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The Future of Chemical and Fuels - Feedstocks and
Process Technologies

edited by M. Bender, H. Blanke, H. Häger, A. Goehrt, A. Jess,
J. A. Lercher, M. Marchionna, J. Sauer, D. Vogt



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Biomass Based Platform Chemical - Promising Value Chains and Major Challenges

R. Palkovits

Institute of Technical und Macromolecular Chemistry, RWTH Aachen, Germany

Abstract

Renewable carbon feedstocks such as biomass and CO₂ present an important element of future circular economy. Especially biomass as highly functionalized feedstock provides manifold opportunities for the transformation into attractive platform chemicals. However, these resources require novel paradigms in process design. Fossil feedstocks are processed in stationary gas-phase processes at elevated temperature. On the contrary, biorefineries are based on processes in polar solvents at moderate conditions to selectively deoxygenate the polar, often thermally instable and high-boiling molecules. Considering “green electrons” provided by renewable energy technologies, also dynamic (electro)catalytic processes become attractive as key technology of a throughout circular economy. Herein, selected value chains via biogenic platform chemicals will be discussed with major emphasis on the valorization of biogenic carboxylic acids by heterogeneous catalysis and electrochemistry.

[1] F. J. Holzhäuser, J. B. Mensah, R. Palkovits, *Green Chem.* (2020) 22, 286-301: (Non-) Kolbe Electrolysis in Biomass Valorisation – A Discussion of Potential Applications

[2] M. O. Haus, Y. Louven, R. Palkovits, *Green Chem.* (2019) 21, 6268-6276: Extending the Chemical Product Tree: A Green Value Chain for the Production of N-Vinyl-2-Pyrrolidones from Biogenic Acids

[3] Delidovich, K. Leonhard, R. Palkovits, *Energy Environ. Sci.* 7 (2014) 2803-2830: Cellulose and Hemicellulose valorisation: An integrated challenge of catalysis and reaction engineering

Improved Catalytic Transfer Hydrogenation of Levulinate Esters with Alcohols over ZrO₂ Catalyst

T. Tabanelli¹, E. Paone², P. Blair Vásquez¹, R. Pietropaolo², N. Dimitratos¹, F. Cavani¹, F. Mauriello¹

¹Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Italy

²Dipartimento DICEAM, Università Mediterranea di Reggio Calabria, Italy

Abstract

Levulinic acid (LA) and its esters (LE) are polyfunctional molecules that can be obtained from lignocellulosic biomass. Because of LA peculiar structure and reactivity, the United States Department of Energy has classified it as one of the top 12 bio-building block chemicals. Nowadays, the most common strategy for its valorization is the chemical reduction in order to obtain valuable compounds such as fuel additives, solvents and intermediates. In particular, γ -valerolactone (GVL) has been proposed both as an innovative "green" solvent (due to its low toxicity, high stability and high boiling point) and as bio-based liquid fuel. GVL may be obtained from LA by catalytic transfer hydrogenation (CTH) through the Meerwein-Ponndorf-Verley (MPV) mechanism. This approach uses organic molecules (e.g. alcohols) as reducing agents for substrates which contain a carbonyl group. The most promising studies published for the CTH of LA and its esters have been performed in liquid phase using batch reactors and ZrO₂ as heterogeneous catalyst. However, high autogenic pressures are needed in order to work in the liquid phase at high temperature with light alcohols. Moreover, the CTH of alkyl levulinates using methanol or ethanol as solvents/H-donor were found to be inefficient in GVL production. Better results can be obtained by using isopropanol in good agreement with the greater tendency of secondary alcohols to release hydrogen. For all these reasons, we decided to synthesize different high-surface-area ZrO₂ (both tetragonal "t" and monoclinic "m") and test their catalytic activity for the gas-phase continuous-flow production of GVL through CTH of LE. In this way, by working at 250°C with a contact time of one second over t-ZrO₂, both ethyl- and methyl- levulinate can be completely converted promoting the formation of GVL with good to excellent yield of 80% and 68% when 2-PrOH and ethanol are used as reducing agents respectively. For the sake of comparison, under batch conditions the CTH of alkyl levulinates using 2-PrOH leads to a comparable GVL yield only after 24h at 250°C. Unfortunately, the ZrO₂ catalyst undergoes to a progressive deactivation during the time-on-stream. This deactivation was correlated to the deposition of heavy carbonaceous compounds over the Lewis acid sites. However, a complete regeneration of the catalyst can be promoted in-situ, in the same reactor, by feeding air at 400°C. As a matter of fact, the similar behavior showed by ethanol may open interesting scenario in the possibility to use bio-ethanol as reducing agent for these kind of reactions. These results represent the very first examples of the CTH of LE under continuous gas-flow conditions ever reported in literature. Furthermore, the effect of the zirconia phases (monoclinic and tetragonal respectively) on the catalytic activity has been further investigated and now the efforts are directed toward the synthesis of zirconia mixed metal oxides (e.g. Ti-doped zirconia) with the aim of further improve both the catalyst activity and stability for the gas-phase continuous flow production of GVL.

Coupled Production of Steel and Chemicals

M. Bender¹, T. Roussiere¹, H. Schelling¹, S. Schuster¹, E. Schwab²

¹BASF SE, ² Dr. Ekkehard Schwab has since retired from BASF

Abstract

In a subproject of the Carbon2Chem[®] Verbundprojekt, we studied a potential production of oxymethylene ethers (OME) as possible diesel fuel components or substitutes. The study was aimed at reducing CO₂ emissions from mobility and steel manufacturing by rededicating steel mill gases to the production of methanol as an important OME precursor.

Six different scenarios for CO₂ emission reduction in steel mills were calculated, in four of which methanol is generated as an OME intermediate from steel mill gases. Potential synergies in raw material and energy streams of the coupled processes were identified. Shared process streams and equipment could lead to savings in capital and operational expenditure.

CO₂ reduction volumes and avoidance costs were calculated for the six scenarios. If coupled with methanol production, natural gas-based direct reduced iron processes offer the chance for quantitative CO₂ emission reduction at the lowest CO₂ avoidance costs. Energy required for this process could be co-fed, e.g., as renewable electricity.

The project was sponsored by the German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung BMBF) under the grant no. 03EK3043A.

Methanol Synthesis with Real Steel-Mill-Gases: Practical Performance Investigations in an On-Site Technical Center

K. Girod¹, S. Schlüter¹, T. Hennig¹, H. Lohmann¹, S. Kaluza^{1/2}

¹Fraunhofer UMSICHT, Oberhausen, Germany

²Faculty of Mechanical and Process Engineering, University of Applied Sciences Düsseldorf, Germany

Introduction

Steel-Mill-Gases are potential alternative sources for CO₂-, CO- and H₂-streams to provide synthesis gas for methanol synthesis. These gases provide promising potential to be utilized as feedstock for bulk chemical production, while simultaneously reducing the CO₂ footprint of the steel mill. The scope of this work is to evaluate the possibility of applying a commercial methanol synthesis catalyst in the conversion of synthesis gas derived from steel mill exhaust gases exhibiting fluctuating compositions. The ongoing experimental work is conducted in the laboratory of the technical center at the thyssenkrupp Steel Europe site in Duisburg, Germany. The investigations are funded by German Federal ministry of Education and Research (BMBF) within the scope of the project Carbon2Chem®.

Methods

First, a process simulation including a kinetic model was developed for the large-scale methanol synthesis using synthesis gas derived from steel mill exhaust gases. The theoretically identified operating points were subsequently applied in a test system that was installed in the technical center, providing direct access to cleaned and optionally conditioned steel mill gases. In order to evaluate, whether detrimental trace compounds remain in the cleaned synthesis gas, methanol synthesis is tested alternately with real gases and synthetic steel mill gases as reference.

Results

First tests with synthetic gas compositions revealed that the CO₂/CO-ratio has a crucial effect on the catalyst performance. As expected, methanol productivity decreased with increasing CO₂ concentration. A minimum CO₂ concentration is required for a high catalyst activity, as the lowest methanol productivity was obtained for pure CO. Apparently, high water and CO₂ concentrations reduce the lifetime of the commercial MeOH-synthesis-catalyst.

Conclusions

Direct access to pre-cleaned steel mill gases is crucial for a realistic assessment of catalyst performance and lifetime. A comparison between real gases and synthetic steel mill gases will reveal the effect of trace compounds might slipping through the gas-cleaning unit.

A New Reactor Concept for Conversion of CO₂ to Methanol

T. Oelmann¹, M. Gorny¹, T. Schuhmann¹, M. Strozyk¹, F. Castillo-Welter², C. Drosdzol², S. Haag²

¹Air Liquide Engineering & Construction, Frankfurt am Main, Germany

²Air Liquide Innovation Campus Frankfurt, Frankfurt am Main, Germany

Abstract

The reduction of carbon footprint as well as the valorization of CO₂ rich gases are of increasing interest for many industries and methanol is a perfect fit for energy storage, for producing clean fuels and will be a building block for producing high value chemicals. Therefore Air Liquide Engineering and Construction (AL E&C) is already proposing a first generation of CO₂ to Methanol plant based on the well-referenced Lurgi Methanol technology with some specific optimizations regarding the CO₂ conversion [1]. It follows the classic synthesis loop design utilizing high recycle ratios to achieve overall high conversion rates. Typically a recycle ratio of around 4 is foreseen. This technology is commercially offered with commercial guarantees on catalyst lifetime and methanol production. Commercially available electrolyzers or other low carbon hydrogen sources will result in first methanol plants based on CO₂ with a capacity up to 1000 mtpd. The most efficient synthesis solution for large scale plants is a Lurgi Megamethanol™ loop with two reaction steps in series to reach single train capacities up to 10000 mtpd. Air Liquide developed and is further optimizing a second generation “CO₂ to Methanol” plant setup (Figure 1). This integrated synthesis loop consists of an “12 in 1” reactor with multiple stages of reaction, gas to gas heat exchange, condensation and interstage product removal (Figure 2). The new multi-stage solution allows very effective conversion rates at reduced recycle rates (down to ~1), reduced costs (CAPEX & OPEX) for low reactive gases like CO₂. Therefore the key features of the “12 in 1” Air Liquide CO₂ to methanol can be summarized in the following points:

- reactor design based on plates
- higher per pass conversion and lower recycle ratio (1 instead 4)
- longer catalyst lifetime
- small footprint & low equipment count
- approx 20% lower CAPEX of the synthesis section
- scalability for a wide range of capacities and feedstock

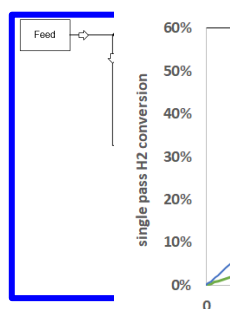


Figure 1: Principle of the CO₂ to methanol multi-stage concept “12 in 1”

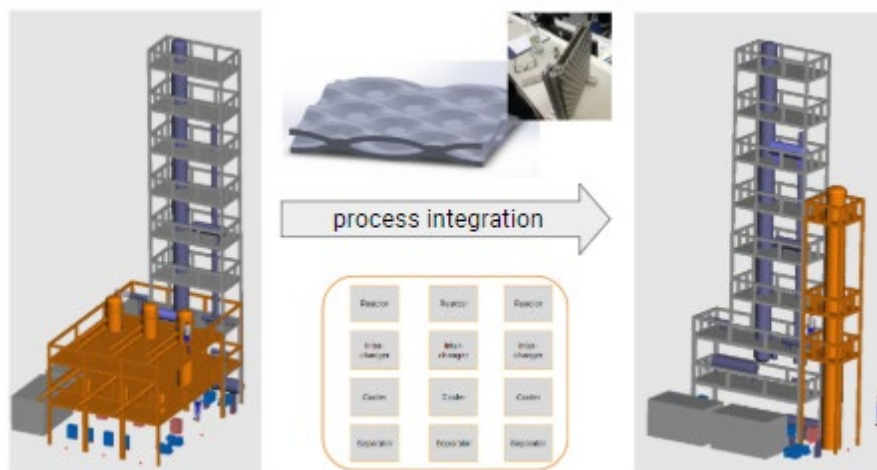


Figure 2: Non integrated 3 stage concept (left) vs fully integrated solution (right)

The multistage reactor concept offers a high potential in the conversion of gases with high inert content. To develop a tailor made solution for these carbon sources a new pilot plant is constructed at Air Liquide Innovation Campus Frankfurt (Figure 3).



Figure 3a: Mega Methanol pilot plant
 Figure 3b: New multi-stage pilot plant

Reference: [1] S. Haag, F. Castillo-Welter, T. Schuhmann, B.A. Williams, T. Oelmann, A. Günther, M. Gorny: *How to Convert CO₂ to Green Methanol* in Challenges for Petrochemistry and Fuels: Integration of Value Chains and Energy Transition DGMK Conference October 10 – 12, 2018 in Berlin, Germany

The Rheticus Project

T. Haas¹, G. Schmid²

¹Evonik Creavis GmbH, Marl, Germany,

²Siemens Gas and Power GmbH & Co. KG, München, Germany

Abstract

Profitable renewable synthesis of chemicals and fuels is a prerequisite for its implementation into current economics. Availability of renewable energy in sufficient quantities and its intermittent character is the main condition. To achieve profitability in a very low fossil energy price scenario Rheticus opens the opportunity to move stepwise into different markets starting from speciality products.

The presented industrial process consists of two major components: Firstly, electricity from wind or solar is stored by electrolysis into energy carriers like hydrogen (H₂) or carbon monoxide (CO). Current density, Faradaic and electrical efficiency and endurance of this upstream process will be discussed. Secondly downstream, a flexible mixture of CO, CO₂ and H₂ is supplied to a multistep anaerobic fermentation process, whereas they are initially converted to acetic acid and ethanol with high carbon efficiency and thus almost without any undesired by-products. The today's economic value is obtained by further condensation of the C₂ products to C₄ and C₆ special chemicals (carboxylates and alcohols). Eventually, finally scaled into the hundreds megawatt range the molecules can be used as fuels.

In the talk a potential solution is addressed by using a commercially available silver-based gas diffusion electrode (used in industrial-scale chlorine–alkaline electrolysis) as the cathode in the CO₂ electrolyser. Electric current densities up to 300 mA cm² were demonstrated for more than 1,200 hours with continuous operation. Faradaic efficiency of the anaerobic fermentation processes was almost quantitative [1].

Evonik and Siemens have decided to move the technology platform toward an industrial scale. The project is named Rheticus [2]. Generally, such an approach is called artificial or technical photosynthesis.

[1] Haas et al. Technical photosynthesis involving CO₂ electrolysis and fermentation; Nature Catalysis 2018, Vol 1. pp 32–39; <https://doi.org/10.1038/s41929-017-0005-1>

[2] <https://press.siemens.com/global/en/pressrelease/research-project-rheticus>
<https://corporate.evonik.com/en/pages/article.aspx?articleId=118401>

Carbon Recycling: Gas Fermentation Turning Sustainable Carbon into Fuels and Chemicals

S. Simpson

LanzaTech Inc., Skokie, Illinois, USA

Abstract

Atmospheric CO₂ has accumulated to levels unprecedented since the Pliocene Epoch (> 2.6 million years ago). Although the effect of elevated atmospheric CO₂ on the climate has been predicted for 60 years, it wasn't until the 2016 Paris Agreement that nations agreed plans to abate atmospheric CO₂ release. These plans necessitate that sustainable carbon resources increasingly displace fossil resources as feedstocks for fuel and chemical production. The economic crisis triggered by the COVID-19 Pandemic has now added urgency to the demands for a move away from traditional polluting production systems. The opportunity being highlighted is that the public finance used to stimulate economic recovery be targeted at a technology that enable a circular, sustainable economic model. Numerous technology solutions have been proposed to enable this transition. Gas fermentation is the most recent of these. This technology uniquely offers a path to produce impactful volumes of sustainable fuels, chemicals and food from abundant, low value above ground carbon feedstocks.

LanzaTech is pioneering the commercialization of a gas fermentation process that allows the continuous production of fuels chemicals from gases at scale. Our first commercial plant is commissioned in China. Further commercial plants are in design or under construction with the process having been demonstrated with live feeds of waste gas from numerous industries and synthesis gas produced from agricultural wastes and municipal waste.

The potential role that gas fermentation could play in enabling a circular economic model has been enhanced through the development of a complete suite of synthetic biology techniques in gas fermenting organisms. This has led to an array of new chemical products being produced from gaseous feedstocks. In this way gas fermentation is a vital bridge in the effort to create value from waste streams as part of an increasingly circular economic model.

Direct Air Carbon Capture and Storage (DACCS) and Direct Air Carbon Capture and Utilization (DACCU)

G. Santori

Institute for Materials and Processes, University of Edinburgh, , Scotland, UK

Abstract

In 2015, the Paris Agreement set the goal to pursue efforts to limit global average temperature increase below 1.5°C above preindustrial levels. Different bodies have independently assessed that this is achievable under optimistic scenarios with a cost: mandatory requirement is the introduction in the energy system of effective negative emission technologies (NETs) in addition to plans for the deployment of point source carbon capture and storage, renewable or nuclear energy. Today, few governments are timidly planning research and development programmes for GHG removal (GGR) technologies. In the UK for example, after invitation of the government, The Royal Society has recently released a policy-setting report where *three possible pathways of NETs are identified among which the option with largest potential (75 MtCO₂/year) consists of the combined adoption of BioEnergy with Carbon Capture and Storage (BECCS) and Direct Air Carbon Capture and Storage (DACCS)*. BECCS is known with good accuracy. Conversely, DACCS is still largely uncertain since the majority of information come from order-of-magnitude estimates (1), forecasts (2), theoretical calculations (3) and proof-of-principle experiments (4, 5). The analyses from these studies are often biased since they are produced by companies tending to promote their specific products. The theoretical feasibility of large scale DAC (without storage) was first proposed by Lackner (6) (founder of Kilimajaro Energy Inc) and Keith (7) (founder of Carbon Engineering Ltd). Other companies have joined later, such as Climeworks Ltd, Global Thermostat LLC and more recently a number of start-ups and research groups proposing processes at technology readiness level (TRL) 1-2. All these actors still need to prove that their DAC ideas can work at large scale. Climeworks Ltd is the only company that has claimed to have actually stored CO₂ underground, with 165 tCO₂ sequestered in an Icelandic geological reservoir over 3 years (8). Unfortunately, this result is unlikely to be replicable since it relies on the specificity of Icelandic waters and rocks and for the share of national renewable energy that it would need. Additionally, the economics of DACCS is uncertain, with costs for capture but excluding storage ranging from \$50 (2) to \$600 per tCO₂ (9). At the time of writing this contribution, EU carbon credits are valued around \$30 per tCO₂ and there is no sound basis to state any threshold which would make DACCS viable. DAC is proposed also in combination with processes that use CO₂, called Direct Air Carbon Capture and Utilization (DACCU). In this solution carbon is kept in a loop. When the overall product life-cycle is assessed, no chemicals have been identified for which DACCU is a NET to date. In most cases DACCU leads to net increase of carbon emissions because of its energy intensity. However, DACCU can still be an option in locations where the CO₂ demand is high and renewable energy in excess. On a market viewpoint, only fuel are chemicals produced at a scale which is large enough to be a real option for climate change mitigation through CO₂ utilization (10) but this comes along with their high cost. Among the negative emission tools, those involving DAC sound attractive on paper but they are also the least explored. If the governmental policies on GGR has to include DAC, governments run the risk of following unreliable plans based on biased data.

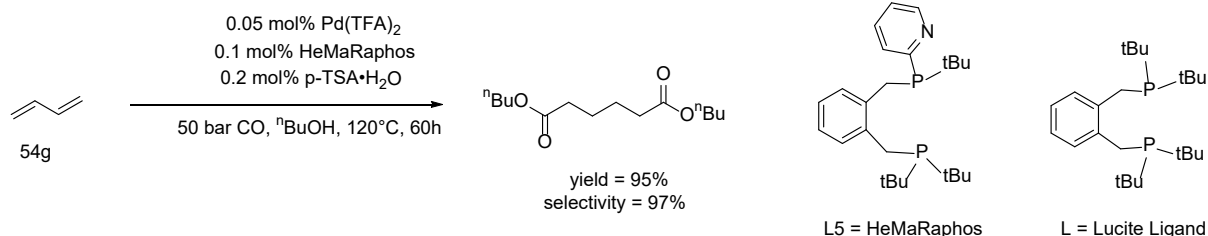
References: 1. K. Z. House *et al.*, *Proc. Natl. Acad. Sci.* **108**, 20428–20433 (2011); 2. M. Fasihi, O. Efimova, C. Breyer, *J. Clean. Prod.* **224**, 957–980 (2019); 3. D. W. Keith, G. Holmes, D. St. Angelo, K. Heidel, *Joule*. **0** (2018), doi:10.1016/j.joule.2018.05.006; 4. T. Wang, K. S. Lackner, A. Wright, *Environ. Sci. Technol.* **45**, 6670–6675 (2011); 5. J. A. Wurzbacher, C. Gebald, N. Piatkowski, A. Steinfeld, *Environ. Sci. Technol.* **46**, 9191–8 (2012); 6. K. S. Lackner, *Sci. Am.* **302**, 66–71 (2010); 7. D. W. Keith, M. Ha-Duong, J. K. Stolaroff, *Clim. Change*. **74**, 17–45 (2006); 8. P. A. E. Pogge von Strandmann *et al.*, *Nat. Commun.* **10**, 1983 (2019); 9. J. Tollefson, *Nat.* 2019 5587709 (2018); 10. S. Deutz *et al.*, *Energy Environ. Sci.* **11**, 331–343 (2018).

Palladium Catalyzed Carbonylation of Challenging Olefins to Esters and Acids

H. Neumann, J. Yang, K. Dong, R. Sang, R. Jackstell, M. Beller
Leibniz-Institute for Catalysis, Rostock, Germany

Abstract

In 1953, Walter Reppe published in "Justus Liebigs Annalen der Chemie" a seminal carbonylation of acetylene with carbon monoxide and a nucleophile using nickel salts as catalysts. [1] The formed methyl acrylates are belonging to an important class of buildings blocks and are synthesized in ton scales. Since this discovery there was a perennial interest both from the industry and academia in Reppe carbonylations. In the late 1980's a big jump ahead was contributed by Drent from Shell AG, who developed highly efficient palladium catalysts in homogenous phase, which surpassed the former catalysts.[2] Based on his results the so called Alpha-Lucite process [3] was set up, where tons of ethylene are converted to methyl propionate in a palladium catalyzed reaction using 1,2-bis((di-*tert*-butylphosphino)methyl)-benzene (Lucite Ligand, L) as an outstanding ligand. Inspired by this success, we developed in cooperation with Evonik AG a ligand system where we modified the Lucite Ligand (L) by replacing one *t*-butyl group on each side with a pyridyl unit. This catalyst system becomes much more active than the Lucite system and is even able to carbonylate internal and tetrasubstituted olefins.[4] Recently, we prepared the unsymmetrical Lucite analogous (L5 = HeMaRaphos) by replacing only one *t*-butyl group with a pyridyl unit. This catalyst is very active for the double carbonylation of 1,3-butadiene to adipinates. [5] Adipinates are important building blocks for many industrial products especially for the Nylon 66 production and have a big economical prominence.



- [1] W. Reppe, Liebigs Ann. Chem., 582, 1 (1953).
[2] G. Kiss, Chem. Rev., 101, 3435 (2001).
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[4] K. Dong, X. Fang, S. Gülak, R. Franke, A. Spannenberg, H. Neumann, R. Jackstell, M. Beller, Nature Communications, 8, 14117 (2017).
[5] J. Yang, J. Liu, H. Neumann, R. Franke, R. Jackstell, M. Beller, Science, 366, 1514 (2019).

Spatially-resolved Gas-phase Measurements on Iron-based Fischer-Tropsch Synthesis in a Fixed-bed Reactor

Florian Wolke¹, Markus Voigt¹, Erik Reichelt¹, Oliver Korup², Matthias Jahn¹, Raimund Horn².

¹Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Dresden.

²Technische Universität Hamburg (TUHH).

Abstract

Even though the development of iron-based catalysts for Fischer-Tropsch synthesis to convert syngas into valuable chemicals like higher alcohols is conducted for about one-hundred years, manifold uncertainties regarding the underlying reaction mechanism are still present. It is well-known that primary products formed by initial reactions can be re-adsorbed and transformed into secondary products via several reaction routes. In order to distinguish the respective pathways and to model the underlying kinetics, spatially-resolved concentration measurements within a fixed-bed reactor would be highly valuable.

Within this study, a commercial compact profile reactor setup is applied for Fischer-Tropsch synthesis. The setup consists of a movable fixed-bed tubular reactor with a central capillary incorporating orifices (0.1 mm diameter) for spatially-resolved sampling and analysis of the gas phase. The results of the gas chromatographic analysis yield high-resolution spatial concentration profiles of short-chained reaction products representing paraffins, olefins, alcohols, aldehydes and CO₂. This approach offers various insights into the occurring reaction pathways and elucidates some aspects of the complex reaction mechanism of iron-based Fischer-Tropsch synthesis. Furthermore, the influence of several promoters like potassium, copper or molybdenum on primary and secondary product formation is studied by this approach and potential optimization pathways are deduced. First attempts to correlate the results with suitable kinetic models are made.

Perspectives for the Intensification of Methane Steam Reforming

Riccardo Balzarotti, Matteo Ambrosetti, Daniele Marangoni, Gianpiero Groppi, Enrico Tronconi
Dipartimento di Energia, Politecnico di Milano, Italy

Abstract

The increasing demand for distributed hydrogen production calls for a downscale of the traditional industrial reformers. The adoption of structured catalysts has been widely investigated as a promising strategy to enhance heat and mass transfer in non-adiabatic reactors: significant advantages with respect to the traditional packed-bed configuration were reported in literature using washcoated open cell foams as structured internals. Nevertheless, many open issues still discourage the adoption of structured reactors at the commercial scale. In order to fill this gap, recently our research group has demonstrated the potential of a new reactor configuration based on highly conductive copper open cell foams as structured internals, which can effectively enhance heat and mass transfer rates in reactors for highly energy-intensive processes (e.g. the steam reforming of methane). The system is made catalytically active by filling the open porosity of the metallic foam with catalytic pellets, thus avoiding many of the typical limitations of the washcoated structured catalysts (i.e. low catalyst inventory and washcoat deposition/adhesion issues). Our experimental results reveal the beneficial effect of introducing a conductive metallic matrix, which enables a more effective conductive heat transfer with respect to that allowed by the convective mechanism prevailing in traditional packed beds operated at flow conditions typical of compact reformers.

Besides (and in parallel to) the benefits obtained by running the process in structured reactors with thermally conductive internals, a new approach to intensified reactor design is gaining attention, aiming at mitigating the environmental impact of chemicals production by reducing the greenhouse gas emissions. The state-of-the-art of chemical industry is characterized by a large use of fossil fuels to meet the heat demand of endothermic processes, which is responsible for a significant portion of greenhouse gas emissions. In fact, the growing availability of electric energy from renewable and sustainable sources is opening new paths for further intensifying highly endothermic processes. In this view, we have recently proposed a breakthrough in the reactor design for highly energy demanding reactions, which directly fulfills the high thermal duty of methane steam reforming by using Joule heating of resistive SiC foams as internal heat generators. The system can be made catalytically active either by washcoat deposition or by packing catalyst pellets in the open porosity of the SiC open cell foam. This innovative configuration holds promise to open new routes for the direct conversion of renewable electric energy into hydrogen, while preventing the CO₂ emissions derived from methane combustion. Experimental tests and detailed numerical simulations are ongoing to validate the potential of the proposed concept.

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How will Climate Change Policy Influence the Future of Chemicals and Fuels: OMV's Route Towards a Sustainable Future

Sebastian Posch

OMV Refining & Marketing GmbH, Vienna, Austria

Abstract

Global awareness on climate change has markedly increased during the last decade. Regional and global emission and climate protection aspirations towards net zero carbon emissions by 2050, such as the European Green Deal pose a great challenge in light of globally increasing demand for energy and petrochemicals that is today largely relying on fossil fuel. Meeting ambitions towards a zero carbon energy supply will require the development and maturing of new technologies on an unprecedented scale, supported by policy makers through funding and adequate regulations.

OMV is already taking a leading role. Leveraging existing assets at its refinery sites, OMV invests significant funds, efforts and resources into the development of sustainable technologies and processes to ensure the supply of circular and green economy-based products and significantly reduce greenhouse gas emissions from operations.

This presentation is subject to three developments that are implemented in the short- to mid-term at OMV refineries:

- **ReOil®:** OMV is a pioneer in the post-consumer plastics sector by developing the ReOil® process within the last years to close the carbon cycle. The ReOil® plant at the Schwechat refinery converts used plastics (polyethylene, polypropylene, polystyrene) under moderate pressure and typical refinery process temperatures, using a solvent, to produce synthetic crude oil. As valuable resources, process outlet products are then intended to be reused in classical refinery processes.
- **Co-Processing:** By 2025, 200,000 tons per year of sustainable, biogenic oils are to be co-processed in the existing refinery processes at OMV refinery sites in Schwechat and Petrobrasi to fulfill the increasing demand for biofuel in Europe in a capital efficient way.
- **Low carbon petrochemicals:** The brand new 60,000 tons per year iso-butene separation plant at the Burghausen refinery site, which is currently in the construction phase, will make a significant contribution to the process intensification of a petrochemical complex and open a new route for petrochemical intermediates at existing refineries. By means of a sophisticated and first of its kind heat integration system, the emission of greenhouse gases during plant operation is reduced significantly.

All measures presented contribute to the reduction of greenhouse gas emissions in different ways and manners and point the way towards a sustainable future with the responsible use of

Direct Hydrogenation of CO₂ to Olefin-rich Hydrocarbons: A Sustainable Process for Basic Chemicals and Fuels

Lucas Brübach, Peter Pfeifer

Karlsruhe Institute of Technology (KIT), Institute for Micro Process Engineering (IMVT)

Abstract

Crude oil is an indispensable feedstock for our today's energy sector and chemical industry. However, the dramatic rise in greenhouse gas emissions and the associated risks of climate change call for a paradigm shift to a transfer to CO₂ neutral technologies. While large parts of the energy sector can be electrified, fuels and chemicals will keep on needing a hydrocarbon-based feedstock. Especially the aviation industry has little or no alternative to continue using liquid hydrocarbon-based fuels. Therefore, there is a high need for processes for the production of sustainable hydrocarbons in the future.

In the last years a two-stage process comprising a high temperature reverse water gas shift reactor and a microstructured low temperature Fischer-Tropsch reactor has been developed at IMVT for the conversion of H₂ and CO₂ to hydrocarbons. However, since the beginning of Fischer-Tropsch research, it is known that CO₂ can also be directly hydrogenated to hydrocarbons using alkali promoted iron catalysts. This so-called modified Fischer-Tropsch process has gained new interest in the last decade. The one-stage process could lead to a significant simplification of power-to-fuel applications and also become a valuable source of basic chemicals. Research has been mainly focused on catalyst development and optimization so far; promoted iron catalysts have shown to be promising candidates. However, modelling and scale up considerations have been addressed by only a few studies. In the project PowerFuel this one-stage process is investigated experimentally and theoretically with the aim to develop a kinetic model that will be assessed with a bench scale setup and a techno-economic analysis.

The poster highlights initial experimental results with supported iron catalysts with a focus on product selectivity and catalyst activity at lab scale. Main challenges of the process, e.g. reaction inhibition by water, are addressed and solutions for the proposed process development are shown. An outlook is given for the next process developments steps towards an adiabatic fixed bed recycle reactor design.

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Oxymethylene Ethers (OMEs) as Diesel Fuels: State of the Art and Perspectives

M. Drexler, U. Arnold, P. Haltenort, J. Sauer

Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Germany

Abstract

Regarding alternative diesel fuels, current research strongly focusses on so-called oxymethylene ethers (OMEs). From a chemical point of view, OMEs are oligomeric acetals with alternating carbon and oxygen atoms and especially OMEs of the type $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ with $n = 3-5$ (OME₃₋₅) exhibit a diesel-like behavior. Despite their favourable fuel characteristics, e.g. extremely low soot and NO_x emissions, availability on a larger scale is still limited and numerous activities aim for an improved production [1].

According to the molecular structure, production of OMEs is based on methanol, formaldehyde and derivatives thereof [1]. The main options are i) the classical process employing the reaction of dimethoxymethane (OME₁, methylal) with trioxane, ii) reactions of methanol with formaldehyde sources and iii) recently reported reactions which are on a comparatively lower level of development. The latter option comprises, among others, reactions of dimethyl ether (DME) with formaldehyde sources, the integrated conversion of CO₂ to OME₁ and direct conversion of methanol to OME₁.

Within this work, the different strategies for OME production are compared concentrating on the starting materials, catalysts, the role of water and the resulting product spectra. All synthesis procedures lead to characteristic OME mixtures which are usually dominated by OME₁. An exception are reactions of DME with formaldehyde sources which can be kinetically controlled so that the content of undesired short chain OMEs can be suppressed [2]. Recent developments in this field will be presented.

In addition to OME production, physico-chemical and fuel characteristics are discussed and different strategies for tuning the properties of OME mixtures are proposed. A largely unexplored option is the synthesis of OMEs with different end groups, e.g. by reactions of higher alcohols with formaldehyde sources [3] or by transacetalization reactions of OMEs in the presence of acidic catalysts [4].

Regarding fuel applications, several studies on chemical, oxidative and thermal stability have been carried out, which will be critically reviewed. In this context, compatibility with commonly used materials and, in the case of fuel blends, compatibility with other fuel components are also considered. Furthermore, recent progress regarding non-fuel applications is described.

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Fischer-Tropsch Synthesis of Higher Alcohols Using Supported Iron-based Catalysts

M. Medicus, M. Merkel, P. Otto, E. Reichelt, M. Jahn
Fraunhofer IKTS, Dresden, Germany

Abstract

Chemical and pharmaceutical industry are generating an growing demand for alcohols as solvents, detergents and additives over the last years that is supposed to further increase in the next decades. Especially so-called higher alcohols that contain more than two carbon atoms per molecule are experiencing high interest [1]. The established higher alcohol production routes depend on fossil fuels and no sustainable alternative has reached industrial applicability so far. However, Fischer-Tropsch synthesis (FTS) which is a well-known process to produce hydrocarbons from syngas is also known to yield oxygenates like alcohols as side-products [1]. Especially iron catalysts show promising higher alcohol selectivities in FTS.

First studies revealed that iron catalysts can be optimized applying chemical promoters like potassium, copper and molybdenum [2]. Furthermore, higher alcohol selectivity depends on the choice of operating conditions e.g. pressure, temperature and H₂/CO ratio of the syngas. However, most studies are focused on laboratory-scale synthesis, while research on formulation and shaping of catalysts for pilot or industrial plants is still widely neglected [3].

Therefore, this study addresses the fundamentals of upscaling of iron-based Fischer-Tropsch catalysts applying Al₂O₃ powders of different particle size and modification as support materials. Furthermore, chemical promotion by K, Cu and Mo was applied to supported catalysts in order to investigate differences between unsupported and supported catalyst systems.

All catalysts were tested regarding conversion and selectivity. Conclusions are drawn on appropriate catalyst-support interactions by the choice of support and precursor materials as well as on optimized impregnation and FTS conditions. Additionally, the influence of chemical promotion is investigated in detail. The gained knowledge will be used as starting point for the production of different supported and structured Fischer-Tropsch catalysts.

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Chemical Upgrading of Bio-Waste Based on a Thermo-Catalytic Pyrolysis and Reforming Process

F. Schmutzler^a, J. Titus^a, J. Neidel^b, V. Palchyk^b, D. Roempler^c, D. Poppitz^a, A. Hornung^b, R. Gläser^a

^a Universität Leipzig, Institute of Chemical Technology, Linnéstr. 3, 04103 Leipzig

^b Fraunhofer UMSICHT, An der Maxhütte 1, 92237 Sulzbach-Rosenberg

^c Fraunhofer IVV, Giggenhauser Str. 35, 85354 Freising

Abstract

Until today, only a fraction of the large amount of bio-waste can be utilized. With the so-called Thermo-Catalytic Reforming (TCR[®]) process, it is possible to convert biomass, e.g., digestates, wood residues and even sewage sludge into a gaseous, liquid and solid phase (TCR[®]-gas, -oil and -char) with high energetic and chemical value.¹⁻³ Depending on the feedstock, the resulting thermally stable TCR[®]-oil is rich in organic components, which can be utilized and upgraded. The BMBF funded project "PhenOlefin" aims to identify, isolate and upgrade organic compounds from TCR[®]-oils to produce value-added chemicals for industrial use. In a first step, Fraunhofer UMSICHT investigates the parameters of the TCR[®]-process under which an oil, with a high phenol content can be obtained. Subsequently, Fraunhofer IVV isolates the phenols from the TCR[®]-oil by means of thermal and chemical separation techniques. The aromatic compounds and alkanes in the remaining organic mixture are catalytically converted by Universität Leipzig to obtain a mixture of olefines. The companies Süd-West-Chemie and Wacker will use the phenols and olefins as precursors to resins and polymers, while Susteen evaluates the process on an industrial scale.

Varying the TCR[®]-feedstock significantly affects the content of phenols obtained in the TCR[®]-oil. Compared to other lignocellulose-based feedstocks digestates deliver the highest yield of phenols (11.5 g/kg feedstock). Increasing the reformer temperature from 773 to 973 K results in a higher yield of phenols (11.8 to 15.4 wt.-%) from digestate. A phenol extraction procedure based on controlled counter-current distillation followed by sequential liquid-liquid extraction yields a liquid phase containing over 90 wt-% phenols. Additionally, it is aimed to upgrade the phenol-poor distillation- and oil-fractions, mainly containing aromatics, naphthenes and long-chain hydrocarbons. For that purpose, the aromatics are converted by hydrogenative ring-opening and successively by dehydrogenation to obtain olefins. For the hydrogenative ring-opening a model mixture consisting of n-tridecane, n-butylcyclohexane, decaline, naphthalene and p-xylene was investigated over different Pt/Al₂O₃ and Pt/zeolite catalysts. Depending on the acid properties of the catalyst, hydrogenation, ring-opening or cracking was observed.

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