



Joint Seminar of BMBF and Siemens "CO₂ Utilization Potential"

22/23 September 2009, Steigenberger Grandhotel Petersberg, Bonn

22 September 2009

General introductory talk

Dr. Johannes Ewers, RWE Power AG

Keynote presentations on "CO₂ utilization on the basis of biological processes"

Dr. Ulrich Schurr, Forschungszentrum Jülich GmbH

Dr. Martin Kerner, SSC Strategic Science Consult GmbH

Keynote presentations on "Inorganic CO₂ utilization, mineralization"

Prof. Hans Geerlings, TU Delft, DelftChemTech

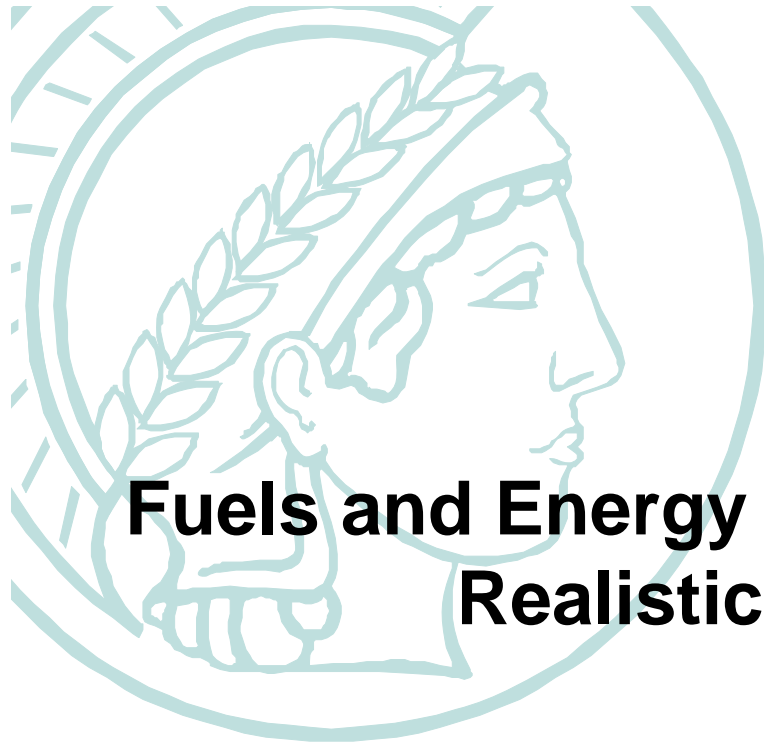
Prof. Ron Zevenhoven, Åbo Akademi University

Keynote presentations on "Alternative fuels and energy sources for industry and transport"

► Prof. Dr.-Ing. Kai Sundmacher, Max-Planck-Institut Dynamics of Complex Technical Systems

Prof. Dr. Eckhard Dinjus, Forschungszentrum Karlsruhe

Joint Seminar of BMBF & Siemens:
„CO₂ Utilization Potential“
Bonn, September 22, 2009



Fuels and Energy Sources by Utilization of CO₂: Realistic Option or Meander?

Liisa Rihko-Struckmann, Hanke-Rauschenbach,
Kai Sundmacher

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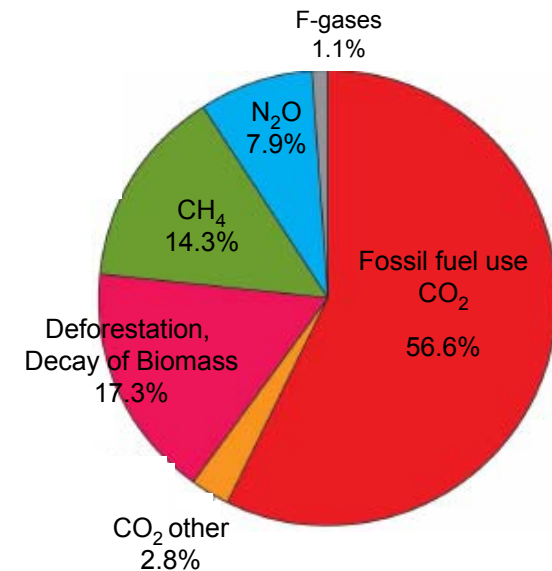
Current Energy Situation: *TO DOs*



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- A) Drastically reduce CO₂ emissions arising from the use of fossil fuels.
- B) Provide sustainable energy sources for transportation and industry at reasonable storage capacities.
- C) Increase the proportion of renewables in the overall energy consumption.

Global greenhouse gas emissions ¹⁾



Key question: *Is it energetically feasible and meaningful to produce liquid fuels from renewable energies by means of chemical reactions which consume fossil CO₂ ?*

1) Rodger et al. Climate Change 2007, IPCC

Why Liquid Fuels?



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	Storage	Grav. Energy Density [kJ/kg]	Vol. Energy Density [kJ/l]	
Storage in Accumulators	Pb accumulator	126	252	
	NiCd accumulator	126	288	
	Ni hydrid accu.	180	576	
	Lithium ion accu.	432	936	
Chemical ¹⁾ Storages	DMC ²⁾	15 780	16 900	RON 105
	Methanol	22 700	18 100	RON 109
	DME	31 700	Pressure dependent	CN > 55
	Gasoline	43 500	32 000	RON 95
	Diesel	42 700	35 000	CN > 51
	Methane	50 000	Pressure dependent	
	Hydrogen	142 200	Pressure dependent	

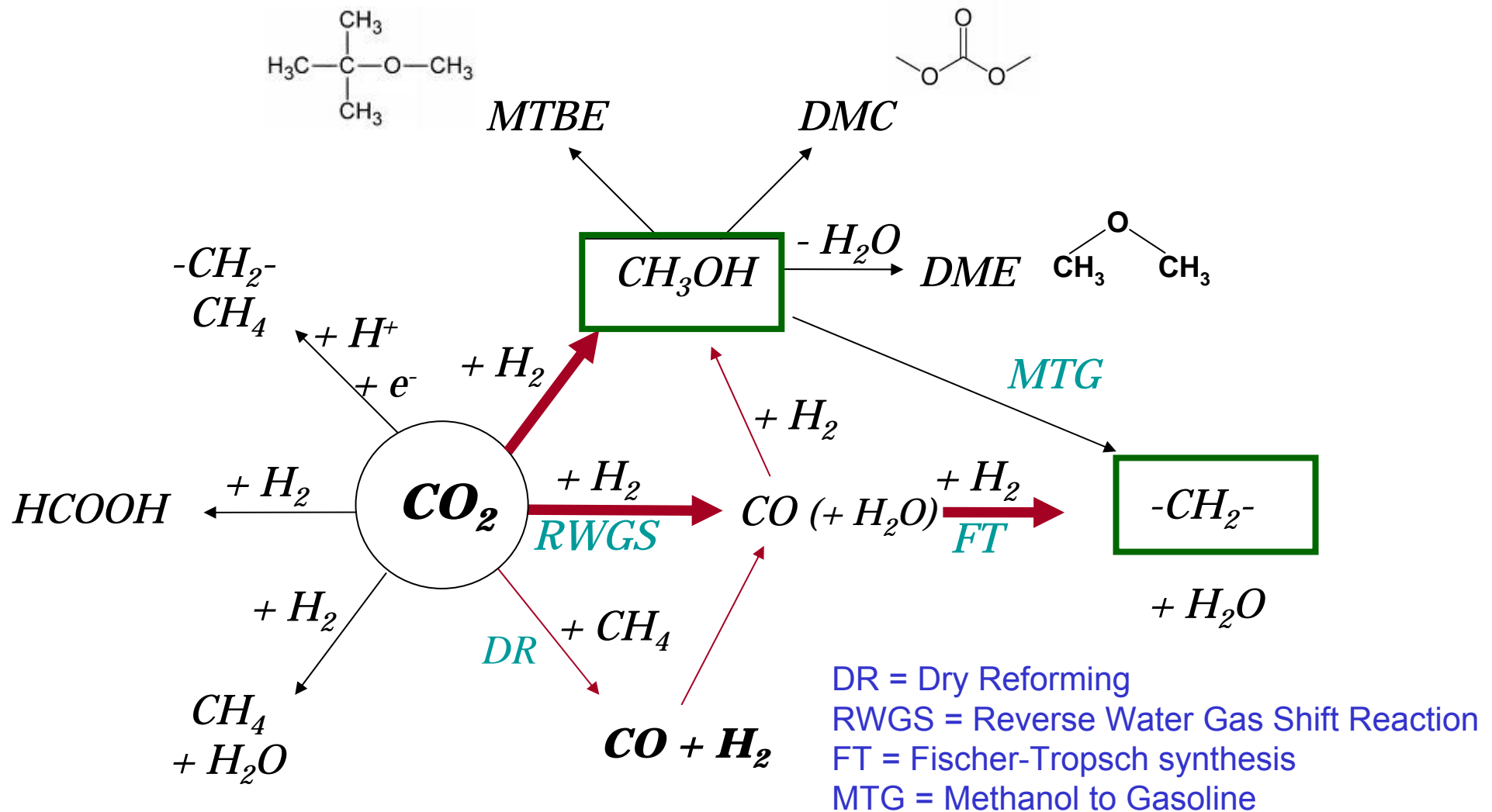
Ref.: Oertel, Fischer, Brennstoffzellen-Technologie - Hoffnungsträger für den Klimaschutz, 2001.
Baehr, Thermodynamik, 1984.

¹⁾ Upper heating value ²⁾ Lower heating value (Wen, Appl. Energy, 2009)

Some Pathways from CO₂ to Liquid Fuels



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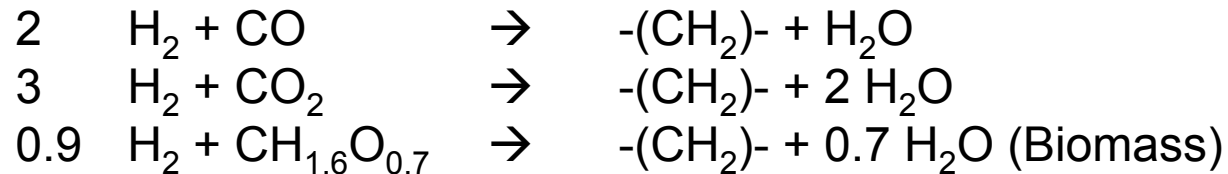
Fischer-Tropsch Synthesis using CO₂



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- Principally CO₂ is a possible raw material for FT synthesis.
- But CO₂ is a less attractive C-source, because C is in a more reduced state.

- **Stoichiometry:**



- **High activity catalysts for RWGS reaction needed:**

- Fe catalysts
- Co catalysts promote unwanted methanation CH₄

- **In-situ removal of H₂O with membrane process:**

- more favourable CO/CO₂ ratio in equilibria: $\text{CO}_2 + \text{H}_2 \longleftrightarrow \text{CO} + \text{H}_2\text{O}$
- more long chain FT Products

References:

G.Schaub, H. Schultz, T. Riedel, *Greenhouse Gas Control Technologies*, Riemer et al. (Edit.), p 367 Elsevier, 1999

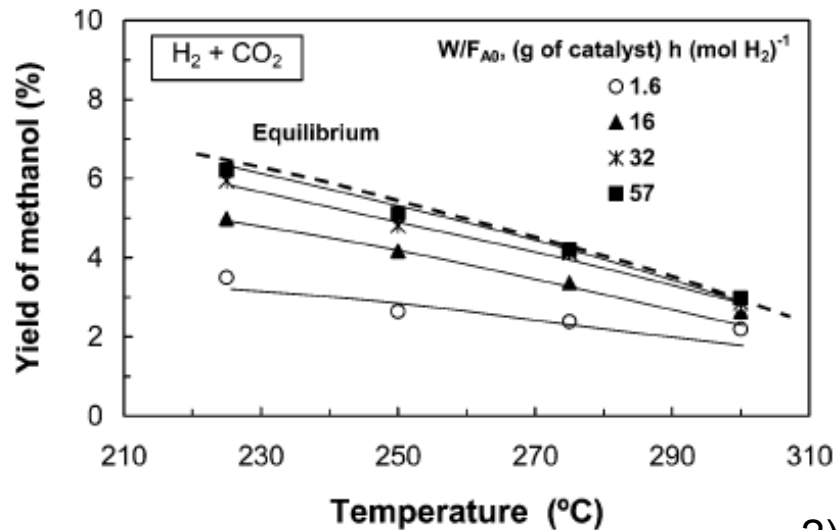
G. Schaub, D. Unruh, M. Rohde, *Stud. in Surf. Sci.* 153 (2004) 17

M. Rohde, D. Unruh, G. Schaub, *Ind. Eng. Chem. Res.* 44 (2005) 9653

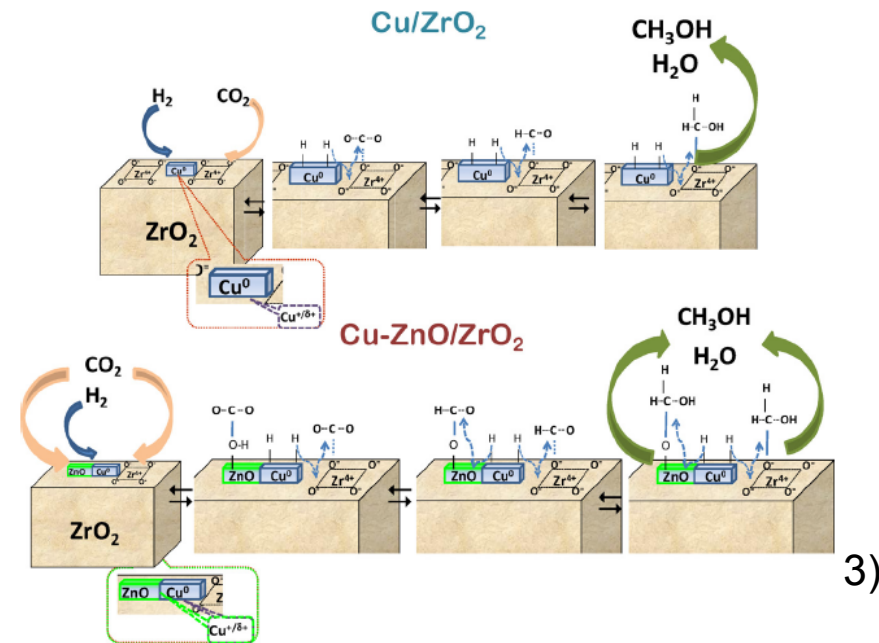
Methanol Synthesis from CO₂



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2)



3)

Fig. 6. Sketch of the catalysts surface and functionality of the various surface sites under CO₂ hydrogenation conditions.

- Commercial CO₂-to-Methanol-Unit under construction ¹⁾

Ref. 1) Olah et al., *Chemical Recycling of CO₂ to Methanol and Dimethyl Ether: From Greenhouse Gas to Renewable, Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons*, *J. Org. Chem.* 74 (2009) 487

2) Aguayo et al., *Ind. Eng. Chem. Res.* 46 (2007) 5522

3) Arena et al., *Appl. Catal.* 350 (2008) 16

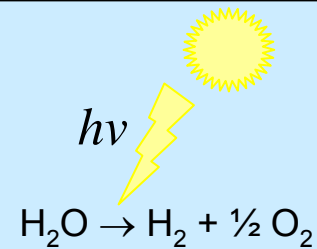
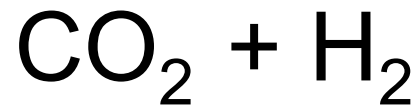
International Activities



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Solar thermal splitting of $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$
(Sandia National Laboratories, USA)

Geothermal Electrolyser for H_2O
(Carbon Recycling Int., Island) ¹⁾



Thermal decomposition of $\text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2$
(Carnol Process® Brookhaven National Laboratory, USA) ²⁾

Photochemical splitting of H_2O (solar)
(Mitsui Chemicals, Japan) ¹⁾

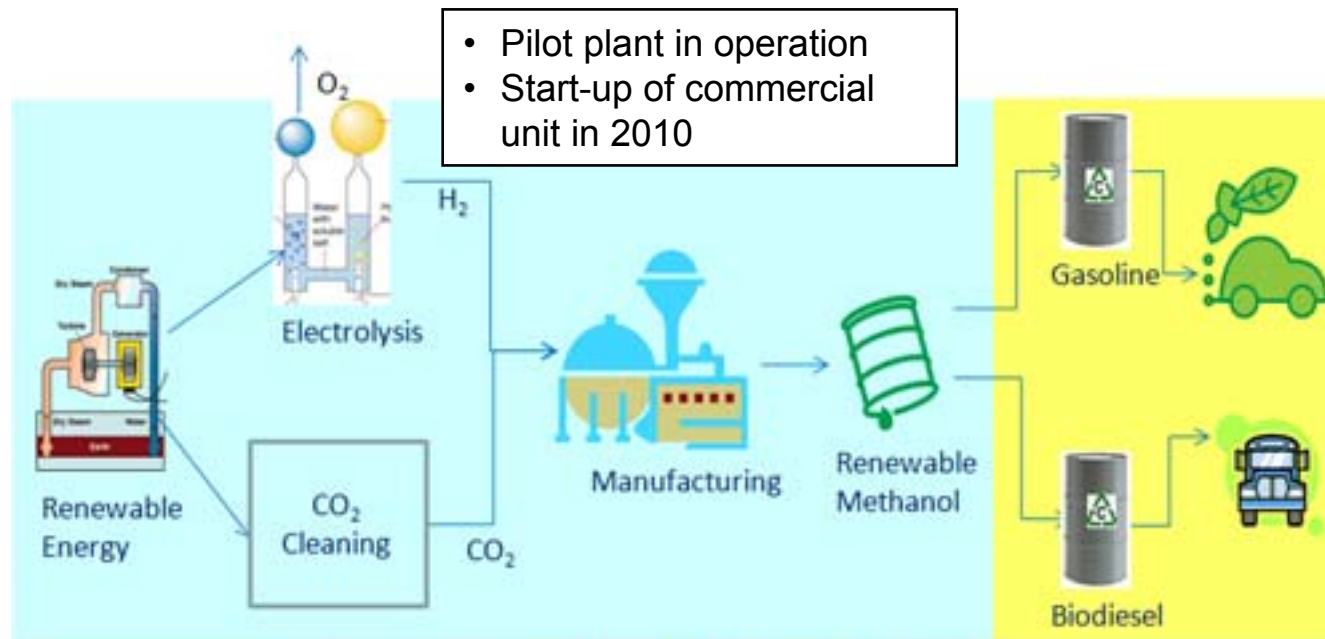
¹⁾ Olah et al., *Chemical Recycling of CO_2 to Methanol and Dimethyl Ether: From Greenhouse Gas to Renewable, Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons*, *J. Org. Chem.* 74 (2009) 487

²⁾ Halmann, Steinberg, *Greenhouse Gas CO_2 Mitigation: Science and Technology*, CRC Press, 1999

Commercial MeOH / DME Process



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- Pilot plant in operation
- Start-up of commercial unit in 2010

CRI Patented Process : Efficiency and Process Intensification

Capture CO_2 from emissions: geothermal, aluminum, and cement
Utilize renewable energy: geothermal, biomass or wind
Produce renewable methanol
Blend gasoline or biodiesel

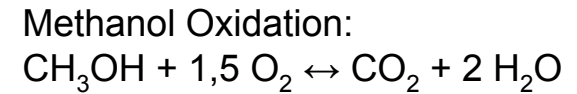
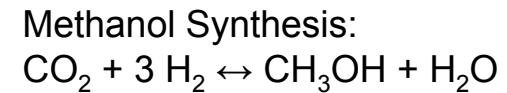
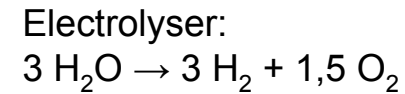
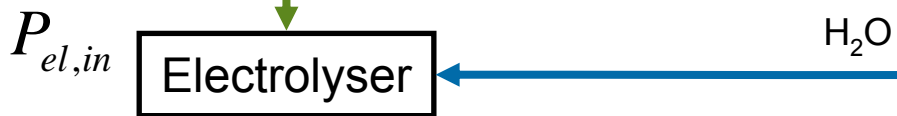
www.carbonrecycling.is

Methanol from Renewable H₂ and Fossil CO₂ for Transportation



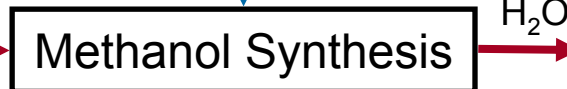
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Power from Renewable Sources (e.g. Wind)



Power Plant

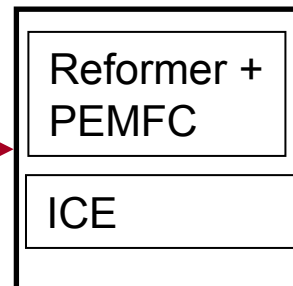
CO₂



CH₃OH



Methanol Oxidation



H₂O CO₂

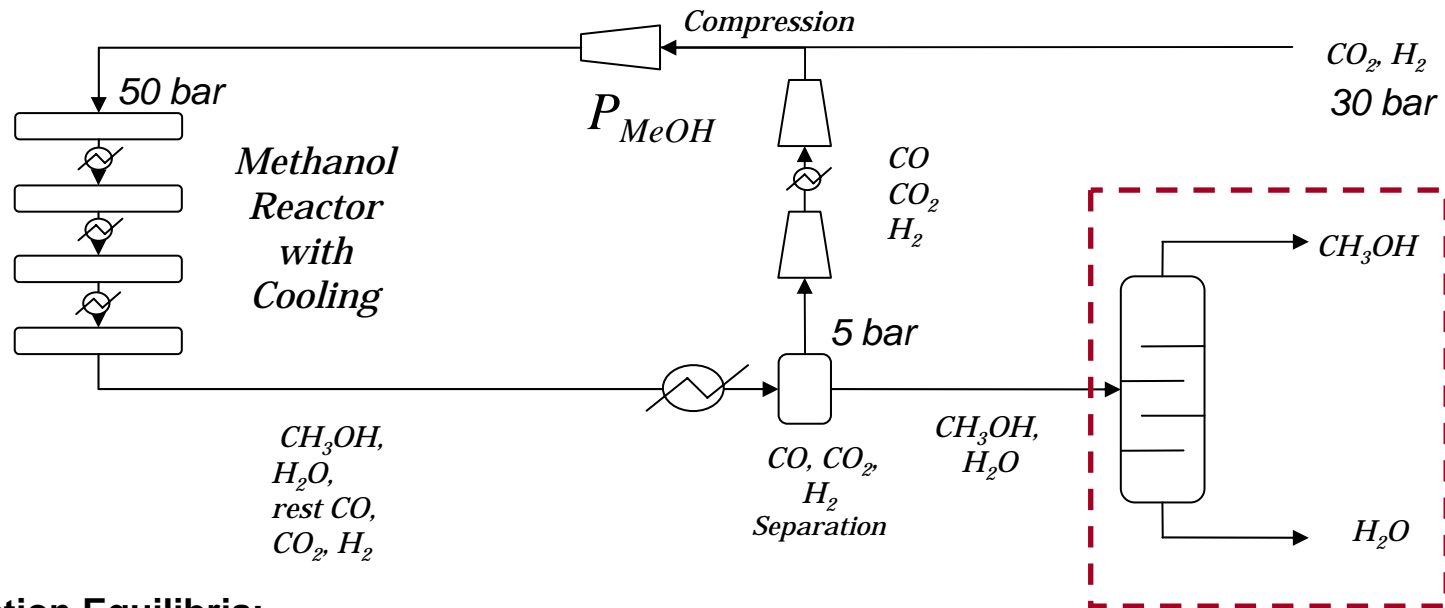
P_{out} Power for Mobility

PEMFC = Proton Exchange Membrane Fuel Cell ($\eta = 38\%$)
 ICE = Internal Combustion Engine ($\eta = 25\%$)

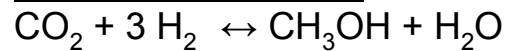
Exergy Analysis of Methanol Synthesis from CO₂



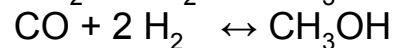
MAX-PLANCK-GESELLSCHAFT



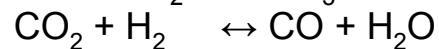
Reaction Equilibria:



$$\Delta_R H(298 \text{ K}) = -49.5 \text{ kJ/mol}$$



$$\Delta_R H(298 \text{ K}) = -190.7 \text{ kJ/mol}$$



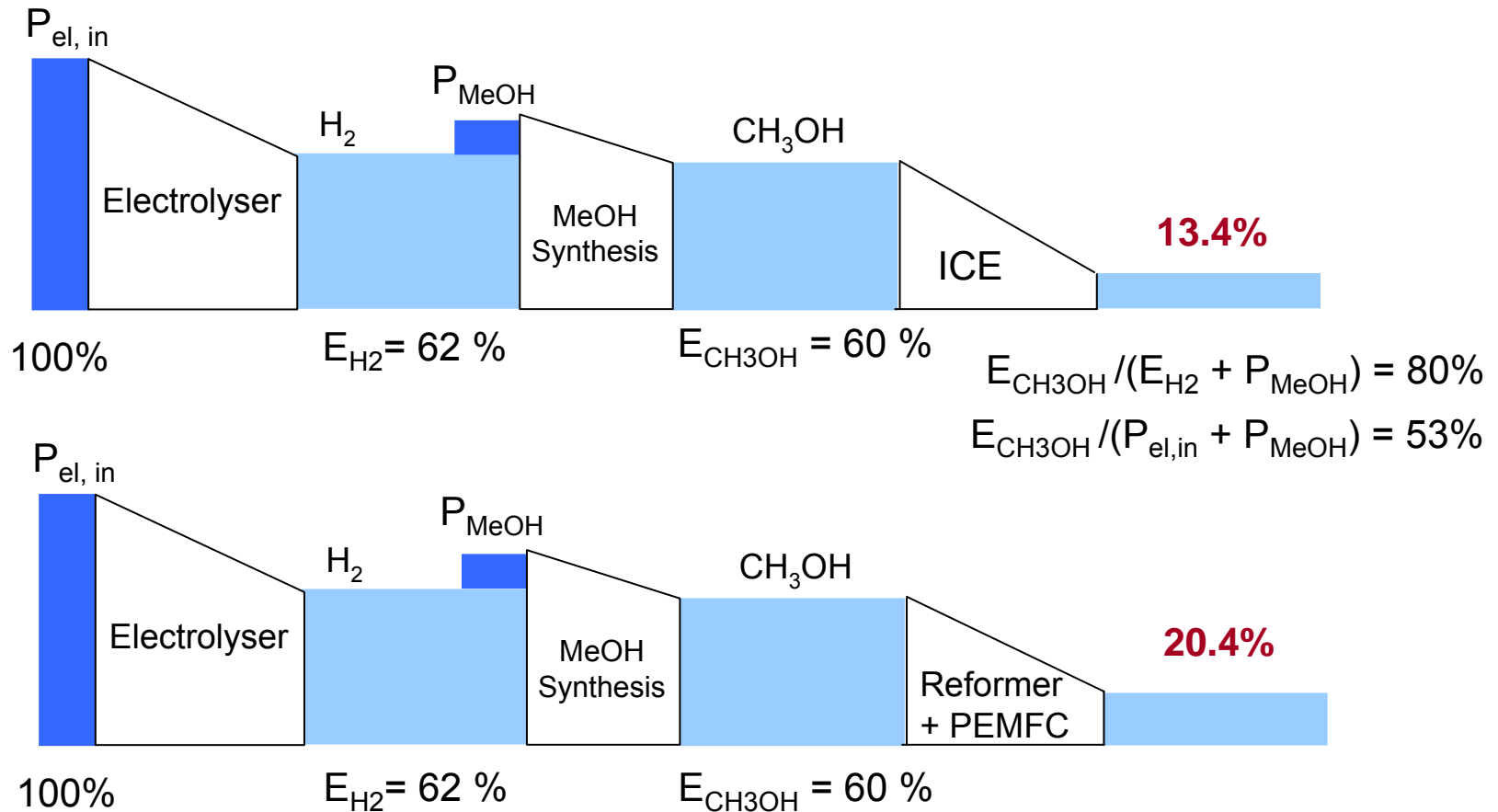
$$\Delta_R H(298 \text{ K}) = 41.2 \text{ kJ/mol}$$

- Recycle with complete conversion
- $n_{\text{feed}}/n_{\text{tot}} = 4.7$
- $p = 50 \text{ bar}$, non-ideal mixture, fugacity coefficients estimated from PSRK equation of state
- $\Delta p = 0.25 \text{ bar}$ in reactors and heat exchange units
- Adiabatic reactor, intermediate cooling, $T_{\text{in}} = 220 \text{ }^\circ\text{C}$
- Compressor efficiency: $\eta = 0.72$
- Simulated with ASPEN

Methanol from CO₂ for Transportation: Exergy Chain Analysis



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MeOH + ICE	880 km (130 l)
MeOH+ Ref + FC	1310 km
Gasoline + ICE	1860 km

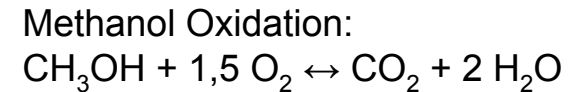
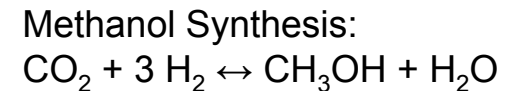
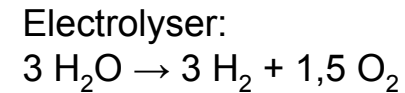
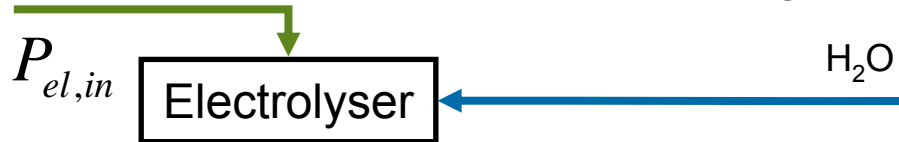
Ref.: *Well to Wheel Analysis*, Concave, EUcar, EU Commission, 2004

Methanol from Renewable H₂ and Fossil CO₂ for Stationary Power Supply



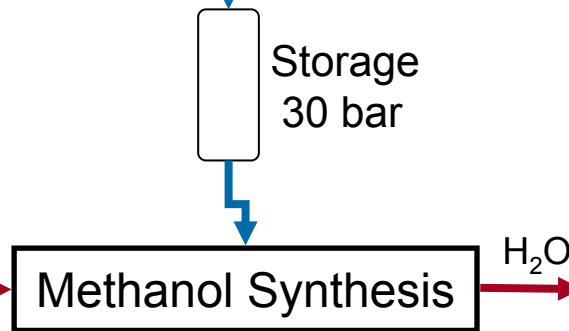
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Power from Renewable Sources (e.g. Wind)

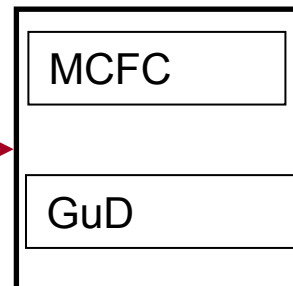


Power Plant

CO₂



Methanol Oxidation



H₂O CO₂

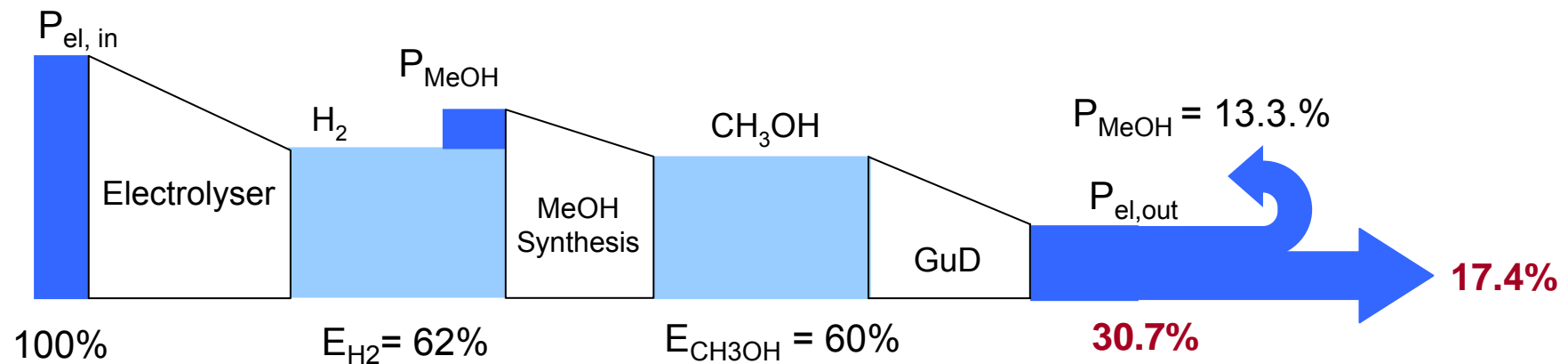
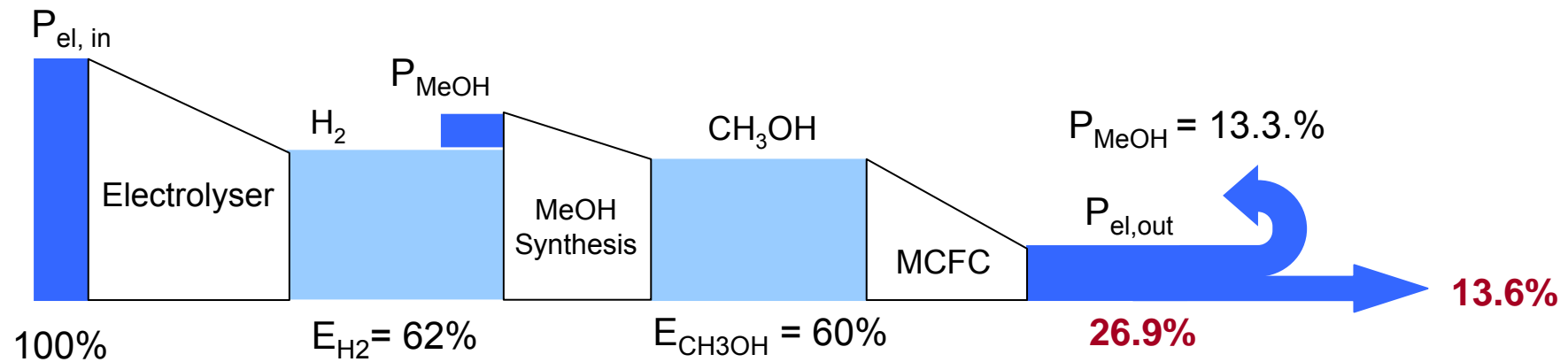
MCFC = Molten Carbonate Fuel Cell ($\eta = 50\%$)
 GuD = Combined Cycle Power Plant ($\eta = 57\%$)

P_{out} Power to Electrical Grid

Methanol from CO₂ for Stationary Power Supply: Exergy Chain Analysis



MAX-PLANCK-GESELLSCHAFT

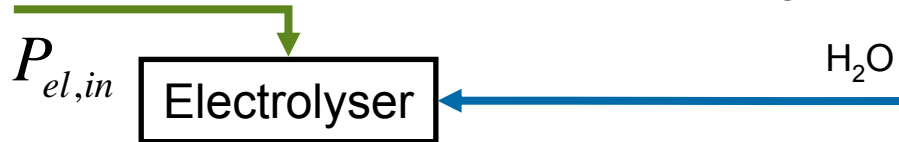


Methanol from Renewable H₂ and Fossil CO₂ for Stationary Power Supply

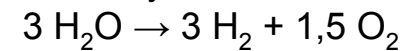


MAX-PLANCK-GESELLSCHAFT

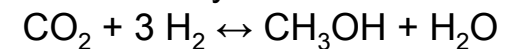
Power from Renewable Sources (e.g. Wind)



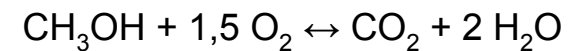
Electrolyser:



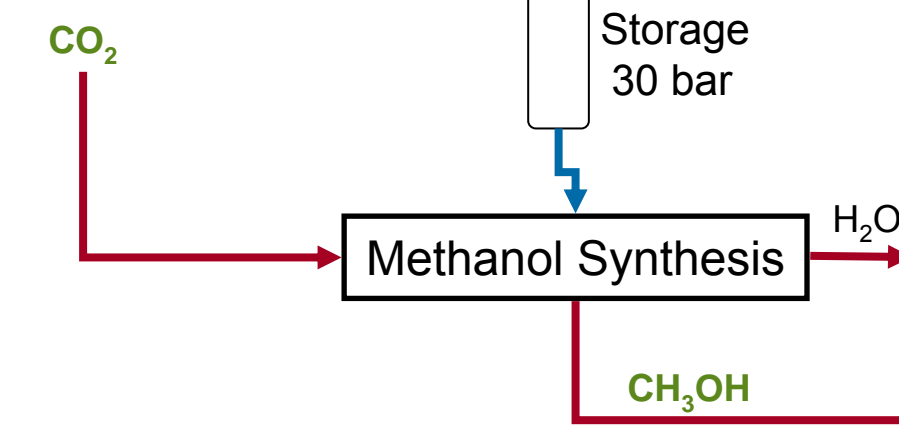
Methanol Synthesis:



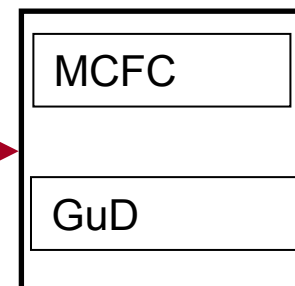
Methanol Oxidation:



Power Plant



Methanol Oxidation



P_{out} Power to Electrical Grid

MCFC = Molten Carbonate Fuel Cell ($\eta = 50\%$)

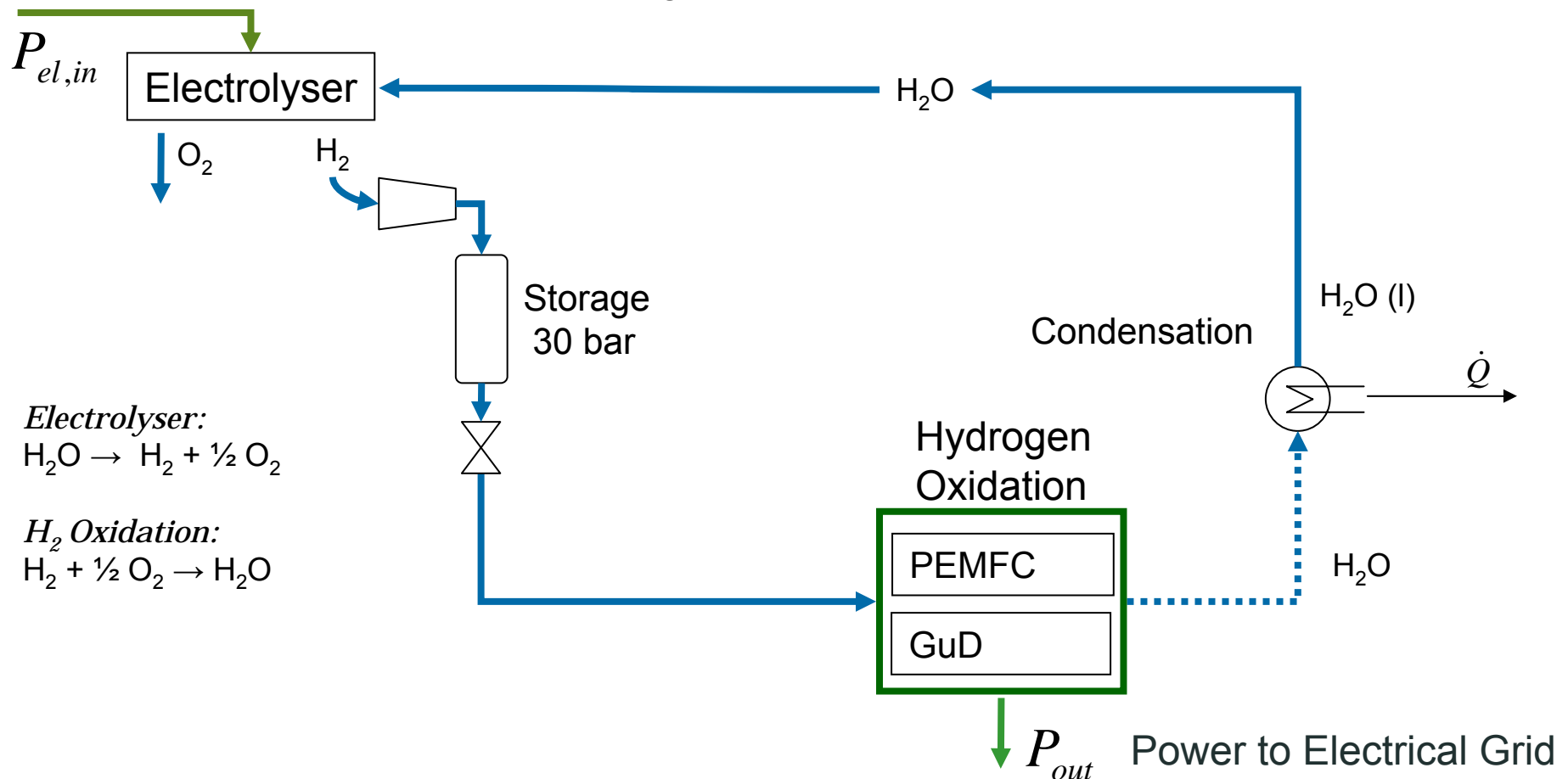
GuD = Combined Cycle Power Plant ($\eta = 57\%$)

Reference Process: Renewable H₂ for Stationary Power Supply



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Power from Renewable Sources (e.g. Wind)



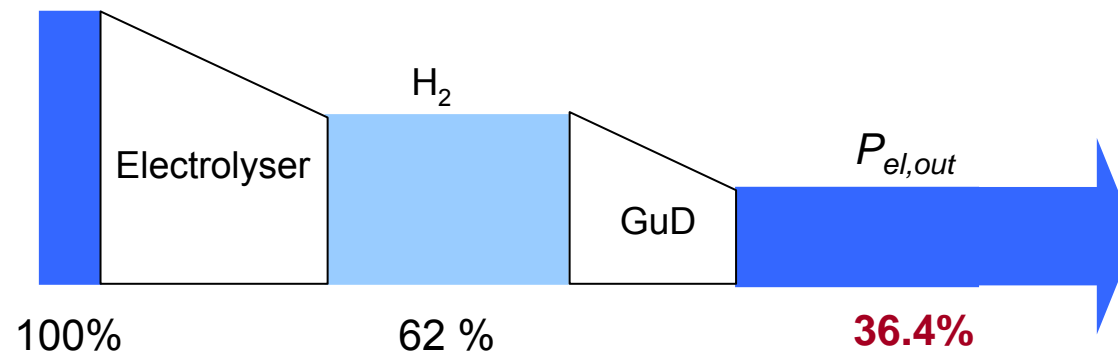
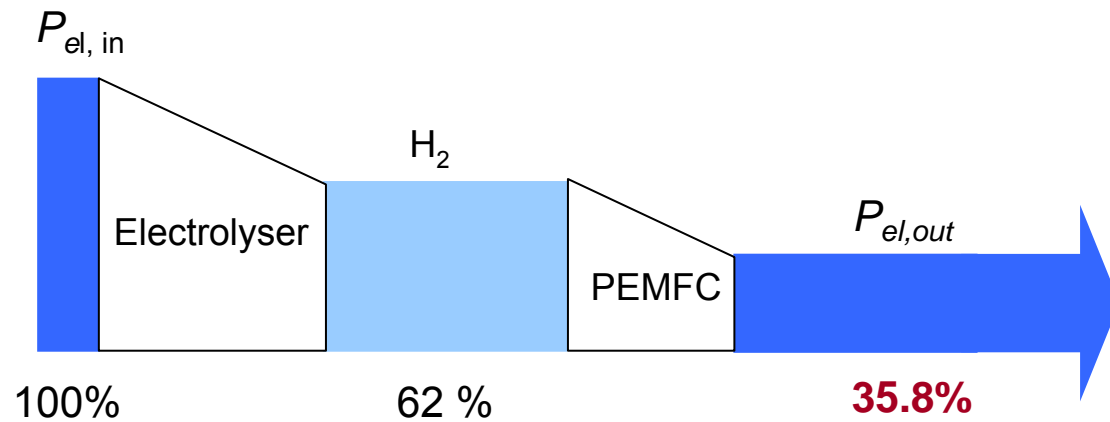
PEMFC = Proton Exchange Membrane Fuel Cell ($\eta = 56\%$)

GuD = Combined Cycle Power Plant ($\eta = 57\%$)

Renewable H₂ for Stationary Power Supply: Exergy Chain Analysis



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Electrolyser: $\eta_{Hu} = 0.63$

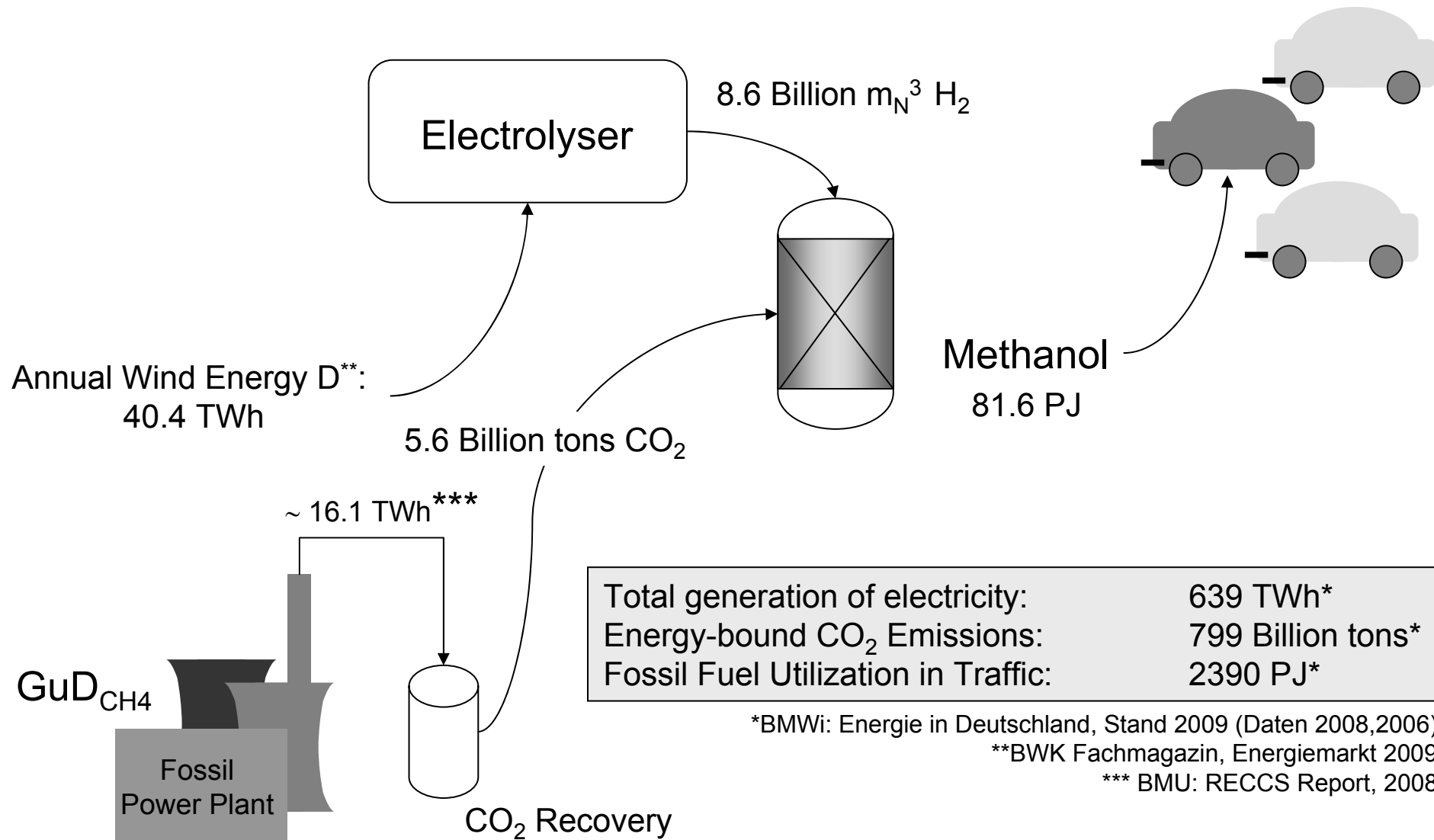
PEMFC: $\eta_{Hu} = 0.56$

GuD: $\eta_{Hu} = 0.57$

Wind Energy to Methanol: Simplified Energetic Analysis for Germany



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Conclusions



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- **Direct avoidance of CO₂ emissions should have the highest priority over all other activities of storage and re-use.**
- Buffering of renewable energy (wind, solar) via electrolysis, H₂ storage and recombustion is attractive and technically feasible, but needs improvement of overall efficiency (in particular: water electrolysis).
- CO₂ based synthesis routes for liquid fuels are principally technical feasible, but need improvement (highly active catalysts for CO₂ activation).
- Efficiency of the route „renewables → liquid fuels, including CO₂ reuse“ is significantly lower than that of grid supply via H₂ storage.
- The integration of this route into the overall energy supply system might temporarily be reasonable.
- Final decisions have to be derived from careful analysis of the overall energy supply system (transportation + stationary power supply).

Global Energy System Analysis



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