\Phi = 0.191$. At $\Phi = 0.5$, OF = 45% approached blowout whereas OF = 55% approached flashback. The selected lean operating point, OF = 0.55 and $\Phi = 0.5$, therefore balances stability and temperature. OH-LIF experiments supported the simulated changes in reaction-zone position and extent when Φ or oxygen fraction was varied.

These results were translated into an oxy-fuel-plus-Organic Rankine Cycle architecture. Compared with a microturbine or conventional internal-combustion engine, the selected layout offers concentrated CO₂ recovery and very low NO_x formation. High-temperature ORC units can reach net efficiencies near 25% for exhaust above 400 °C, although a conservative efficiency of 0.15 was adopted for preliminary 5 MW net-electric sizing, together with combustion efficiency 0.975, a 0.95 design margin and heat-exchanger efficiency 0.75. The CFD operating window supplies the combustion constraints required for reliable plant-level optimization (Table 3).

The comparison with SOFC illustrates a recurring trade-off. Oxy-combustion has lower round-trip efficiency, but potentially simpler fuel flexibility, larger unit sizes and concentrated CO₂ capture. SOFC offers higher electrical efficiency and modularity but currently faces higher stack cost, thermal cycling constraints and durability requirements. The 3PGG architecture can accommodate both, allowing the optimum choice to depend on scale, heat demand, electricity prices and operational flexibility rather than on a single conversion metric.

Table 3. Validated oxy-fuel modelling choices and stability indicators.

Item	Selected result
Diffusion-flame mesh	≈100,000 cells
Diffusion chemistry	DRM19: 19 species, 84 reactions
Maximum stable CO ₂ -rich coflow	up to 92 wt% CO ₂
Premixed model	Hu chemistry + P1 + k- ω BSL
Lean stability limit at 60% O ₂	blowout below $\Phi = 0.191$
Selected operating point	OF = 0.55; $\Phi = 0.50$

3.4 Steady-state integration and scale-up performance

The 1 MW AEC-MET model located the optimal Sabatier temperature between 340 and 380 °C. At the 345 °C design point, 100 m² of AEC active area operated at 0.53 A cm⁻² and the first-law P2G efficiency was 53.8%. The energy balance assigned 28.6% of input power to electrolyser heat dissipation and 11.1% to Sabatier heat. This decomposition shows why heat integration and higher-temperature electrolysis are important: SOEC development could potentially reduce losses by 10-15% relative to AEC or PEM electrolysis, provided durability and cycling are solved.

Commercial-scale integration was evaluated for a net-electric target near 16 MW (Table 4). In the SOFC case, 38.66 MW renewable electricity produced 445 kmol h⁻¹ H₂ and 111 kmol h⁻¹ CH₄. The SOFC delivered 14.80 MW and the Rankine bottoming cycle 1.20 MW using 724 kmol h⁻¹ steam at 15 bar, giving 41.4% overall electrical efficiency. In the OFC case, 71.98 MW renewable input generated 828 kmol h⁻¹ H₂ and 206 kmol h⁻¹ CH₄; oxy-fuel conversion produced 10.74 MW and the Rankine cycle 5.26 MW using 3,167 kmol h⁻¹ steam, for 22.2% efficiency.

The scaled methanation section operated at 15 bar with 99.69% H₂/CO₂ conversion and 99.94% methane selectivity. A catalyst inventory of 743.79 kg produced 110.71 kmol h⁻¹ CH₄. After dehydration, the gas contained 98.67 mol% CH₄, 0.09% CO₂, 1.22% H₂ and 0.01% H₂O, with no CO predicted. This composition is suitable for considering injection into a natural-gas distribution line, although final compliance must be checked against the applicable national grid specification and measurement basis.

Table 4. Integrated 16 MW-scale process results.

Metric	SOFC route	OFC route
Renewable electricity input / MW	38.66	71.98
H ₂ production / kmol h ⁻¹	445	828
CH ₄ production / kmol h ⁻¹	111	206
Primary G2P output / MW	14.80	10.74
Rankine output / MW	1.20	5.26
Overall electrical efficiency / %	41.4	22.2

The SOFC route requires almost half the renewable input for the same net-electric output and is therefore preferred when electricity efficiency dominates. The OFC route rejects more recoverable heat, making its relative position more favourable in cogeneration applications. Both cases reveal that the methanator itself can reach pipeline-quality performance; the system penalty is governed primarily by electrolysis and G2P conversion, not by methane selectivity. Consequently, development priorities should emphasize low-cost electrolyzers, heat recovery, SOFC lifetime and flexible operation rather than marginal increases in already near-quantitative methane purity.

3.5 Energy management and the operational value of sector coupling

The 15 min EMS (Table 5) demonstrated that integrated conversion can lower operating expenditure even when round-trip efficiency is imperfect. Baseline costs for the representative winter, spring, summer and autumn days were €7,131.7, €4,383.7, €3,443.4 and €5,918.8. Configuration A (SOFC) reduced them to €4,982.0, €2,676.0, €1,178.1 and €3,816.4, corresponding to reductions of approximately 30%, 39%, 66% and 36%. Configuration B (Allam/oxy-combustion) achieved €4,571.9, €2,163.9, €1,061.2 and €3,508.0, or 36%, 51%, 69% and 41% reductions.

Table 5. EMS operating cost for representative seasonal days.

Season	Baseline / €	SOFC / €	Reduction / %	Allam-OFC / €	Reduction / %
Winter	7,131.7	4,982.0	30	4,571.9	36
Spring	4,383.7	2,676.0	39	2,163.9	51
Summer	3,443.4	1,178.1	66	1,061.2	69
Autumn	5,918.8	3,816.4	36	3,508.0	41

In configuration A, grid-electricity purchases fell to zero in all four simulated days; operating cost was entirely associated with methane purchase. The EMS kept the SOFC running because its slow thermal dynamics and the gas/electricity price relationship made steady conversion preferable. In configuration B, the Allam block remained at its 40% minimum load because shutdown was uneconomic. Summer photovoltaic production then created a small surplus: €11.68 of electricity-sale revenue compared with €2.35 of purchased electricity. The electrolyser operated in every season except winter; in spring and summer, internally produced methane was stored and later dispatched.

These patterns show that the principal benefit was avoided electricity purchase, not export revenue. The integrated cases bought more methane, but the additional gas cost was lower than the avoided grid-electricity cost. The result is case-specific and depends on tariff assumptions, yet it demonstrates the operational mechanism by which a multi-carrier network creates value. Storage and conversion need not be used continuously; they should respond to renewable availability, load, price and component constraints.

At city scale, the unconstrained renewable-expansion case activated P2G to absorb summer photovoltaic surplus and transported CO₂ from an industrial furnace to methanators. The reference CITY-S0 case achieved only about 11% emission reduction at an annualized cost of €64.5 million and did not exchange O₂ or CO₂ between nodes. CITY-UC achieved 26.6% emission reduction. With a 40% decarbonization constraint ($\epsilon = 0.60$), electricity imports nearly halved from 61.1 to 33.8 GWh year⁻¹, a 5 MW ICE-OFC operated much of the year and an inter-node O₂ line of 175.3 m³ h⁻¹ was selected. Thus the additional pipelines acquire value only when the optimization has sufficient renewable surplus and a meaningful carbon constraint.

3.6 Multi-objective transition pathways, economics and LCA

The national-scale optimization separated the transition into three stages. Renewable electricity and heat pumps first decarbonized electricity and low-temperature heat. Above approximately 60% renewable penetration, synthetic methane became advantageous for high-temperature heat and seasonal storage of summer solar generation. This stage ended near 80%, when the gas network was saturated with synthetic methane and electricity plus low- and high-temperature heat were largely decarbonized. Transport conversion dominated the final stage.

The endpoint depended on the environmental objective. When cost and direct CO₂ emissions were minimized, complete decarbonization was technically achievable through extensive electrification of transport, but the marginal cost of removing the last 15% of emissions increased sharply. When cost and total ReCiPe damage were optimized, renewable penetration stopped near 85% and transport was not fully converted. In that formulation, life-cycle burdens of additional electric vehicles or e-fuels outweighed the damage avoided by replacing the remaining fossil fleet. This does not imply that fossil transport is intrinsically preferable; rather, it illustrates that technology inventories, system boundaries and environmental indicators materially influence the optimized pathway.

Economic scale-up identified electrolysis as the dominant cost centre. For 25 years and 8,000 h year⁻¹, the alkaline-electrolysis block had an estimated CAPEX of €198 million and annual OPEX of €16 million, yielding LCOH = €190 MWh⁻¹. Installed methanation equipment cost was €6.6 million with €5 million year⁻¹ OPEX and LCOM = €66 MWh⁻¹, compared with a project reference fossil-gas commodity range of €30-60 MWh⁻¹. For methane production alone, the estimated minimum selling price fell from €86.5 MWh⁻¹ in a 2024 scenario to €63.1 MWh⁻¹ in 2030 and €45.2 MWh⁻¹ in 2050, mainly through assumed hydrogen-cost reduction.

The SOFC reference stack cost was €4,711 kWh⁻¹; electricity production through the SOFC was estimated at €95.1 MWh⁻¹. The 15 MW oxy-fuel combustion/turbine section had CAPEX of approximately €17.0 million, while the complete integrated OFC route reached €479.69 MWh⁻¹. The latter is not currently competitive with the project reference range of €60-225 MWh⁻¹ for photovoltaic generation plus batteries. However, the comparison does not capture all services: very long storage duration, carbon circulation, oxygen valorization, heat and network resilience. Those services should be monetized explicitly in future business cases rather than treated as qualitative co-benefits.

LCA (Table 6) confirmed that electricity origin controls climate performance. For hydrogen alone, wind electricity gave GWP20/GWP100/GWP500 values of 1.24/1.07/1.00 t CO_{2-eq} t⁻¹ H₂, below the 3 t CO_{2-eq} t⁻¹ H₂ target. Photovoltaic electricity gave 4.46/3.81/3.57 t CO_{2-eq} t⁻¹ H₂, exceeding that hydrogen-specific threshold on the adopted inventory. After methanation, the synthetic-fuel comparison was favourable for both sources. Wind-based methane yielded GWP100 = 9.9 g CO_{2-eq} MJ⁻¹ HHV (11.0 on an LHV basis), whereas photovoltaic-based methane yielded 34.8 g CO_{2-eq} MJ⁻¹ HHV (38.6 LHV). Both are below 28.2 g CO_{2-eq} MJ⁻¹ only in the wind case if the strict 70% reduction is calculated directly from 94 g; however, the project report assessed all considered synthetic-methane scenarios as compliant under its applied methodology and boundaries. This sensitivity deserves transparent reconciliation before regulatory certification.

Table 6. Life-cycle greenhouse-gas results reported by the project.

Energy source / product	GWP horizon	Result
Wind H ₂	100 y	1.07 t CO _{2-eq} t ⁻¹ H ₂
PV H ₂	100 y	3.81 t CO _{2-eq} t ⁻¹ H ₂
Wind CH ₄ , HHV / LHV	100 y	9.9 / 11.0 g CO _{2-eq} MJ ⁻¹
PV CH ₄ , HHV / LHV	100 y	34.8 / 38.6 g CO _{2-eq} MJ ⁻¹

The apparent discrepancy between the numerical photovoltaic methane intensity and a direct 70%-reduction threshold illustrates why functional unit, energy basis, allocation, CO₂ accounting and regulatory methodology must be reported explicitly. It does not alter the robust ranking: wind-powered electrolysis delivered the lowest impacts, photovoltaic electricity remained substantially below the fossil comparator, and heat recovery—excluded from the conservative fuel-only LCA—could further improve the integrated cycle. Future work should update Ecoinvent inventories, distinguish attributional and consequential decisions, include pipeline construction and leakage, and test alternative sources of captured CO₂.

4. Conclusions

An integrated P2G/G2P system with a three-pipeline CH₄/O₂/CO₂ grid was developed from functional materials to commercial-scale models. The experimental programme established GDC-compatible reversible solid-oxide electrodes, quantified the effect of Pd loading in methane-fed cells and demonstrated stable low-temperature methanation over 36 wt% Ni/CeO₂. The integrated electrolyser-methanator-SOFC apparatus converted electrolytic hydrogen at approximately 89% for 3 h with near-complete methane selectivity and low CO formation, providing laboratory proof of the closed conversion chain.

Validated oxy-fuel CFD and OH-LIF experiments defined CO₂ dilution and stability limits, including a selected lean premixed point at OF = 0.55 and Φ = 0.50. Scale-up simulations predicted 99.69% methanation conversion and a dry gas containing 98.67 mol% CH₄. For approximately 16 MW net output, the SOFC route achieved 41.4% electrical efficiency and clearly outperformed the 22.2% OFC route, whereas the latter retained advantages in concentrated CO₂ capture, heat availability and potential large-scale implementation.

System coordination was as important as component efficiency. The EMS reduced representative seasonal operating costs by 30-66% with SOFC and 36-69% with Allam/oxy-combustion by substituting dispatchable gas conversion and stored synthetic methane for grid-electricity purchases. City and national optimizations showed that inter-node CO₂/O₂ exchange and power-to-methane become increasingly valuable when renewable surplus, high-temperature heat and stringent decarbonization constraints are considered.

The main barriers are economic and durability-related rather than fundamental methane chemistry. Electrolysis dominated both energy losses and cost; SOFC stack cost and lifetime remain critical; and the complete OFC pathway was not competitive with the adopted photovoltaic-plus-battery benchmark. LCA showed a strong dependence on electricity supply, with GWP100 methane intensities of 9.9 g CO_{2-eq} MJ⁻¹ HHV for wind and 34.8 for photovoltaic electricity. Regulatory compliance should be confirmed using a harmonized functional unit and accounting method.

Overall, the 3PGG concept is technically credible as a circular infrastructure strategy that exploits existing methane assets while enabling renewable-hydrogen storage, oxygen valorization and recoverable CO₂ circulation. The next step should be a 10-100 kW pilot integrating dynamic operation, heat recovery, methane storage and measured pipeline-grade composition, followed by long-duration catalyst and SOFC testing. Demonstration should be accompanied by updated techno-economic and consequential LCA models that value resilience, long-duration storage and avoided carbon-transport costs.

Acknowledgements

The authors gratefully acknowledge the Italian Ministry of Environment and Energy Sustainability (MASE, formerly MITE) for funding the project “RSH2A_000018 - Stoccaggio e distribuzione di idrogeno attraverso una strategia power-to-gas/gas-to-power con cattura ed utilizzo completi del carbonio - Hydrogen storage and distribution through power-to-gas strategy, with full carbon capture and utilization-CUP: F57G25000180006” in the frame the European Union Next-GenerationEU, Piano Nazionale di Ripresa e Resilienza (PNRR) – Missione 2 “Rivoluzione verde e transizione ecologica”, Componente 2 “Energia rinnovabile,

idrogeno, rete e mobilità sostenibile”, Investimento 3.5 “Ricerca e sviluppo sull'idrogeno” (bando A).

All the colleagues from the University of Genoa, Milan and Padua (ca. 40 people) involved in the collection and elaboration of the present data are gratefully acknowledged.

References

- [1] A. International Energy, Global Hydrogen Review 2024, IEA, 2024.
- [2] A. Züttel, Hydrogen storage methods, *Naturwissenschaften*, 91 (2004) 157–172.
- [3] A. Buttler, H. Spliethoff, Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review, *Renew Sust Energ Rev*, 82 (2018) 2440–2454.
- [4] M. Thema, F. Bauer, M. Sterner, Power-to-Gas: Electrolysis and methanation status review, *Renew Sust Energ Rev*, 112 (2019) 775–787.
- [5] M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, Renewable Power-to-Gas: A technological and economic review, *Renewable Energy*, 85 (2016) 1371–1390.
- [6] K. Stangeland, D. Kalai, H.L. Li, Z.X. Yu, CO methanation: the effect of catalysts and reaction conditions, *Enrgy Proced*, 105 (2017) 2022–2027.
- [7] J.J. Gao, Q. Liu, F.N. Gu, B. Liu, Z.Y. Zhong, F.B. Su, Recent advances in methanation catalysts for the production of synthetic natural gas, *Rsc Advances*, 5 (2015) 22759–22776.
- [8] S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz, J. Lefebvre, P. Prabhakaran, S. Bajohr, Review on methanation – From fundamentals to current projects, *Fuel*, 166 (2016) 276–296.
- [9] M. Tommasi, L. Rotasperti, A. Gramegna, A. Di Michele, M. Galloni, E. Falletta, F. Galli, C. Hammond, G. Ramis, I. Rossetti, Ni/Al₂O₃ and Ni/TiO₂ catalysts for CO₂ methanation: structure-performance relationship and optimization, *Appl. Catal. A*, submitted.
- [10] Commission Delegated Regulation (EU) 2023/1185, Official Journal of the European Union, 2023.
- [11] Directive (EU) 2018/2001 on the promotion of the use of energy from renewable sources, Official Journal of the European Union, 2018.

Power2ValueChemicals – Integrated Process Development for Evaluating Electrolytically Produced CO from CO₂ for Industrial Applications

L. Steinwachs¹, A. Vorholt²

¹MPI for Chemical Energy Conversion, Molecular Catalysis, Mülheim an der Ruhr, Germany, ²MPI für Chemische Energiekonversion, Molekulare Katalyse, Mülheim an der Ruhr, Germany

Carbon monoxide is an essential building block in the chemical industry and is used on a large Scale. Since carbon-containing raw materials like coal, natural gas, and petroleum are to be completely eliminated from production chains as part of the defossilisation of the chemical industry, new production routes are needed to provide CO in sufficient quantities as a climate-neutral feedstock. One way to achieve this while keeping the carbon cycle closed is the co-electrolysis of carbon dioxide to CO using sustainably produced electricity.

As part of the Power2ValueChemicals project, the Forschungszentrum Jülich plans the installation and continuous operation of a low-temperature CO₂-to-CO electrolyzer developed by Siemens Energy in various operating modes. In the second part of the project, the continuous conversion of the electrolysis gas through a homogeneously catalyzed methoxycarbonylation reaction will be carried out to evaluate the economic and ecological potential of the electrolysis gas for the chemical industry. For this purpose, a mini-plant will be planned and built at the Max Planck Institute for Chemical Energy Conversion.

To ensure the continuous operation of the process, an efficient method for catalyst recycling is required. Therefore, various commercially available membranes were investigated regarding their catalyst retention performance. The differing retention characteristics of the active and deactivated catalyst species were examined and taken into account during the membrane selection process.

Based on these findings, a process was designed, and a corresponding mini-plant was constructed to enable the continuous operation of the reaction using the selected membrane system for efficient catalyst recycling.

Bridging the Gap in MDI Value Chains: A Dual-Metric Evaluation of Circularity and Carbon Footprint from CO Production to MDI Synthesis

T. E. Korkut¹, A. Uguina²

¹Air Liquide Forschung und Entwicklung GmbH, Frankfurt am Main, Germany, ²Air Liquide, Frankfurt, Germany

Carbon Monoxide (CO) serves as the foundational building block for a vast array of high-value chemicals, most notably Methylene Diphenyl Diisocyanate (MDI), the essential precursor for the polyurethane industry. As the chemical sector faces increasing pressure to defossilize, the reliance on Carbon Footprint (CFP) as the sole sustainability indicator is being challenged. This research introduces a comprehensive framework that integrates a dedicated inhouse Circularity Metric alongside traditional CFP to provide a more nuanced understanding of resource management and climate impact.

The study evaluates the sustainability profile of the CO-to-MDI value chain by examining various feedstock pathways, including fossil, biogenic and recycled carbon. By utilizing a simplified in-house carbon circularity matrix, we analyze the sustainability benefits from the initial CO production stage through to the MDI intermediate. This dual-metric approach allows for the identification of "circularity-positive" pathways that may be obscured when viewing the process through a solely emission based lens.

Our findings demonstrate that while CFP identifies the immediate climate impact, the circularity metric reveals the long-term strategic value of keeping carbon within the industrial technosphere. By stopping the analysis at critical gates, such as CO production, and then extending it to complex intermediates like MDI, this research provides a strategic roadmap for the chemical and polymer industries. The resulting framework enables decision makers to prioritize technologies that offer the best balance between greenhouse gas reduction and material loop closure, ensuring a resilient transition toward a circular economy.

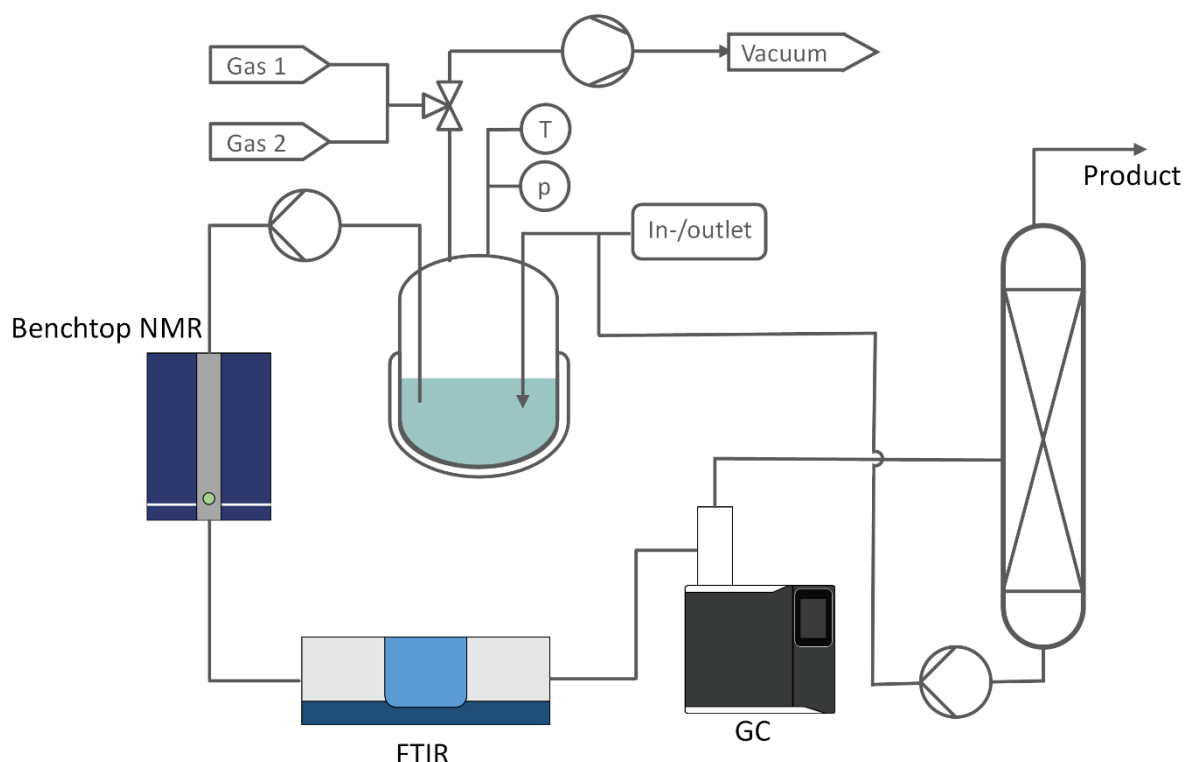
Operando Spectroscopy to Investigate Molecular Catalysts in Flow

R. Medhekar¹, A. Sobolev², M. Gerlach², C. Hamel², W. Leitner^{1,3}, A. J. Vorholt¹

¹MPI Chemical Energy Conversion, Mülheim an der Ruhr, Germany, ²Otto-von-Guericke-Universität Magdeburg, Magdeburg, Germany, ³RWTH Aachen, Aachen, Germany

High catalyst stability is an important property necessary for good catalytic performance, especially when continuous processes with physical separation steps are considered.[1] Catalyst deactivation greatly affects the catalyst performance leading to reduced conversion and selectivity. This can result in varied product streams, reduced reaction, and higher process costs, and in general a reduced process performance.[2] Studying the catalytic system and understanding the deactivation mechanisms, to then control the reaction conditions before the product quality actually declines, could result in more stable product qualities. *Operando* spectroscopy is an emerging tool for studying the catalytic system, which utilizes real-time analytical techniques, carried out under reaction conditions.[3]

In our work, *operando* spectroscopic techniques are used to investigate the catalytic cycle of hydroformylation of 1-decene, catalyzed by a Rhodium catalyst complex. For this purpose, a miniplant is set up in which the reaction mixture from the reactor is pumped through the NMR, FTIR and GC.[4]



Flowsheet of operando miniplant

With this *operando* setup, it is possible to detect unstable intermediates formed during the reaction and thus analyze the catalytic cycle. In this work, the hydroformylation of 1-decene was successfully monitored. In addition, different start-up methods were investigated to study their effect on the conversion and selectivity obtained, while simultaneously correlating these effects with the observed catalytic species. Furthermore, the effect of mass transfer limitations on the formed catalytic species, and the resulting selectivity was studied.

In addition, the effect of downstream processing, such as distillation, on the catalyst system are to be investigated, and methods for prolonging and restoring catalytic activity are to be developed and used for process control in order to obtain a stabler continuous process.

This work is funded by the Deutsche Forschungsgemeinschaft under project number 537105915.

References:

- [1] J. M. Dreimann, E. Kohls, H. F. W. Warmeling, M. Stein, L. F. Guo, M. Garland, T. N. Dinh, A.J. Vorholt, (2019), In Situ Infrared Spectroscopy as a Tool for Monitoring Molecular Catalyst for Hydroformylation in Continuous Processes, *ACS Catalysis*, 4308–4319
- [2] R. H. Crabtree, (2015), Deactivation in Homogeneous Transition Metal Catalysis: Causes, Avoidance, and Cure, *Chemical Reviews*, 127–150
- [3] K. Köhnke, N. Wessel, J. Esteban, J. Jin, A. J. Vorholt and W. Leitner, (2022), Operando monitoring of mechanisms and deactivation of molecular catalysts, *Green Chemistry*, 1951–1972
- [4] N. Wessel, R. S. Medhekar, M. Sonnenberg, H. Stieber, W. Leitner, A.J. Vorholt, (2024), Catalyst in sight: the use of Benchtop NMR spectrometers to maintain the activity of Pd-PPh₃ catalysts, *ACS Catalysis*, 10679-10688

Phosphorus-Modified Catalysts in the Dehydrogenation of n-Heptane as a Model Compound for Pyrolysis Oil Upgrading

C. Schweiger, P. Schühle

Institute of Chemical Reaction Engineering, Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen, Germany

The recycling of plastic waste is a key component in the transition towards a circular carbon economy. In particular, pyrolysis enables the conversion of complex plastic waste streams into hydrocarbon-rich feedstocks. Such pyrolysis oils typically contain significant fractions of linear mid-chain alkanes, which are energetically valuable but of limited utility as chemical intermediates [1]. In this context, catalytic dehydrogenation of n-alkanes to linear olefins represents an attractive upgrading route, since linear olefins are important platform chemicals for the production of, e.g., detergents and polymers. However, due to high temperatures required for alkane dehydrogenation, conventional Pt/Al₂O₃ catalysts are prone to deactivation caused by coke deposition and metal particle sintering. In order to tailor catalytic selectivity and improve stability, catalyst modification represents a promising approach. Among other promoter elements, phosphorous (P) has gained interest due to its capability to alter both steric and electronic properties of active metal clusters as well as the support material's surface characteristics [2]. Previous studies on different dehydrogenation systems have already demonstrated benefits of P-modification, including improved olefin selectivity and stability against sintering [3][4]. Therefore, P-modified Pt-based catalysts are investigated in this study for the dehydrogenation of n-heptane, serving as a model compound representative of linear alkanes present in plastic pyrolysis oils. The synthesized catalysts are evaluated in a continuous fixed-bed reactor setup. In comparison to an unmodified Pt/Al₂O₃ catalyst, initial variations in phosphorus loading already indicate improvements in heptane conversion and olefin selectivity by 11% and 15%, respectively. In addition, parameter studies are being performed for both unmodified Pt/Al₂O₃ and P-modified catalysts aiming to identify differences in activity, selectivity, and deactivation behavior under varying reaction conditions. Furthermore, Pt-catalysts supported on SiO₂ will be employed in order to examine the influence of the support material and its interaction with the P-promoter. By combining of extensive characterization and catalytic testing, this work aims to provide fundamental insights into structure-performance relationships of phosphorus-modified dehydrogenation catalysts for the upgrading of plastic-derived hydrocarbon feedstocks.

References:

- [1] Dai et al., (2022), Pyrolysis technology for plastic waste recycling: A state-of-the-art review, Progress in Energy and Combustion Science, 101021
- [2] Stöber et al., (2022), A Highly Stable Bimetallic Transition Metal Phosphide Catalyst for Selective Dehydrogenation of n-Heptane, ChemCatChem, 18
- [3] Ellert et al., (2024), Phosphorus-modification of Pt/Al₂O₃ catalysts improves dispersion and cycloalkane dehydrogenation activity, Journal of Catalysis
- [4] Kou et al., (2021), Structural and Catalytic Properties of Isolated Pt²⁺ Sites in Platinum Phosphide (PtP₂), ACS Catalysis

Multiscale Study of CH₄ Pyrolysis: From Kinetics to Fluidized Reactor Operation with C-valorization in the Steel Industry

M. Orsenigo¹, V. Piazza^{1,2}, G. Dall'Osto³, C. Negri¹, L. Castoldi¹, G. Groppi¹, M. Maestri¹, C. Mapelli³, A. Beretta¹

¹Politecnico di Milano, Dipartimento di Energia, Milan, Italy, ²Politecnico di Milano, Milan, Italy,

³Politecnico di Milano, Dipartimento di Meccanica, Milan, Italy

Introduction. Catalytic methane pyrolysis ($\text{CH}_4 \leftrightarrow 2\text{H}_2 + \text{C}_{(\text{s})}$, $\Delta H^\circ = 75 \text{ kJ/mol}$) is emerging as a route for CO_x-free hydrogen with solid carbon co-generation. In this work, Fe-Al₂O₃ catalysts were investigated at different scales and reactor configurations. Solid characterization elucidated mechanisms of C-growth and served to assess the potential valorization of spent catalyst in steelmaking as reducing agent for waste iron recovery (Fig1).

Methods. Fe-Al₂O₃ (5-100wt.%Fe) catalysts were prepared by fusion-decomposition from nitrate salts. Pyrolysis tests were performed in thermobalance (TG, 4mg), packed (PBR, 0.75g) and fluidized (FBR, 3.5g) bed reactors, at varying temperature, feed composition, space velocity. Fresh, reduced, spent catalysts were characterized (BET, XRD, SEM, TEM, Raman). The reduction potential of spent catalyst was assessed *via* carbothermal conversion of Fe_xO_y into Fe⁰, using waste mill-scale as iron source [1] ($\text{Fe}_x\text{O}_y + y\text{C}_{(\text{s})} \leftrightarrow x\text{Fe}^0 + y\text{CO}_{(\text{g})}$).

Results and discussion. From thermogravimetric analyses, the equimolar Fe-Al₂O₃ showed the best performances in terms of activity and C-accumulation capacity. This catalyst was tested in PBR, showing a rapid decrease in CH₄ conversion at increasing CH₄ feed and temperature due to formation of encapsulating-C. Stable operations were demonstrated by reducing the GHSV to 1 NL/h/g_{cat} at 750 °C, achieving the highest C-load of 5 g_C/g_{cat}. A dynamic reactor model was used to derive kinetic expressions for methane pyrolysis and deactivation rate over a wide operating range. Afterwards, pyrolysis tests were carried out in FBR, achieving stable bubbling fluidization regime and enabling longer experiments, spent discharge and post-characterization. The formation of ordered C-nanotubes was observed, leading to a growth in particle size, and reduced density. The spent-materials also exhibited a promising reduction degree (>80%,) and iron recovery ratio, when tested in the carbothermic smelting processes of mill-scale above 1375 °C.

These findings highlight the potential of Fe-Al₂O₃ catalysts to combine high H₂ productivity and C-load, both essential for process commercialization [2]. The resulting C-loaded catalysts could replace iron ore and anthracite in steel industry. Integrating bio-streams as feedstocks would enhance these advantages, producing CO_x-negative H₂ and increasing C-market value.

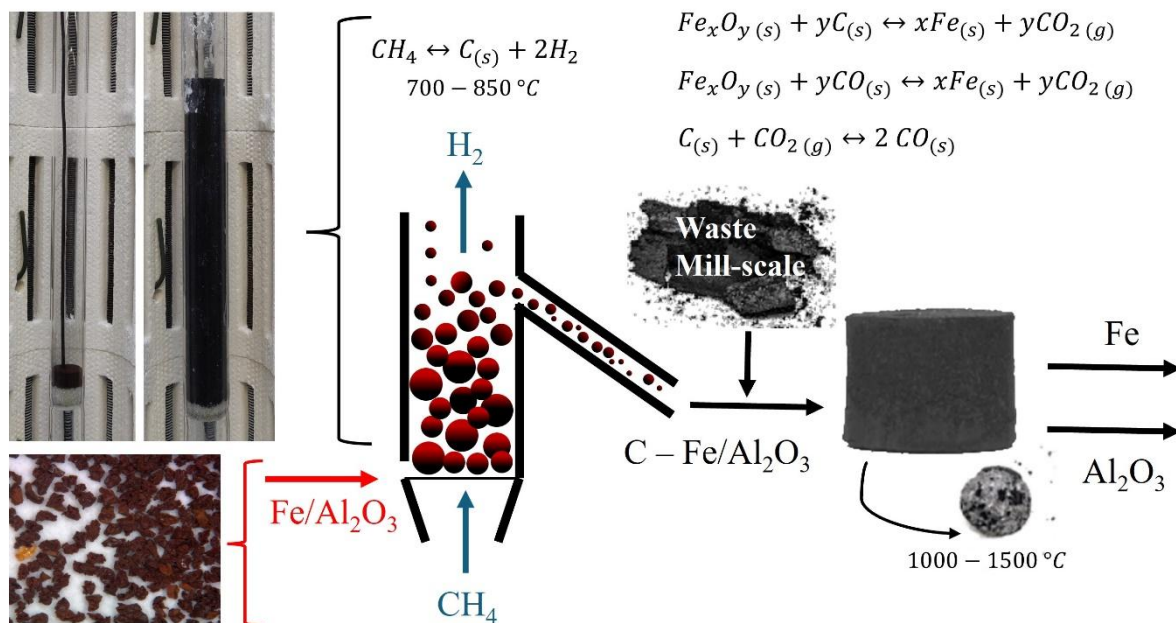


Fig1: Scheme of CH₄ pyrolysis in FBR with utilization of spent catalyst for carbothermic reduction of mill-scale

References:

- [1] Gianluca Dall'Osto, Davide Mombelli, Sara Scolari, Carlo Mapelli, (2024), Role of the Biogenic Carbon Physicochemical Properties in the Manufacturing and Industrial Transferability of Mill Scale-Based Self-Reducing Briquettes, *Metals*, 882, <https://doi.org/10.3390/met14080882>
- [2] Alessandro de Cataldo, Paolo Colbertaldo, Alessandra Beretta, Gianpiero Groppi, José Luis Pinilla, Isabel Suelves, Stefano Campanari, Matteo C. Romano, (2025), Blueish hydrogen production via methane pyrolysis and remote CO₂ capture and storage, *International Journal of Hydrogen Energy*, 149723, <https://doi.org/10.1016/j.ijhydene.2025.05.353>

Reconstructing the Kinetics of Biomass Pyrolysis from bio-components

Contributions: Application to Rice Husk

E. Benedetto¹, V. Piazza^{1,2}, A. Guarnieri¹, M. Y. Suleiman³, L. C. Pariani⁴, P. D'Arrigo⁴, T. Faravelli⁴, A. Frassoldati⁴, L. Lietti¹, A. Beretta¹, P. Debiagi³

¹Politecnico di Milano, Dipartimento di Energia, Milan, Italy, ²Politecnico di Milano, Milan, Italy,

³University of Nottingham Ningbo China, Ningbo, China, People's Republic of, ⁴Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica, Milan, Italy

Understanding biomass pyrolysis kinetics is essential for the optimization of thermochemical conversion processes; however, whether the pyrolysis behavior of real lignocellulosic biomass can be reliably described through an additive kinetic approach, which forms the basis of lumped kinetic models, remains a key open question. In this work, the adequacy of this hypothesis is investigated by focusing on the pyrolysis of a real biomass, namely rice husk.

The study starts with the experimental investigation of rice husk pyrolysis by thermogravimetric analysis coupled with mass spectrometry (TG-MS), providing detailed information on devolatilization behavior and product speciation [1][2]. The rice husk sample was then characterized through chemical fractionation, allowing the quantification of its main constituents. The individual pyrolysis behaviors of these constituents were combined additively according to the fractionation results and directly compared with the experimental evidence obtained for rice husk. In parallel, previously developed lumped kinetic models for the single constituents were also combined according to the experimentally determined biomass composition, enabling the evaluation of the capability of the additive modelling approach to reproduce the behavior of a real feedstock. The comparison between experimental TG-MS data and model predictions shows that the additive kinetic model satisfactorily reproduces both the overall devolatilization profile (Fig1) and the main trends in product speciation of rice husk pyrolysis, with only minor discrepancies. These results provide strong and encouraging evidence that additive lumped approaches can effectively describe the pyrolysis of real lignocellulosic biomasses. Ongoing work is focused on the detailed investigation of possible interactions among biomass components through the study of binary and ternary mixtures.

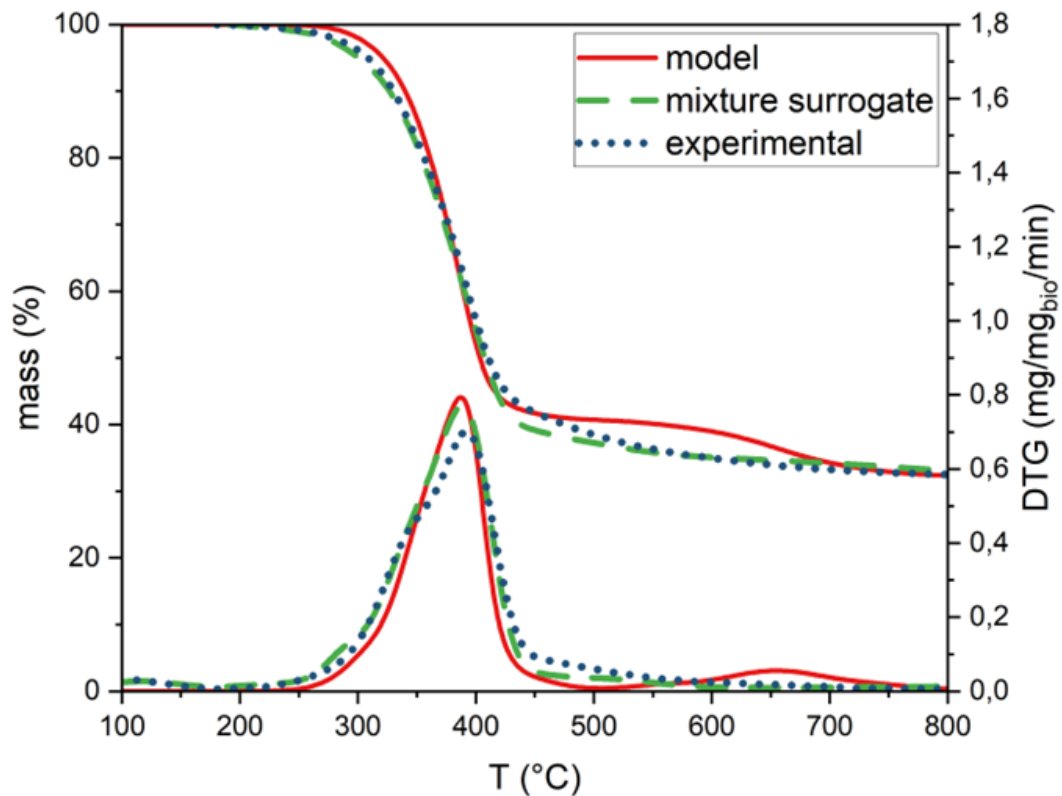


Fig.1: TG and DTG curves for rice husk: comparison between experimental data and predicted behavior by mixture surrogate and CRECK-S model

References:

- [1] Veronica Piazza, Roberto Batista da Silva Junior, Alessio Frassoldati, Luca Lietti, Stefano Chiaberge, Chiara Gambaro, Andrea Siviero, Tiziano Faravelli, Alessandra Beretta, (2024), Detailed speciation of biomass pyrolysis products with a novel TGA-based methodology: the case-study of cellulose, *Journal of Analytical and Applied Pyrolysis*, 106413, <https://doi.org/10.1016/j.jaap.2024.106413>
- [2] Muhammad Yusuf Suleiman, Eleonora Benedetto, Veronica Piazza, Luca Lietti, Alessio Frassoldati, Tiziano Faravelli, Alessandra Beretta, Paulo Debiagi, (2025), Kinetic modelling of biomass pyrolysis: A new lumped scheme for xylan-based hardwood hemicellulose, *Energy Conversion and Management: X*, 101130, <https://doi.org/10.1016/j.ecmx.2025.101130>

Recrystallisation of Pyrolysis Carbon into Graphitic Materials

S. Schütz^{1,2}, G. Stubbe¹, G. Bendel², G. Sorrentino², T. E. Müller^{2,*}

¹VDEh-Betriebsforschungsinstitut GmbH, Düsseldorf, Germany

²Carbon Sources and Conversion, Ruhr-Universität Bochum, Germany

Methane pyrolysis is a promising route for hydrogen production without direct CO₂ emissions [1]. However, the economic viability of methane pyrolysis strongly depends on the utilization of the solid carbon co-product [2]. Although pyrolysis carbon contains only minor impurities, its morphology and particle structure generally do not fulfil the requirements for established carbon black applications [3]. The transformation of pyrolysis carbon into graphitic materials therefore represents an important step toward closed carbon cycles.

In this work, a molten-metal recrystallisation process for the valorisation of pyrolysis carbon is presented [4]. The process concept originates from catalyst systems originally developed for the formation of carbon nanotubes and graphitic nanostructures from hydrocarbons [5]. Amorphous carbon is first dissolved in molten iron and subsequently precipitated through controlled cooling of the melt. Under oxygen-free conditions, graphitic carbon structures form on the melt surface, analogous to previously reported carbon precipitation phenomena in metal–carbon systems [6]. After proof of concept, an experimental reactor was developed to investigate process scalability. Inductive heating enables precise thermal control of the molten metal, while inert gas injection through a sparger separates graphitic particles from the melt surface and transports them pneumatically to a cyclone separator. A cyclic setup additionally allows continuous recharging of pyrolysis carbon.

SEM investigations reveal graphitic crystals with diameters of approximately 100 µm and thicknesses below 5 µm (Figure 1). Raman spectroscopy and XRD analysis confirm the formation of highly ordered graphitic structures with only minor deviations from a pristine hexagonal lattice. Ongoing process optimization focuses on reducing crystal thickness and the number of atomic layers toward graphene nanoplatelets.

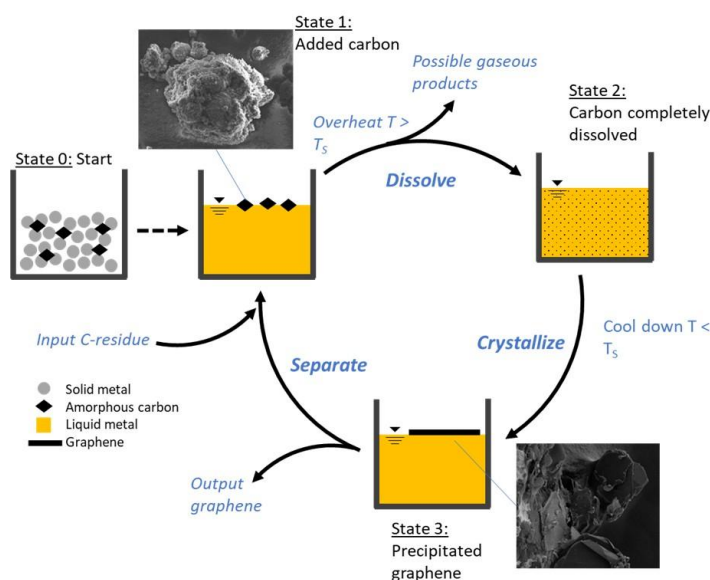


Figure 1: Concept of the molten-metal recrystallisation process for transforming amorphous pyrolysis carbon into graphitic carbon materials.

The results demonstrate the successful transformation of a low-value carbon co-product into high-value graphitic materials. Potential applications include polymers, conductive inks, specialty cement, and batteries, thereby linking methane pyrolysis with advanced carbon-material value chains.

References

- [1] G. Kreysa, Climate Protection by an Alternative Use of Methane—The Carbon Moratorium, *ChemSusChem*, 2009, 2, 49–55.
- [2] C. Tsiklios, M. Hermesmann, P. Stumm, and T. E. Müller, Comparative analysis of hydrogen vs. methane pipeline transport systems with integrated methane pyrolysis for low-carbon hydrogen supply, *Appl. Energy* 2025, 383, 125276.
- [3] S. R. Patlolla, K. Katsu, A. Sharafian, K. Wei, O. E. Herrera, and W. Mérida, A review of methane pyrolysis technologies for hydrogen production, *Renew. Sustain. Energy Rev.*, 2023, 181, 113323.
- [4] S. Wölfelschneider, M. Hensmann, D. Panke, and T. E. Müller, Graphene Nanoparticles from Amorphous Carbon via Molten Metal Recrystallization, *ACS SRM*, 2025, 2, 1643–1650.
- [5] T. E. Müller, D. G. Reid, W. K. Hsu, J. P. Hare, H. W. Kroto, and D. R. M. Walton, Synthesis of nanotubes via catalytic pyrolysis of acetylene: A SEM study, *Carbon* 1997, 35, 951–966.
- [6] S. Amini, J. Garay, G. Liu, A. A. Balandin, and R. Abbaschian, Growth of large-area graphene films from metal-carbon melts, *J. Appl. Phys.* 2010, 108, 094321.

Environmental Assessment of CO₂-based Pathways to Short-Chain Alkenes

J. H. Westerbarkei¹, M. Hebenbrock¹, V. Hagen², T. E. Müller¹

¹Carbon Sources and Conversion, Ruhr-Universität Bochum, Germany, ²Rubokat GmbH, Bochum, Germany

The transition toward defossilised chemical value chains requires resilient processes for the production of carbon carriers, fuels, and platform chemicals independent of fossil feedstocks. Short-chain alkenes are among the most important building blocks of the chemical industry, yet their current production relies predominantly on fossil naphtha and light hydrocarbons. Fischer–Tropsch-type CO₂ hydrogenation offers a promising route to close carbon cycles by converting captured CO₂ and renewable hydrogen into olefinic products. However, the environmental performance of such pathways depends strongly on hydrogen sourcing, electricity supply, process efficiency, and integration into future carbon capture and utilization infrastructures [1].

This contribution presents a life-cycle-based environmental assessment of catalytic CO₂ hydrogenation toward C₂–C₆ alkenes using ruthenium-based catalysts. Experimental data from laboratory-scale investigations were combined with reactor and process simulations to derive mass and energy balances for technically relevant process scenarios. These data served as the basis for a cradle-to-gate life cycle assessment benchmarked against conventional fossil-based olefin production.

The results demonstrate that the environmental impact of CO₂-based alkene production is currently dominated by the energy demand associated with hydrogen generation. Scenarios based on today's electricity mixes and industrial CO₂ sources exhibit higher global warming potentials than established fossil-based pathways. In contrast, scenarios relying on renewable electricity, green hydrogen, improved process efficiency, and closed carbon cycles reveal substantially improved environmental performance. Under favourable conditions, CO₂-based alkene production can approach or even outperform conventional fossil-based routes in terms of global warming potential (Figure 1).

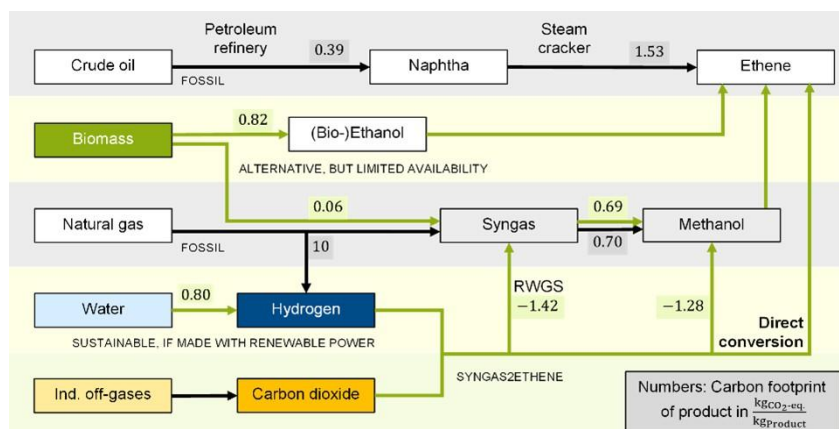


Figure 1: Comparison of fossil and alternative pathways toward ethene production, including indicative carbon footprints of key intermediates and products (kg CO₂-eq. per kg product).

Sensitivity analyses identify hydrogen sourcing, electricity supply, product selectivity, and heat integration as key parameters for reducing environmental impacts. The results demonstrate that catalytic development must be coupled with process design, energy system integration, and life-cycle assessment to unlock the full potential of CO₂ utilization for resilient and defossilised chemical

production [2].

References

- [1] Hermesmann, M.; Tsiklios, C.; Müller, T. E. The environmental impact of renewable hydrogen supply chains: Local vs. remote production and long-distance hydrogen transport. *Applied Energy* 2023, 351, 121920.
- [2] Liese, T.; Graef, I.; Heck, F.; Hagen, V.; Müller, T. E. Produktion von Ethen aus Recycleströmen und erneuerbaren Kohlenstoffquellen als eine nachhaltige und ökonomische Route zu Grundbausteinen der chemischen Industrie; Technische Informationsbibliothek: Hannover, 2025.

From Ammonia Synthesis to CO₂-based Alkenes: Repurposing Industrial Iron Catalysts

J. H. Westerbarkei¹, V. Hagen², T. E. Müller¹

¹Carbon Sources and Conversion, Ruhr-Universität Bochum, Germany, ²Rubokat GmbH, Bochum, Germany

The defossilization of the chemical industry requires resilient pathways for the production of basic chemicals such as ethylene. One promising approach is the repurposing of established industrial catalyst systems for carbon capture and utilization (CCU). This work investigates an industrial iron-based ammonia synthesis catalyst for the formation of hydrocarbons and short-chain alkenes from CO₂ and H₂. Due to structural similarities between ammonia synthesis and Fischer–Tropsch catalysts, hydrocarbon formation under CO₂/H₂ atmospheres is expected [1].

Initial catalytic investigations already demonstrate pronounced activity under CO₂-containing feed gas. By varying temperature, H₂/CO₂ ratio, and gas hourly space velocity, conversions of 70–80% and selectivities toward C₂–C₆ alkenes of up to 17% were achieved. Besides CO formed via the reverse water–gas shift reaction, methane and higher hydrocarbons are produced. Increasing temperature particularly promotes methane formation, while alkene selectivity decreases (Figure 1).

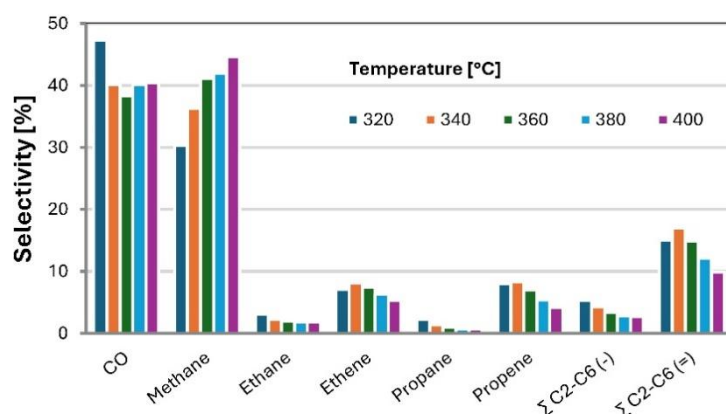


Figure 1: Influence of temperature on product distribution (25 barg; 320–400 °C; H₂/CO₂/N₂ = 66/24/10).

Catalytic screening is performed in fixed-bed and Berty reactors to investigate reaction kinetics under gradient-free conditions. Particular focus is placed on comparing CO₂ and CO as carbon sources and on evaluating the influence of nitrogen-containing feed gases. Catalyst characterization before and after reaction is carried out using BET, XPS, SEM-EDX, TG-MS, and ICP-OES analysis.

The results demonstrate that established ammonia synthesis catalysts show significant potential for the CO₂-based production of hydrocarbons and alkenes. The combination of catalytic activity, existing industrial relevance, and compatibility with CO₂/H₂-based feedstocks highlights their potential for resilient and defossilised chemical production pathways [2].

References:

- [1] Dry, M. E. *The Fischer–Tropsch process: 1950–2000*. Catalysis Today 2002, 71, 227–241.
- [2] Liese, T.; Graef, I.; Heck, F.; Hagen, V.; Müller, T. E. Produktion von Ethen aus Recycleströmen und erneuerbaren Kohlenstoffquellen als eine nachhaltige und ökonomische Route zu Grundbausteinen der chemischen Industrie; Technische Informationsbibliothek: Hannover, 2025.

DME from Crude Methanol

A. Schaadt, S. Feuerbach, F. Nestler, M. Gierse, R. Szolak
Fraunhofer ISE, Freiburg

Introduction

Hydrogen and its derivatives, such as methanol and dimethyl ether (DME), are essential for the defossilisation of the transport, industrial, and energy sectors. This is also addressed in the Hightech Agenda of the BMFTR. e-Fuels, chemicals, and energy carriers are various applications of DME, which are of significant relevance for future industrial value creation in Germany. Furthermore, Germany relies on the large-scale import of renewable energies, sustainable energy carriers, and raw materials for industry. Innovative technologies for the production of e-fuels also enhance Germany's geopolitical independence and resilience.

DME offers several advantages over other energy carriers, but there are still research gaps that need to be addressed. Fraunhofer ISE, which has long-standing expertise in the field of DME [1-7], addresses these topics. For example, Fraunhofer ISE has developed a novel process (INDIGO, patent filed) using reactive distillation, in which the thermodynamic reaction equilibrium is bypassed by coupling synthesis and distillation (see Fig. 1). INDIGO reduces energy requirements, plant complexity, and investment costs. In cooperation with our industrial partner, thyssenkrupp Uhde, the aim is to increase the technological maturity of this innovative and efficient process developed by Fraunhofer ISE for the production of DME and to prepare for its industrial implementation. We achieved the world's first DME production directly from crude methanol (Carbon2Chem pilot plant [8]).

The hydrogen carrier ammonia, frequently discussed in this context, has a lower H₂ storage capacity compared to DME and requires significant water resources in sunny countries that often suffer from water scarcity [2]. The efficient transport of hydrogen via DME allows for large-scale global use of H₂, enabling a CO₂-neutral supply to the industry, transport sector, and energy economy. Additionally, the transport of hydrogen using DME would be conducted through a non-toxic, ozone-friendly, and non-hazardous hydrogen carrier.

Furthermore, DME, as a platform molecule, offers many applications: as an intermediate for further synthesis of aviation fuels, gasoline, and other refinery products, as well as for blending with LPG (up to 20% possible without user-side adjustments).

The proposed presentation will provide an overview of the opportunities and challenges of DME and draw conclusions regarding technology and economics.



Figure 1: PN50 distillation column with a total height of 7.5 meters at Fraunhofer ISE, serving as a platform for DME and SAF process development.

References

- [1] Semmel, M.; Kerschbaum, M.; Steinbach, B.; Sauer, J.; Salem, O. (2023): Optimized design and techno-economic analysis of novel DME production processes. In *Reaction Chemistry & Engineering*. DOI: 10.1039/D3RE00333G.
- [2] Schühle, P.; Stöber, R.; Semmel, M.; Schaadt, A.; Szolak, R.; Thill, S. et al. (2023): Dimethyl ether/ CO_2 - a hitherto underestimated H_2 storage cycle. In *Energy & Environmental Science* 16 (7), pp. 3002–3013. DOI: 10.1039/D3EE00228D.0.
- [3] Semmel, M.; Bogatykh, I.; Steinbach, B.; Sauer, J.; Repke, J.; Salem, O. (2023): Demonstration and experimental model validation of the DME synthesis by reactive distillation in a pilot-scale pressure column. In *React. Chem. Eng.* (8), pp. 2309–2322. DOI: 10.1039/D3RE00200D.
- [4] Kubas, D.; Semmel, M.; Salem, O.; Krossing, I. (2023): Is Direct DME Synthesis Superior to Methanol Production in Carbon Dioxide Valorization? From Thermo-dynamic Predictions to Experimental Confirmation. In *ACS Catal.*, pp. 3960–3970. DOI: 10.1021/acscatal.2c06207.
- [5] Semmel, M.; Steiner, L.; Bontrup, M.; Sauer, J.; Salem, O. (2022): Catalyst screening and reaction kinetics of liquid phase DME synthesis under reactive distillation conditions. In *Chem. Eng. J.*, p. 140525. DOI: 10.1016/j.cej.2022.140525.
- [6] Cholewa, T.; Semmel, M.; Mantei, F.; Güttel, R.; Salem, O. (2022): Process Intensification Strategies for Power-to-X Technologies. In *ChemEngineering* 6 (1), p. 13. DOI: 10.3390/chemengineering6010013.
- [7] Semmel, M.; Ali, R. E.; Ouda, M.; Schaadt, A.; Sauer, J.; Hebling, C. (2021): Power-to-DME: a cornerstone towards a sustainable energy system. In Giuseppe Spazzafumo (Ed.): *Power to Fuel. How to Speed Up a Hydrogen Economy*: Elsevier, pp. 123–151.
- [8] Nestler, F., Voß, J., Fastabend, A., Niemeier, T., Ruland, H. and Hadrich, M.J. (2024), *Methanol Synthesis from Sustainable Feedstocks – A Quantitative Side Product Analysis*. *ChemieIngenieurTechnik*, 96: 1166–1176. <https://doi.org/10.1002/cite.202400009>