Methane pyrolysis – a new source of H_2 with low CO_2 emissions

„Finance for innovation: Towards the ETS Innovation Fund“ – Workshop organized by the European Commission, Brussels, 23 March 2017

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Hydrogen – a versatile chemical substance

Large additional amount of H_2 is required in the future for different applications

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Chemicals – today‘s major use (60 million t H_2/y globally)

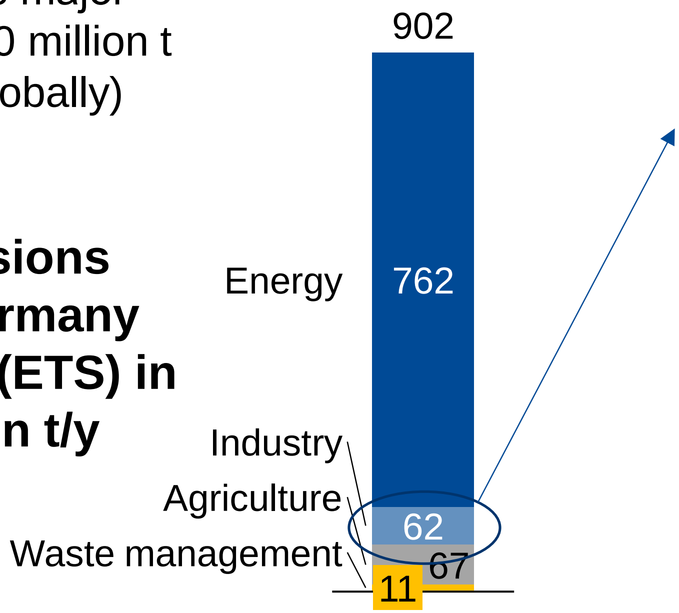
CO_2 utilization
below example

Fuel

Energy storage

Energy carrier

CO_2 emissions in Germany 2015 (ETS) in million t/y



~10 million tons H_2/y required for utilization of industrial 62 million tons CO_2/y
→ H_2 with low CO_2 emissions and low cost is important for competitiveness in industrial production

Illustrative numbers for water electrolysis

- 1 400 large water electrolyzers
- Electrical power 60 GW (Germany today: 180 GW)
- Electricity consumption 500 TWh p.a. (Germany today 600 TWh/y)

Comparison of conventional and new H_2 production processes

Methane pyrolysis is the most cost competitive H_2 process at low CO_2 emission

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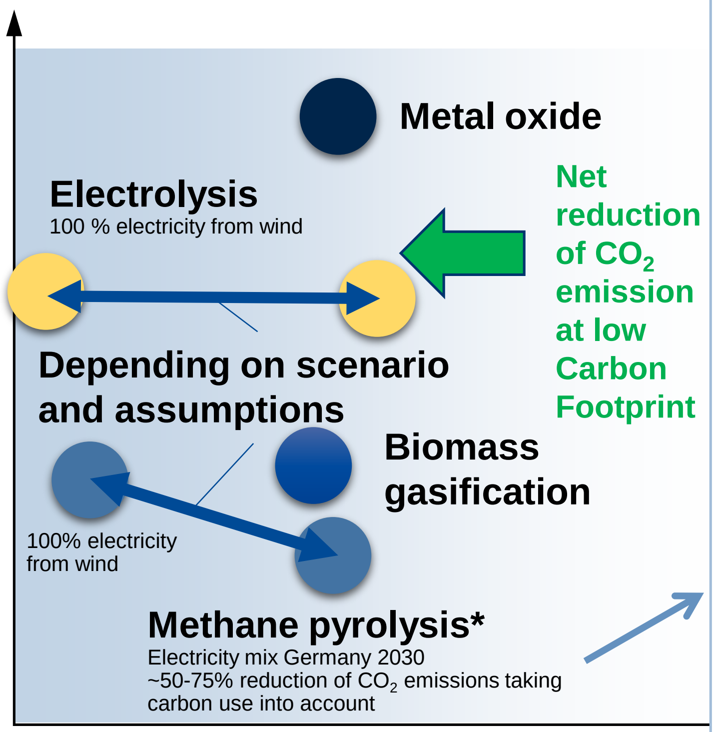
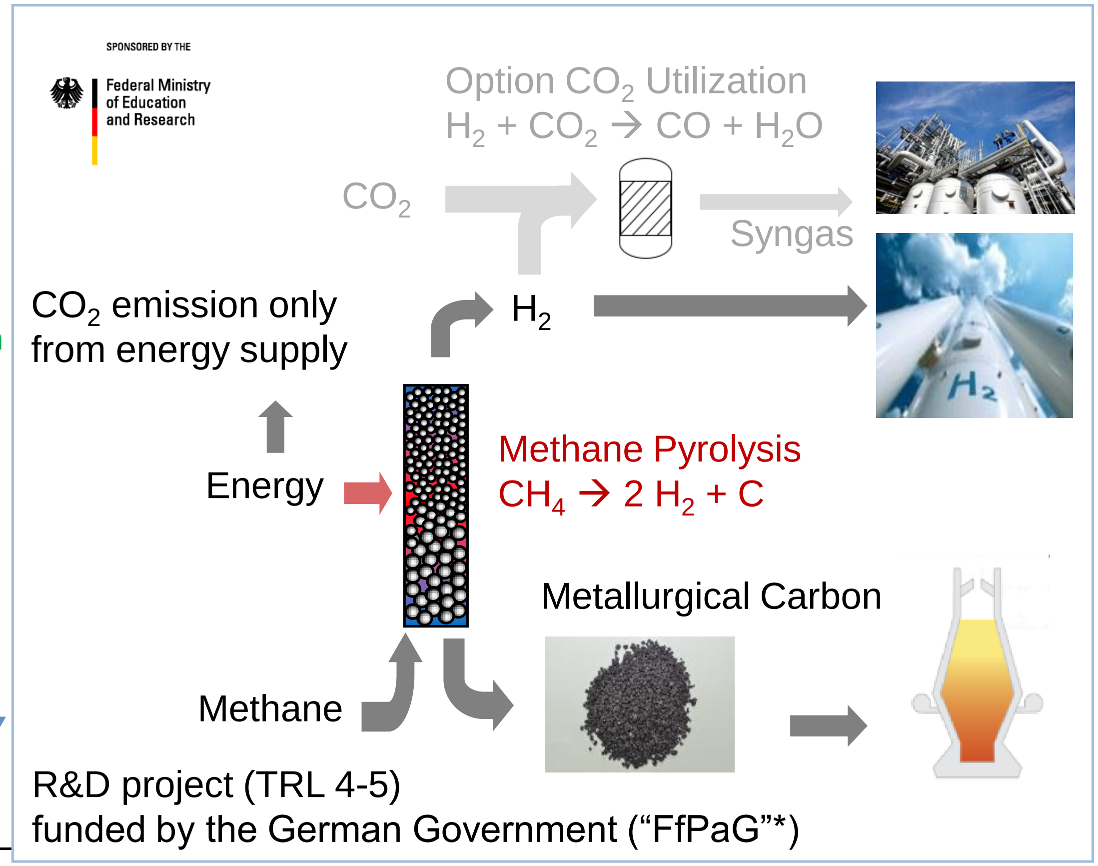
Hydrogen production cost





Carbon Footprint [kg CO_2 / kg H_2]

Project outlook and financing aspects

Risks and project financing

- breakthrough process development
- carbon utilization in metallurgy
- industrial scale reference required
- CAPEX and OPEX support

Pilot Unit

~€20-40 million investment
(start-up ≥2020, TRL 6-7,
~1000 Nm³/h H_2, ~2 000 t/y carbon)

Reference/demonstration unit on commercial scale

~€100 million investment
(start-up ≥2024, TRL 8-9,
~20 000 Nm³/h H_2, ~40 000 t/y carbon)

Ongoing

R&D-Project funded by the German Ministry of Education and Research
July 2013- July 2017
Total R&D cost €25 million

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Pyrolysis reaction video-images

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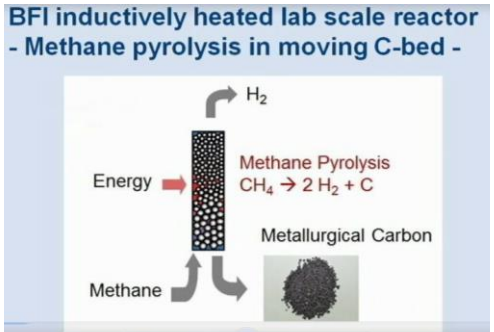

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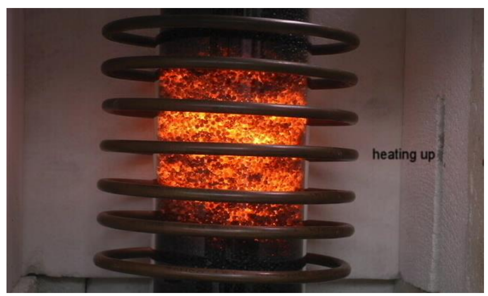

Methane pyrolysis

Experimental units

Lab scale - Methane pyrolysis (BASF)
Reaction kinetics, carbon formation, fluid dynamics, materials of construction

Lab/Technikum scale - Methane pyrolysis (BASF)
Heat input, carbon formation, fluid dynamics,
materials of construction

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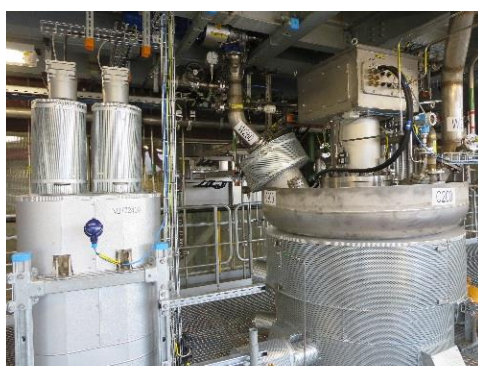

Semi-Pilot scale - Methane pyrolysis (BASF)
Carbon samples, reactor design,
materials of construction

Methane pyrolysis – carbon footprint

Cradle-to-gate analysis

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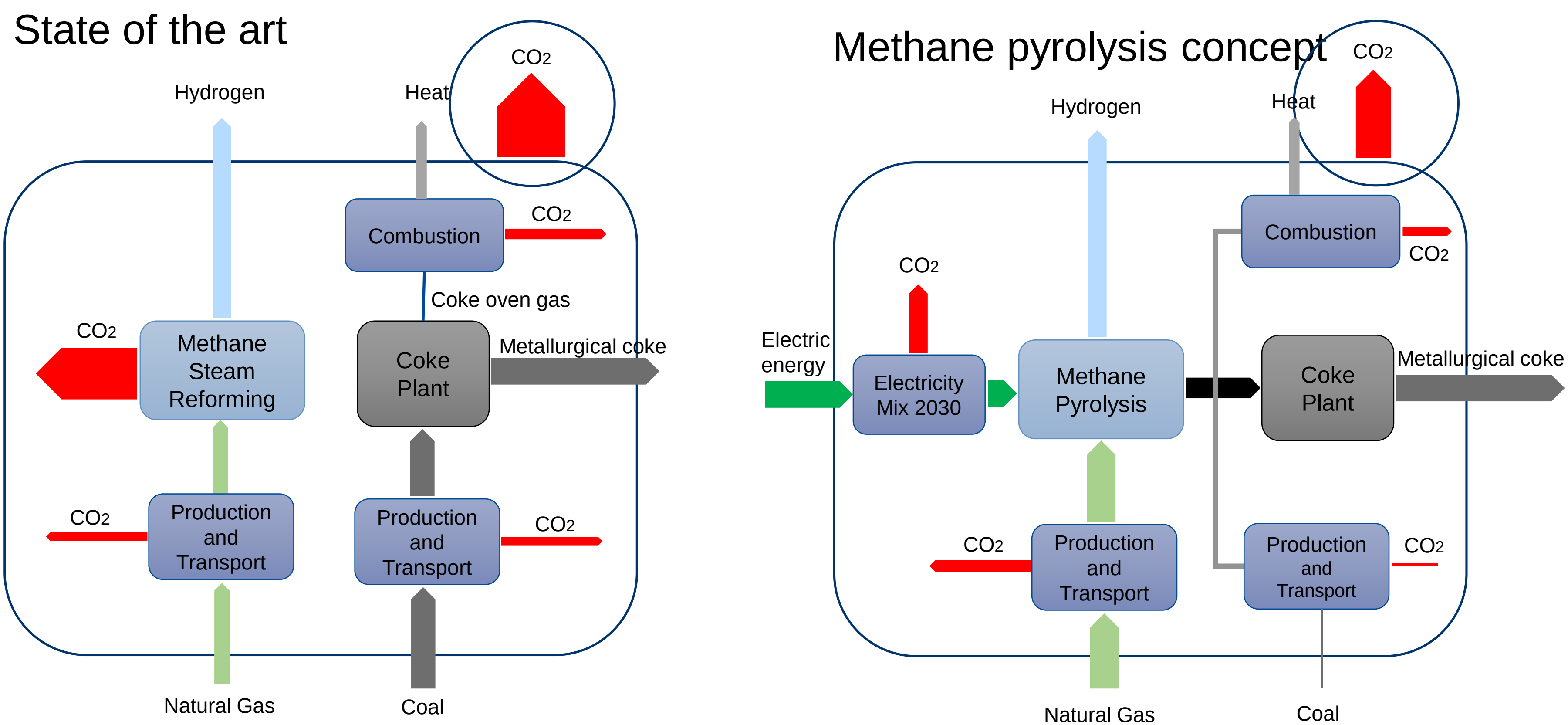


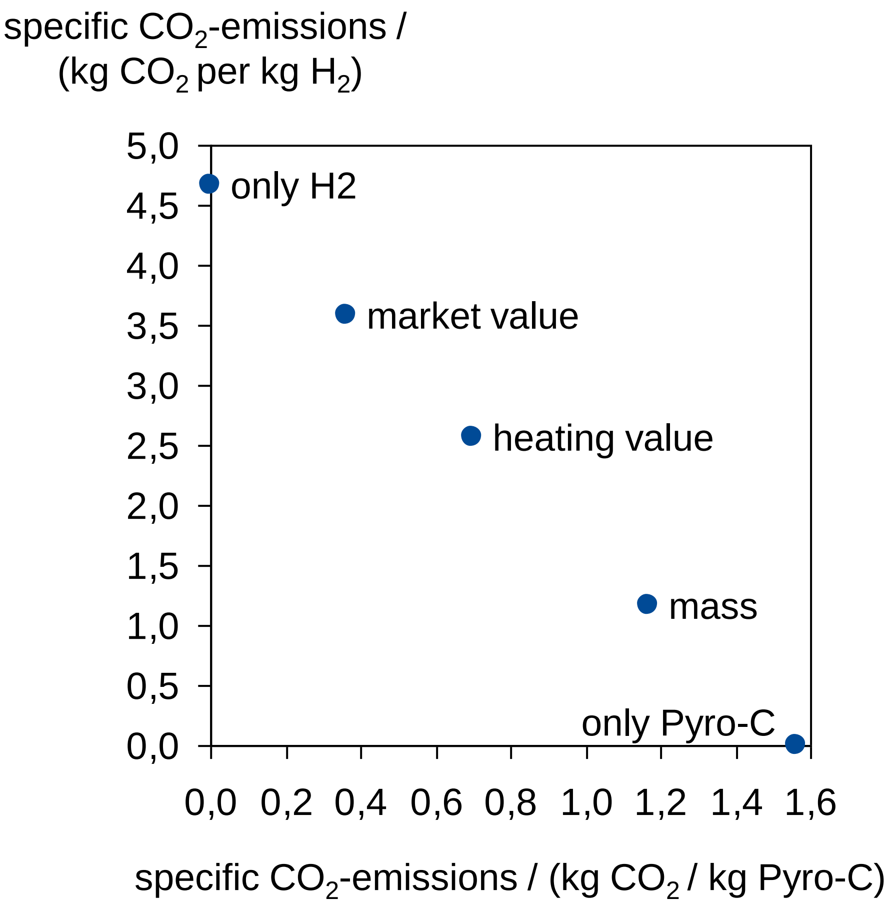
Up to ~50 % reduction of CO_2-emissions for the same production of hydrogen, metallurgical coke and heat – allocation not included.

Methane pyrolysis – carbon footprint

Effect of emission allocation

Allocation of 4,67 t* of CO_2 for based on different rules

- Market value: H_2: 2 000 €/t, C: 200 €/t
- Heating value: H_2: 120 GJ/t, C: 33 GJ/t
- Mass: H_2: 1 t, C: 3 t
- For heating value: 2,6 kg CO2 / kg H2 corresponds to 22 kg CO_2 / GJ H_2 with electricity grid-mix 2030 (well-to-tank report data for comparison: electrolysis via renewable electricity 9,1 kg/GJ, conventional reference value ~90 kg/GJ)

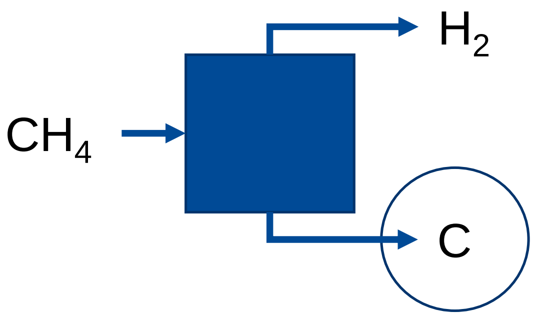


* see previous page: 4,37 t CO_2 (pyrolysis) + 1,17 t CO_2 (coking plant using Pyro-C) – 0,87 t CO_2 (direct and indirect emissions for heat in coking plant system) = 4,67 t CO_2

Methane pyrolysis

Business case

Coupled production of hydrogen and carbon by thermal decomposition of methane



Established product, locally produced,
500 (fuel value) - 1 000 (US) – 2 000 (NWE) EUR/t

New for the markets: pure and in bulk amount, transportable, 3 kg C / kg H2
Established carbon products: 100 – 1 000 EUR/t, commodities, specialties

- Carbon product is value driver of the process
- Special high temperature process and introduction of new technology – cooperation in consortium

Methane pyrolysis

Economics and carbon utilization

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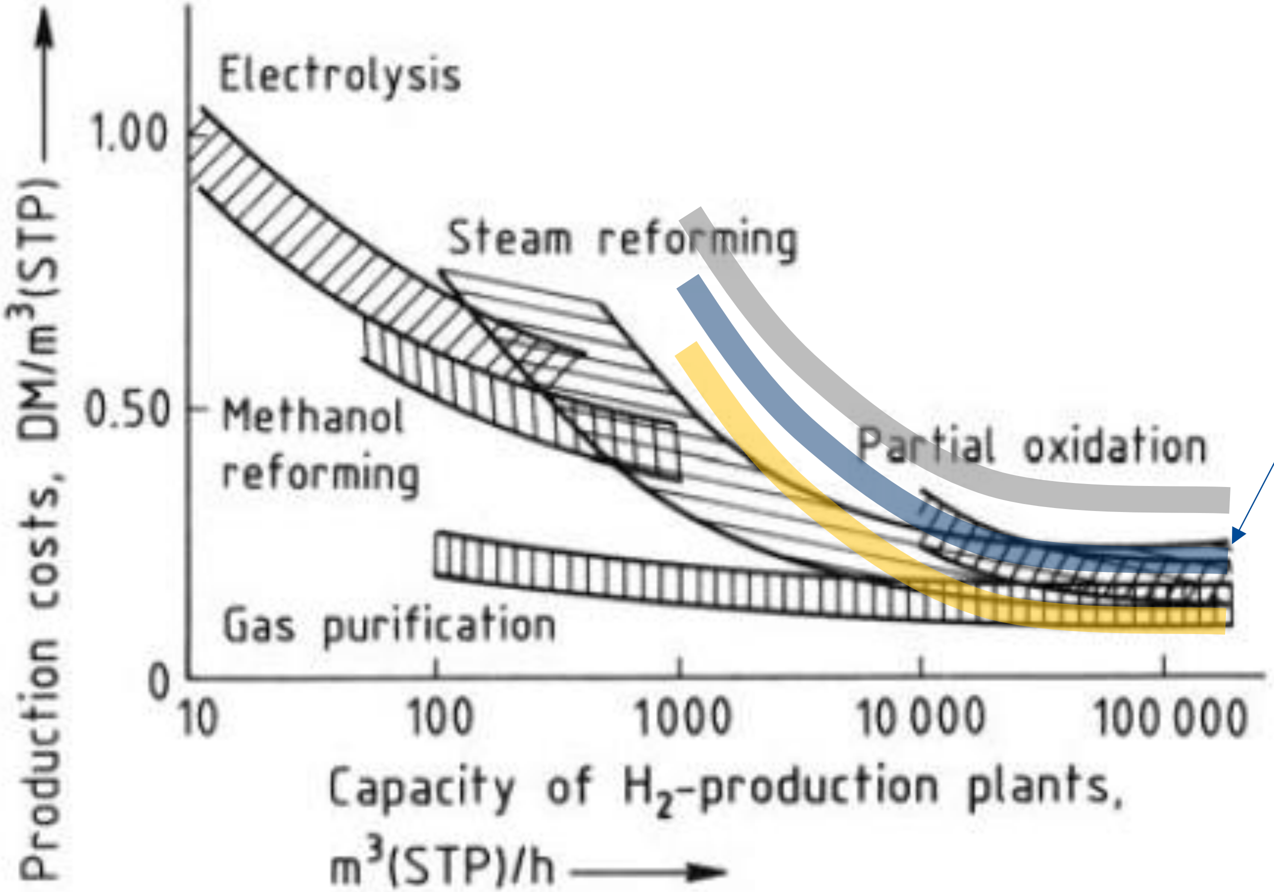
Lohmüller, 1984



Estimates for methane pyrolysis depending on value of pyrolysis carbon

Several projects since ~1900, sample production max ~1kg/h, no commercial realization, FfPaG* first targeting ~5-10 kg/h carbon

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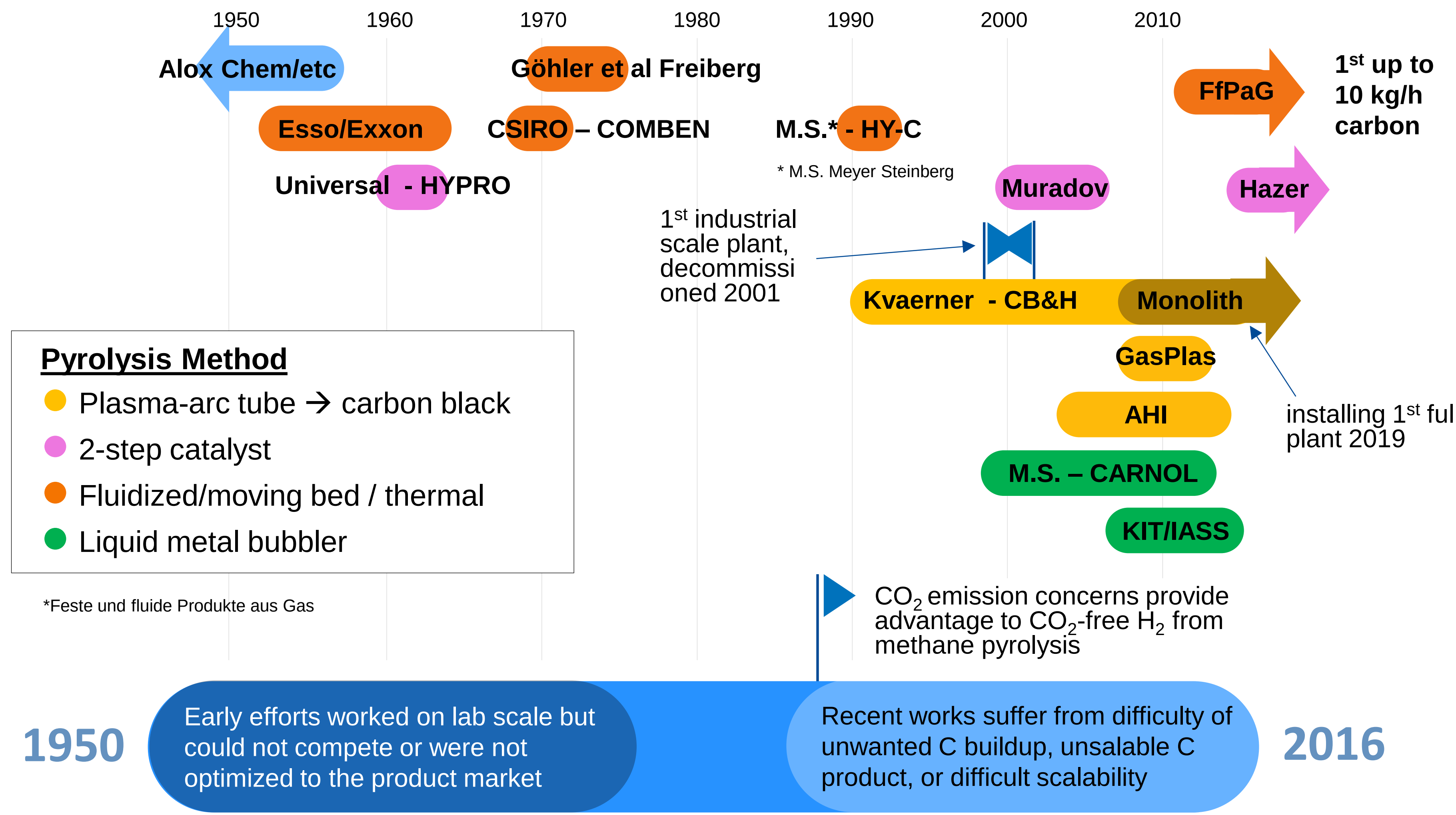

CO_2 activation

Carbon dioxide utilization

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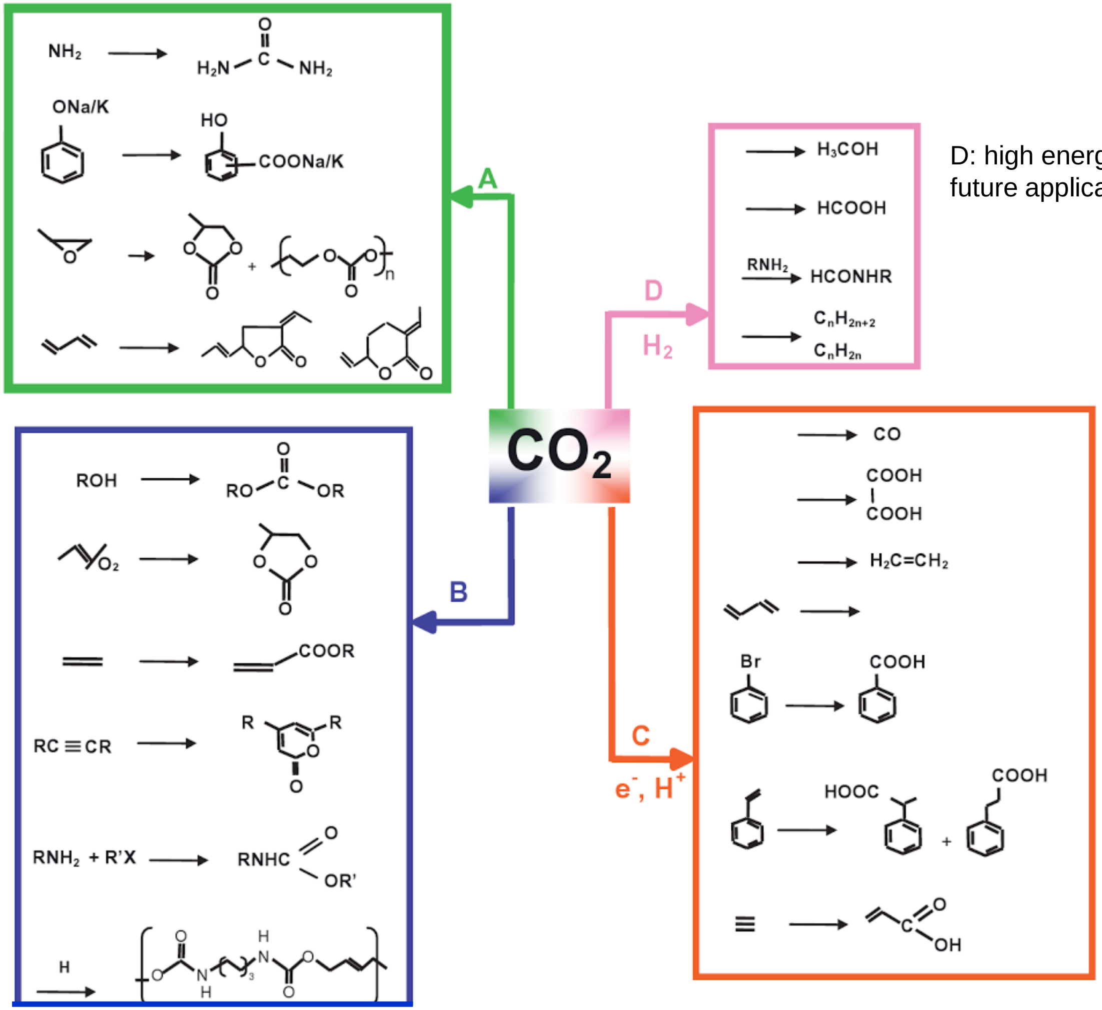
A: low energy input, CO2 incorporation, processes on stream

B: low energy input, CO2 incorporation, processes under advanced study



D: high energy input, future applications

C: high energy input, future applications, obtainable by electrolysis

Source: Aresta, M.(Ed.) VCH-Wiley, 2010 „Carbon dioxide as Chemical Feedstock“

CO_2 utilization projects at BASF

- 2009 – 2012 CO_2 as polymer component
- 2009 – 2011 Photocatalytic CO_2 reduction
- 2011 – 2014 Solar thermal production of chemicals from H_2O and CO_2
- 2011 – 2014 Sodiumacrylate from CO_2 and ethen
- 2012 – 2015 Dimethylther from CO_2 and CH4
- 2013 – 2016 Methane pyrolysis and CO_2-activation
- 2016 – Formaldehyde from CO_2
- 2016 - OME from steel plant process gas