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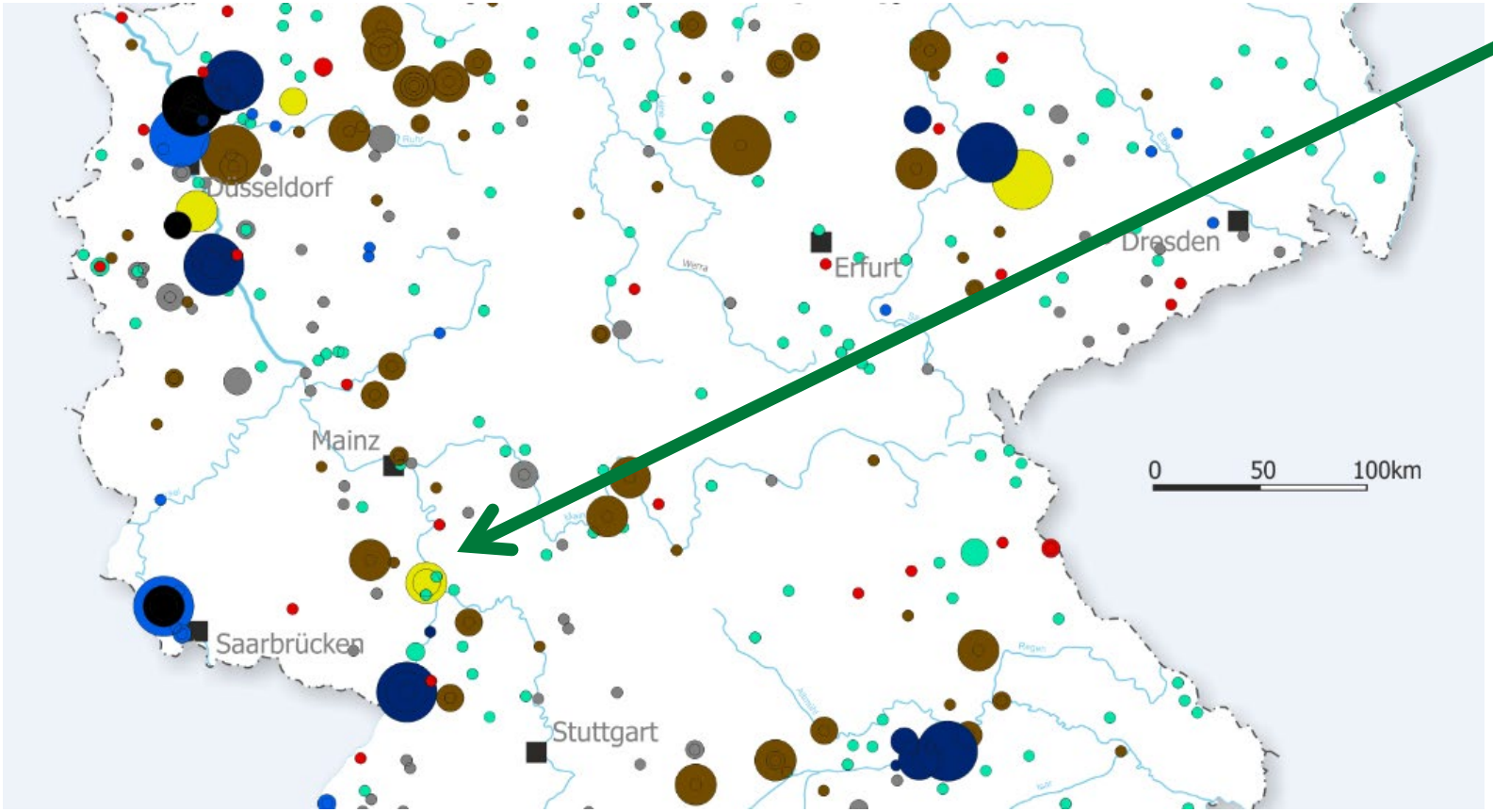
Niedersächsische Energietage, November 6, 2019, Hannover

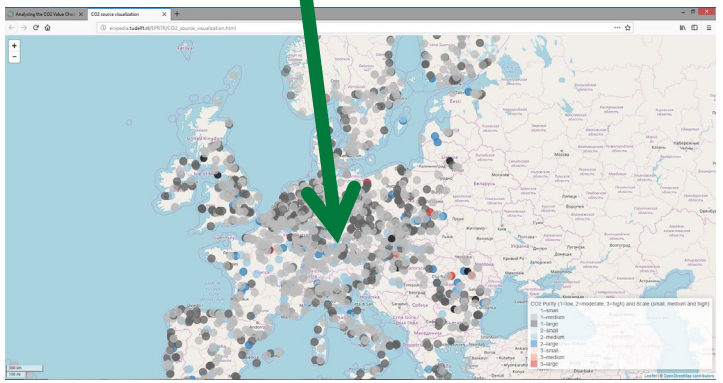
Methane Pyrolysis – a potential new process for hydrogen production without CO_2 emission

Dr. Andreas Bode
BASF SE - Program leader Carbon Management R&D

Industrial Greenhouse Gas emissions in Germany and Europe



BASF Ludwigshafen



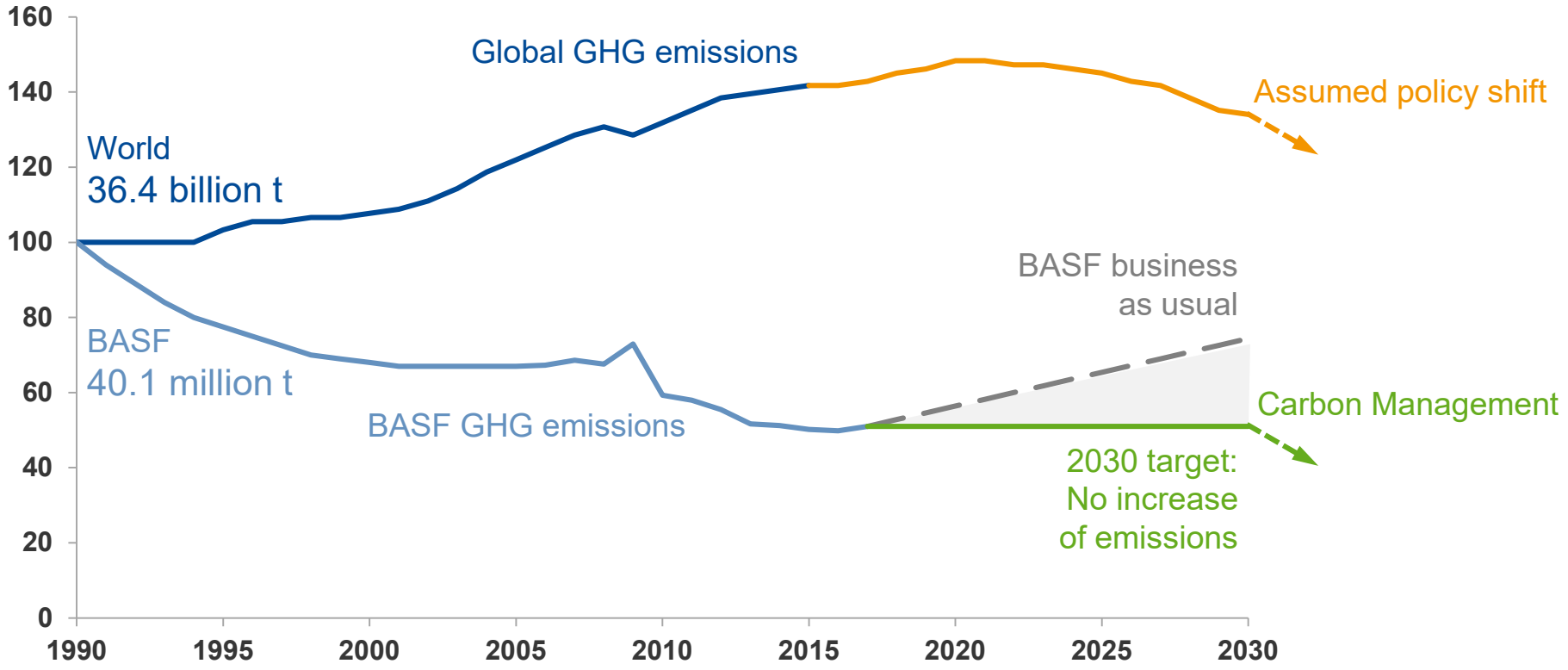
Data from the European Trading Scheme for Greenhouse Gas emissions are published in EU database (here: TU Delft, EnCO2re-project)

Source: J. Gerling, BGR Hannover 2018, personal communication

Our target: CO_2-neutral[1] growth until 2030

Absolute GHG emissions

Indexed (1990 = 100)



[1] BASF operations excluding the discontinued oil and gas business. The goal includes other greenhouse gases according to the Greenhouse Gas Protocol, which are converted into CO_2 equivalents.

Carbon Management at BASF: climate target 2030 and further reductions in the long term in scope

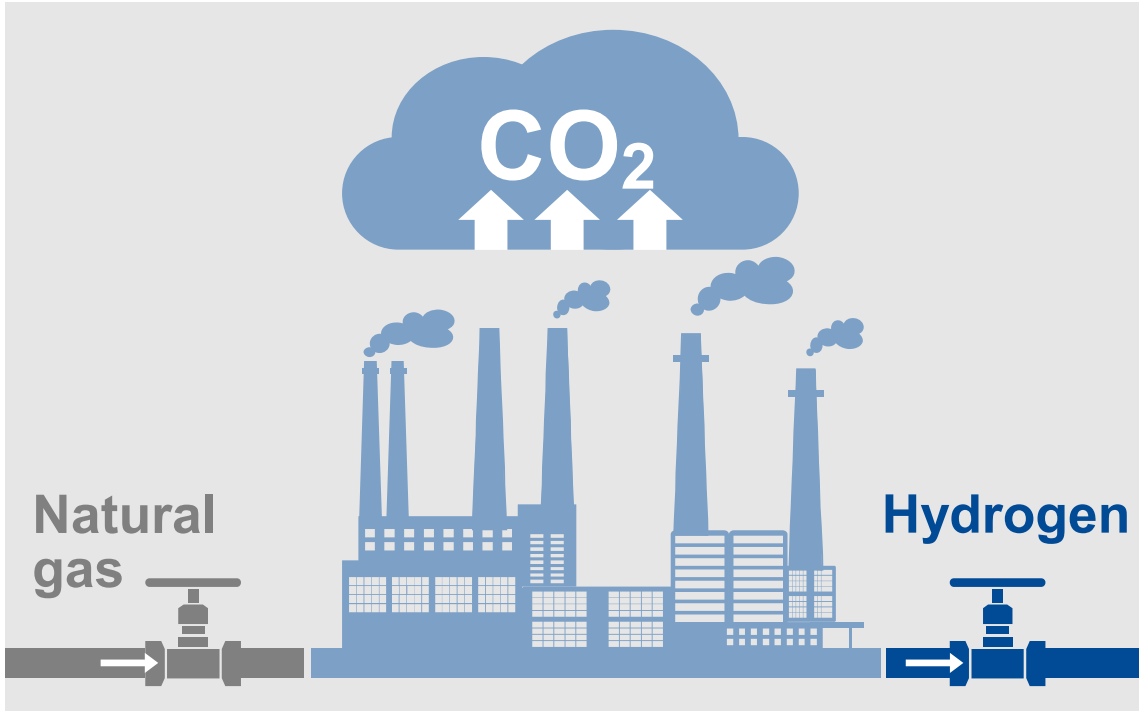
Reducing the CO_2 emissions from our production by improving energy and process efficiency

Increasing the share of renewable energies in our global power supply

Developing breakthrough technologies for low emission production in a research & development program

CO_2 – the burden of hydrogen

- Today's main production method at a global level is steam reforming of natural gas
- Hydrogen is mainly used for ammonia production, petroleum refining, and chemicals production like cyclohexane, aniline, metals, etc.
- BASF Ludwigshafen
  - hydrogen capacity: 300 kt per year
  - optimized production network including side-product hydrogen and on-purpose production

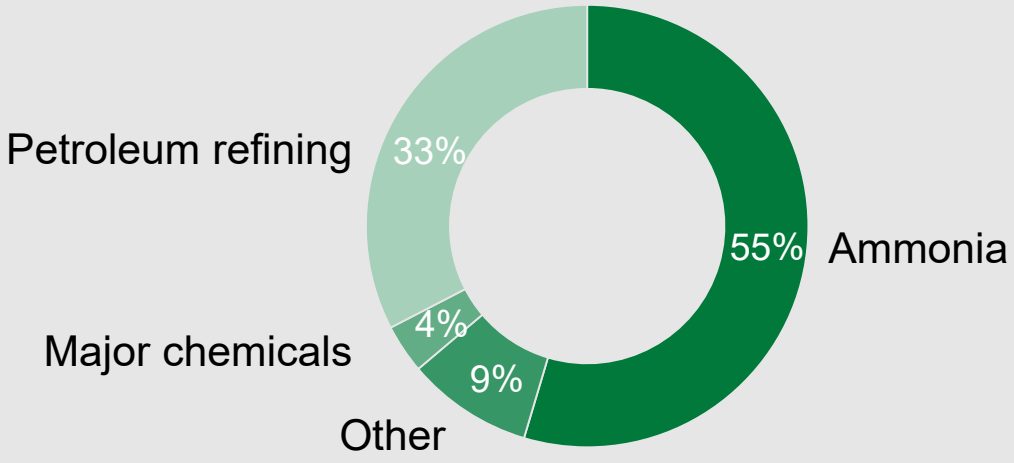


Production of 1 metric ton of hydrogen by steam reforming of natural gas generates ~9 metric tons* of CO_2
→ globally ~1% of the anthropogenic GHG emissions

* Benchmark 8.85 t CO_2/t H_2, Sector-specific guidance, European Commission, 2011

Beyond the chemical industry: Hydrogen is discussed for many future applications

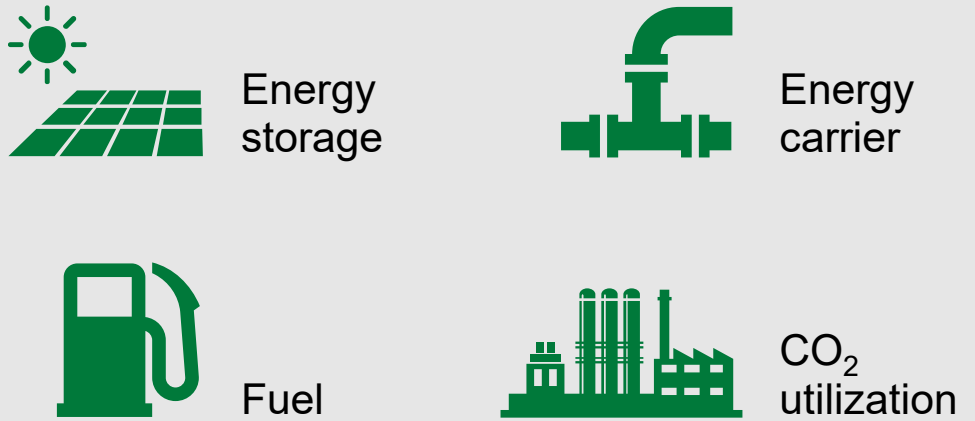
Chemicals – major use today



Market size 56 million t per year

Source: CEH Report „Hydrogen“ 2018 without hydrogen in synthesis gas

Future applications



The increasing demand in existing markets and future applications drive the need for a new clean hydrogen production technology

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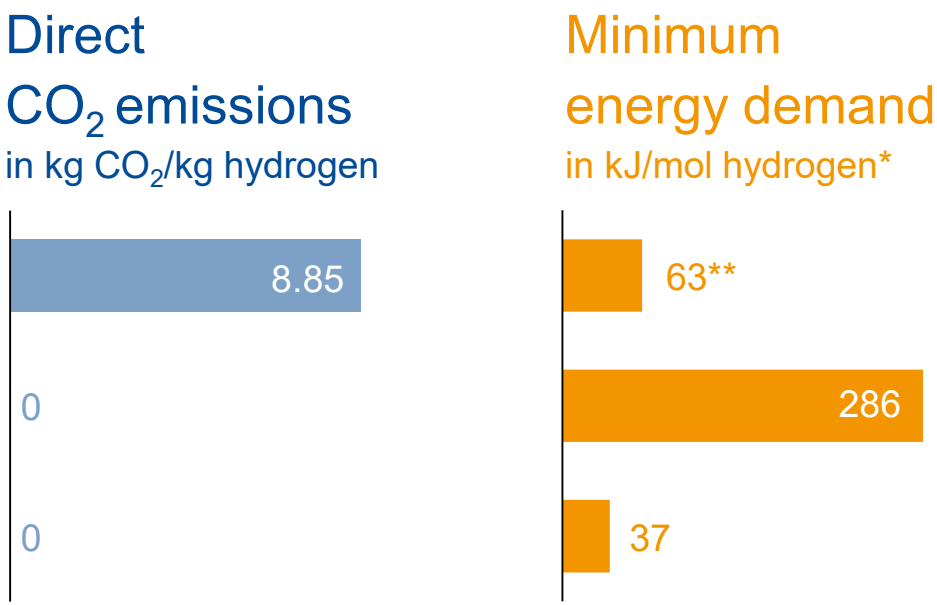
Towards a new clean hydrogen production technology

State of the art	Steam reforming of natural gas	**$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$**
Option 1	Water electrolysis	$2H_2O \rightarrow 2H_2 + O_2$
Option 2	Methane pyrolysis	$CH_4 \rightarrow 2H_2 + C$

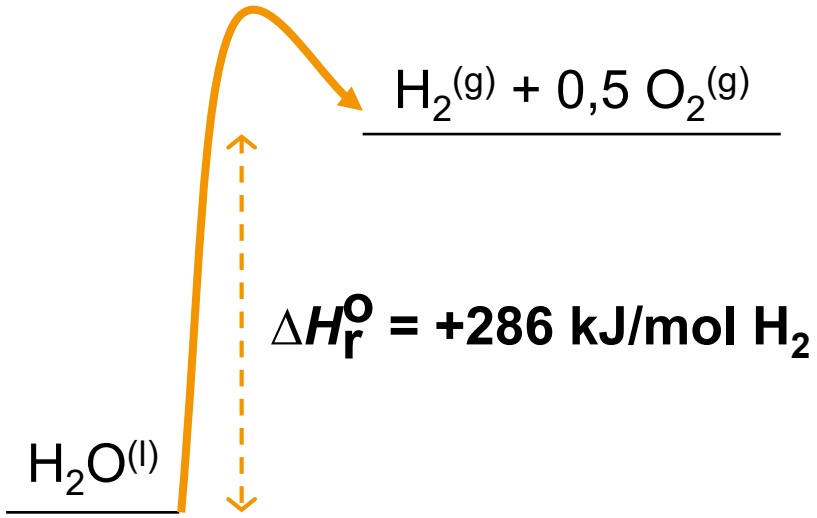


Water electrolysis and methane pyrolysis yield clean - CO_2-free - hydrogen

* Standard reaction enthalpy as approximation
** using liquid water, with gaseous water 41 kJ/mol

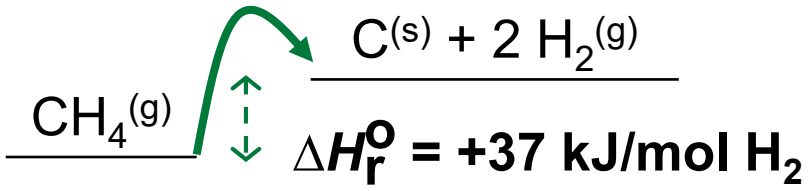
Water electrolysis or methane pyrolysis?

H_2 from water electrolysis



- Very high energy demand
- Water as a raw material
- First small industrial-scale plants

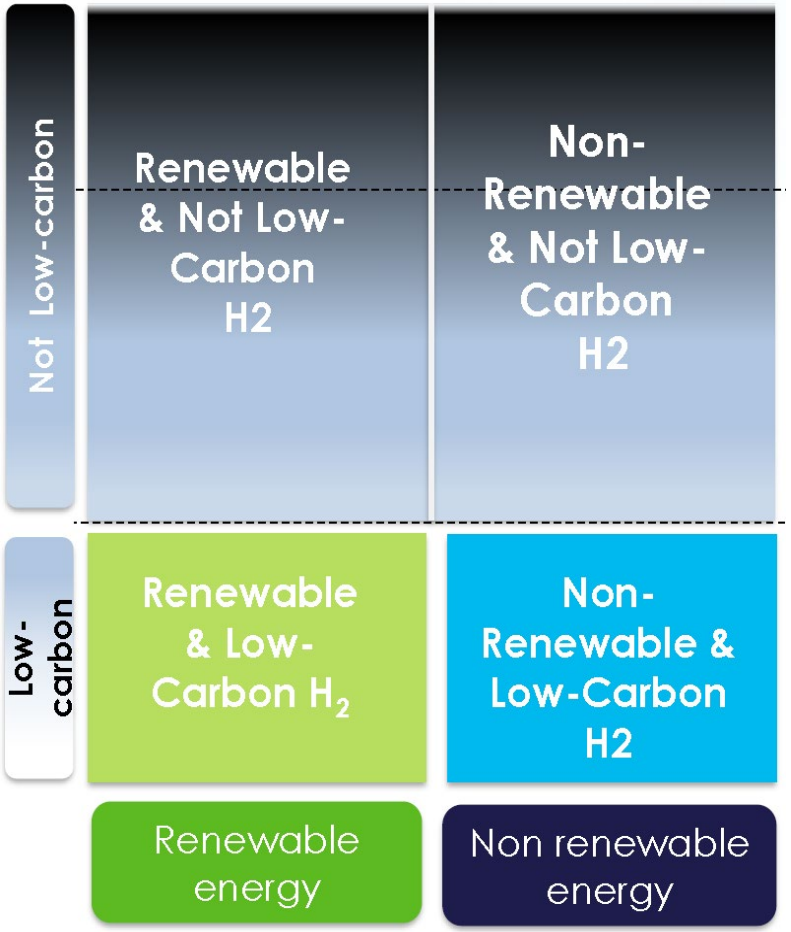
H_2 from methane pyrolysis



- Low energy demand
- Fossil raw material
- Solid carbon as 2nd product
- First pilot plants

Standard reaction enthalpy as approximation

H_2 from methane pyrolysis allows for green or blue certificate application depending on power source and feedstock



Benchmark emissions intensity threshold (=91 g CO_2eq/MJ H_2)*

-60%**

Low-carbon threshold (=36,4 g CO_2eq/MJ H_2

Source: F. Barth "CertifHy – Developing a European guarantee of origin scheme for green hydrogen. CertifHy.eu, 05.11.2019

* Best Available Technology = Natural gas steam methane reforming >95% of hydrogen market
** cfr RED reduction requirement for biofuels in 2018

- Certification scheme by CertifHy is active
- New definitions for green and decarbonized gases are under discussion
- Methane pyrolysis using
  - grey electricity and natural gas would apply for blue certification
  - Green electricity and biogas for green certification

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BASF leads a consortium evaluating methane pyrolysis since 2013

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Federal Ministry of Education and Research

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thyssenkrupp

THE LINDE GROUP Linde

hte the high throughput experimentation company

BFI

tu technische universität dortmund

2013 – 2017 Basic, ambitious R&D

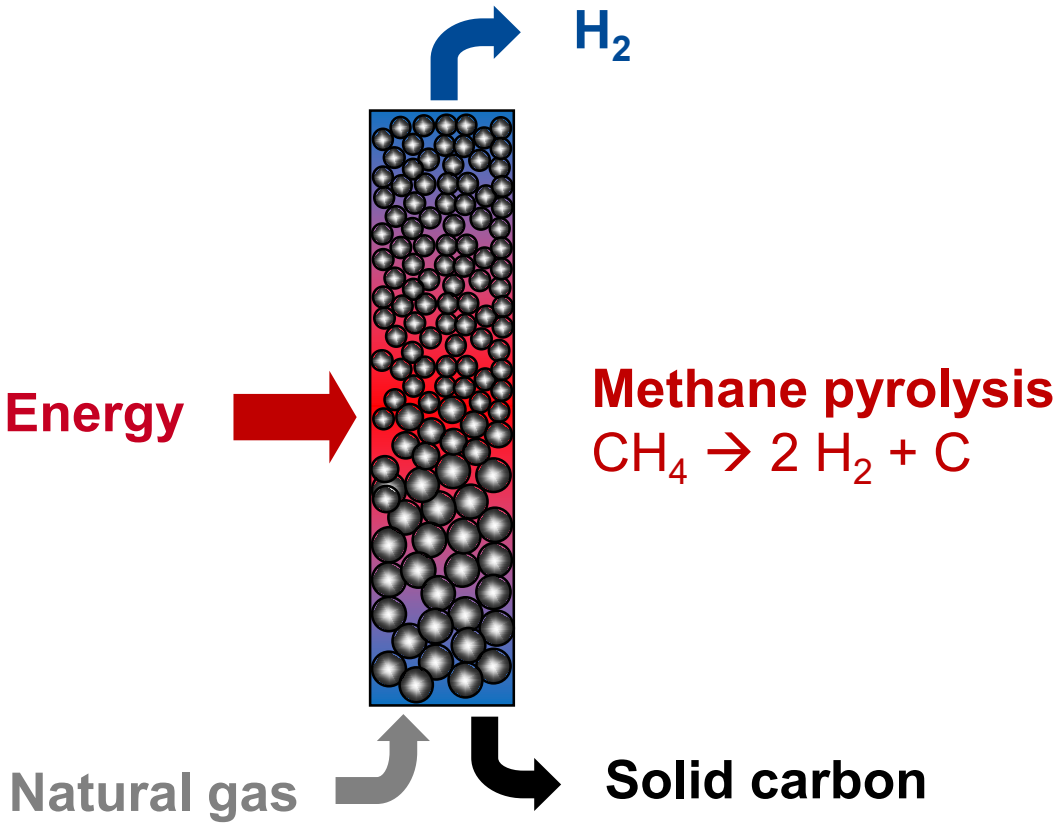
Theoretical and experimental assessment of various reactor concepts

Carbon sample production on 100 kg scale

Results

- Successful operation on lab scale
- Identification of promising reactor concepts
- **Successful carbon sample production and application testing**
- But: reactor was ruined during sample production

First moving carbon beds for methane pyrolysis: Combined reaction and heat integration



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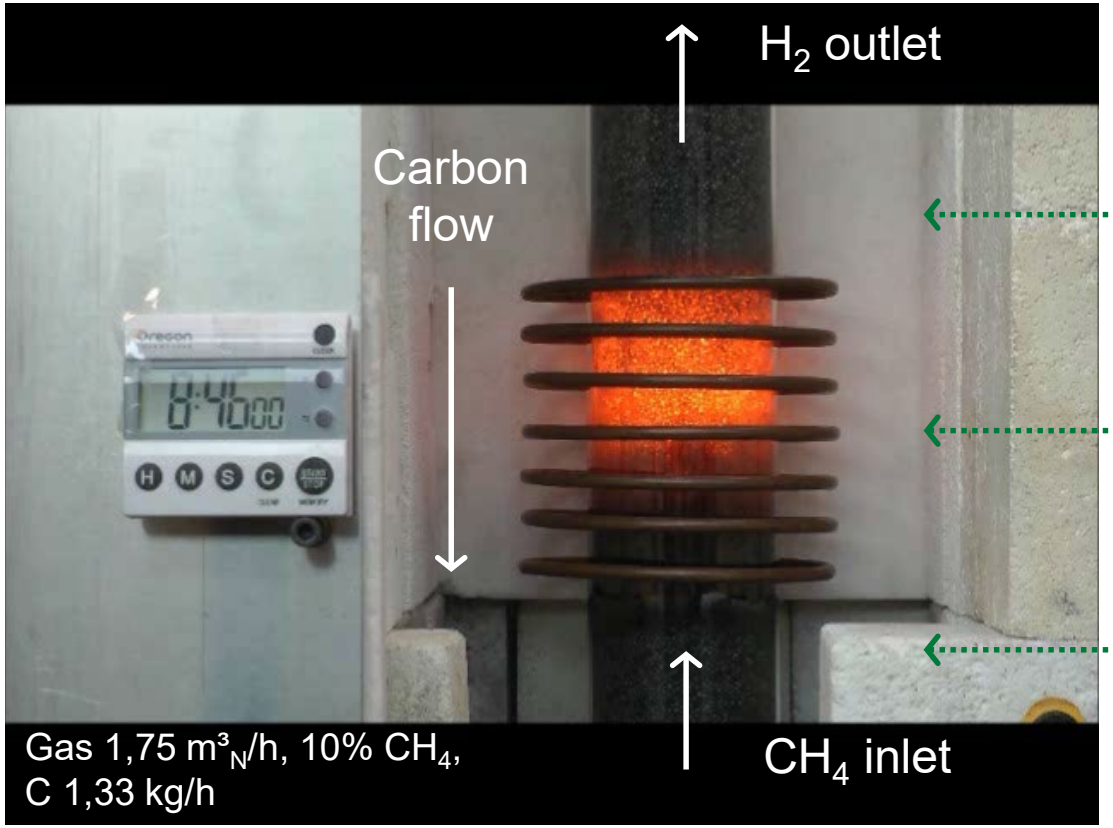
First video observation of methane pyrolysis on a moving carbon bed in glass lab reactor



H_2 cooling and carbon pre-heating

Reaction zone heated by induction

Carbon cooling and CH_4 pre-heating

Reactor is operated at BFI in Düsseldorf

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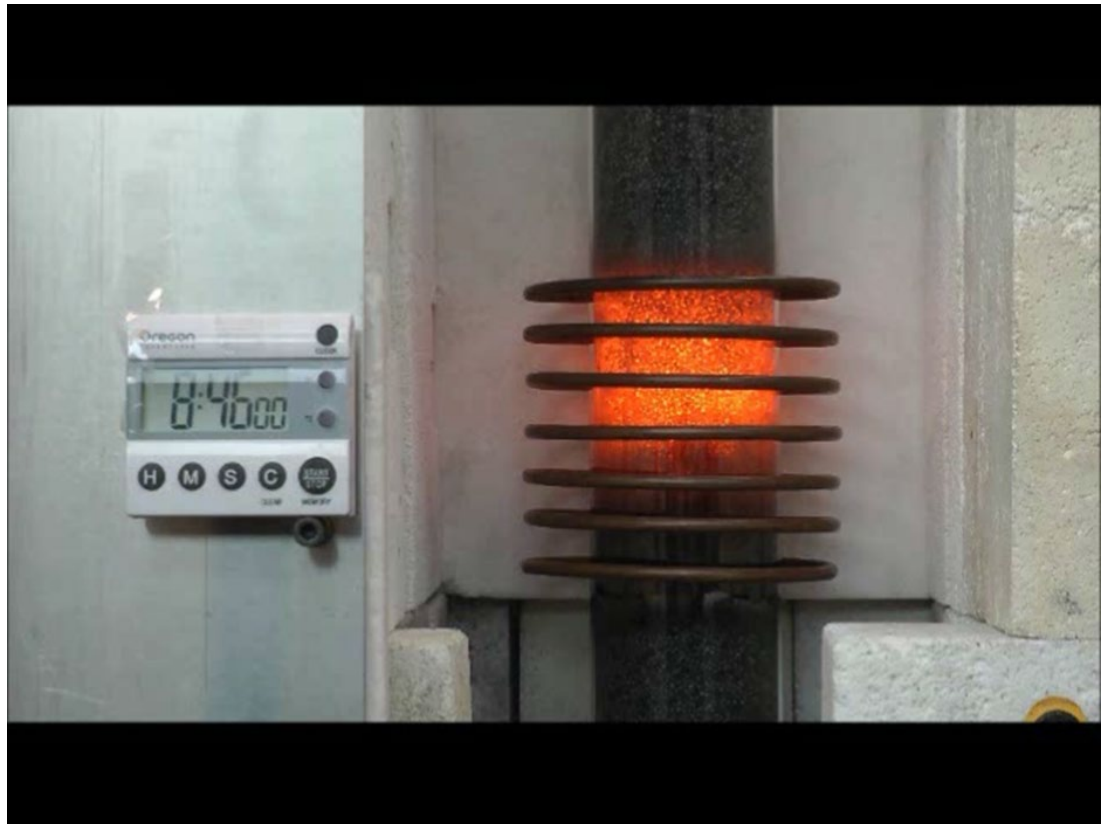
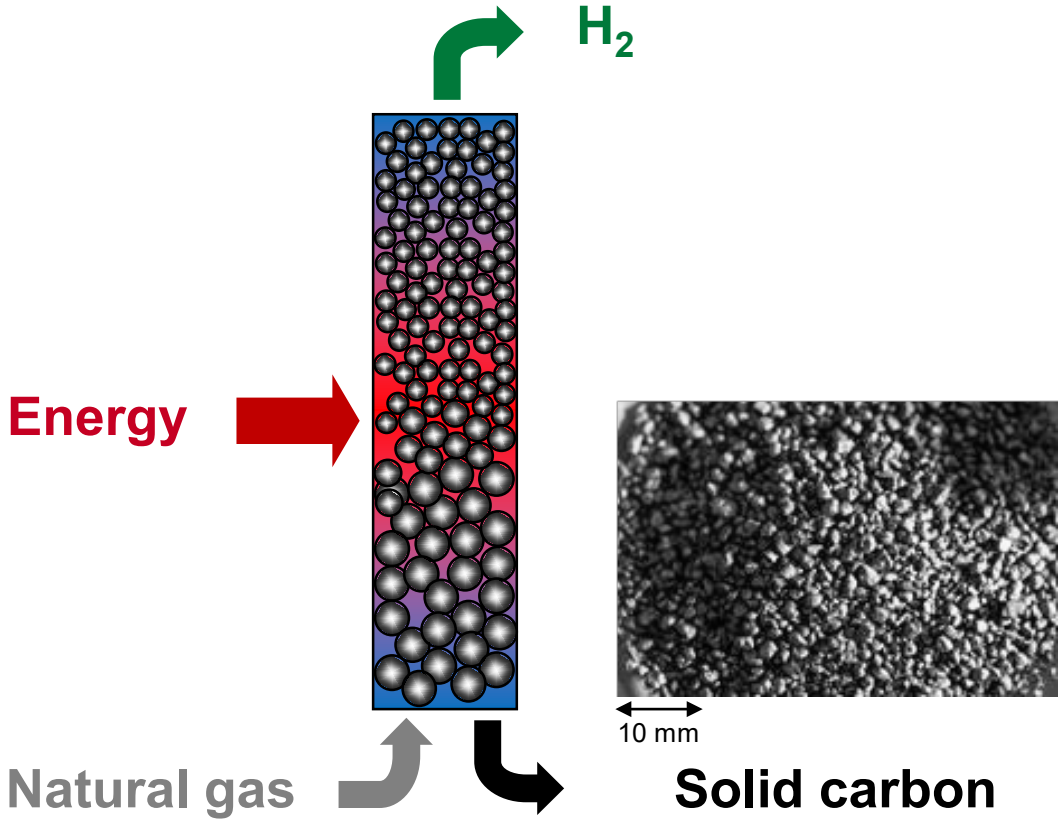
From lab to pilot scale: Process challenges



- Need for basic R&D and **new reactor design**
- Heating concept needed to overcome the low radial heat transfer from the wall into the reactor core
- Manage inhomogeneous flow and pulsations
- High-temperature materials required

BASF strives for first stable operation on large lab scale

Is the solid carbon the showstopper?

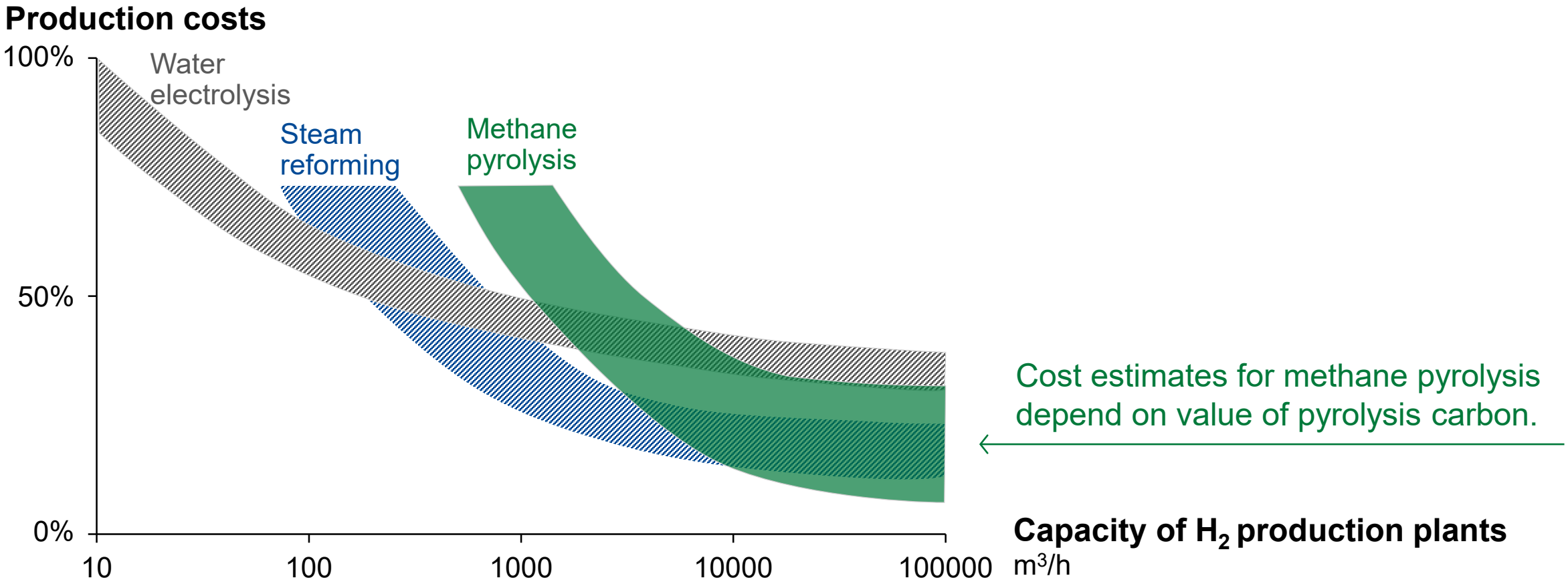


Options for carbon utilization and storage

1. Utilization in major carbon markets
   - Aluminum – positive tests
   - Steel – positive tests
   - Others (tires, concrete admixtures, …)
2. Storage/sequestration
   - Soil improver / Terra preta
   - Filling material

Outlet needed for 3 kg carbon per kg hydrogen

Is methane pyrolysis cost competitive?



Cost estimates for methane pyrolysis depend on value of pyrolysis carbon.

Carbon sales price or cost for storage is critical

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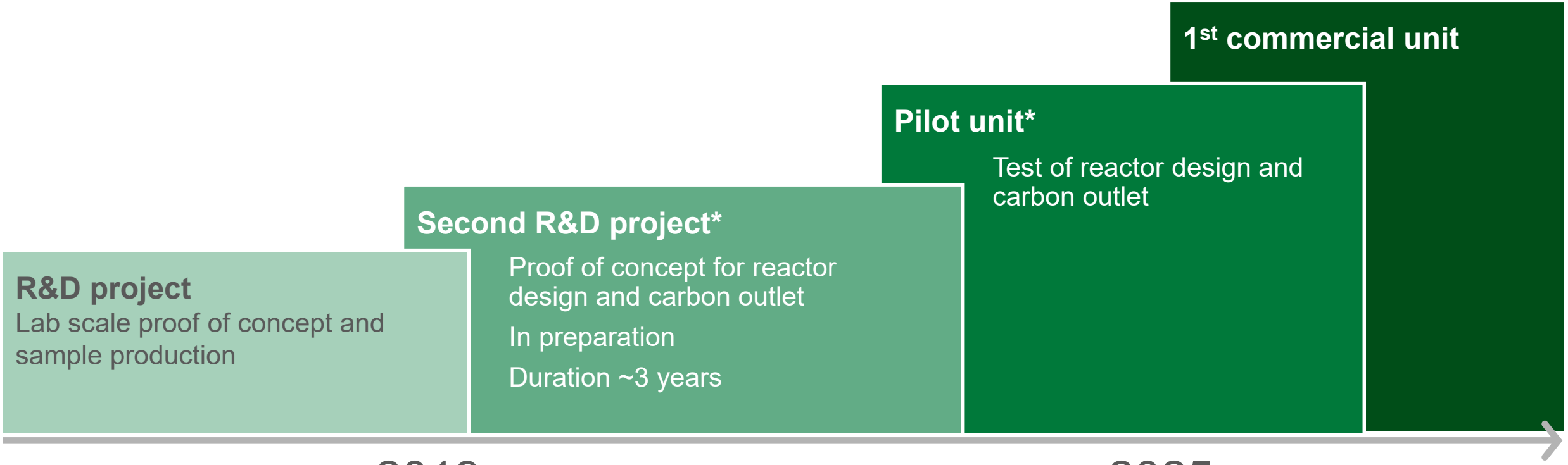
Project outlook – methane pyrolysis for clean hydrogen



Second R&D project with

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* Government funding will be necessary due to high technological and commercial risk

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