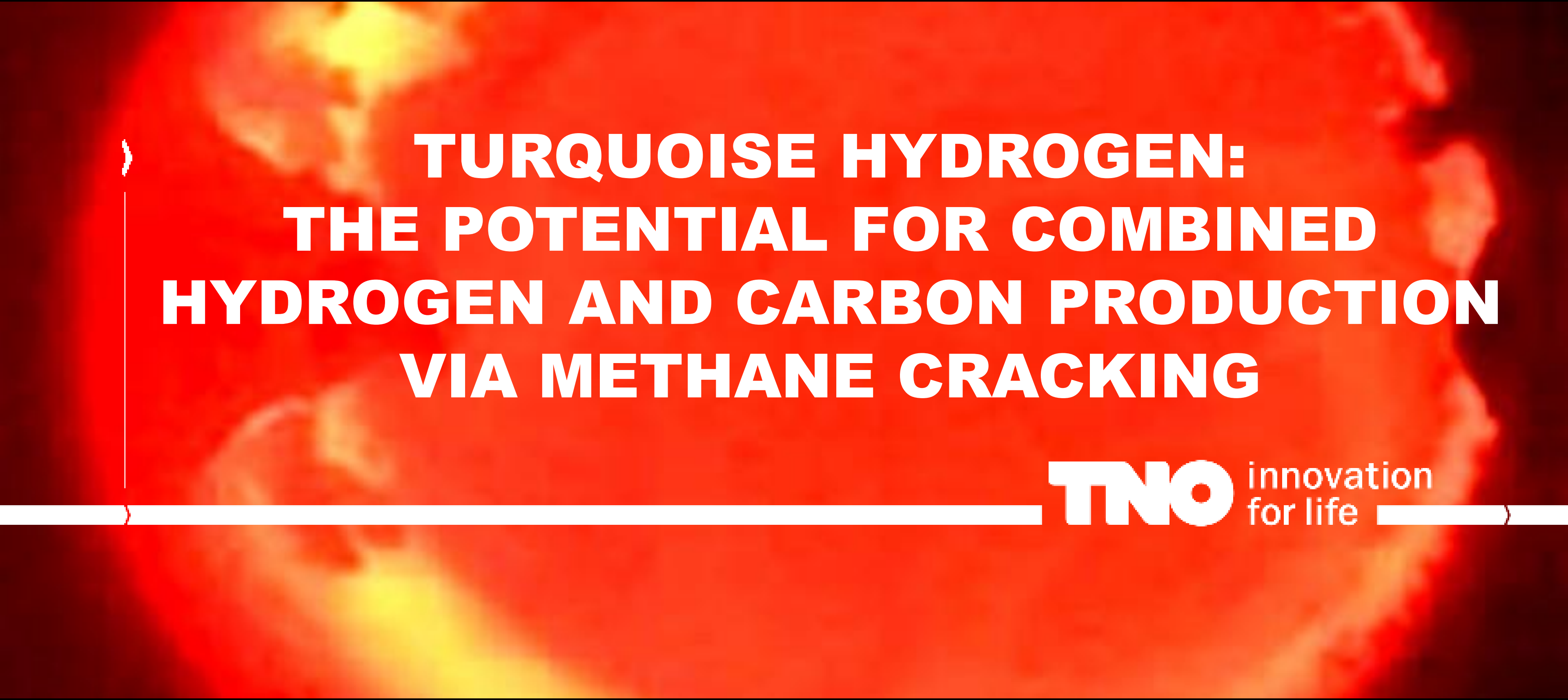

TURQUOISE HYDROGEN: THE POTENTIAL FOR COMBINED HYDROGEN AND CARBON PRODUCTION VIA METHANE CRACKING

TNO innovation for life

Rajat Bhardwaj, Jan Willem Konemann, Earl Goetheer

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Part-time professor TUDelft
CO2 utilisation/mechanical engineering

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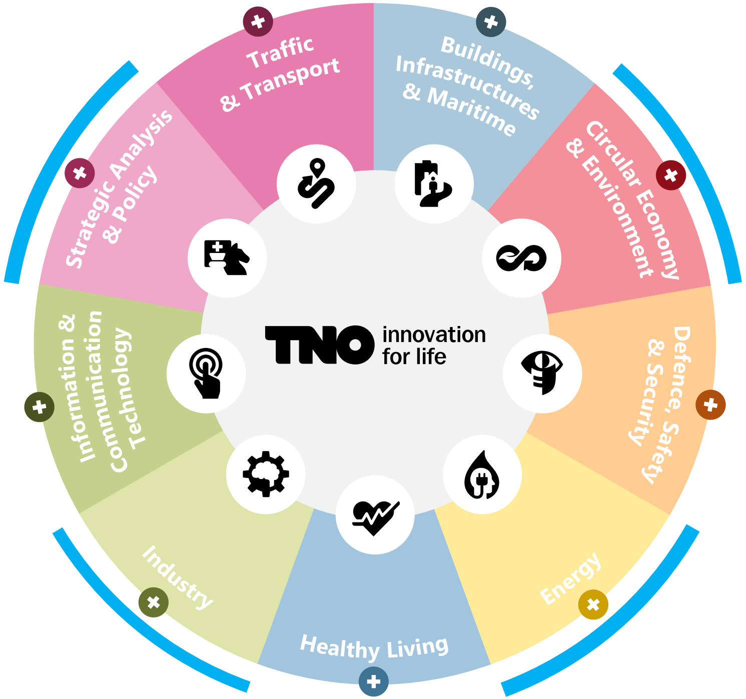
OUR MISSION & APPROACH

TNO connects people and knowledge to create innovations that boost the competitive strength of industry and the wellbeing of society in a sustainable way.

This is our mission and the professionals of TNO have used their knowledge and experience to this end for more than eighty years.

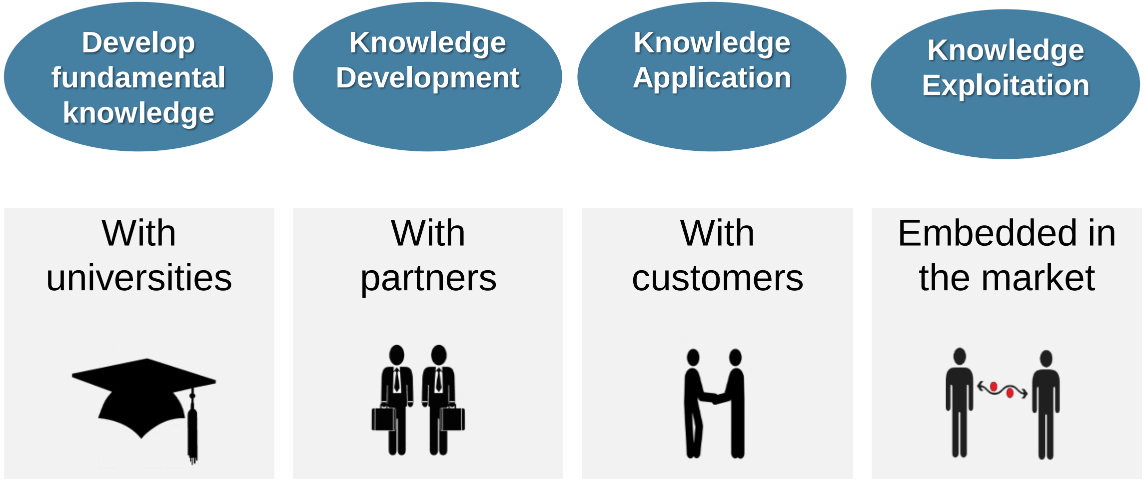
‘INNOVATION FOR LIFE’



Our dedicated pockets of technology & knowledge development and a multidisciplinary approach towards the market and our customers

THE POWER OF TNO

- Active in all steps of the knowledge development process
- Multidisciplinary: combination of knowledge domains
- Cross fertilization: tap into expertise from other markets and applications
- Independent



Develop fundamental knowledge

With universities

Knowledge Development

With partners

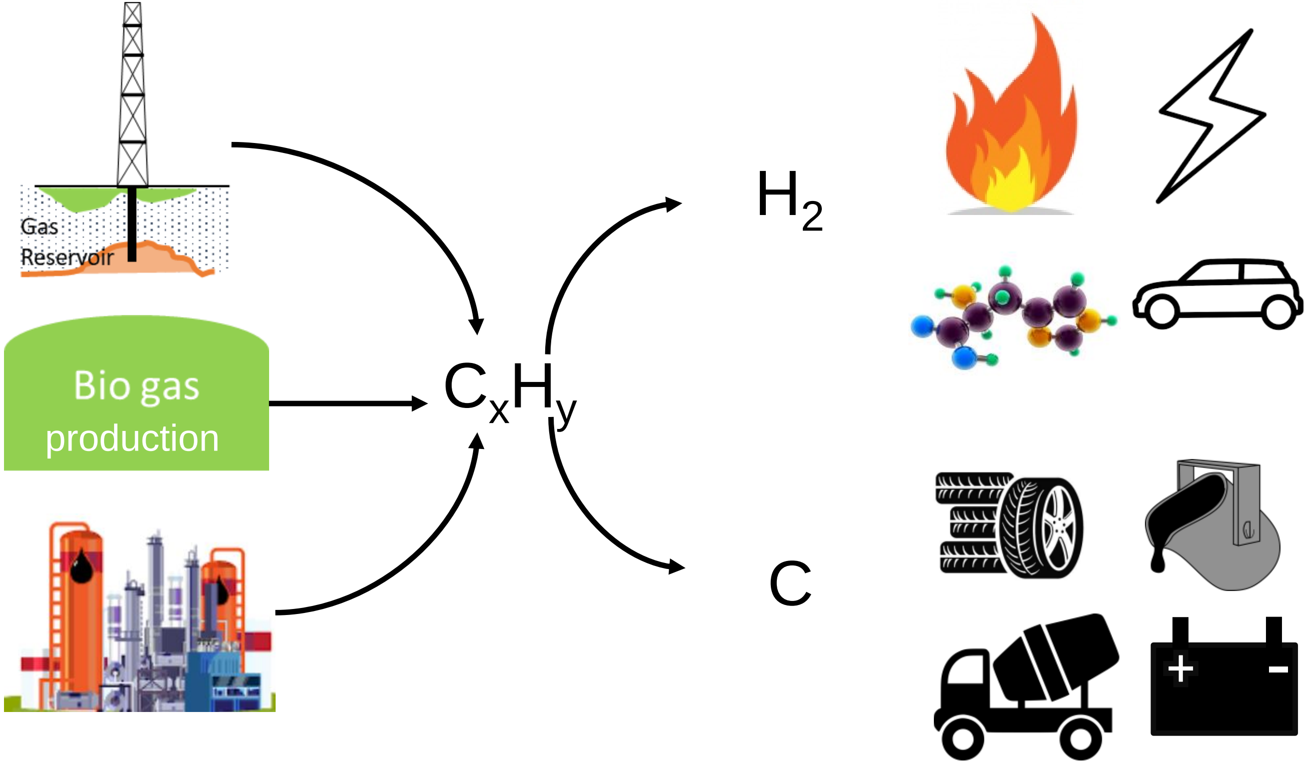
Knowledge Application

With customers

Knowledge Exploitation

Embedded in the market

WHY DO LARGE SCALE PYROLYSIS?



Bio gas production

C_xH_y

H_2

C

9 – 11

tonnes CO_2/ton H_2

2.5 – 4.5

tonnes CO_2/ton C

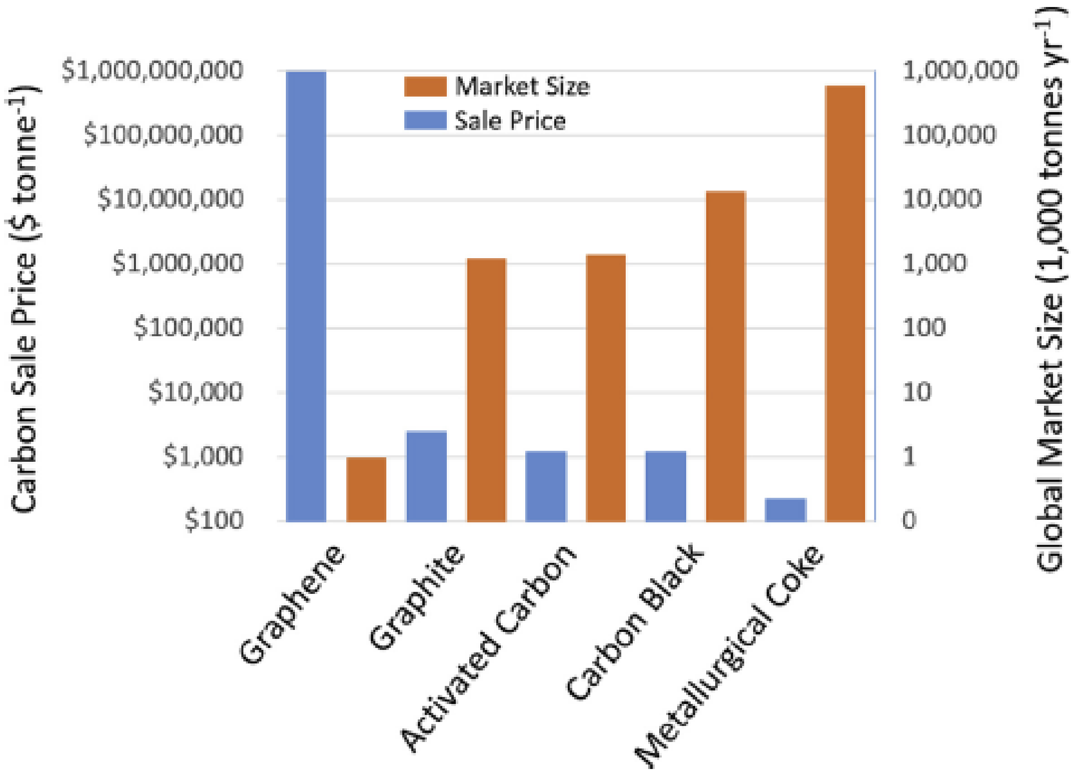
ABUNDANT RAW MATERIALS

H_2 & C ARE BASE PRODUCTS

>90% CO_2 REDUCTION

(0 – 2.5 ton CO_2/4 ton product)

CARBON MARKET FOR DIFFERENT PRODUCTS

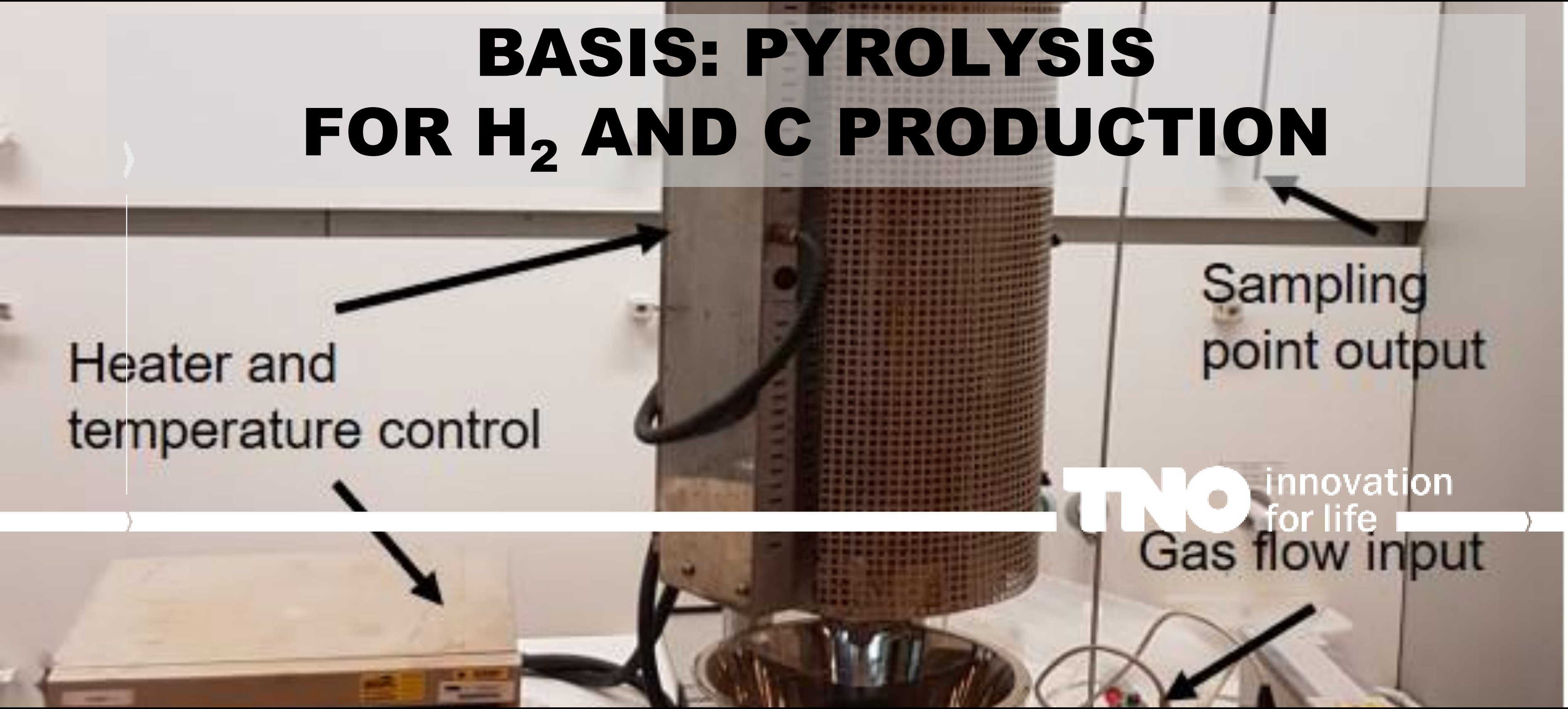


Tuneable carbon technology development can accommodate variety of products.

doi.org/10.1016/j.ijhydene.2017.12.081c

CONTENTS

BASIS: PYROLYSIS FOR H_2 AND C PRODUCTION

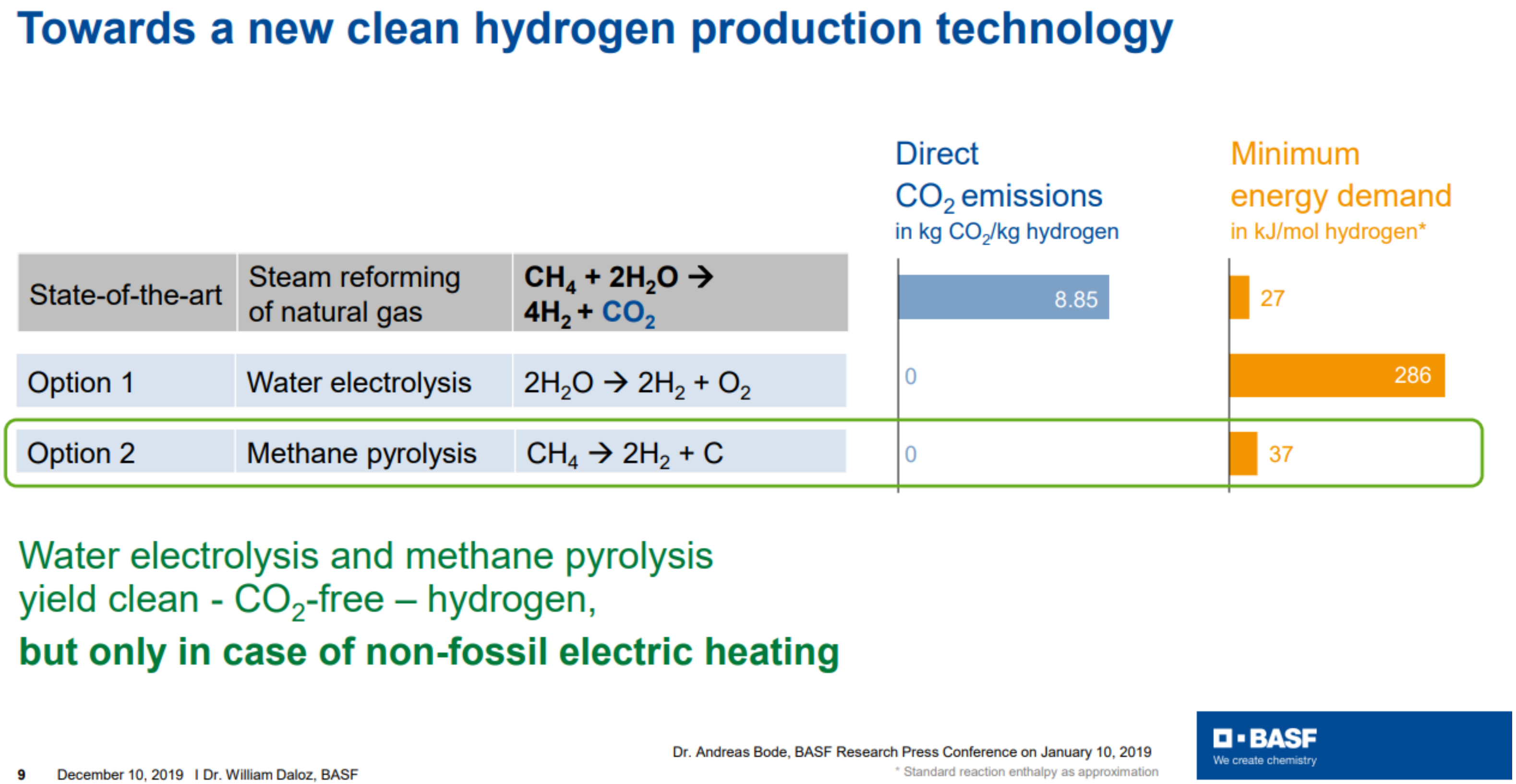


BASIS: PYROLYSIS (MOLTEN METAL) TECHNOLOGY

		$\Delta H_{Thermodynamic}$
Steam methane reforming*	$CH_4 + 2\,H_2O \rightarrow CO_2 + 4H_2$	41 kJ/mol H_2
CO_2 reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	124 kJ/mol H_2
Hydrolysis	$H_2O \rightarrow \frac{1}{2}\,O_2 + H_2$	283 KJ/mol H_2
Pyrolysis	$CH_4 \rightarrow C + 2H_2$	38 KJ/mol H_2

* Water gas shift is included in the reaction equation.

- At 100% conversion, energy/mole reaction is similar for reforming and pyrolysis.
- Steam reforming results in CO_2 problem; Pyrolysis results in (solid) carbon product.



Towards a new clean hydrogen production technology

			Direct CO_2 emissions in kg CO_2/kg hydrogen	Minimum energy demand in kJ/mol hydrogen*
State-of-the-art	Steam reforming of natural gas	**$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$**	8.85	27
Option 1	Water electrolysis	$2H_2O \rightarrow 2H_2 + O_2$	0	286
Option 2	Methane pyrolysis	$CH_4 \rightarrow 2H_2 + C$	0	37

Water electrolysis and methane pyrolysis yield clean - CO_2-free – hydrogen,

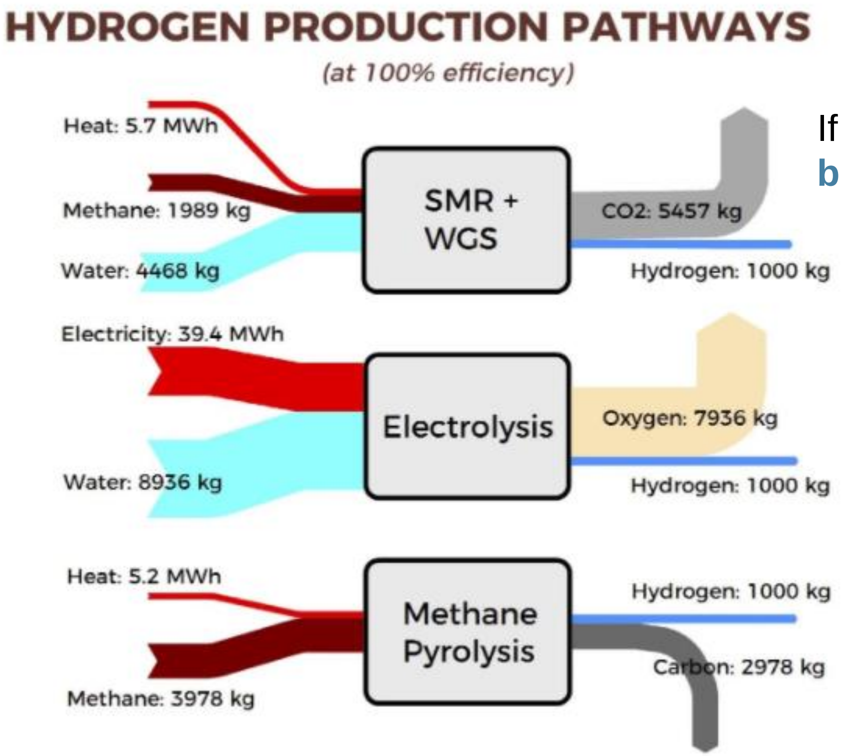
but only in case of non-fossil electric heating

Dr. Andreas Bode, BASF Research Press Conference on January 10, 2019

* Standard reaction enthalpy as approximation

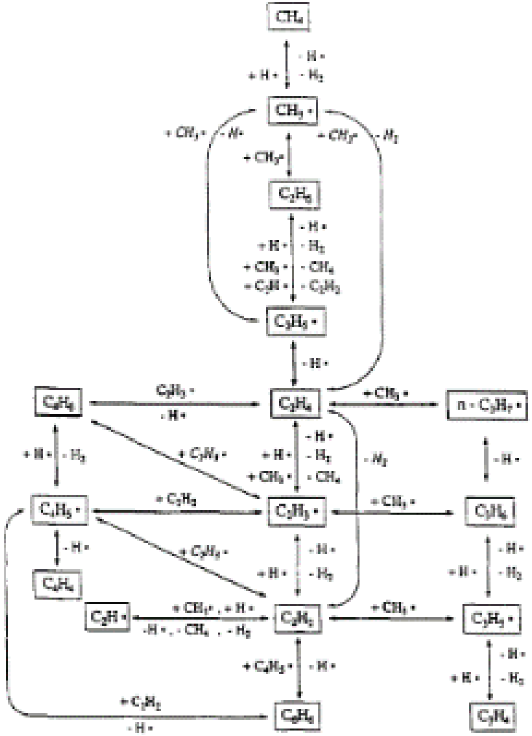
BASF We create chemistry

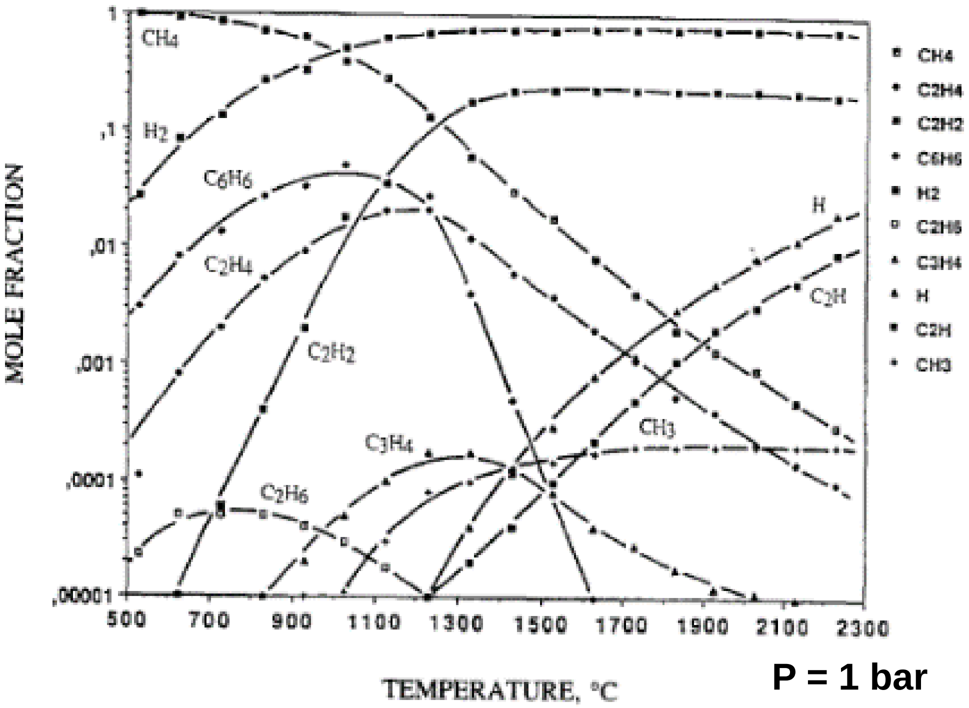
- **Grey hydrogen**
- **Green hydrogen**
- **Turquoise hydrogen**



If CO_2 stored than **blue hydrogen**

THERMODYNAMICS OF METHANE PYROLYSIS





P = 1 bar

High temperature is favour carbon formation.
H_2 dilution, fast reaction and temperature quench lead to higher carbon atoms products.

doi.org/10.1016/0378-3820(94)00109-7

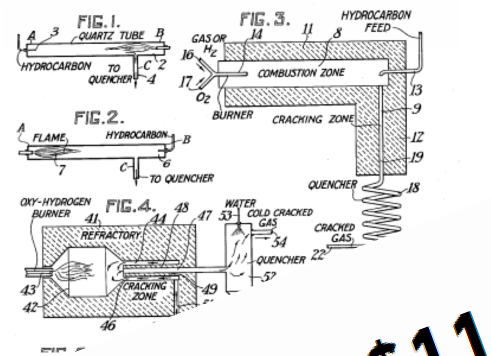
TIMELINE: METHANE PYROLYSIS

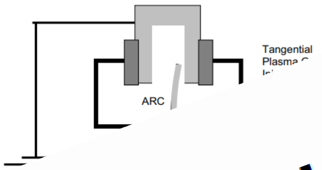
ENERGY

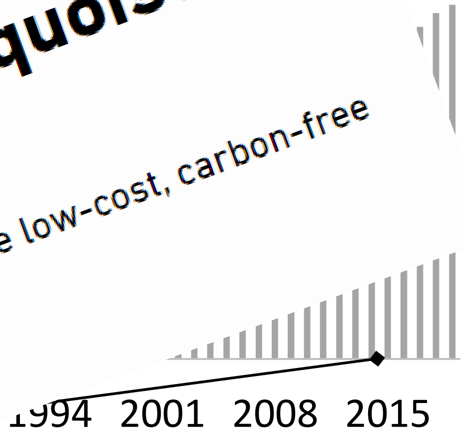
C-Zero Raises $11.5M to Scale Up 'Turquoise Hydrogen' Technology

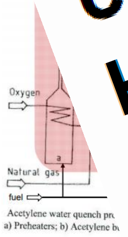
Breakthrough Energy Ventures and Eni Next back the startup's plan to make low-cost, carbon-free hydrogen from natural gas.

JEFF ST. JOHN | FEBRUARY 09, 2021







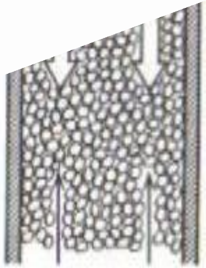


Acetylene water quench pr
a) Preheaters; b) Acetylene b

BASF

cetylene

Monolith Materials

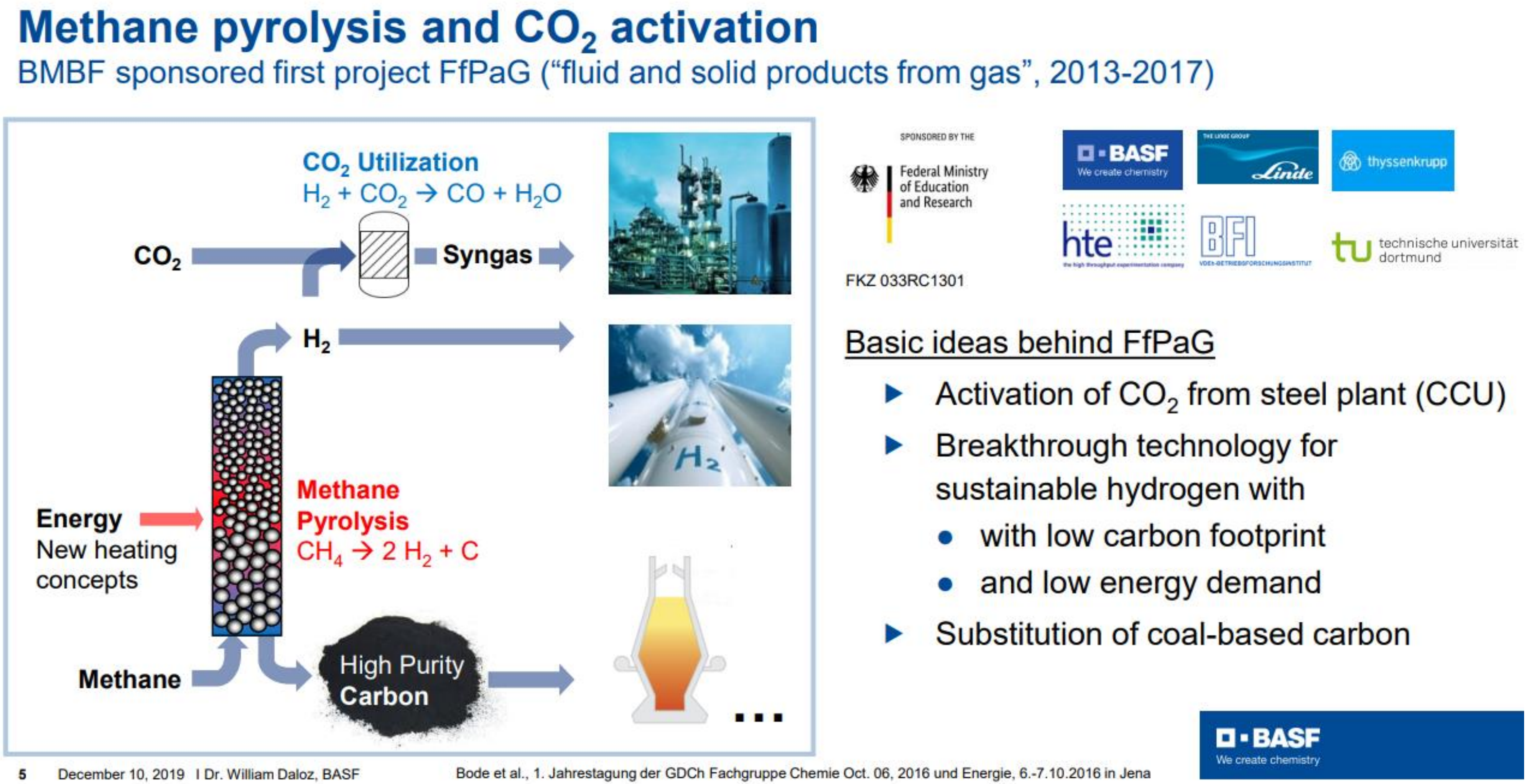


BASF

HAZER Group

Groups in UK, US, Spain, Germany, Netherlands are working including companies such as GAZPROM, GASPLAS, ThyssenKrupp, Air Liquide and others.

Formation and separation of carbon has been a major challenge throughout.



Methane pyrolysis and CO_2 activation

BMBF sponsored first project FfPaG (“fluid and solid products from gas”, 2013-2017)

CO_2 Utilization

$H_2 + CO_2 \rightarrow CO + H_2O$

CO_2

Syngas

H_2

Methane Pyrolysis

$CH_4 \rightarrow 2\ H_2 + C$

Energy

New heating concepts

Methane

High Purity **Carbon**

...

SPONSORED BY THE

Federal Ministry
of Education
and Research

FKZ 033RC1301

Basic ideas behind FfPaG

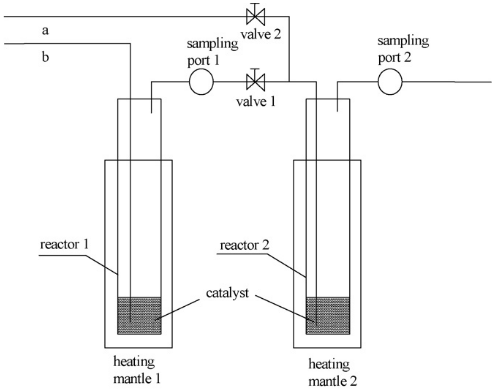
- Activation of CO_2 from steel plant (CCU)
- Breakthrough technology for sustainable hydrogen with
  - with low carbon footprint
  - and low energy demand
- Substitution of coal-based carbon

5 December 10, 2019 I Dr. William Daloz, BASF

Bode et al., 1. Jahrestagung der GDCh Fachgruppe Chemie Oct. 06, 2016 und Energie, 6.-7.10.2016 in Jena

NEW DEVELOPMENTS: CATALYSTS

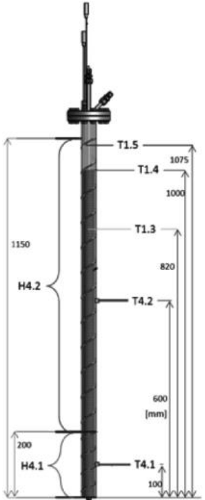
Mg molten metal batch setup



doi:10.1016/j.molcata.2007.12.018

~20% conversion

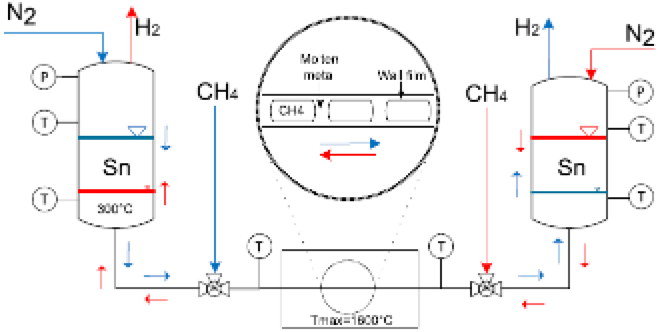
Tin bubble column reactor



http://dx.doi.org/10.1016/j.ijhydene.2015.04.062

~40% conversion

Capilary slug flow reactor



http://dx.doi.org/10.1016/j.ijhydene.2016.12.044

~80% conversion

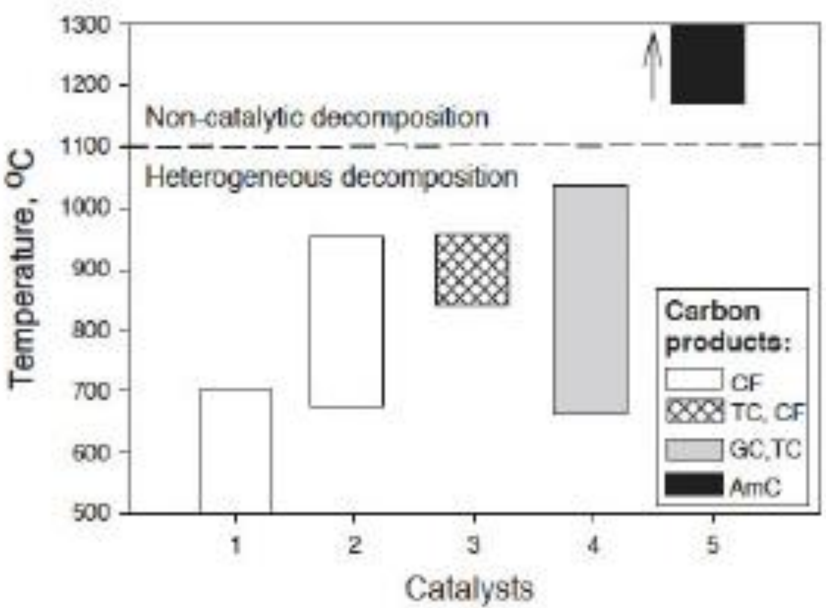
Ni-Bi bubble column reactor

Upham et al., Science 358, 917–921 (2017)

~95% conversion

Advantages of inherently designed separation and floatation of carbon.
Tuning of carbon quality by different conditions and (Ni-Bi) catalyst.

IMPACT OF TEMPERATURE CONDITIONS AND CHOICE OF METAL ON CARBON FORMATION

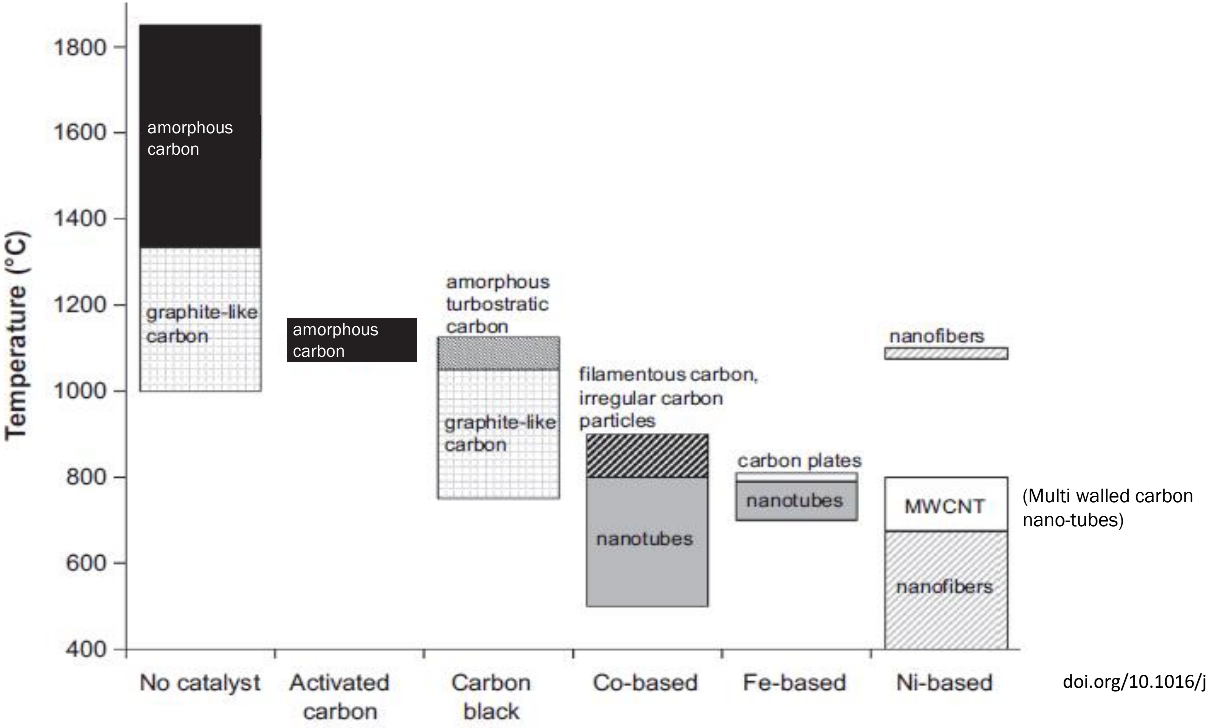


Decomposition Catalysts: 1:Ni-based, 2 :Fe-based, 3:carbon-based, 4:Co, Ni, Pd, Pt, Cr, Ru, Mo, and W catalysts, 5:non-catalytic decomposition.

Carbon products: CF:carbon filaments, TC:turbostratic carbon, GC:graphitic carbon, AmC:amorphous carbon.

The quality of carbon produced is dependent on the Temperature – catalyst combination.

WHY MOLTEN MELT PYROLYSIS: CARBON QUALITY



doi.org/10.1016/j.enconman.2016.08.060; Muradov et al.

Flexibility in quality of carbon produced with temperature – catalyst combination.

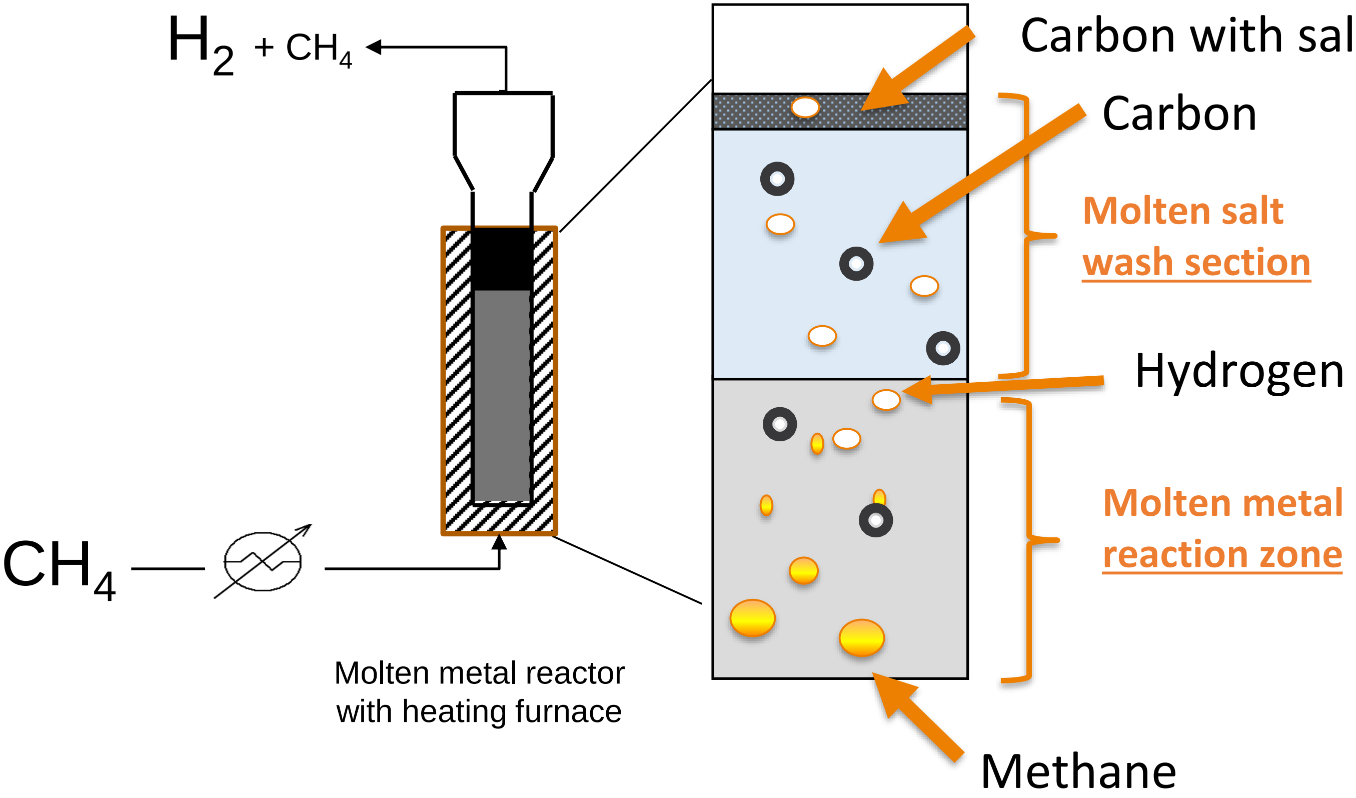
WHY MOLTEN MELT PYROLYSIS?

Technology	TRL	Scalability	Conversion per pass	Flexibility			
				Energy **(for dissociation)**	**Carbon**	**Other products**	**Operation**
Plasma DC arc	9	Limited, cannot work at high pressure	high	Electricity only	Amorphous carbon	Extendable to chemical production	Flexible on/off with thermal losses.
Plasma micro wave	2 - 4		un-certain				
Molten Melt	2 - 4	Scalable, can work at high pressure	high	Can be H_2, fuel or electricity (induction)	Flexible	Extendable to chemical/ power production	Preferably base load continuous
Fluidized bed	5-6	Scalable, can work at high pressure	low	H_2, fuel. electicity[1] (induction)	carbon on carbon	Do not know	Preferably base load continuous

1. Graphite based seed material can be heated with induction heater in a fluidized bed.
2. High pressure estimated range of 30 -60 bars.

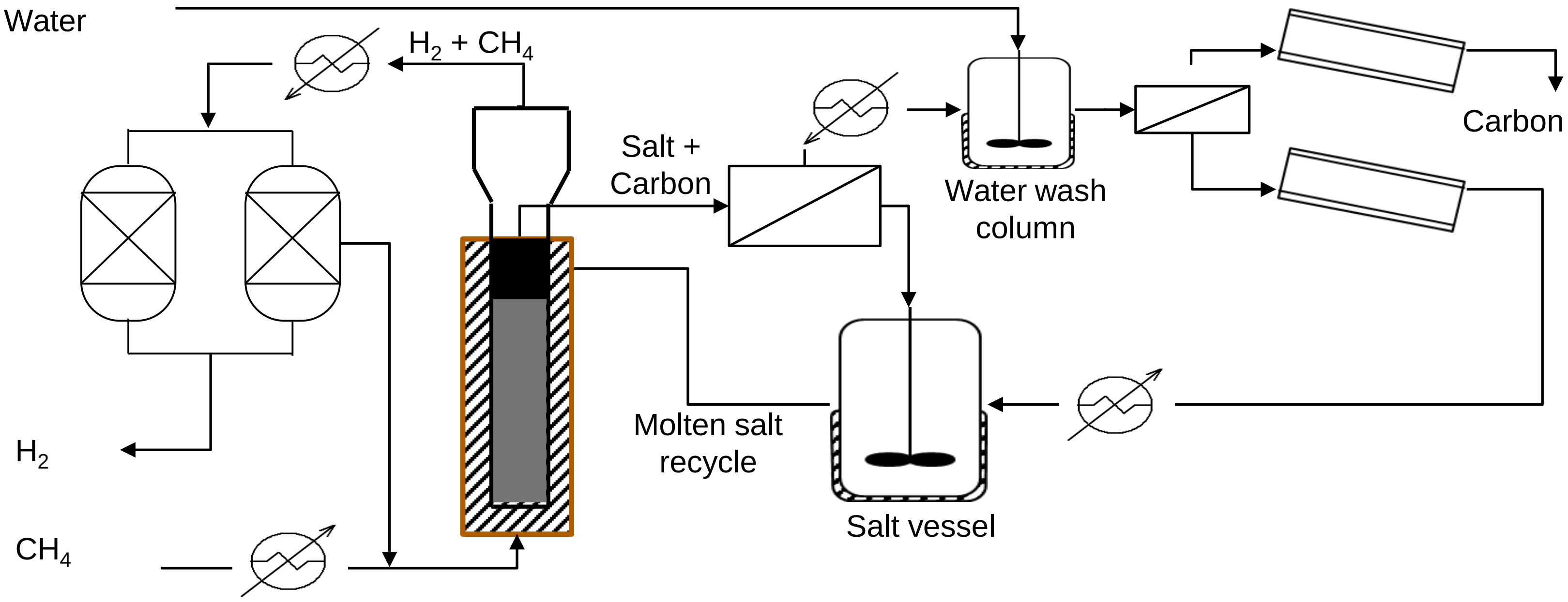
There is not yet a clear winner for methane pyrolysis technology (AVFRY analysis).

EMBER PRINCIPLE



Molten metal reactor
with heating furnace

PROCESS FLOW DIAGRAM WITH CARBON REMOVAL



PSA purification

Molten metal reactor with heating furnace

Carbon – salt filter

Carbon – water filter

Dryers

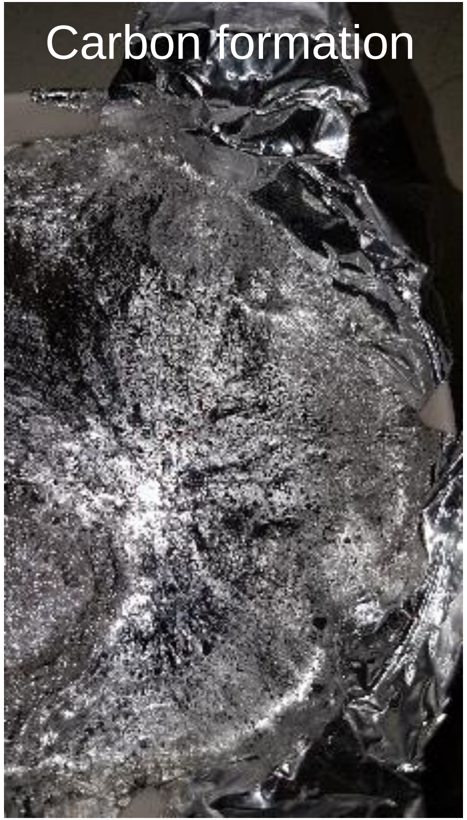
Pyrolysis reactor and carbon separation in a continuous operation.

EXPERIMENTAL VALIDATION

TNO innovation for life

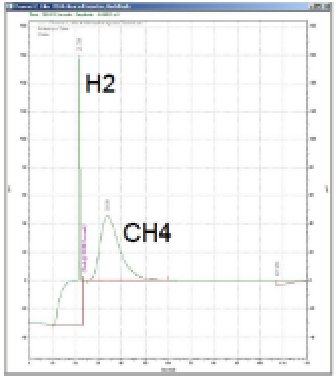
PROOF OF CONCEPT TESTING (CRACKING)


Experimental Setup


Carbon formation

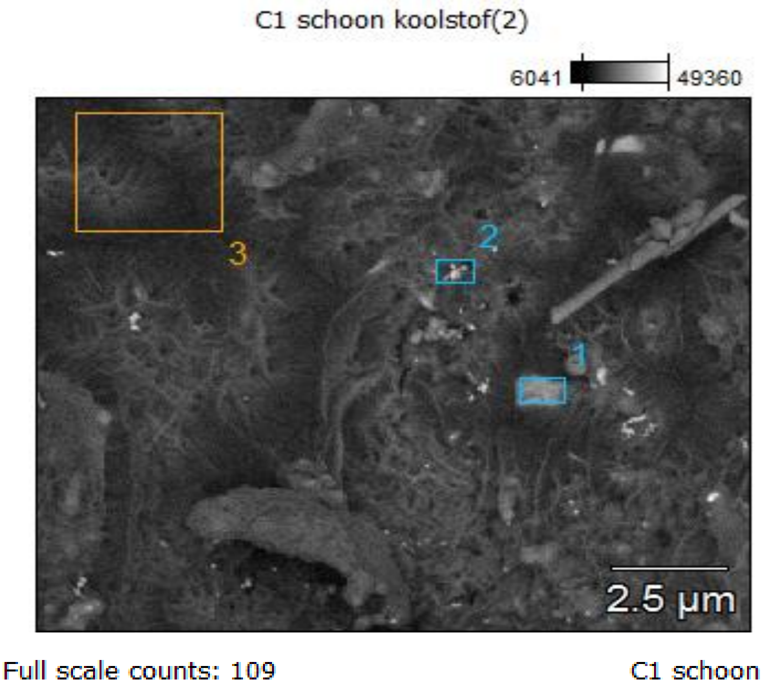

Carbon formation

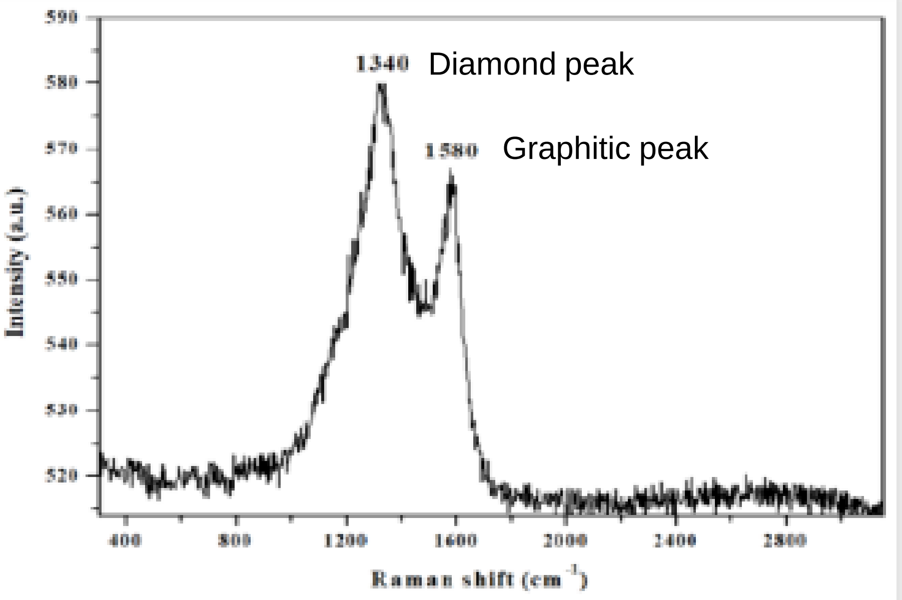
H_2 formation



Upto 90% conversion to products from cracking experiments was successfully achieved.

RESULTS: CARBON ANALYSIS





- Carbon is formed with graphitic characteristics.
- Rod like structures are seen.
- Impurities of gallium (upto 30%) is detected.

PROOF OF CONCEPT TESTING (SEPARATION OF CARBON)

Initial materials

Gallium

\+

Salt

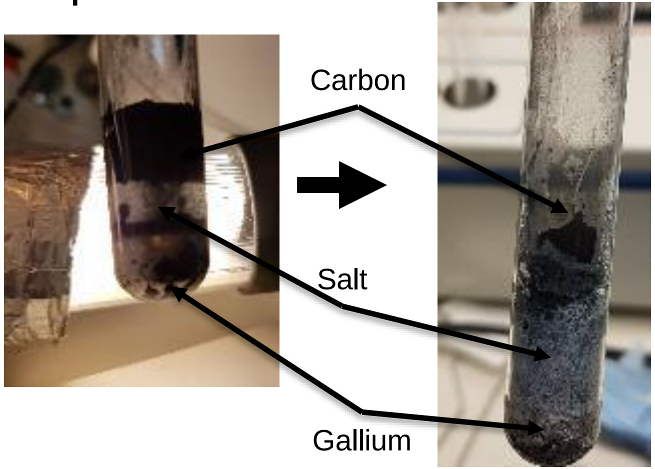
\+

Carbon
Particle size: < 100 µm.

Initial mix

High temperature Separation

Cooling @ room temperature



Re-arrangement of carbon, salt and molten metal. Carbon separated on top due to its low density.

Salt solidifies, metal remains liquid around room temperature and carbon is separated at top.

Separation

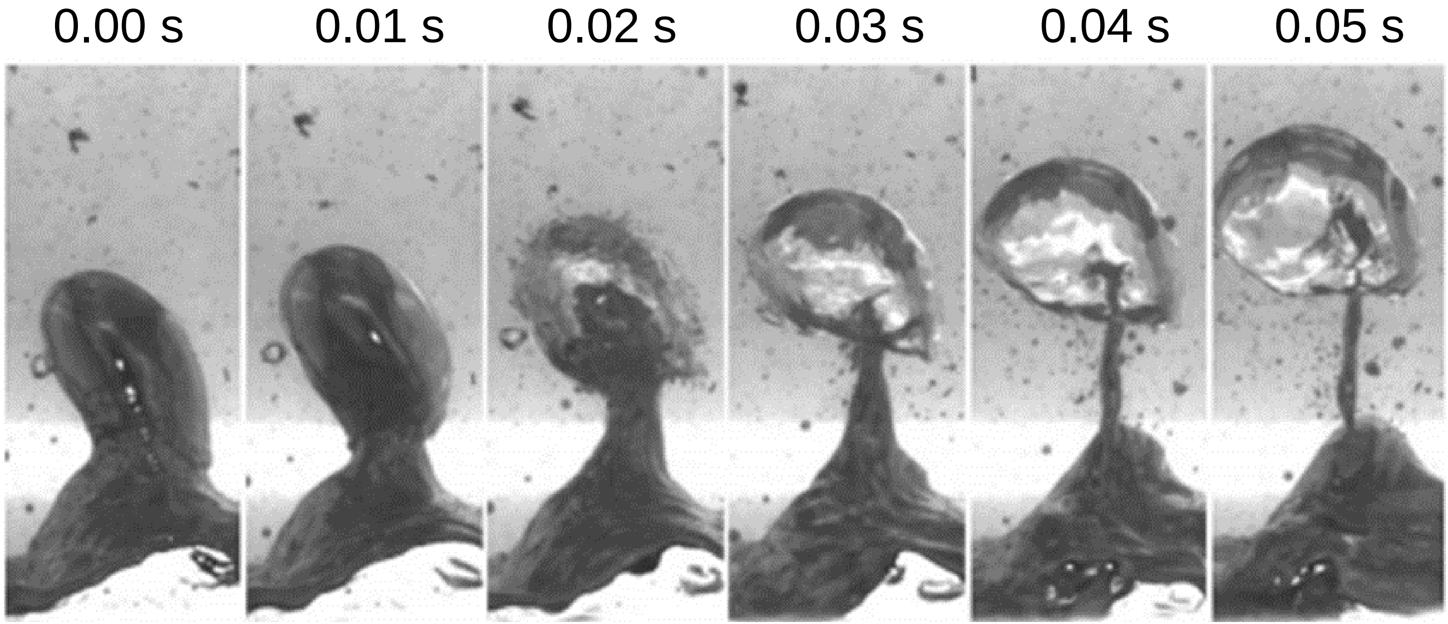
> 96% carbon was recovered in the salt layer with continuous bubbling of gas.

SALT SELECTION

- Key parameters:
  - Density : Intermediate density between carbon and molten metal;
  - Salt adhesion to carbon: Low to prevent wetting of carbon by salt.
  - Cost and safety: To limit the overall cost of production and handling.
  - Residence time of salt wash: Long enough to be able to wash metal layer from the carbon.
  - Melting point and vapor pressure: Low vapor pressure at reaction temperature.

Out of an initial list of 35 salts, seven salts were experimentally tested.

SALT SELECTION - WETTABILITY



Adhesion of graphite on salt ~ (Cation radius)^2/ Anion radius

NaBr, NaCl are more preferable than CsCl and KBr

Adapted from doi.org/10.1016/j.msea.2007.11.093

SALT SELECTION – DENSITY

Separation by flotation

Low density salt

High Density salt

- Separation due to flotation and density differences successfully achieved.
- NaCl, NaBr $ZnCl_2$ able to separate by flotation; NiCl, CuCl, $MgCl_2$ by density.

DOWNSTREAM PROCESSING: FILTRATION

Initial state Final state

Pore size – 4 – 8 µm

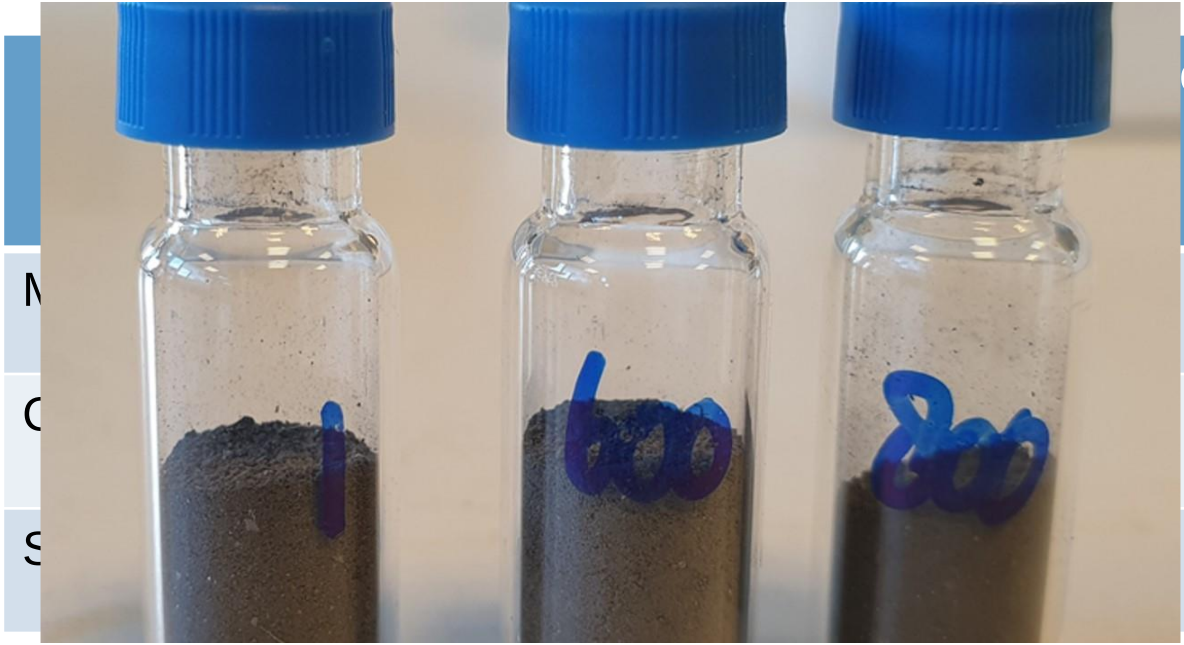
Initial state Final state

Pore size – 25 – 50 µm

- Both filters are able to separate salt from carbon – salt homogeneous mix.
- Filter with poresize of 25 - 50 micrometer has higher rate of filteration than 4 – 8 micrometer filter.

DOWNSTREAM PROCESSING – FILTRATION AND CLEANING

	d
M	
C	
S	

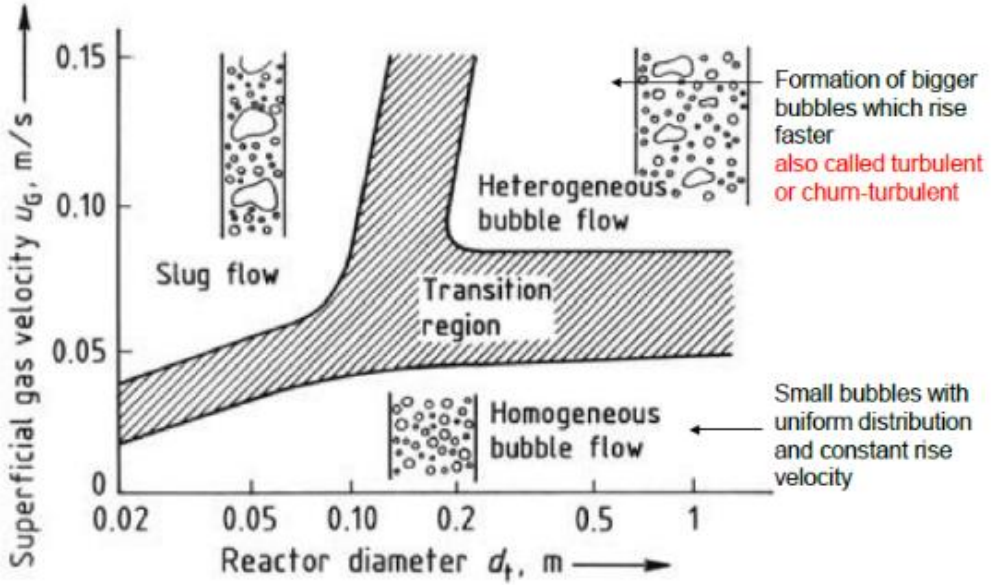


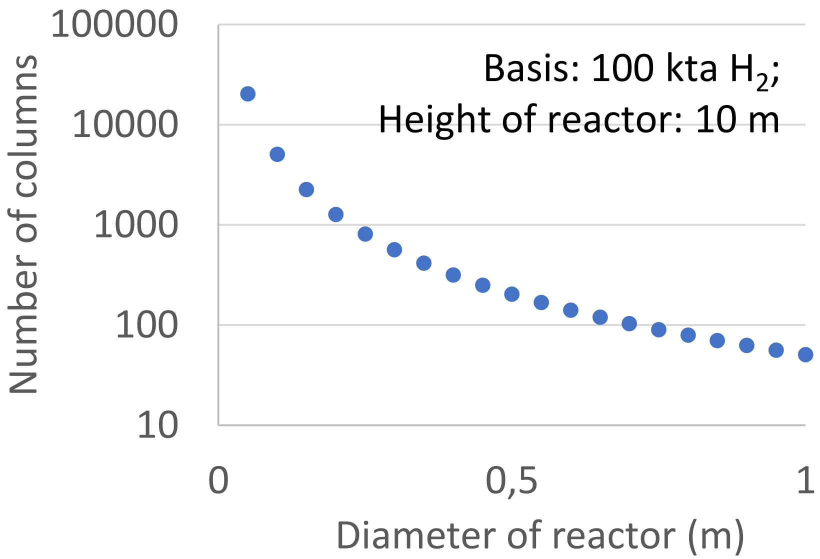
- Metal chlorides/ bromides have shown successful separation and cleaning of carbon.

Adapted from doi.org/10.1016/j.carbon.2019.05.041

SCALE UP, OPTIMIZATION AND REACTOR DESIGN

BUBBLE SIZE AND HYDRODYNAMICS





Basis: 100 kta H_2;
Height of reactor: 10 m

- Normal bubble sizes (~1-5 mm) limit scaling up of reactor.
- 100 Kta H_2 production would mean at least 100 columns of diameter of 0.75 m and 10 m in height ~ 600 m^3.

INTENSIFIED REACTOR DESIGN: MICROBUBBLE INJECTION

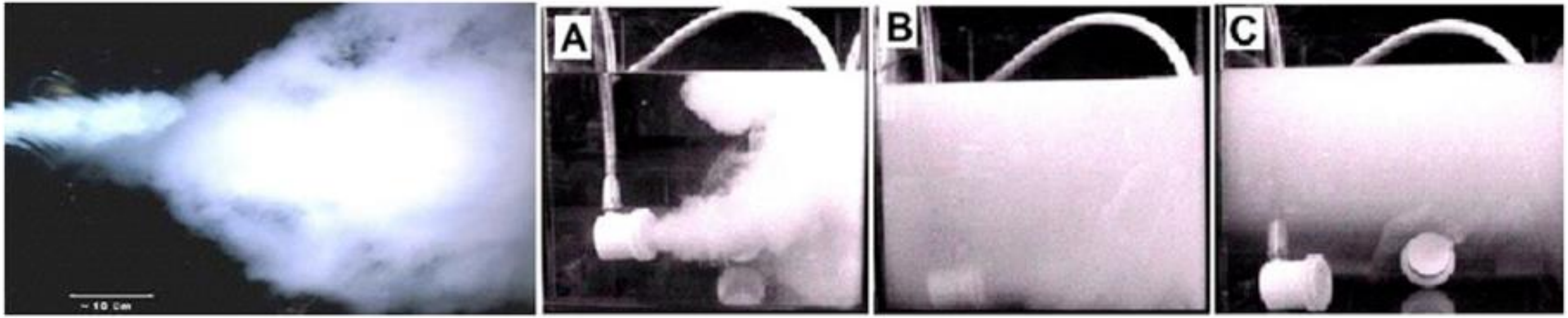


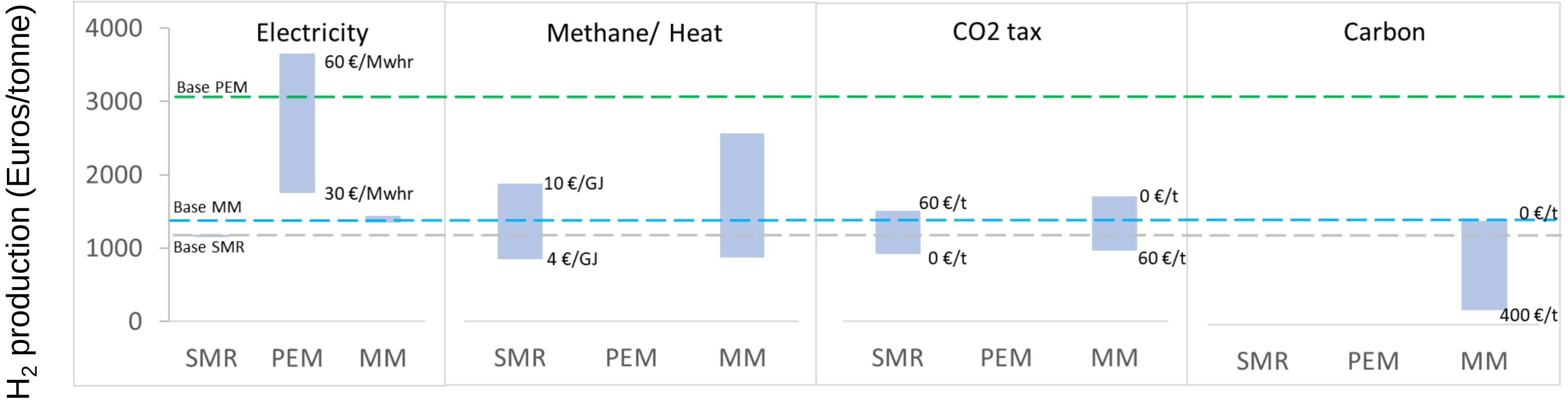
Figure 1. Microbubble sparging [Seitz 2010]. Sparging is stopped at image B and image C is 120 s later. Manufacturer claim for bubble size is ~1 µm, though the implied rise velocity is consistent with a radius of ~20 µm, perhaps with smaller bubbles having dissolved.

- 100 X increase in surface area.
- 5 X decrease in rise velocity.
- 500 X decrease in reactor volume.

TECHNO-ECONOMICS AND BUSINESS CASES

WHAT ABOUT ECONOMICS?

Marginal cost estimates (excluding CAPEX and profits)



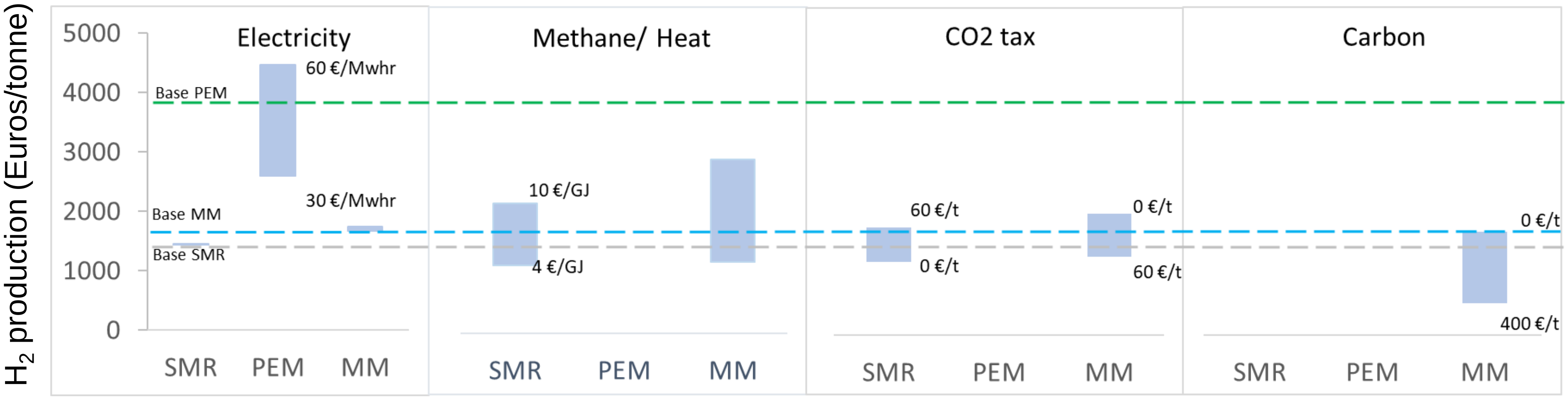
- Cost competitive with H_2 via SMR at
  - CO_2 tax/ credits of 36 euros/tonne (without sales of carbon) or
  - Solid carbon price of 260 euros/ tonne (without CO_2 tax or CO_2 credit) or
  - Solid carbon price of 80 euros/tonne and CO_2 tax/ credit of 26 euros/tonne CO_2.

Base case values:

Electricity	50	EUR/MWh	Carbon	0	EUR/t
Gas/ Heat	6	EUR/GJ	Steam	21	EUR/t
CO2 tax	25.96	EUR/t	Carbon credit	25.96	EUR/t

WHAT ABOUT ECONOMICS?

Comparison cost estimates (inclusive CAPEX)

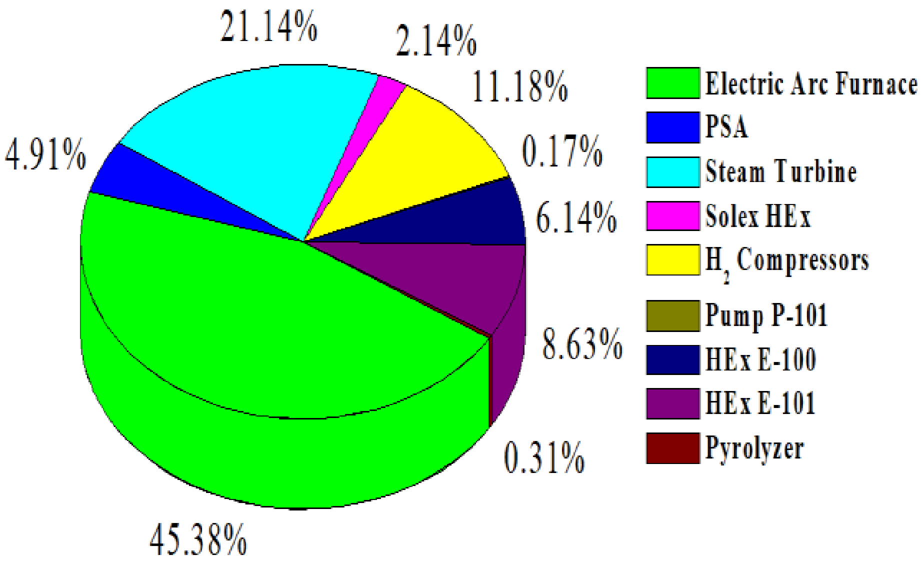


- Cost competitive with H_2 via SMR at
  - CO_2 tax/ credits of 38 euros/tonne (without sales of carbon) or
  - Solid carbon price of 270 euros/ tonne (without CO_2 tax or CO_2 credit) or
  - Solid carbon price of 95 euros/tonne and CO_2 tax/ credit of 26 euros/tonne CO_2.

Base case values:

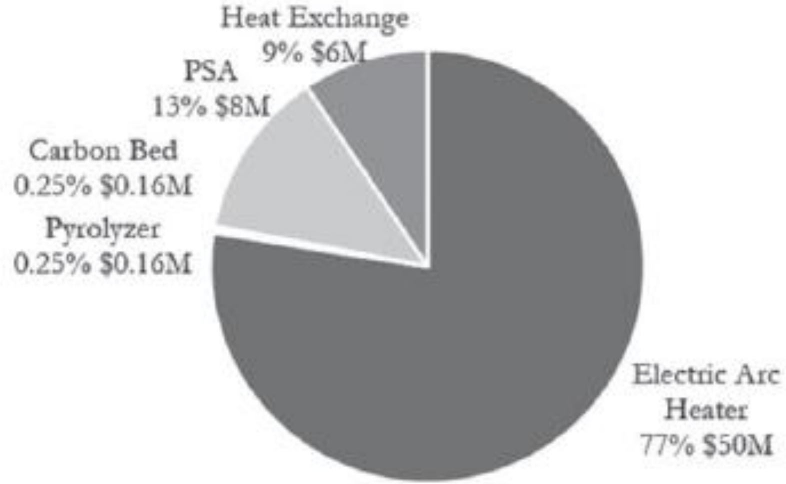
Electricity	50	EUR/MWh	Carbon	0	EUR/t
Gas/ Heat	6	EUR/GJ	Steam	21	EUR/t
CO2 tax	25.96	EUR/t	Carbon credit	25.96	EUR/t

BREAKDOWN CAPITAL COSTS FOR EQUIPMENT



TU/e – TNO estimates

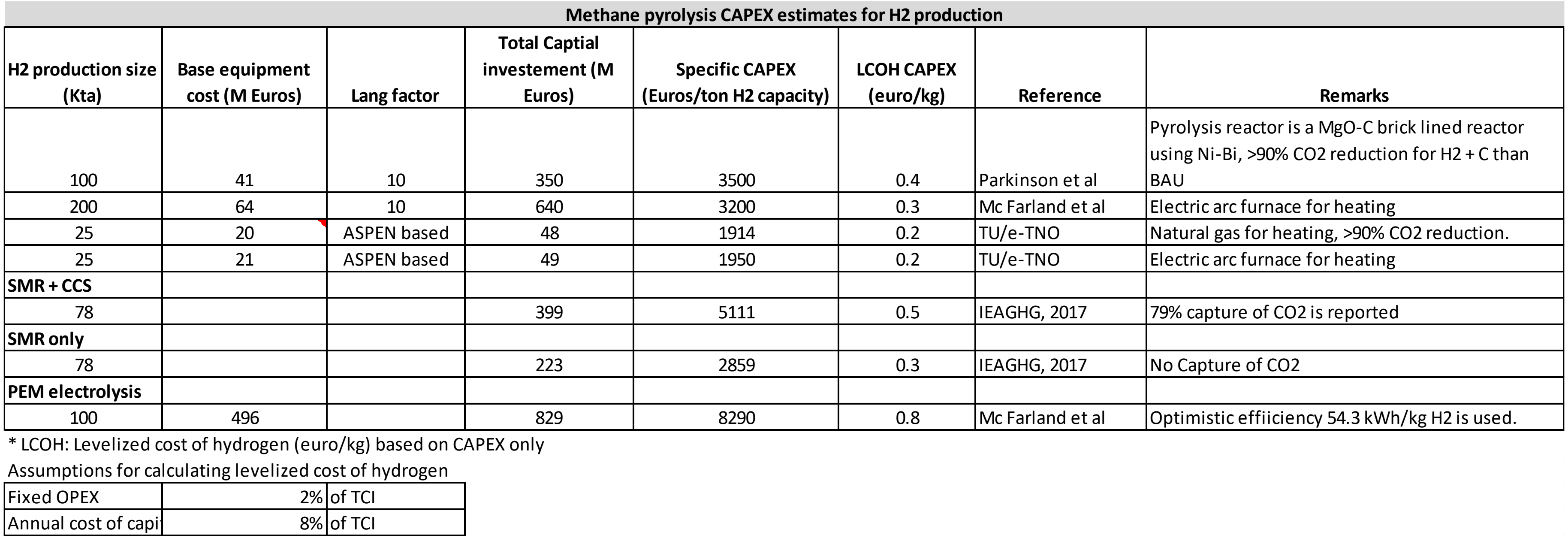
(Equipment cost: 21 Million euros for 25 kta H_2 production)



Parkinson et al.

(Equipment cost: 64 Million euros for 200 kta H_2 production)
Lang factor 6-10, TCI: 320 – 640 Million euros)

CAPEX ESTIMATES (BACKGROUND)



Methane pyrolysis CAPEX estimates for H2 production

H2 production size (Kta)	Base equipment cost (M Euros)	Lang factor	Total Captial investement (M Euros)	Specific CAPEX (Euros/ton H2 capacity)	LCOH CAPEX (euro/kg)	Reference	Remarks
100	41	10	350	3500	0.4	Parkinson et al	Pyrolysis reactor is a MgO-C brick lined reactor using Ni-Bi, >90% CO2 reduction for H2 + C than BAU
200	64	10	640	3200	0.3	Mc Farland et al	Electric arc furnace for heating
25	20	ASPEN based	48	1914	0.2	TU/e-TNO	Natural gas for heating, >90% CO2 reduction.
25	21	ASPEN based	49	1950	0.2	TU/e-TNO	Electric arc furnace for heating
SMR + CCS							
78			399	5111	0.5	IEAGHG, 2017	79% capture of CO2 is reported
SMR only							
78			223	2859	0.3	IEAGHG, 2017	No Capture of CO2
PEM electrolysis							
100	496		829	8290	0.8	Mc Farland et al	Optimistic effiiciency 54.3 kWh/kg H2 is used.

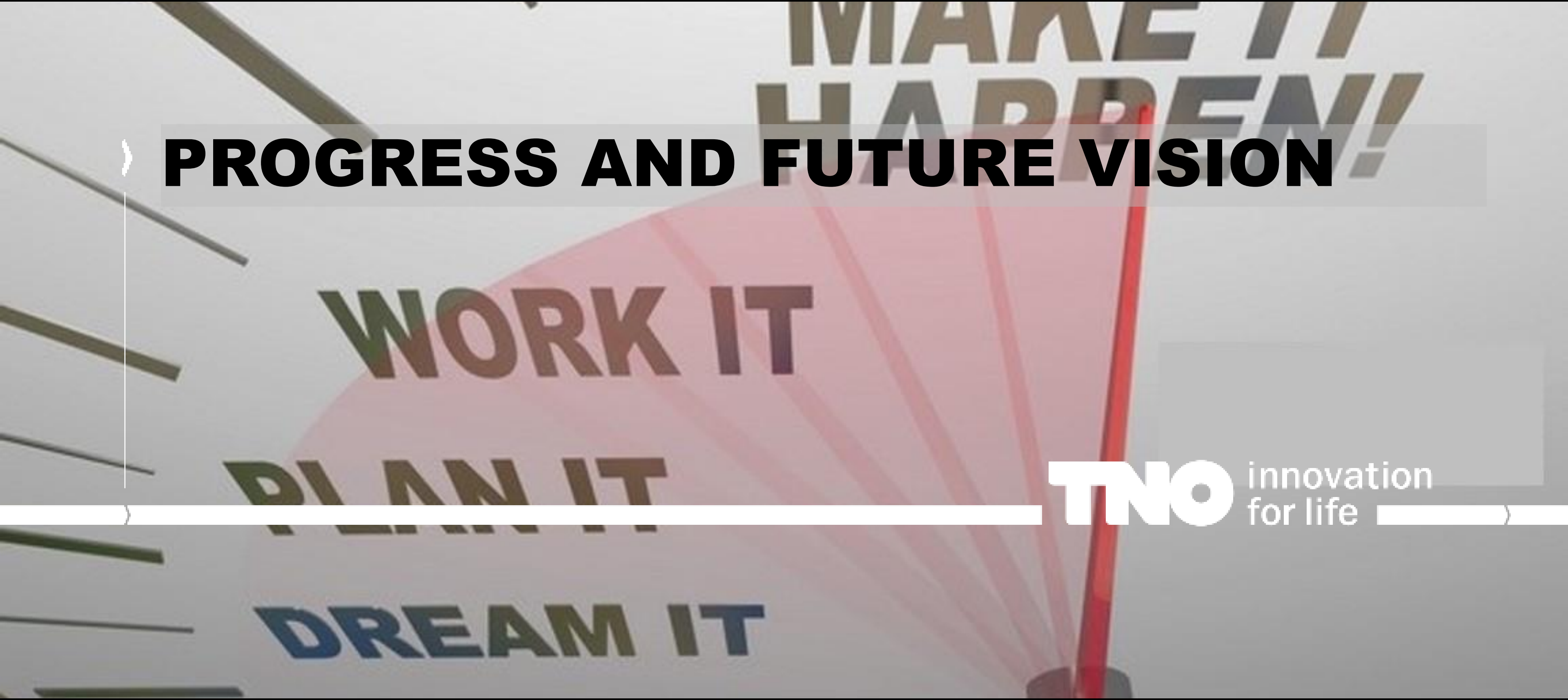
* LCOH: Levelized cost of hydrogen (euro/kg) based on CAPEX only

Assumptions for calculating levelized cost of hydrogen

Fixed OPEX	2%	of TCI
Annual cost of capi	8%	of TCI

- CAPEX estimates for pyrolysis lie in similar ‘ballpark’ as those of conventional SMR (~300 euros/tonne H_2 produced).
- Accuracy of cost estimates although done with same principles, is expected to be much more certain for SMR.
- >45% of CAPEX in pyrolysis is for (electric) furnace– reactor which is expected to decrease with process intensification.

PROGRESS AND FUTURE VISION



PROPOSED APPROACH

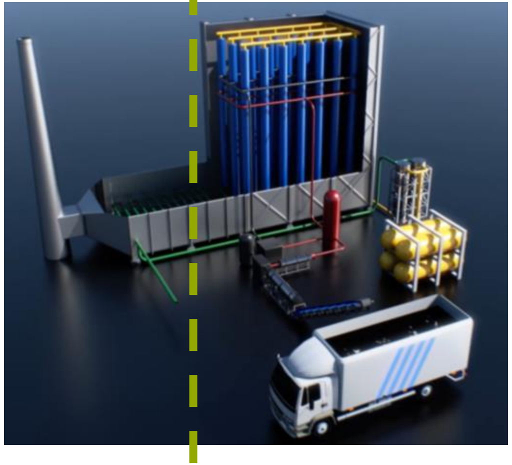
Proof of concept

Bench Scale

Continuous Process

Pilot Plant

Demonstration Plant



Today

In 2030

FUTURE OUTLOOK AND APPROACH

TECHNOLOGY PROGRESS STATUS

TRL 1 - 3			**TRL 3 - 6**			**TRL 6 - 9**
Conceptual design	Proof of concept	Techno economic evaluation	Optimization and batch scale pilot	Scale up continuous operation	Pilot plant	Commercial scale demonstration and application.
Established proof of concept for removal of carbon.			Identified main steps and questions for progressing technology.			Gained interest from companies for demonstration.

Timeline

2019

2020

2023

2025

2030

Bench Scale

- Continuous production-separation reactor.
- Tuning carbon quality with process conditions.
- Impact of variation in feedstock & impurities.
- Optimization of individual unit operations.

Continuous Process

- Scale up and effect of hydrodynamics.
- Optimization DSP with integrated reactor.
- Duration tests and de-risking for pilot.

Pilot Plant

- Scale up swing operation & single tube.
- Duration tests and de-risking for integration for site(s).

+ Continuous improvements with the cost estimates for the reactor and overall plant.

WORK PLAN TIMELINE - EMBER PYROLYSIS TECHNOLOGY

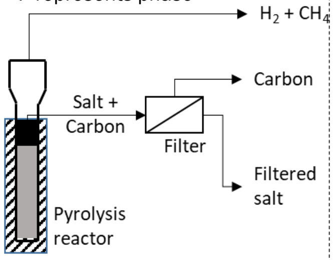
P0. Proof of concept

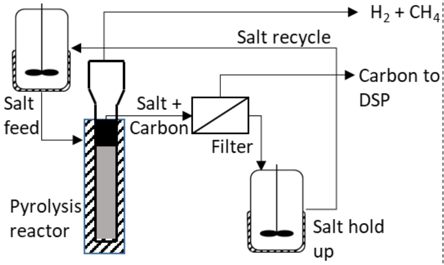
P1. Bench Scale

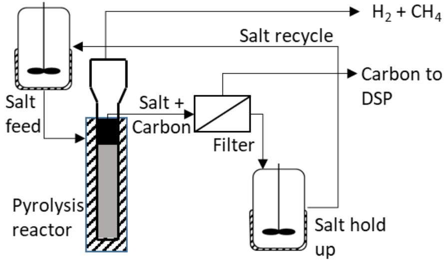
P2. Continuous Process

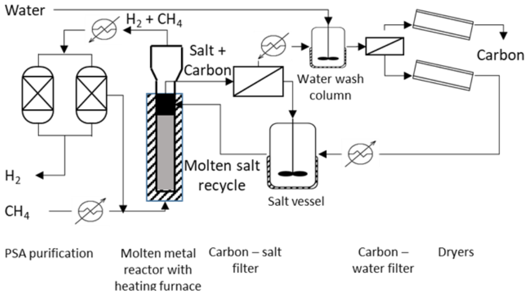
P3. Pilot Plant

* P represents phase







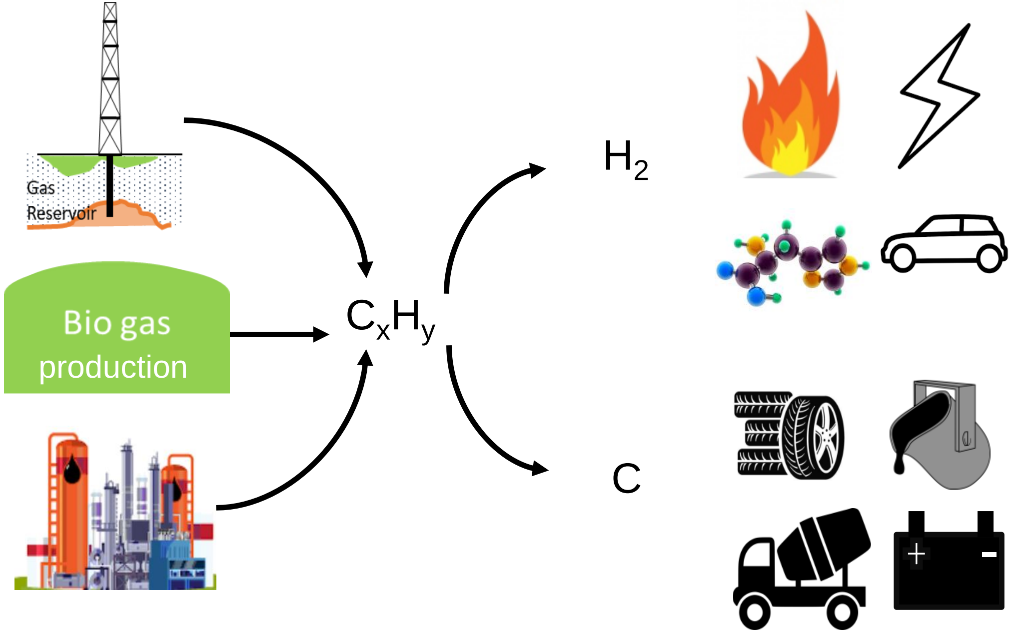


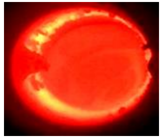
2019	2020 - 2022	2021 - 2023	2022 - 2025
Proof of concept lab scale demonstration of carbon separation.	(semi)Continuous lab scale demonstration carbon separation with salt recycle.	Continuous scale up of salt recycle and carbon separation.	Pilot scale up including downstream purification of carbon and H_2
1000 mm x 35 mm reactor; 0.04 m^3/hr H_2; 0.1 tonnes/year scale	1000 mm x 50 mm reactor; 0.04 m^3/hr H_2; 0.1 tonnes/year scale	10 L reactor; 4.5 m^3/hr H_2; 3 - 12 tonnes/year scale	20-100 L reactor; upto 500 tonnes/year scale

• Proof of concept of salt wash concept.
• Separation of carbon from metal using molten salts.
• Analysis of quality of carbon.
• Screening of filter size for the purification of carbon.
• Screening and selection of optimum salts for separation.
	• Addition of salt recycle loop for semi-continuous separation of carbon.
	• Tuning carbon quality with process conditions and hydrodynamics.
	• Impact of variation in feedstock & impurities.
	• Optimization of salt recycle loop and filtration.
	• Extension of lab scale tests (50 mm reactor) at high pressure(s).
		• Scale up to (semi)continuous process.
		• Impact of furnace – material selection on performance.
		• Effect 5 x increase in diameter on production and performance of EMBER concept.
		• Duration tests and de-risking for pilot.
		• Extension of continuous process at high pressures.
			• Scale up and effect of hydrodynamics and performance.
			• Optimization DSP with integrated reactor. These include
			  • Water wash of carbon and removal of salt.
			  • Drying of salt and drying of carbon.
			  • Heat transfer integration.
			• Duration tests and de-risking for demonstration.

Each stage involves design of setup, procurement of hardware, analysis of products, techno-economic evaluations for different value chains and engagement with stakeholders.			

CONCLUSION: WHY DO LARGE SCALE PYROLYSIS?





Conventional	**EMBER**
9 – 11 tonnes CO_2/ton H_2	**0-2.5 TONNES CO2/ TON H2 + 3 TON C**
2.5 – 4.5 tonnes CO_2/ton C	

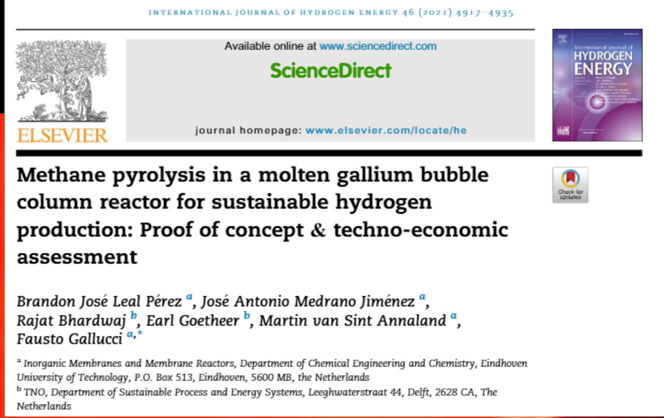
ABUNDANT RAW MATERIALS

H_2 & C ARE BASE PRODUCTS

EMBER: a cost effective process for producing hydrogen and carbon

Ember

WOULD YOU LIKE TO KNOW MORE?



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Methane pyrolysis in a molten gallium bubble column reactor for sustainable hydrogen production: Proof of concept & techno-economic assessment

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THANK YOU FOR YOUR ATTENTION

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