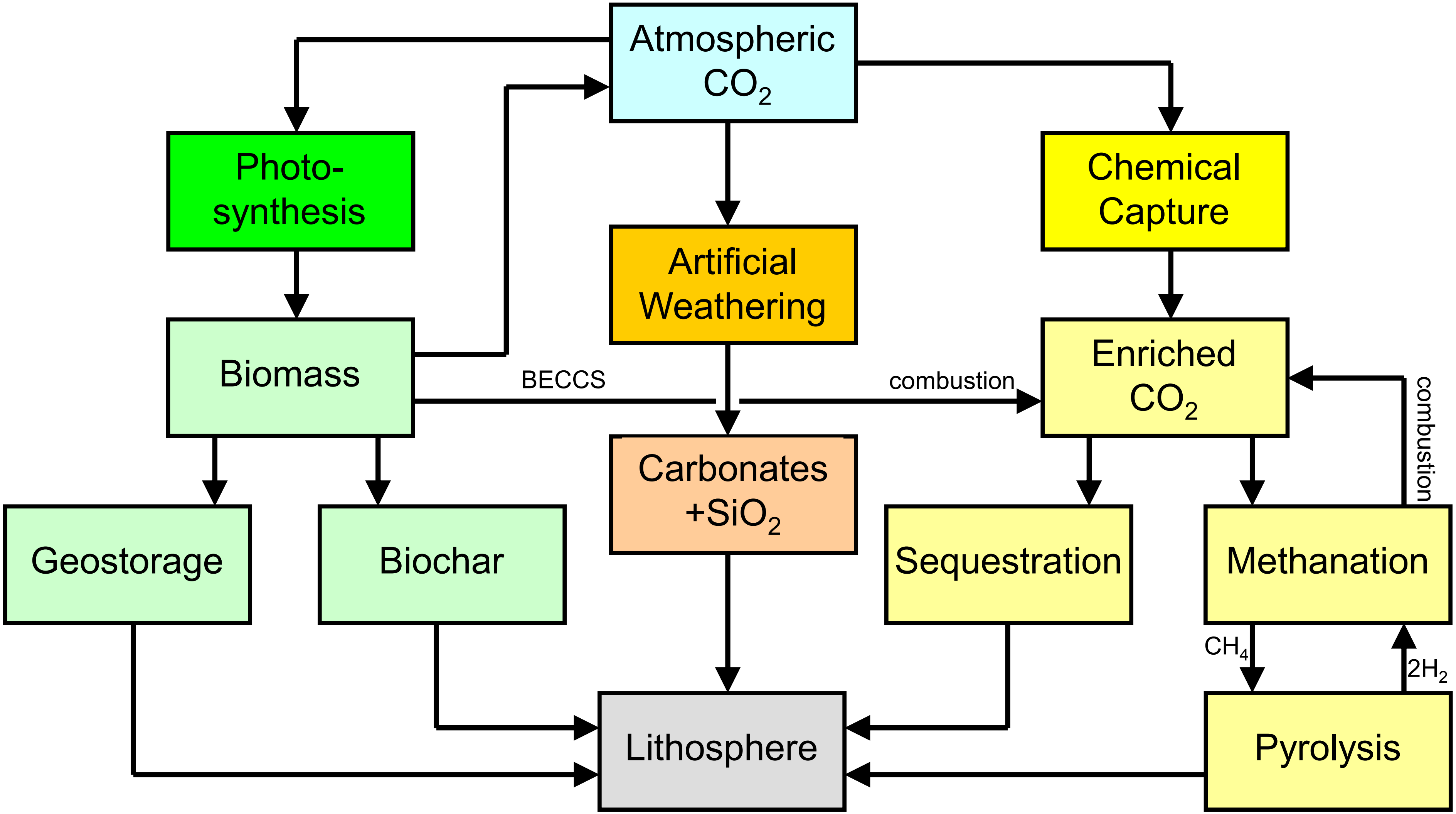
Power-to-Gas with Direct-air-capture

David Agar
Yu Qiao
Jan Haertel
Yee Tong Voon

UKCCS
Air Capture Workshop
London, 20.02.2015

Contents

Direct-air-capture

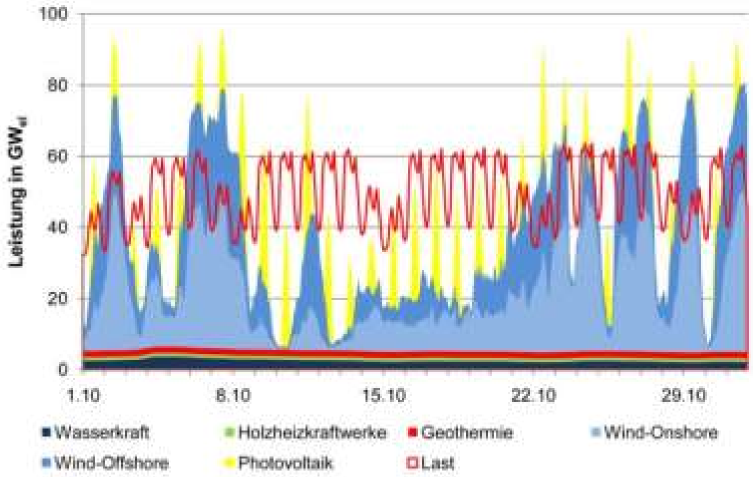


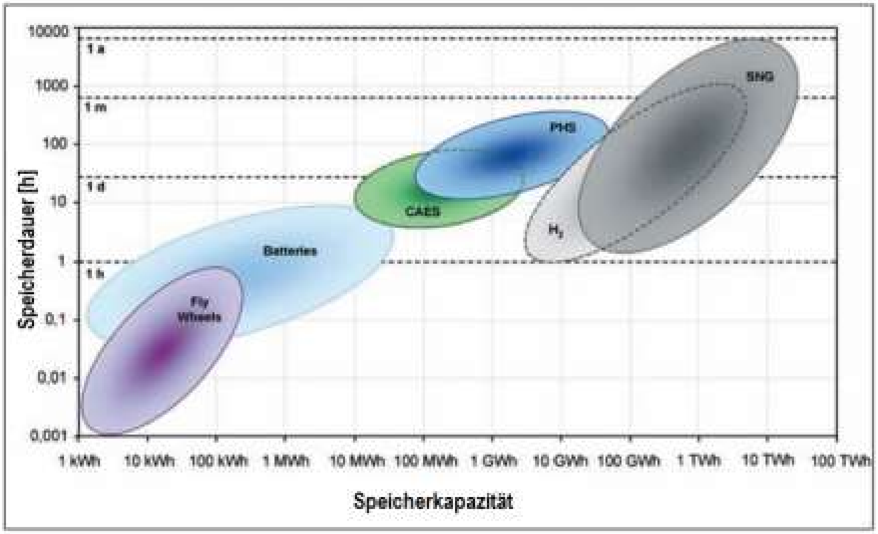
Power-to-gas

- **German Energy ‚Turnaround‘**
  - §1 Abs.2 EEG 2014
  - 2025: 40-45%
  - 2035: 55-60%
  - Supply fluctuations endanger grid stability

- **Storage of renewable power**
  - balancing supply and demand
  - 2030: excess power available

- **Storage technologies**
  - Batteries
  - Compressed air (CAES)
  - Hydroelectric (PHS)
  - Power-to-heat
  - **Power-to-Gas (PtG)**





Source: Trost et al. (2012)

Sabatier methanisation reaction

$$CO_2 + 4H_2 \; \square \qquad 2H_2O$$

$\Delta_R H_{298K}$ = -164.9 kJ/mol CO_2
= - 3.75 MJ/kg CO_2
(plus latent heat)

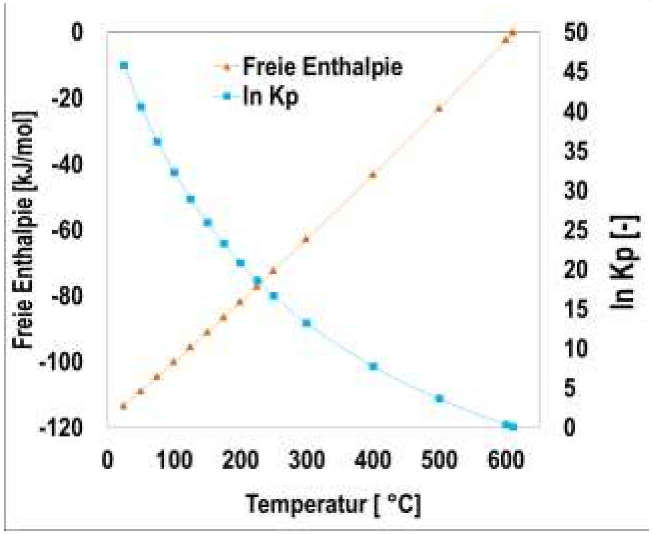
$\Delta_R G_{298K}$ = -113.5 kJ/mol CO_2

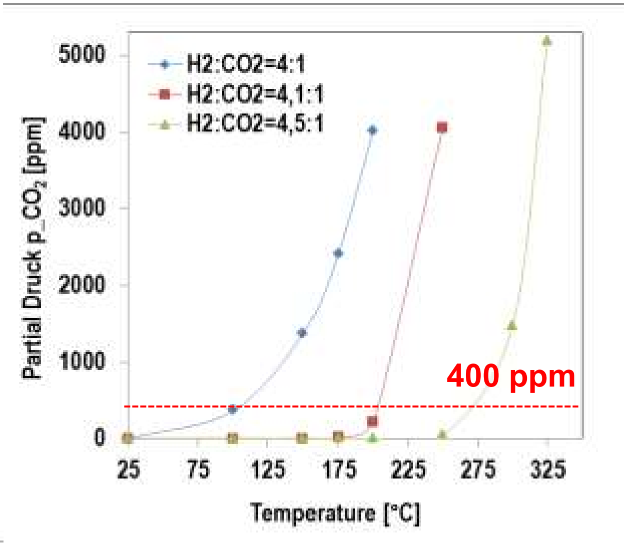
$\Rightarrow K_{P,298K} = 7.86 \times 10^{19}$

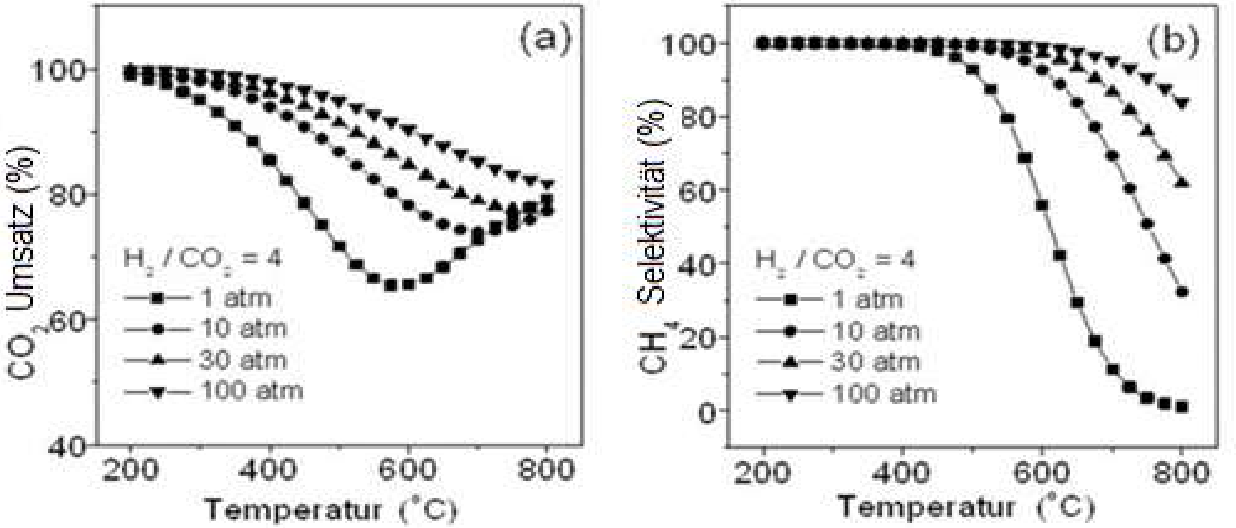
T [K]	**$H_2:CO_2$ [mol/mol]**	**$y_{CO2,eqm}$ [ppm]**
298	**4**	**71**
523	**4**	**21 700**
523	**4.25**	**370**

Retro-shift side-reaction: $CO_2 + H_2 \leftrightarrows CO + H_2O$ is negligible

Sabatier methanisation reaction

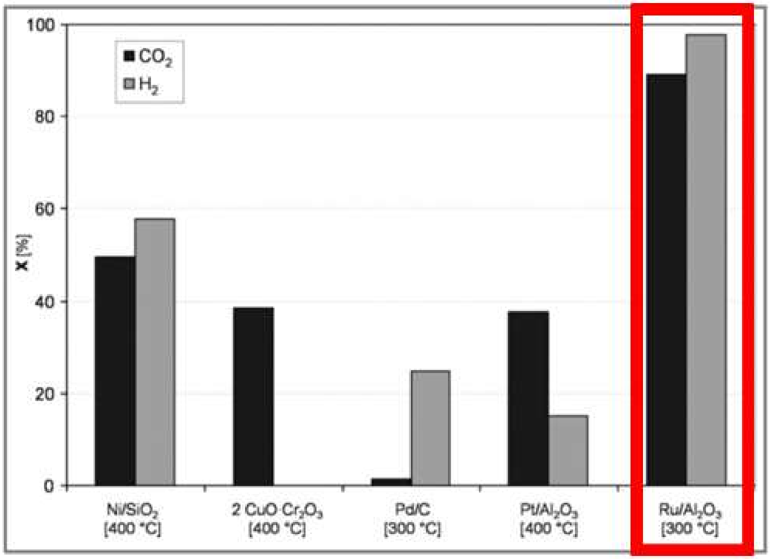




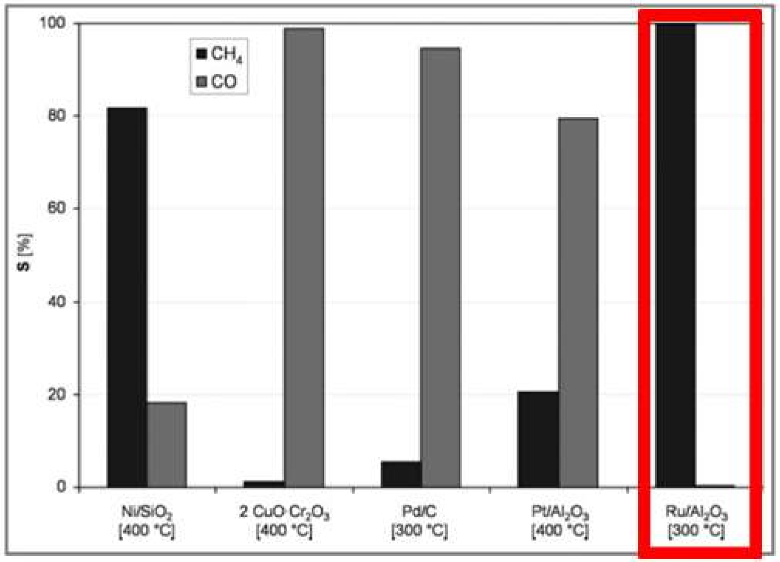


Gao et al. (2012)

Sabatier methanisation reaction



Conversion



Selectivity

- **Kinetics**
  - novel Ru/Al_2O_3 catalysts
  - Temperature window: 270-350°C
- **Heat removal**
  - Adiabatic reactor + intermediate cooling + isothermal reactor
  - 50 K / %CO_2

Schoder (2013)

German patent DE10226424A1 08.01.2004

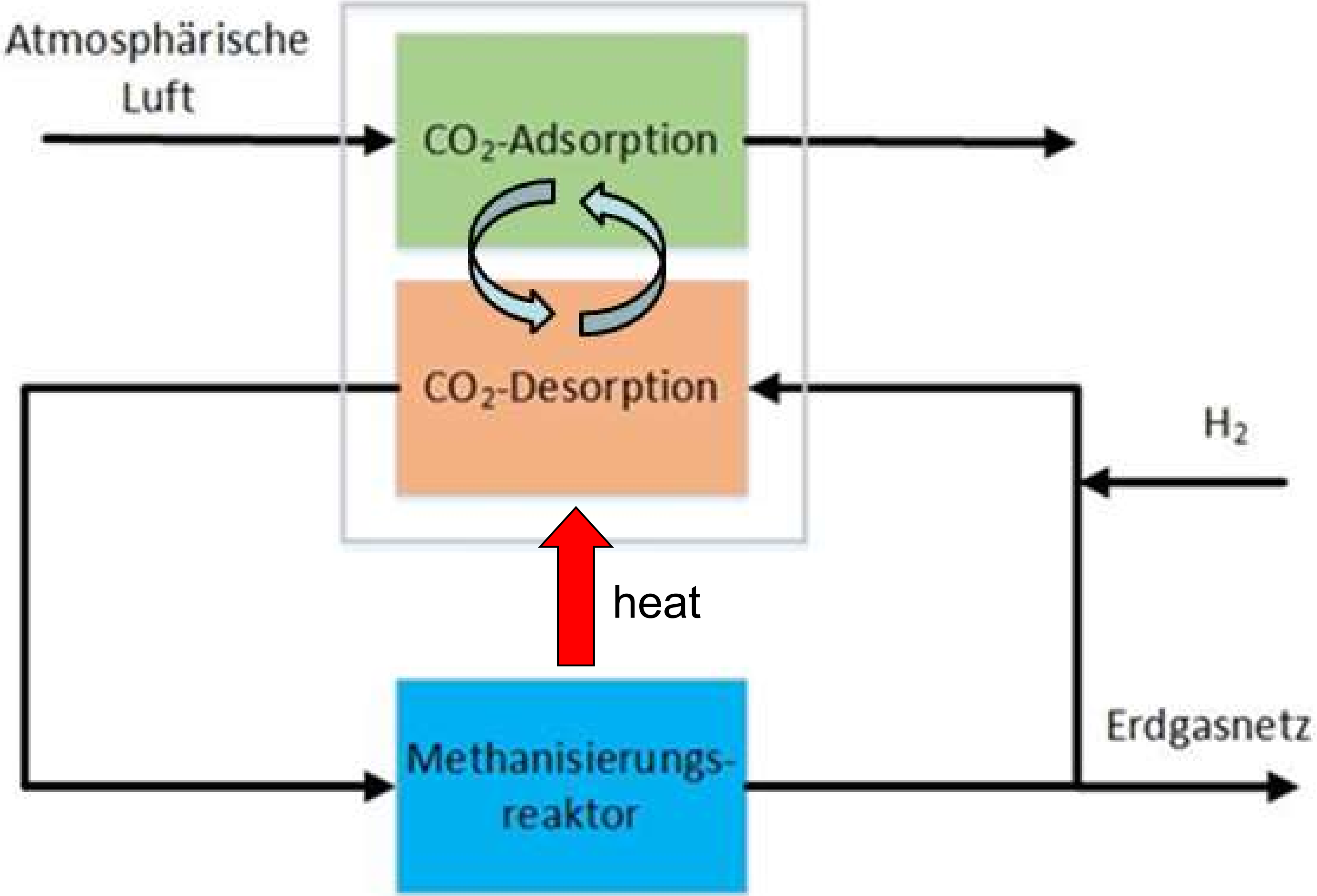
CO_2 sources

- **Industrial purge gases (100%)**
- **Biogas (50%)**
- **Cement flue gases (30%)**
- **Coal combustion (15%)**
- **Natural gas combustion (5%)**
- **Atmosphere (400 ppm)**

Power-to-gas logistics

- **Renewable power generation**
- **Flexible CO_2-source**
- **District heating consumer**
- **Natural gas transport & storage infrastructure**
- **CO_2-sequestration site**
- **Power-Gas-Power efficiency: 30-38%** (wikipedia)

Power-to-Gas (PtG) with Direct-Air-Capture (DAC)



http://co2now.org/ (24.09.2014)

Ad(b)sorbents

- **Caustic and carbonates**
- **Polyethylenimine impregnated resin**
- **AEAPDMS functionalised cellulose**
- **Hyperbranched aminosilica**
- **TEPA on PMMA**
- **Lewatit VP OC 1065**
- **MOF + Amines…**

Ad(b)sorbents

- **Adsorbents have no volatility losses**
- **Adsorbents reduce oxidative degradation**
- **Support increases heat capacity**
- **Moisture reduces CO_2-capacity**
- **Absorption simplifies heat exchange**

$$Q_r = \frac{1-\theta}{q_w} C_{PS}\left(T_{de} - T_{ad}\right) - \Delta_R H$$

Zhang et al., Chem. Engng. Sci. 116:306-316 (2014)

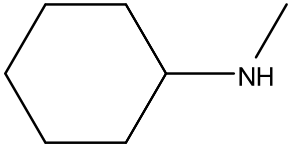
Regeneration techniques

- Thermal
- Vacuum
- Stripping
- Displacement
- Reaction

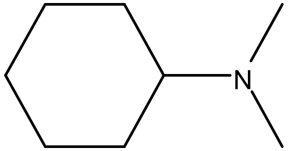
Agar ‚Do's and Don'ts of adsorptive reactors' Ch. 7 in ‚Integrated chemical processes' (2005)

Regeneration techniques

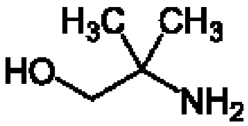
- **Thermomorphic biphasic solvents**



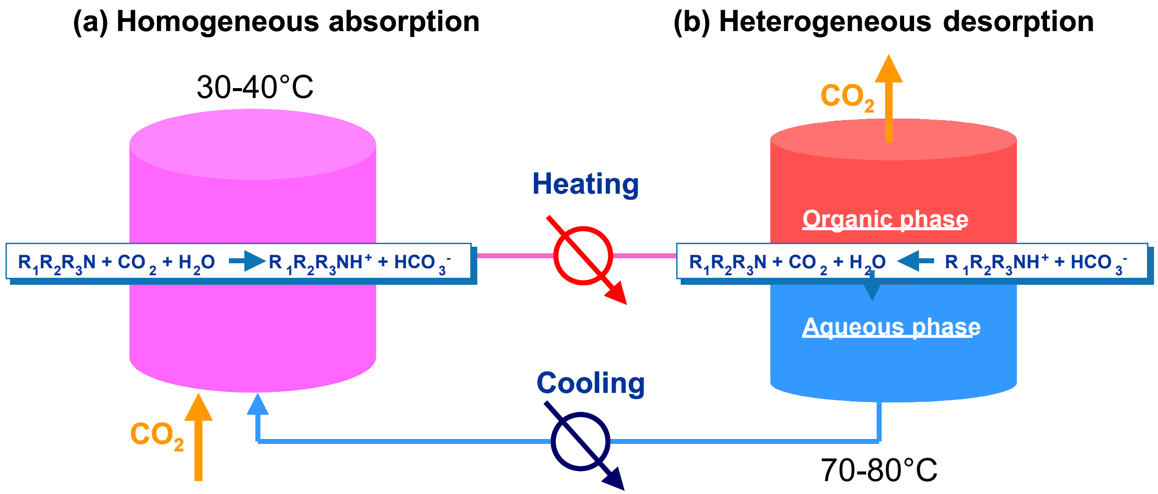
MCA

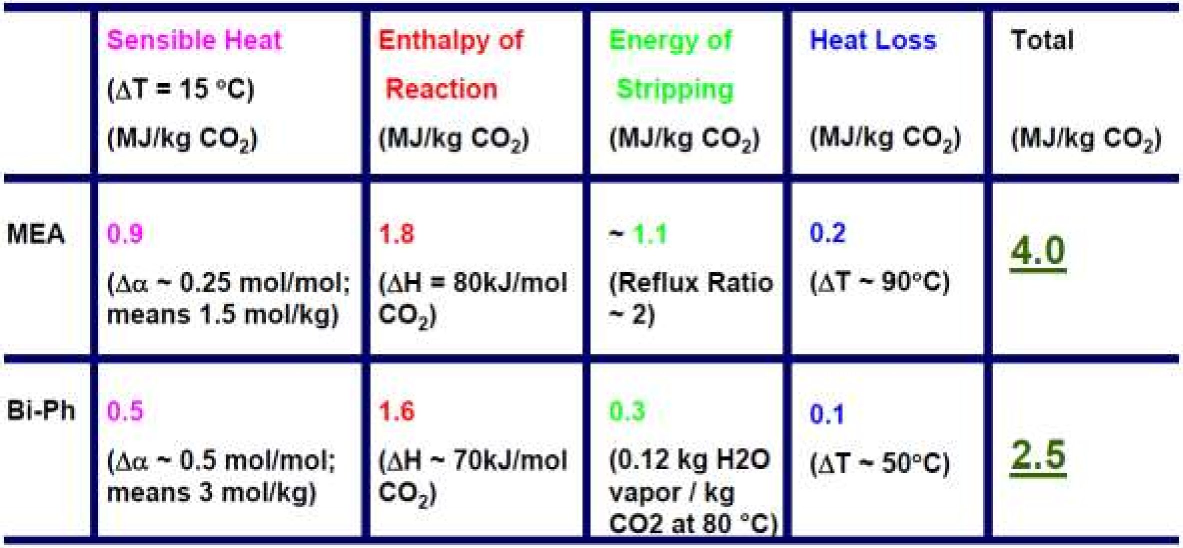


DMCA



AMP





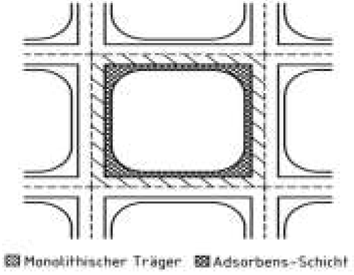
	Sensible Heat (ΔT = 15 °C) (MJ/kg CO_2)	Enthalpy of Reaction (MJ/kg CO_2)	Energy of Stripping (MJ/kg CO_2)	Heat Loss (MJ/kg CO_2)	Total (MJ/kg CO_2)
MEA	0.9 ($\Delta\alpha$ ~ 0.25 mol/mol; means 1.5 mol/kg)	1.8 (ΔH = 80kJ/mol CO_2)	~ 1.1 (Reflux Ratio ~ 2)	0.2 (ΔT ~ 90°C)	4.0
Bi-Ph	0.5 ($\Delta\alpha$ ~ 0.5 mol/mol; means 3 mol/kg)	1.6 (ΔH ~ 70kJ/mol CO_2)	0.3 (0.12 kg H2O vapor / kg CO2 at 80 °C)	0.1 (ΔT ~ 50°C)	2.5

German Patent DE 102006036228 03.08.2006

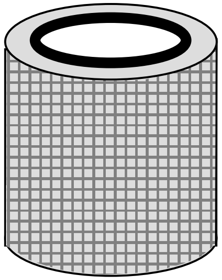
Ad(b)sorbents

www.hamon.com
M. Dittmar DIssertation 2013

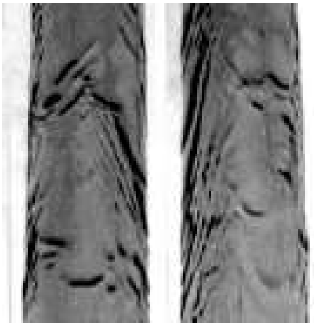
- **Monolithic supports**



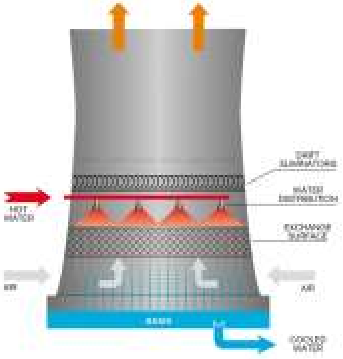
- **Adsorbent mechanically immobilised on heat exchanger surface**



- **Wavy falling film absorbers**



- **„Cooling tower“ contactor with thermal draft**



H_2 sources

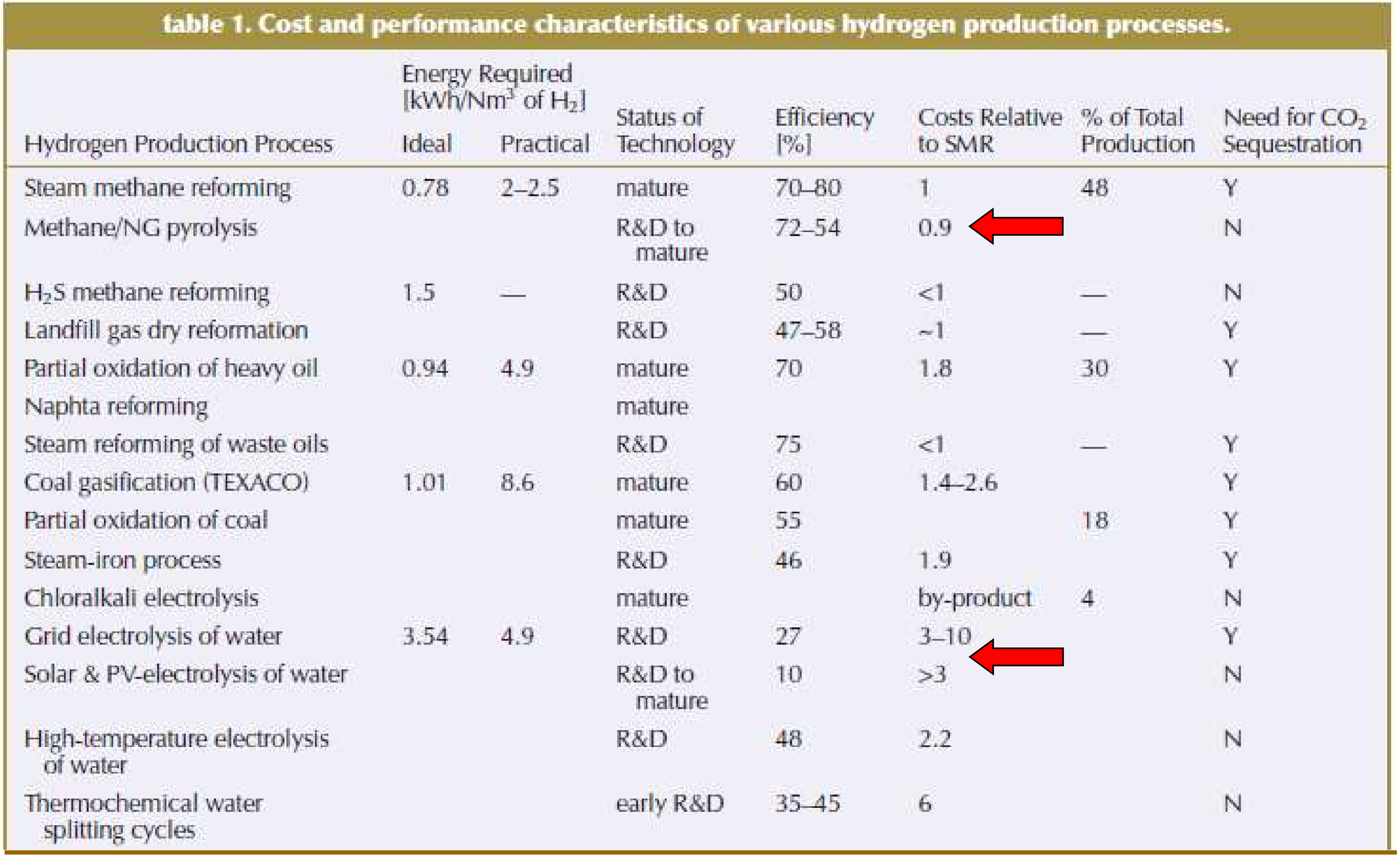


table 1. Cost and performance characteristics of various hydrogen production processes.

	Energy Required [kWh/Nm³ of H_2]						
Hydrogen Production Process	Ideal	Practical	Status of Technology	Efficiency [%]	Costs Relative to SMR	% of Total Production	Need for CO_2 Sequestration
Steam methane reforming	0.78	2–2.5	mature	70–80	1	48	Y
Methane/NG pyrolysis			R&D to mature	72–54	0.9		N
H_2S methane reforming	1.5	—	R&D	50	<1	—	N
Landfill gas dry reformation			R&D	47–58	~1	—	Y
Partial oxidation of heavy oil	0.94	4.9	mature	70	1.8	30	Y
Naphta reforming			mature				
Steam reforming of waste oils			R&D	75	<1	—	Y
Coal gasification (TEXACO)	1.01	8.6	mature	60	1.4–2.6		Y
Partial oxidation of coal			mature	55		18	Y
Steam-iron process			R&D	46	1.9		Y
Chloralkali electrolysis			mature		by-product	4	N
Grid electrolysis of water	3.54	4.9	R&D	27	3–10		Y
Solar & PV-electrolysis of water			R&D to mature	10	>3		N
High-temperature electrolysis of water			R&D	48	2.2		N
Thermochemical water splitting cycles			early R&D	35–45	6		N

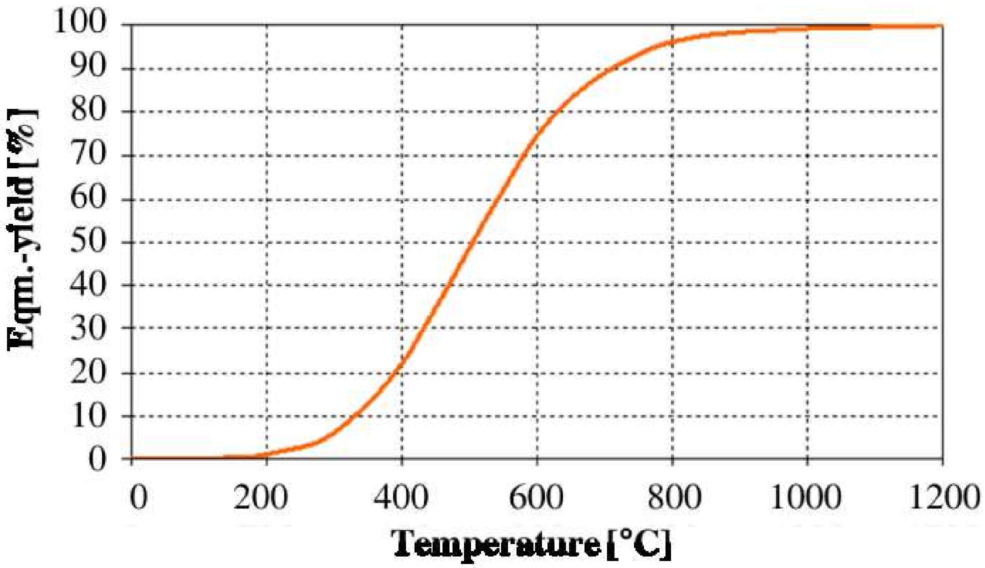
T-Raissi & Block, IEEE Power & Energy 2(6):40-45 (2004)

H_2 sources – methane pyrolysis

- Thermodynamics

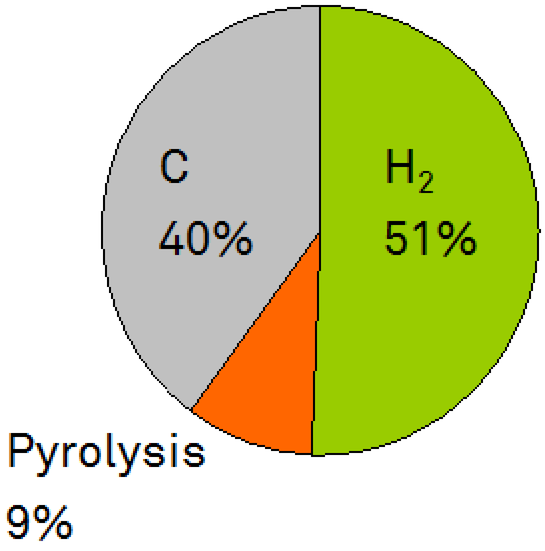
$$CH_4 \leftrightarrows C + 2H_2$$

$$\Delta H_{1000°C} = +91.7\ kJ\ mol^{-1}$$



- Total energy balance of methane pyrolysis

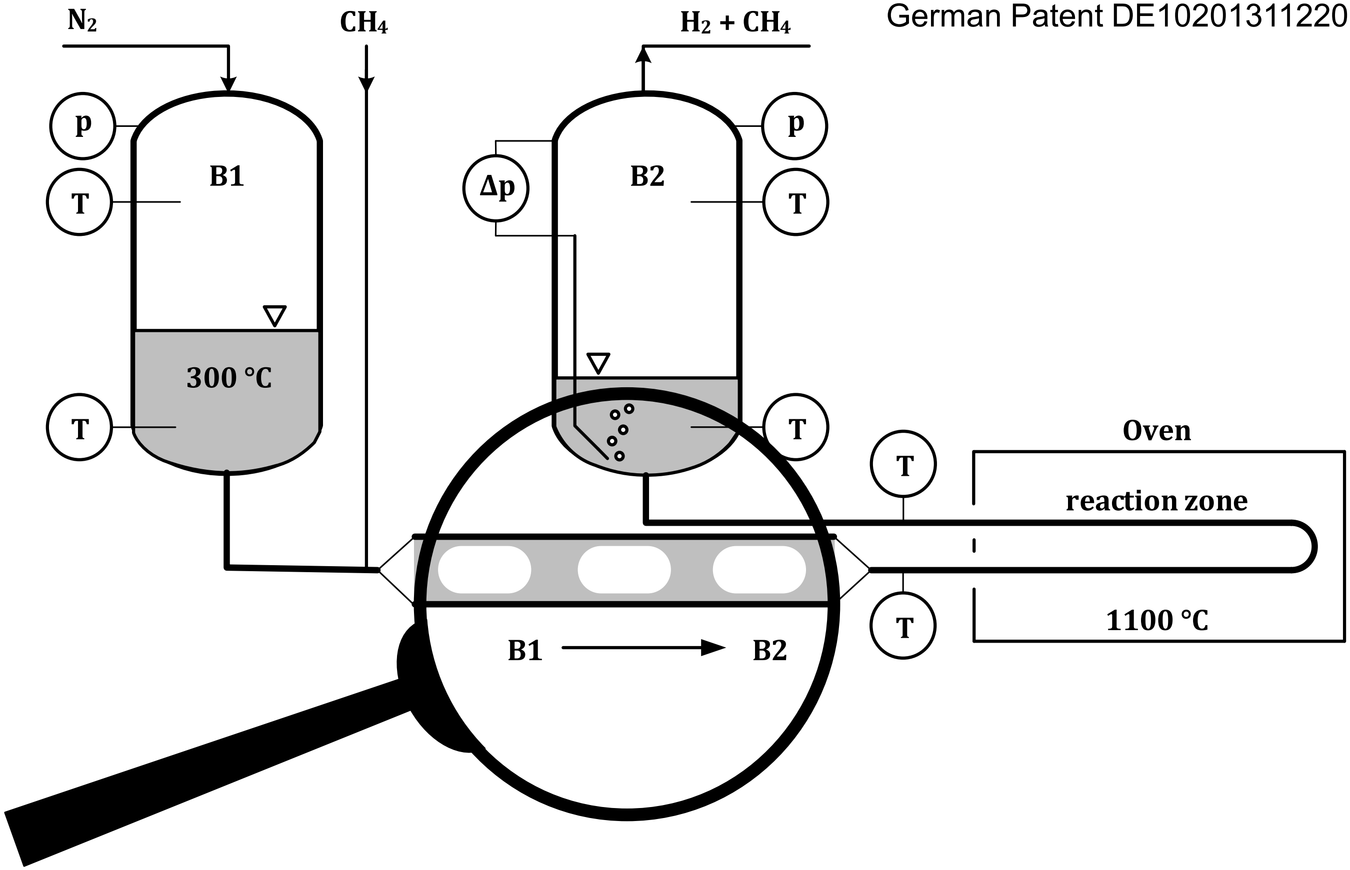
100% = net heat of combustion of methane



Kreysa, Agar, Schultz, DGMK-Tagungsericht 4-6.10.2010

H_2 sources - methane pyrolysis

German Patent DE102013112205 11.06.2013



- **Convective heat supply**
- **Molten-metal slug-flow reactor**

Take-home messages

- Good fit between PtG & DAC
- Energy demand for CO_2-capture < 4 MJ/kg
- CO_2-free H_2 via CH_4-Pyrolysis

Acknowledgement

Thank you for your attention

Yu Qiao, M.Sc.
CVT – G1-6.22
BCI -TU-Dortmund
D-44227 Dortmund, D
Tel.: (+49) 231 - 755 5332
E-Mail: yuqiao@bci.tu-dortmund.de