Produktion von **Wasserstoff**
Fokus **Methanpyrolyse**

MONTANUNIVERSITÄT LEOBEN

RIC Leoben

VTiU

Robert OBENAUS-EMLER

Head of Innovation and R&D Portfolio Management at RIC

Markus LEHNER

Head of the Chair of Process Technology and Industrial Environmental Protection

WHERE RESEARCH MEETS FUTURE

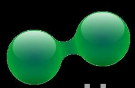
1

Hydrogen

Hydrogen 1 H 1.008 g 1 2.11

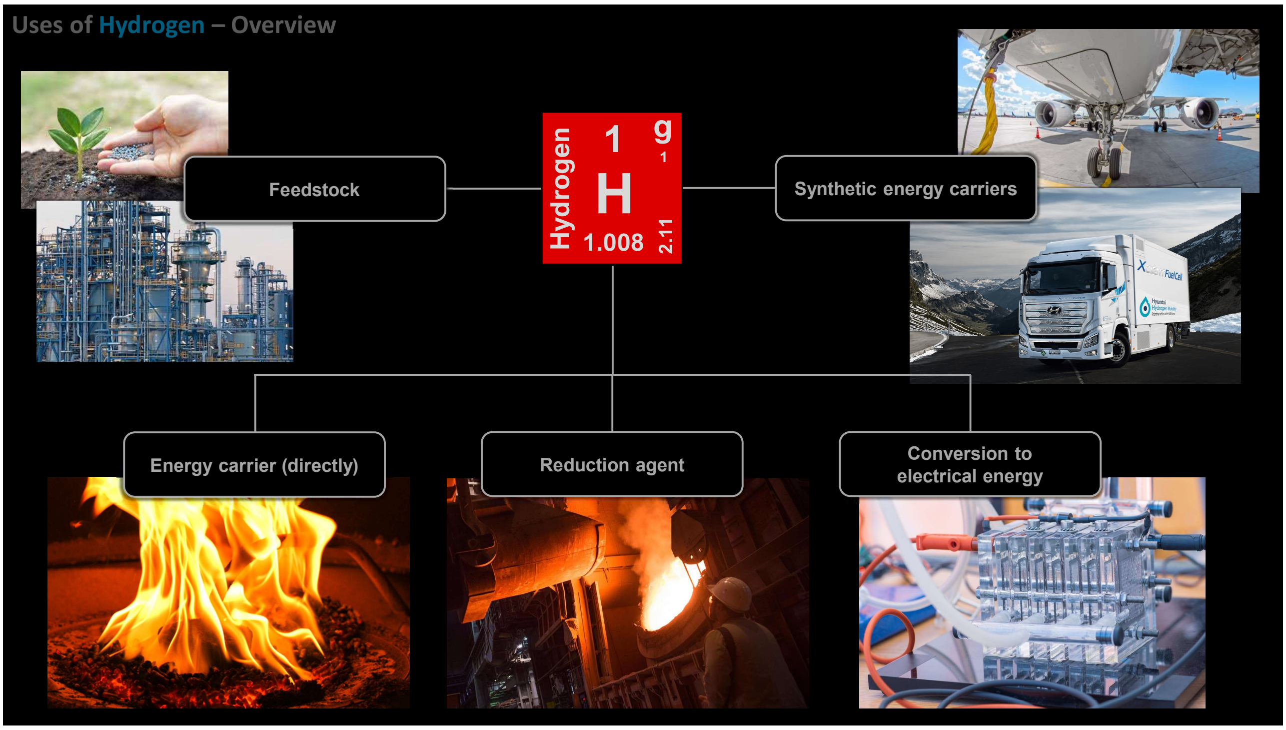
- lightest element
- most abundant element in the universe
- major constituent of our sun
- share in the Earth's crust: 2,9 %
- mostly in compounds
- colour- and odourless gas
- **energy source**

  H_u = 33 kWh / kg

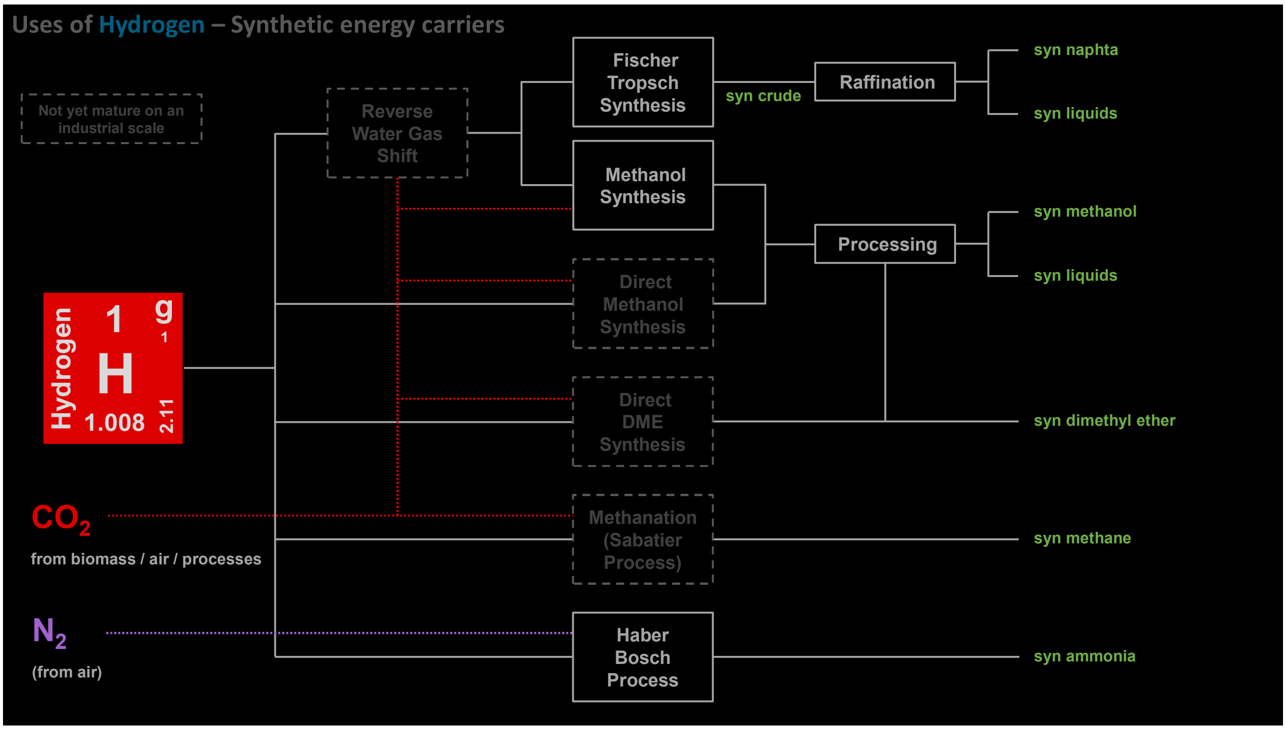


H_2

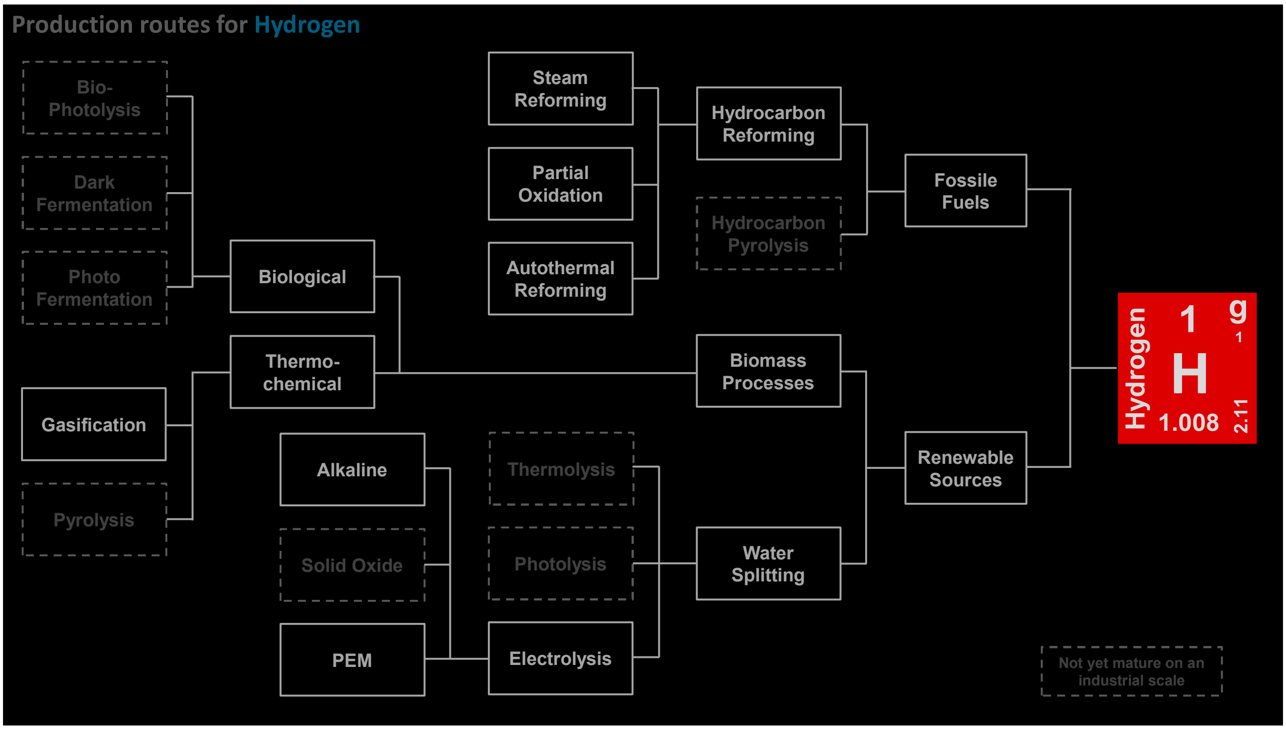
2

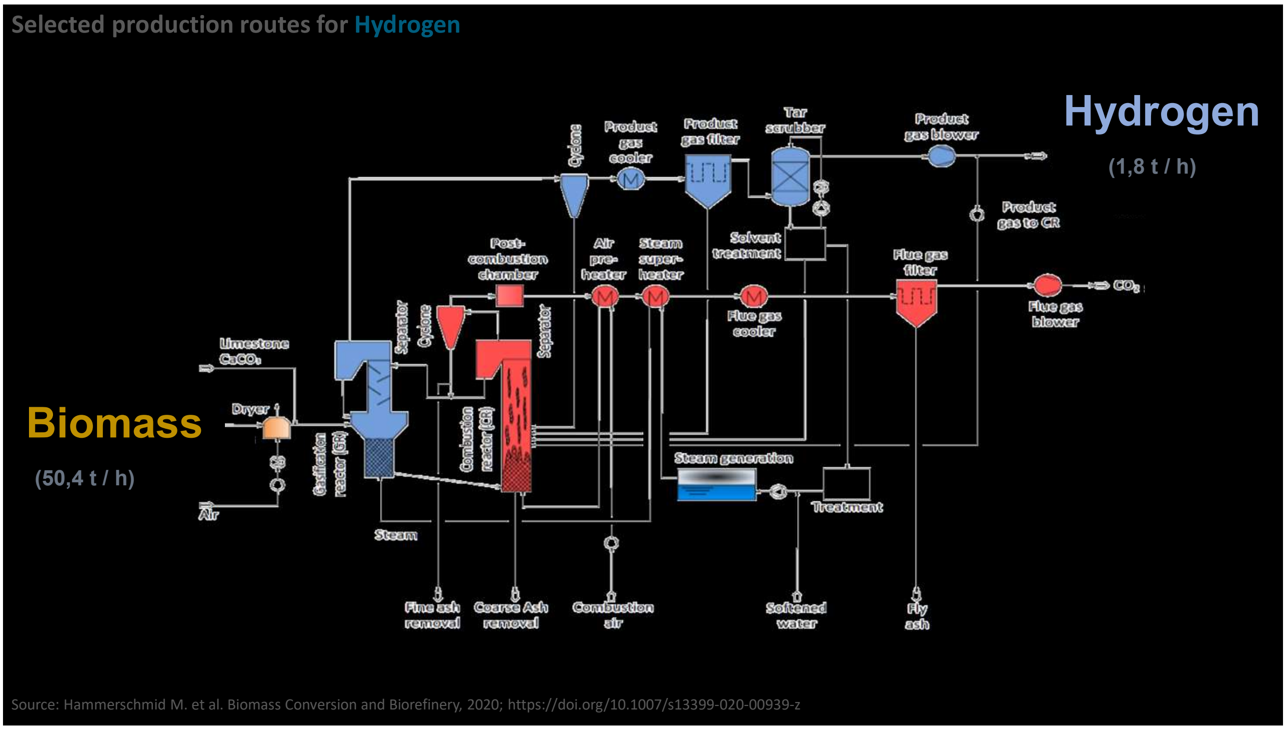

Uses of Hydrogen – Overview
Hydrogen
1
g
1
H
1.008
2.11
Feedstock
Synthetic energy carriers
Energy carrier (directly)
Reduction agent
Conversion to electrical energy

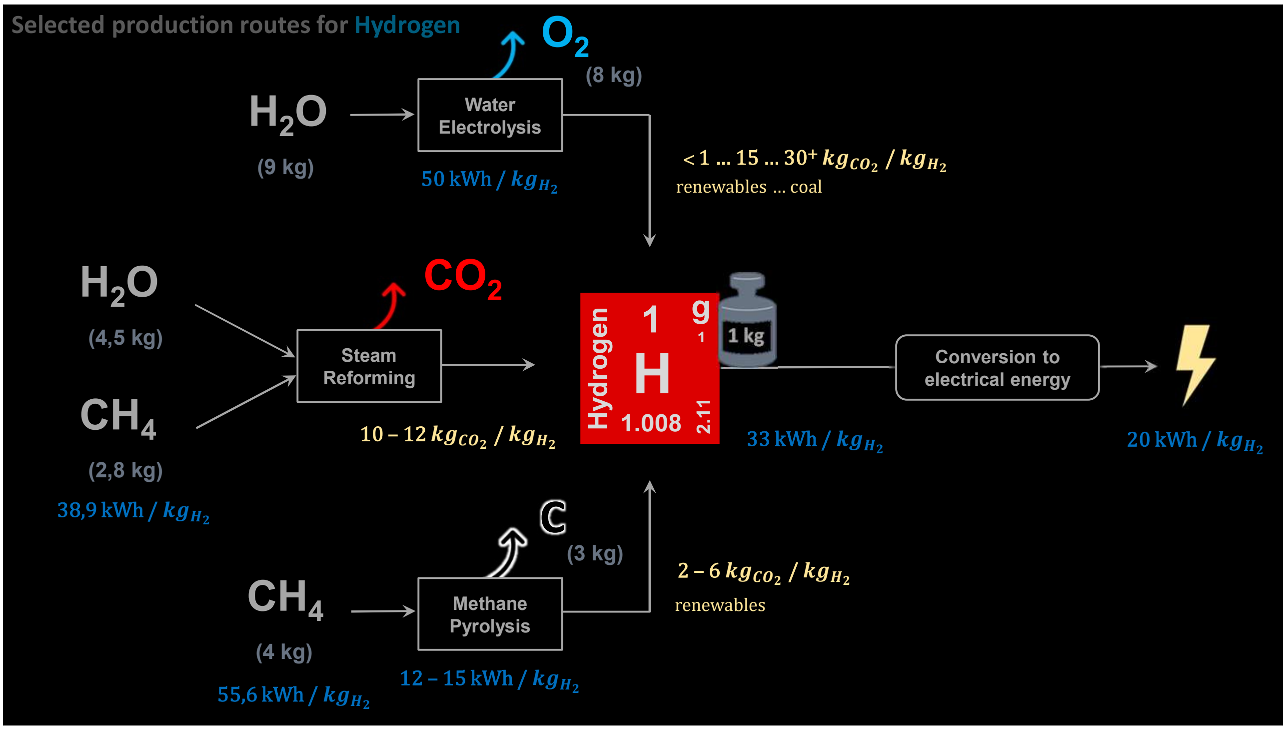
3


Uses of Hydrogen – Synthetic energy carriers
Not yet mature on an industrial scale
Reverse Water Gas Shift
Fischer Tropsch Synthesis
syn crude
Raffination
syn naphta
syn liquids
Methanol Synthesis
Processing
syn methanol
syn liquids
Direct Methanol Synthesis
Hydrogen
1
g
1
H
1.008
2.11
Direct DME Synthesis
syn dimethyl ether
CO2
from biomass / air / processes
Methanation (Sabatier Process)
syn methane
N2
(from air)
Haber Bosch Process
syn ammonia

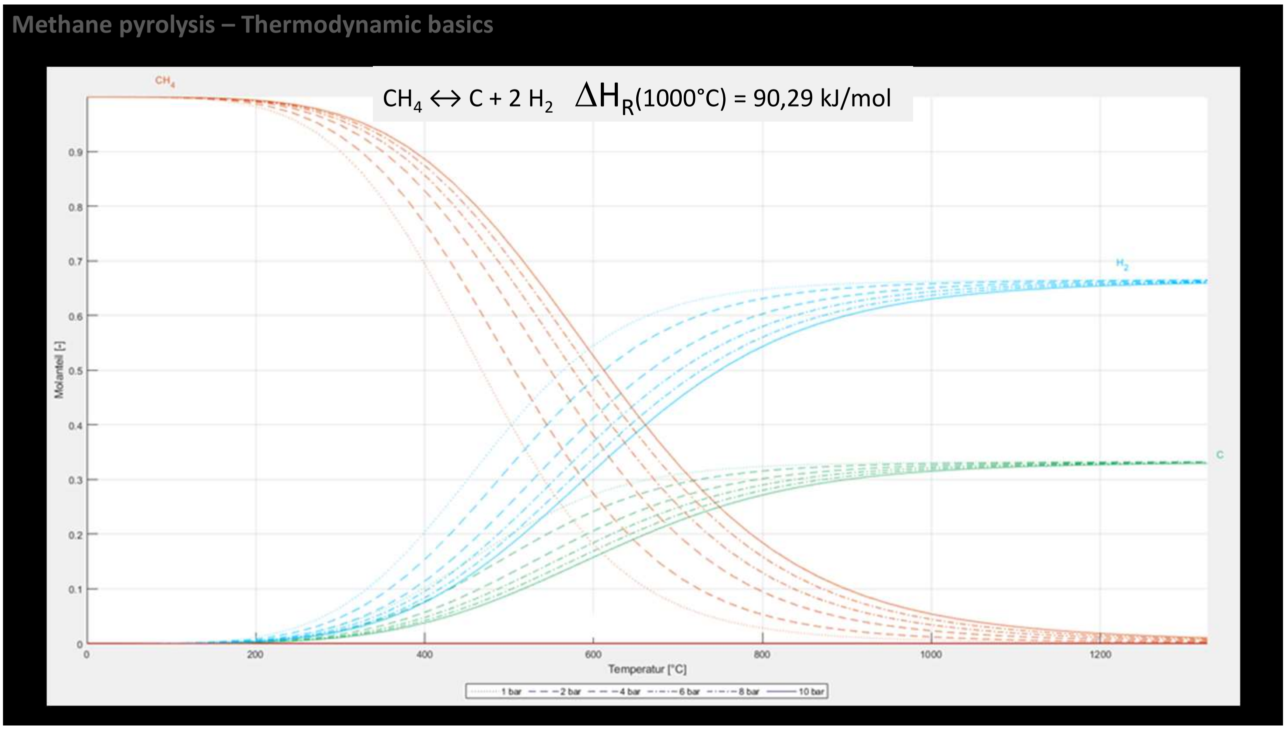
4


Production routes for Hydrogen
Bio-Photolysis
Dark Fermentation
Photo Fermentation
Biological
Thermo-chemical
Gasification
Pyrolysis
Steam Reforming
Partial Oxidation
Autothermal Reforming
Hydrocarbon Reforming
Hydrocarbon Pyrolysis
Fossile Fuels
Biomass Processes
Renewable Sources
Alkaline
Solid Oxide
PEM
Thermolysis
Photolysis
Electrolysis
Water Splitting
Hydrogen
1
H
1.008
g
1
2.11
Not yet mature on an industrial scale


Selected production routes for Hydrogen
Hydrogen
(1,8 t / h)
Biomass
(50,4 t / h)
Cyclone
Product gas cooler
Product gas filter
Tar scrubber
Product gas blower
Product gas to CR
Solvent treatment
Post-combustion chamber
Air pre-heater
Steam super-heater
Flue gas cooler
Flue gas filter
Flue gas blower
CO₂
Limestone CaCO₃
Dryer
Air
Separator
Cyclone
Separator
Gasification reactor (GR)
Combustion reactor (CR)
Steam generation
Treatment
Steam
Fine ash removal
Coarse Ash removal
Combustion air
Softened water
Fly ash
Source: Hammerschmid M. et al. Biomass Conversion and Biorefinery, 2020; https://doi.org/10.1007/s13399-020-00939-z


Selected production routes for Hydrogen
O2
(8 kg)
H2O
(9 kg)
Water Electrolysis
50 kWh / kgH2
< 1 … 15 … 30+ kgCO2 / kgH2
renewables … coal
H2O
(4,5 kg)
CO2
Steam Reforming
CH4
(2,8 kg)
38,9 kWh / kgH2
10 – 12 kgCO2 / kgH2
Hydrogen
1
g
1
H
1.008
2.11
1 kg
Conversion to electrical energy
33 kWh / kgH2
20 kWh / kgH2
C
(3 kg)
2 – 6 kgCO2 / kgH2
renewables
CH4
(4 kg)
55,6 kWh / kgH2
Methane Pyrolysis
12 – 15 kWh / kgH2

7


Methane pyrolysis – Thermodynamic basics
CH4 ↔ C + 2 H2 ΔHR(1000°C) = 90,29 kJ/mol
CH4
H2
C
Molanteil [-]
Temperatur [°C]
1 bar
2 bar
4 bar
6 bar
8 bar
10 bar

8

Methane pyrolysis – Technology and reactor concepts

$CH_4 \leftrightarrow C + 2\,H_2 \quad \Delta H_R(1000°C) = 90{,}29\ kJ/mol$

Methane decomposition				
	Thermal Cracking		**Thermo-catalytic Cracking**	
Technology	**Molten liquid baths:** • Metals (Sn, Cu, Fe, …) • Salts	**Plasma:** • Microwave • Direct current arc • Dielectric barrier discharge • DC radio frequency	**Metal based catalyst:** • Fe, Ni, Cu and others on ceramic supports	**Carbon based catalyst:** • Activated carbon • Carbon black • Graphite
Reactor concepts	Bubble column Capillary reactor	Vortex flow reactor Fluid-wall reactor	Fluidized bed Packed bed Moving bed	

Methane pyrolysis – Literature review

	Catalytic	Molten metal / salt	Plasma	Thermal
Temperature [°C]	550 - 1000	700 - 1300	Ambient - 1500	750 - 1800
Methane flow rate [ml/min]	8 - 1920	5 - 200	0,3 - 3600	10,5 - 8000
Conversion [%]	5 - 100	18 - 95	15 - 100	33 - 100
Inner diameter [mm]	4 - 90	20 - 40	4 - 142	7 - 73
Length [mm]	350 - 1200	150 - 1270	100 - 280	350 - 2500

Catalytic pyrolysis

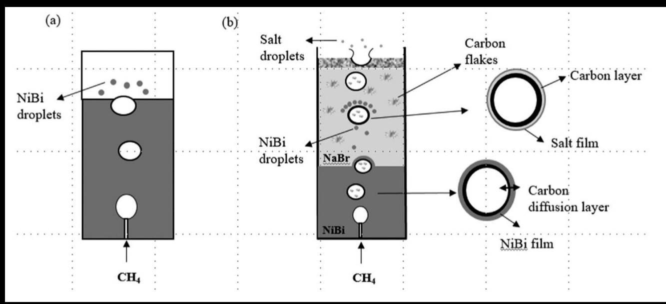
- **Metallic catalysts**: mostly Ni and Fe (with or without carrier), also Co
- **Multi-component systems**: Ni-Mg-Al-O, Cu-Ni alloys
- **Promoters**: Pd, Pt, K_2CO_3
- **Carriers**: Al_2O_3, SiO_2, Activated carbon
- **Carbon based catalysts**: Activated carbon, carbon black, porous carbon, coke, carbon nano fibres
- **Deactivation over time**

Catalytic pyrolysis

- **Advantages of metallic catalysts**
  - Higher activity
  - Production of CNF or CNT as the Carbon product
- **Advantages of carbon-based catalysts**:
  - Cheaper
  - Resist higher temperature
  - No separation of produced carbon necessary
  - High resistance to catalyst poisons

Liquid metal / liquid salt

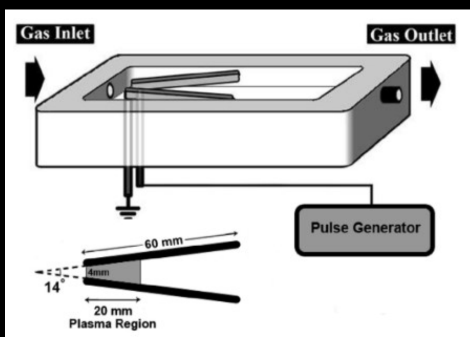
- Predominantly Sn, sometimes alloys (Ni-Bi, In-Bi-Sn, Ga-In-Sn, …)
- Liquid salts as reaction media (system $MnCl_2$-KCl) or as a layer on the liquid metal (NaBr, KBr, KCl)
- $MnCl_2$-KCl und Ni-Bi show catalytic activity
- **Challenges**:
  Operational capacity,
  continuous operation



Source: Rahimi N. et al. (2019)

Plasma

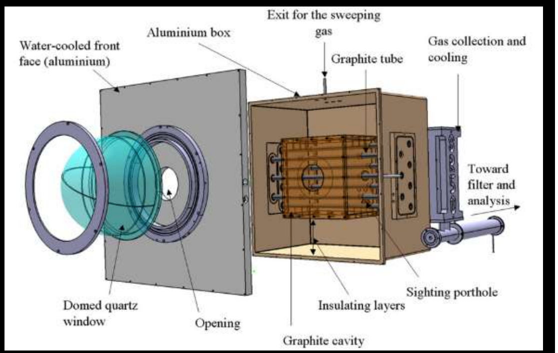
- Predominantly non-thermal plasma with various setup of electrodes
- Mostly Ar or N_2 as a carrier gas
- Carbon product often gaphitic
- **Problems**: Carbon deposition, H_2 yield, and selectivity



Source: Majidi Bidgoli et al. (2017)

Thermal cracking

- Mostly diluted with Ar or N_2 as carrier gas
- Maximum H_2 yield: 84 – 99 %
- Mostly carbon black as product
- **Problems**: Carbon deposition, production of by-products (e.g. C_2H_2)



Source: Rodat et al. (2010)

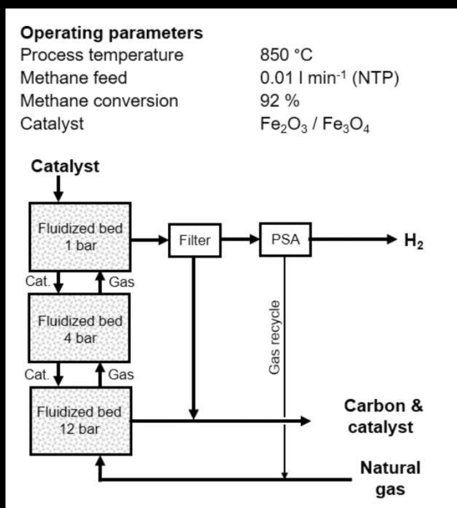
Challenges and TRL

- All known technologies have **TRL 2 – 4** (if H_2 is the intended product)
- Plasma technologies for carbon black production have TRL 6 – 8 (H_2 as a by-product)
- **Problems**: Scalability and continuous operation, valorisation of carbon

Company	Method	TRL	Remarks
Florida Energy Center	Catalytic	3	Last publication 2005, terminated
Hazer	**Catalytic**	**3**	**Cascade fluidized bed, ongoing**
UOP	Catalytic	4	Cat. regeneration by CO_2 generation, SMR substitute
KIT	**Molten metal**	**3**	**Ongoing**
Arenius	Molten metal	-	Unclear status, no further information found
BASF, Linde	**Thermal**	**4**	**Ongoing**
Monolith Materials	**Plasma**	**8**	**Carbon black production, ongoing**
Atlantic Hydrogen	Plasma	5	Went bankrupt under pilot plant construction
Gazprom	Plasma	3	Operation of lab plant, no further plans publ.
GasPlas	Plasma	-	Lab scale
Hope Cell	Plasma	-	One patent available, no further information publ.
HiiROC	**Plasma**	**?**	**Only PR information available**
Graforce	**Plasma**	**5 - 6**	**Demo plant in operation in Berlin**

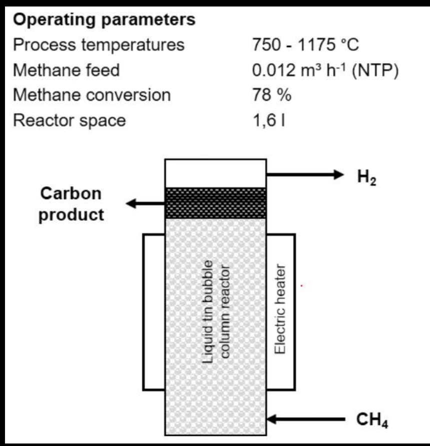
Hazer

- Fluidised bed reactor with iron ore
- Three reactors operating at different pressures
- Continuous catalyst flow
- Pilot plant wit a capacity of 5,5 kg/d (Hydrogen and carbon)
- Demo plat (100 t/a) currently under construction - Intended feed: Biogas



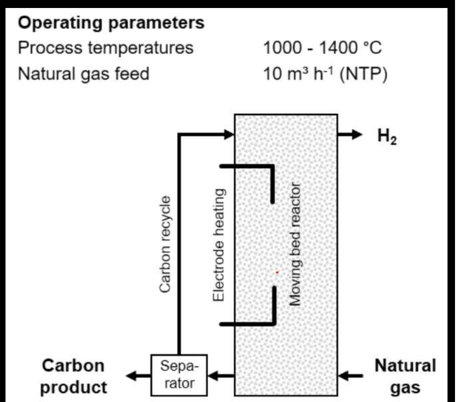
KIT

- Liquid metal bath (Sn)
- Bubble column reactor at 1200°C
- Carbon not removed at lab scale reactor
- Upscaling currently under discussion



BASF

- Projects:
  - 'Solid and fluid products from gas' (Linde, Thyssenkrupp, TU Dortmund, RU Bochum, hte, VDEh)
  - 'Me^{2}H$_2$' (KIT, Thyssenkrupp, TU Dortmund, Universität Bochum, VDEh)
- Process development and valorisation of C
- Moving bed reactor with solid carbon pellets
- Electrically heated to 1400°C
- Demo plant for continuous operation planned



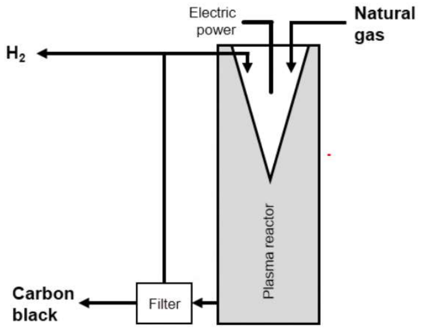
Methane pyrolysis – Overview of industrial developments

Monolith Materials

- Based on Kvaerner process
- Plasma reactor for carbon black production
- Pilot plant in operation till 2018
- Demo plant Olive Creek
- H_2 as plasma gas and heat carrier

Operating parameters Seaport-plant	
Temperature reaction zone	2100 °C
Natural gas feed	144 m³ h⁻¹ (NTP)
Methane conversion	94 %
Plasma power (electr.)	0.85 MW

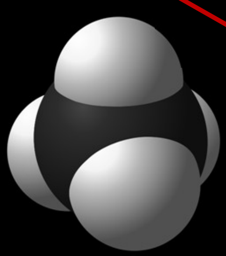
Operating parameters Olive-Creek-plant (under construction)	
Carbon black output	10 - 15 kt a⁻¹



21

Valorisation options for **Carbon**

CH_4



74,9 % C

25,1 % H

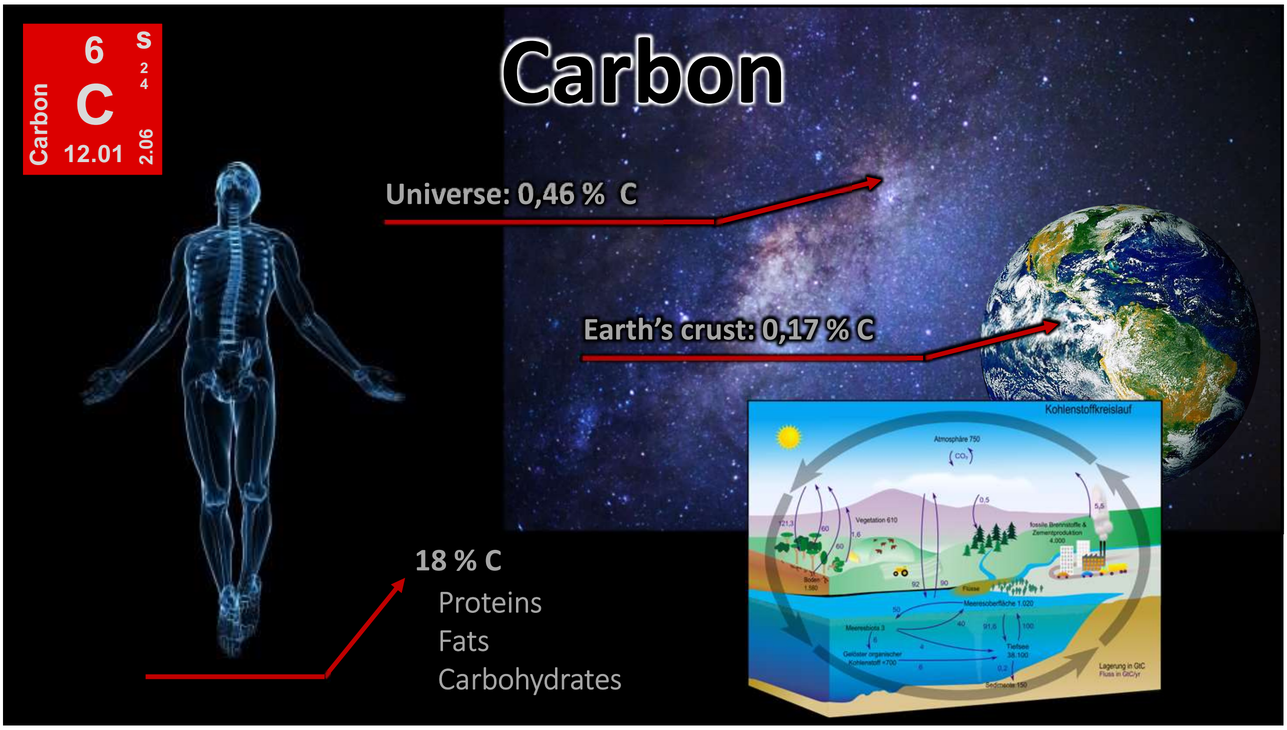
1 kg H_2 → 3 kg C

Steel production in 

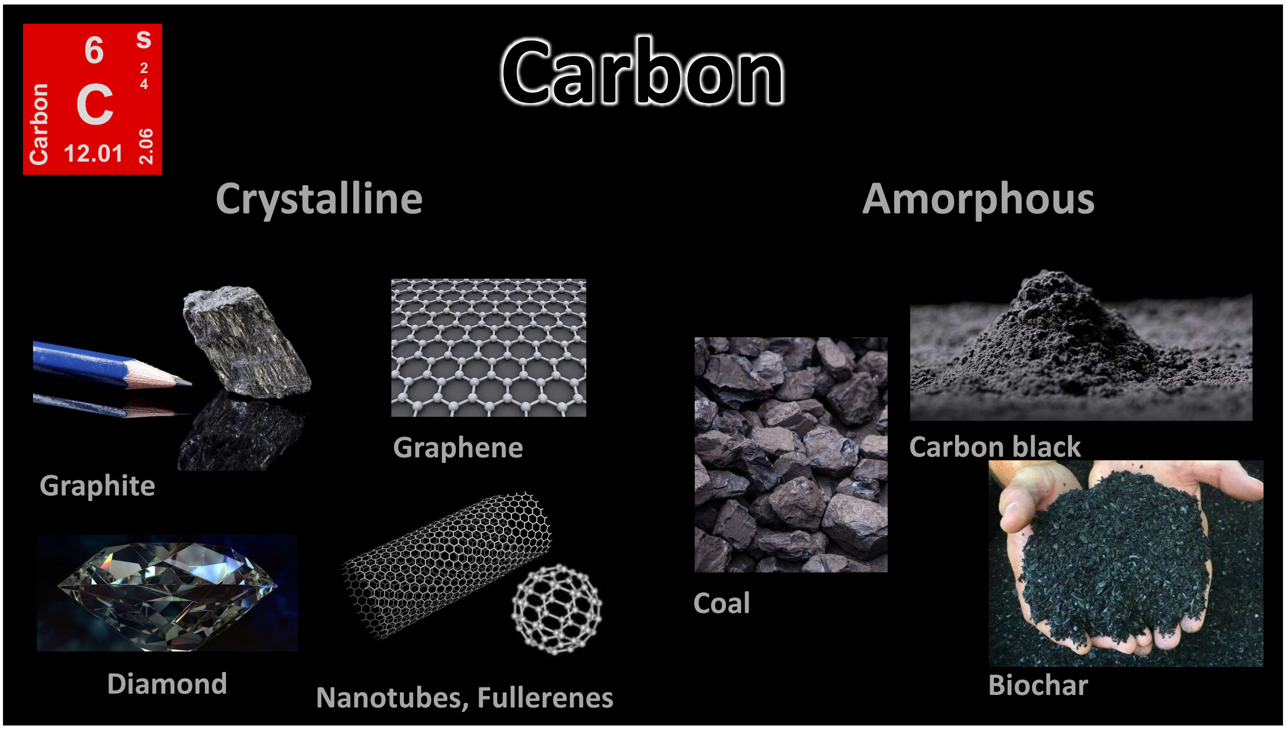
500 000 t H_2 → 1 500 000 t C

every year !

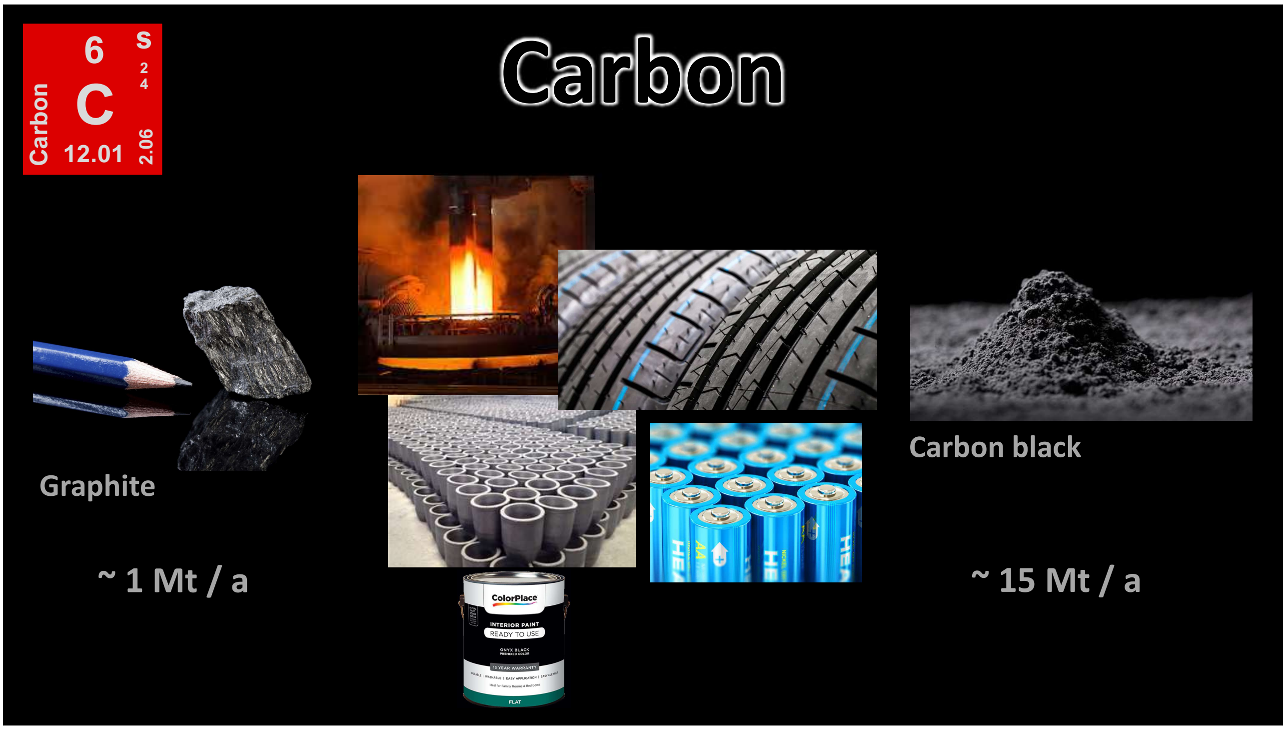
22


Carbon
6
C
12.01
Carbon
Universe: 0,46 % C
Earth's crust: 0,17 % C
18 % C
Proteins
Fats
Carbohydrates
Kohlenstoffkreislauf

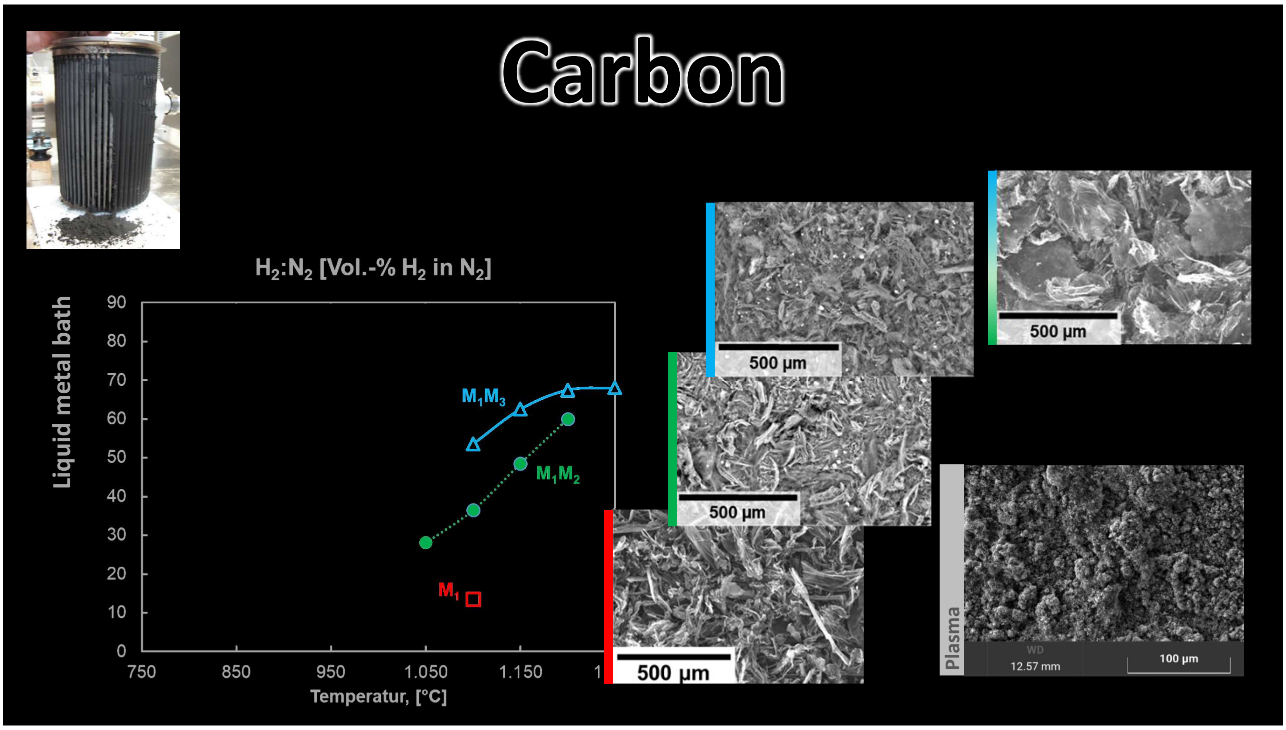
23


Carbon
6
C
12.01
Carbon
Crystalline
Amorphous
Graphite
Graphene
Diamond
Nanotubes, Fullerenes
Coal
Carbon black
Biochar

24


6
S
2
4
C
Carbon
12.01
2.06
Carbon
Graphite
~ 1 Mt / a
ColorPlace
INTERIOR PAINT
READY TO USE
Carbon black
~ 15 Mt / a

25

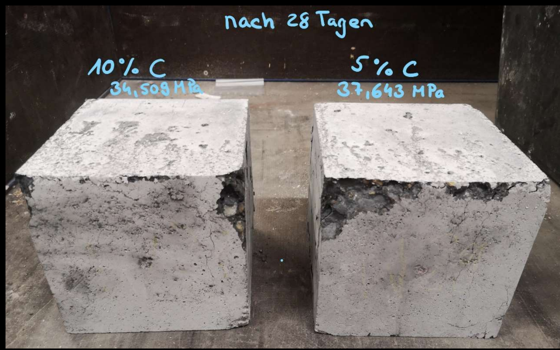

Carbon
H2:N2 [Vol.-% H2 in N2]
Liquid metal bath
90
80
70
60
50
40
30
20
10
0
750
850
950
1.050
1.150
Temperatur, [°C]
M1M3
M1M2
M1
500 µm
500 µm
500 µm
500 µm
Plasma
WD
12.57 mm
100 µm

26

High volume applications of Carbon

(1) Construction industry

Isolation materials

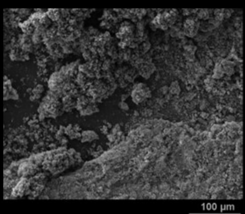


Substitution of cement in concrete

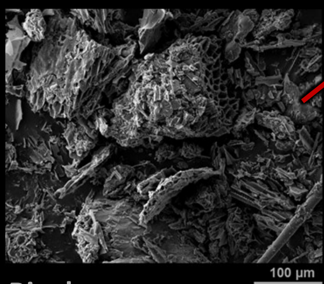
High volume applications of Carbon

(2) Agriculture

Amazon basin
(450 BC – 950 AC)



Carbon from pyrolysis



Biochar

Terra preta soils

- ☑ Water retention capacity
- ☑ Nutrient storage
- ☑ Habitat for microorganisms
- ☑ Creation of humus

Hydrogen, Carbon and Pyrolysis

MONTAN UNIVERSITÄT LEOBEN

ric Leoben

Explanatory video

YouTube

Montanuniversität Leoben – RIC Leoben

WO AUS FORSCHUNG ZUKUNFT WIRD