THE HYDROGENATION OF CO_2 TO SUSTAINABLE ENERGY CARRIERS – PTL CONCEPT

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Fraunhofer-Institute for Solar Energy systems ISE

EWACC 2015 Conference

Nicosia - Cyprus, 16-18. June 2015

www.ise.fraunhofer.de

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AGENDA

- Overview about Fraunhofer ISE
- Challenges and motivation
- What is Power to Liquid – PtL Concept?
- Our Energy Storage Activities
- PtL Technology Progress at ISE
- Ph. D. Research Focus
- Summary

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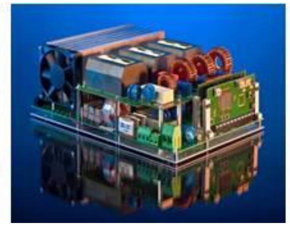
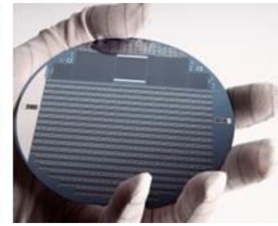
12 Business Fields




- Silicon - Photovoltaics
- III-V- and Concentrated Photovoltaics
- Dye-, Organic and Novel Solar Cells
- Photovoltaic Modules and Power Plants
- Energy Efficient Power Electronics
- Solar Thermal

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   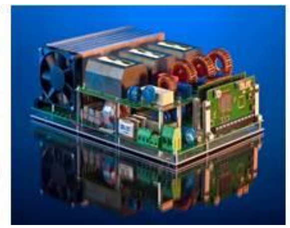 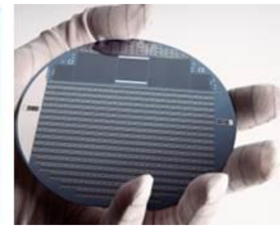 

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- Solar Thermal
- Energy Efficient Buildings
- Hydrogen- and Fuel Cell Technologies
- Emissions Free Mobility
- Storage Technologies
- System integration and Net – Power, Heat, Gas
- Energy Systems Analysis

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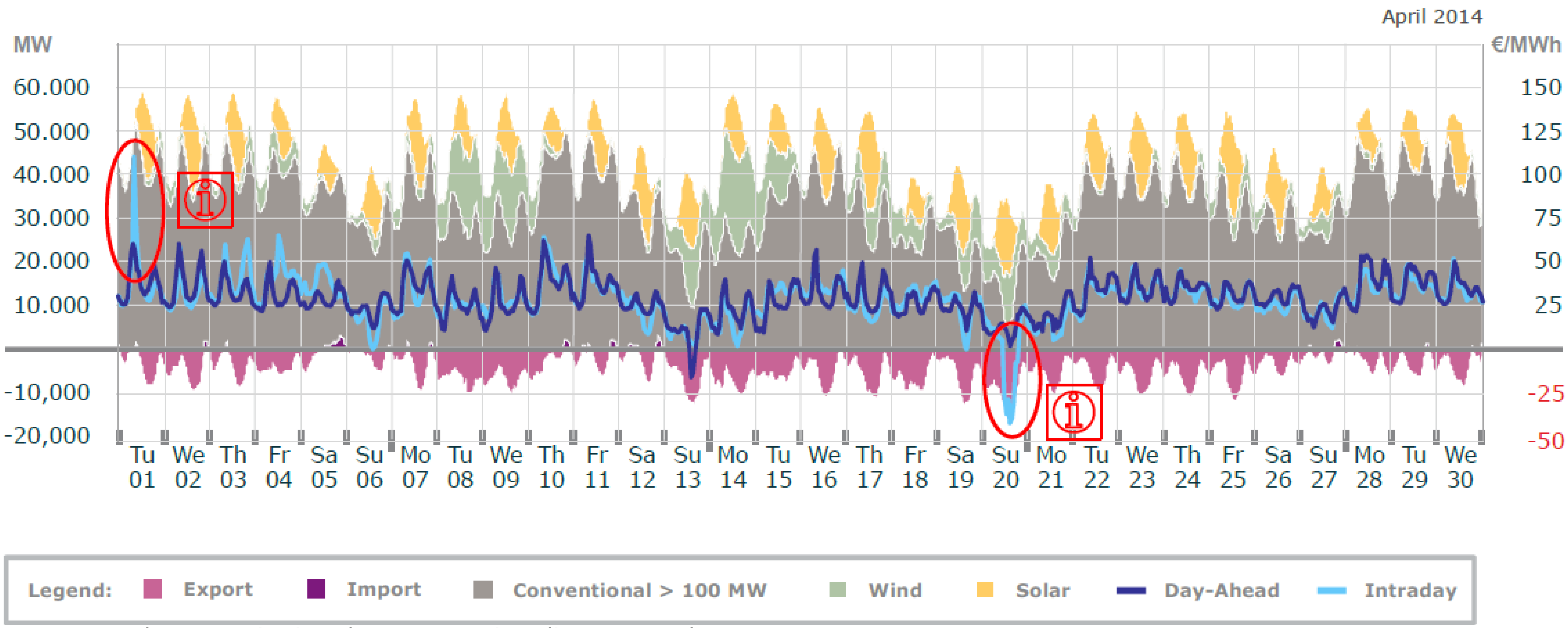
Motivation: Fluctuating Nature of Renewable Resources

- On Easter Sunday April 20th 11:00 - 18:00 electricity cost -39.18 €/MWh
- PV and wind production combined were about 4 GW higher than projected, the actual load was up to 4 GW lower than projected. The combined projection error was over 7 GW between 1 and 2 pm.



Erneuerbare Energien im Jahr 2013. BMWi, Berlin vom 28. Februar 2014 Burger, B., Stromerzeugung aus Solar- und Windenergie im Jahr 2014, Fraunhofer ISE

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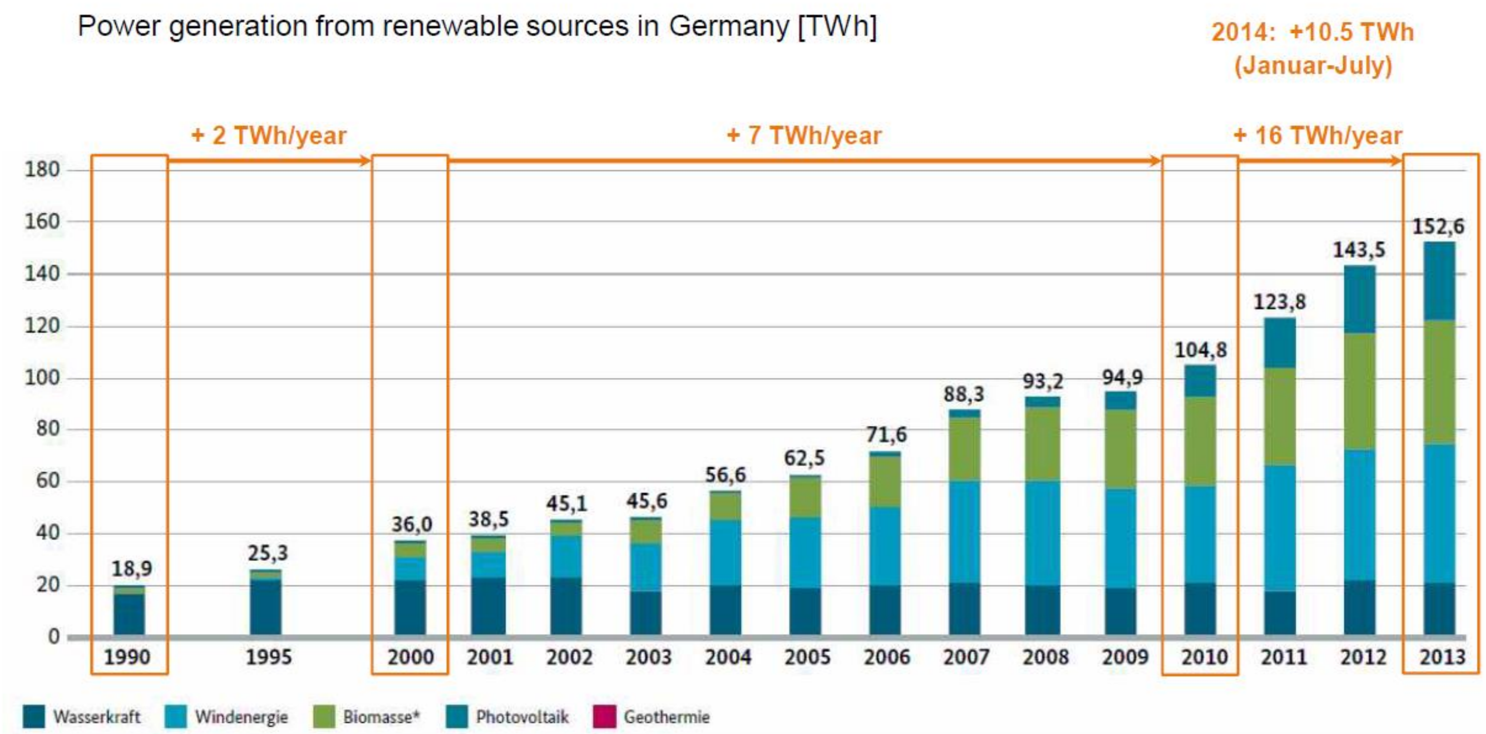
Motivation: RE Capacity Expansion

- German RE Share is targeted to reach 80% of total power production by 2050
  - „Residual Power“ 2012 Approx. 0.5 %/385 GWh



Alexander Tremel, 2014 Electrolysis and chemical synthesis –Linking energy system and chemical industry, Siemens Corporate Technology

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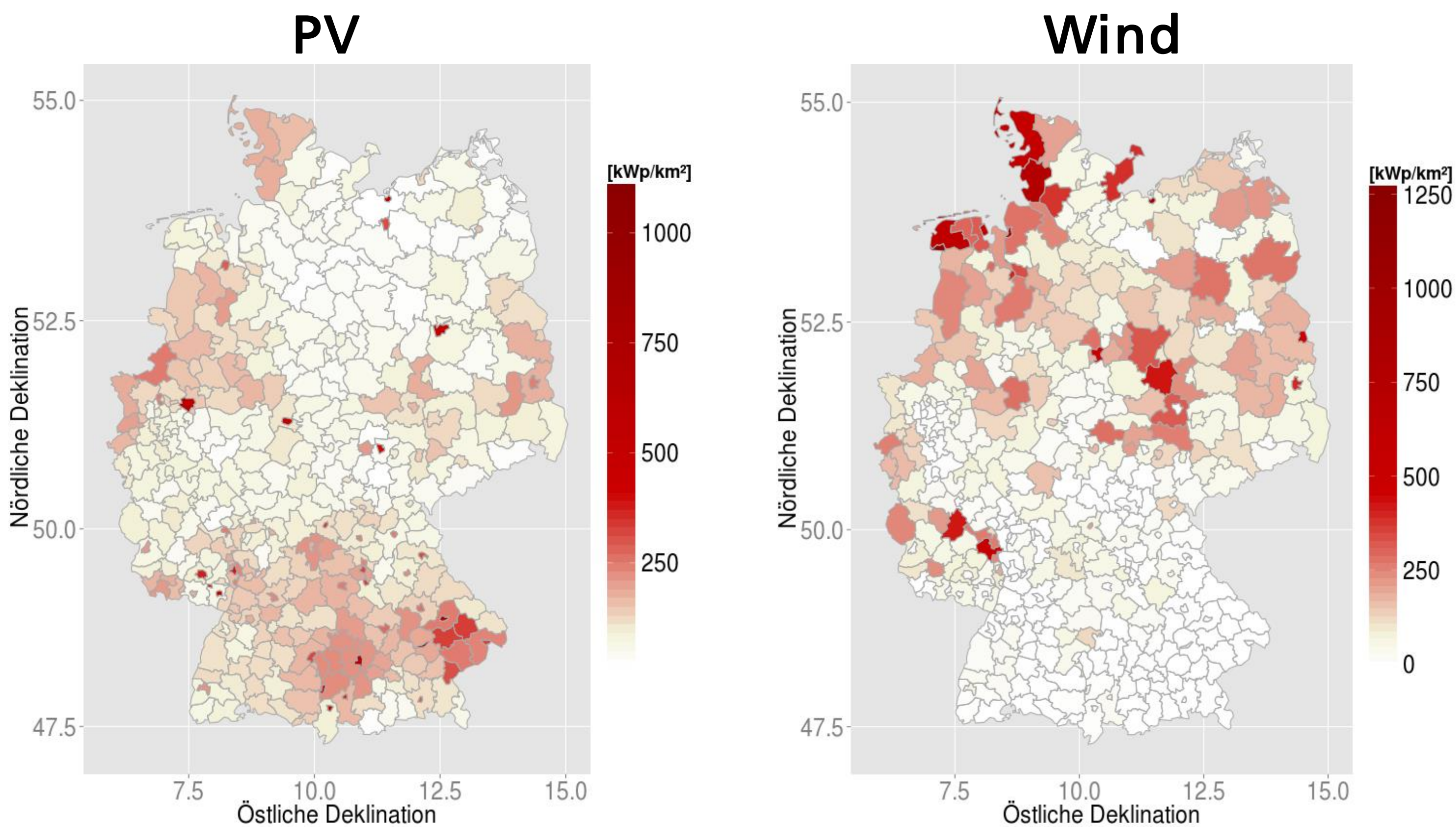
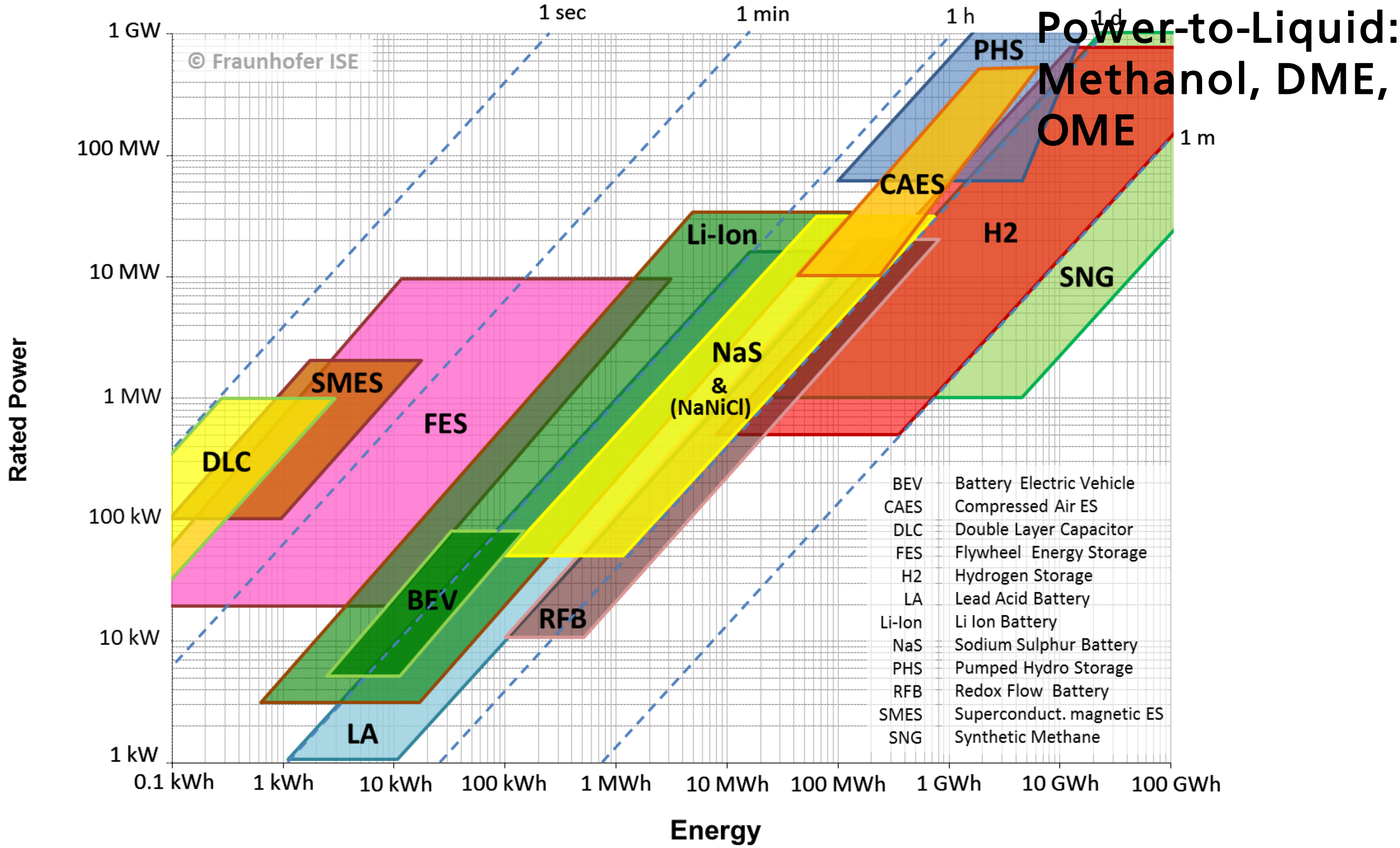
Motivation

- Regional Imbalances



Own Data,
Daten: Energiemap 2014

Only Chemical Storage allows energy storage in TWh range and for long periods



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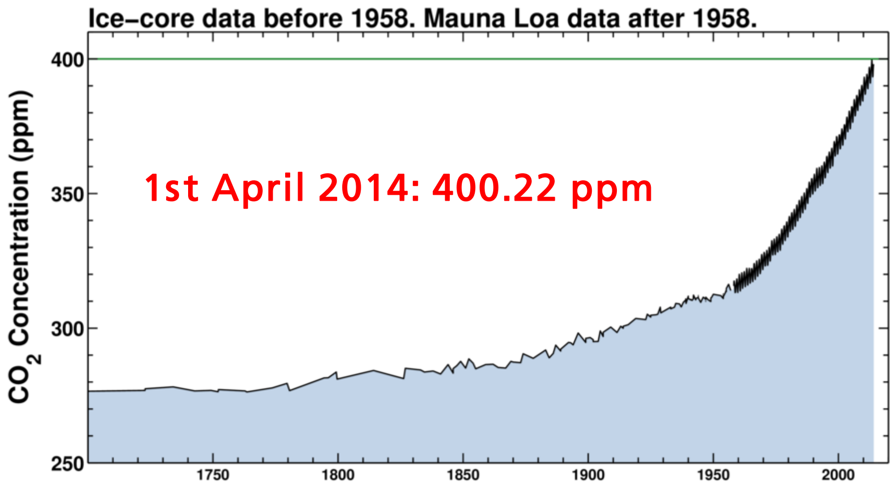
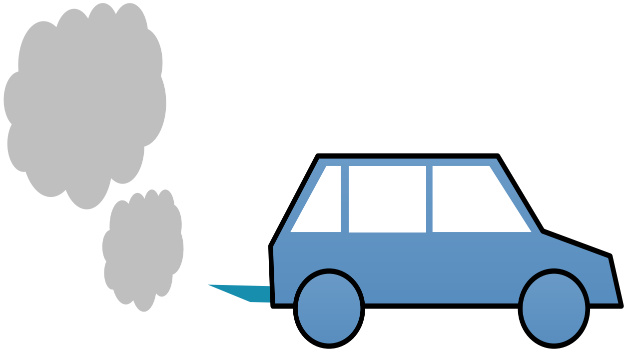
Motivation

- Security of Supply (Ukraine)/Raw Material Reserves
- High CO_2 emissionen (> 0,24 t $CO_{2\ eq}$/t Methanol)
- Worldwide defined limits for CO_2 emissions (i.e. Euro 6)



Source: http://keelingcurve.ucsd.edu/



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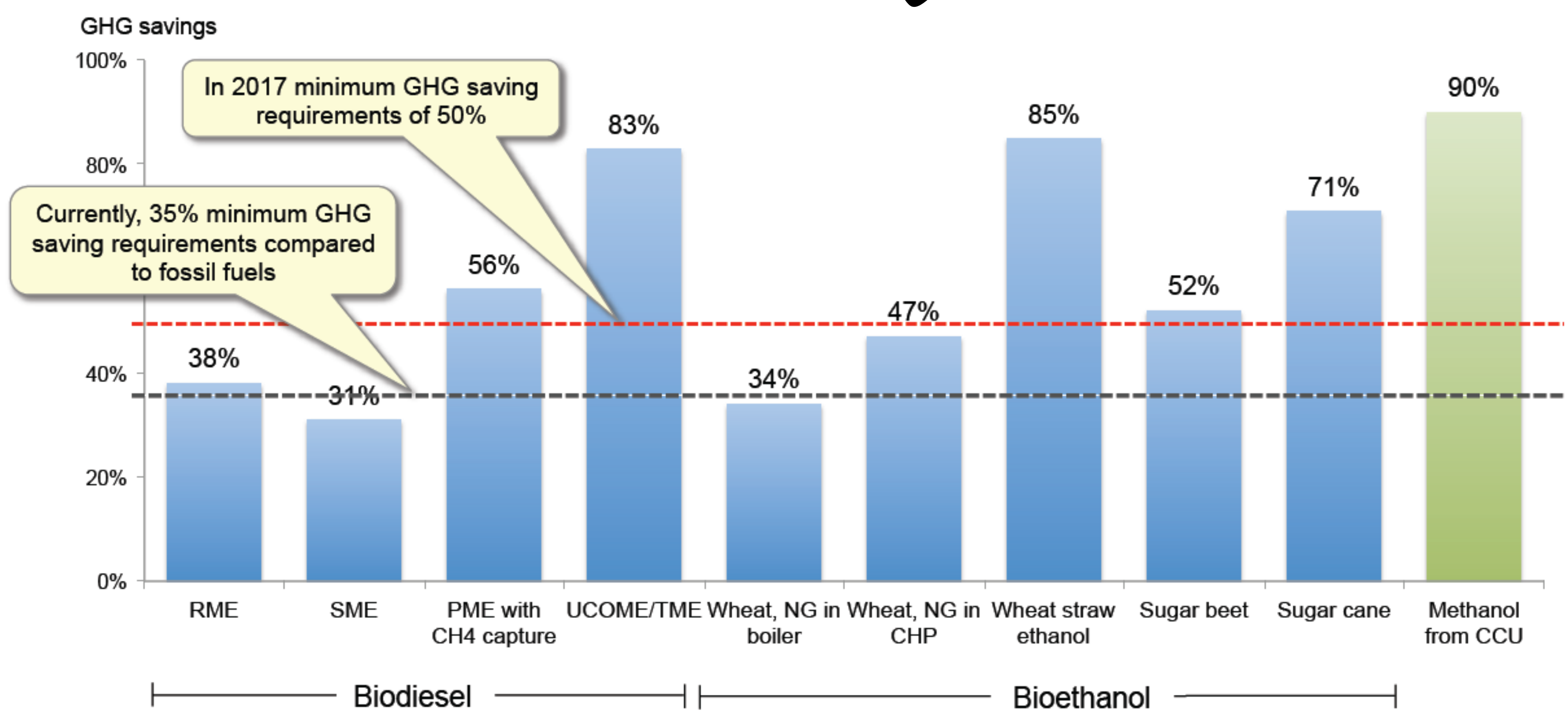
GHG Savings: Certification of Methanol Pilot Plant in Iceland through ISCC

Conventional biofuels will have problems reaching rising GHG emission thresholds

- Ecology ✓



GHG emission savings from Directive 2009/28/EC. Individual value for Methanol derived by electrolysis using geothermal energy

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Norbert Schmitz (2013) 2nd Conference on CO_2 as Feedstock for Chemistry and Polymers

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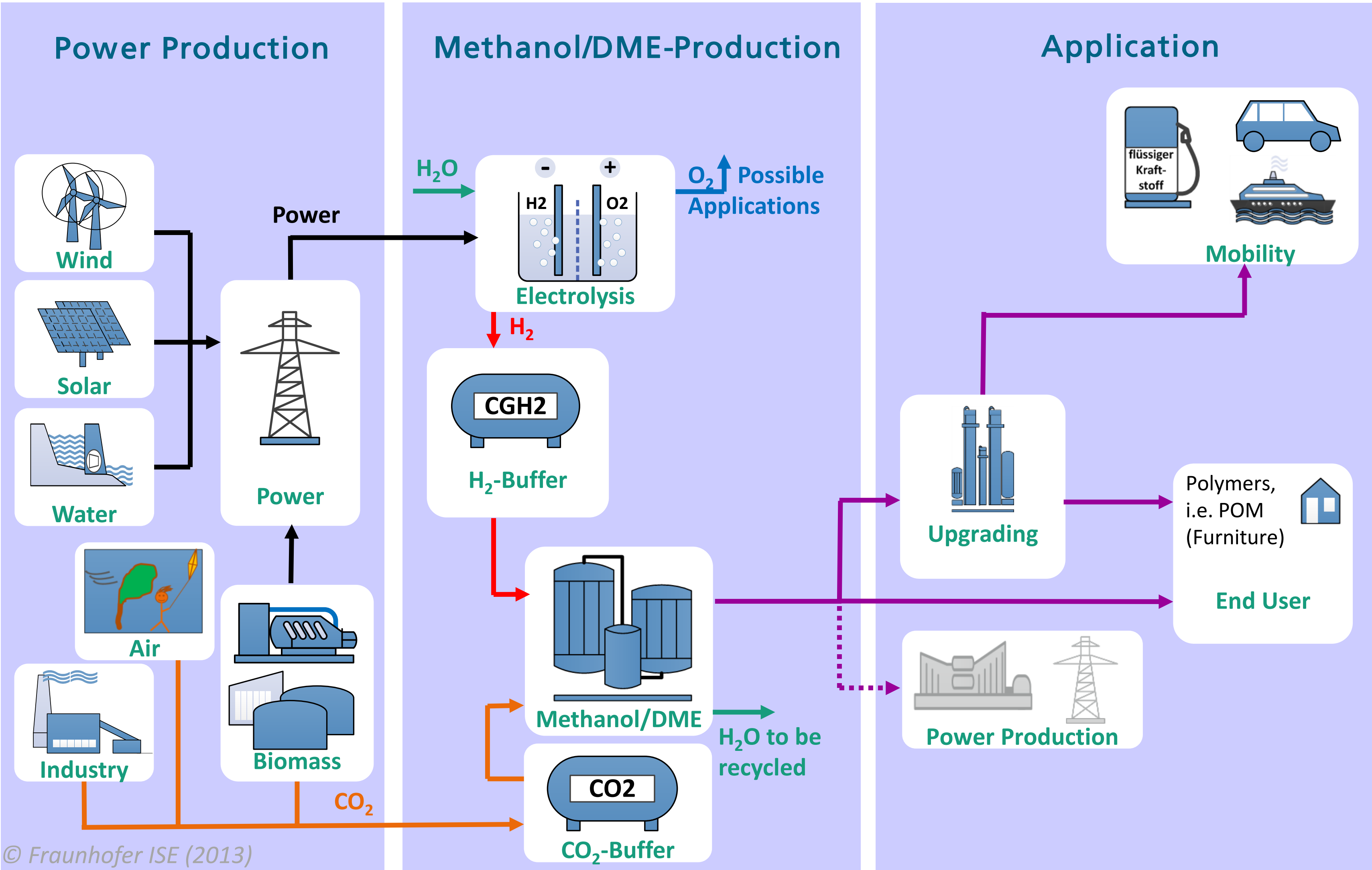
Overall Process Chain - PtL



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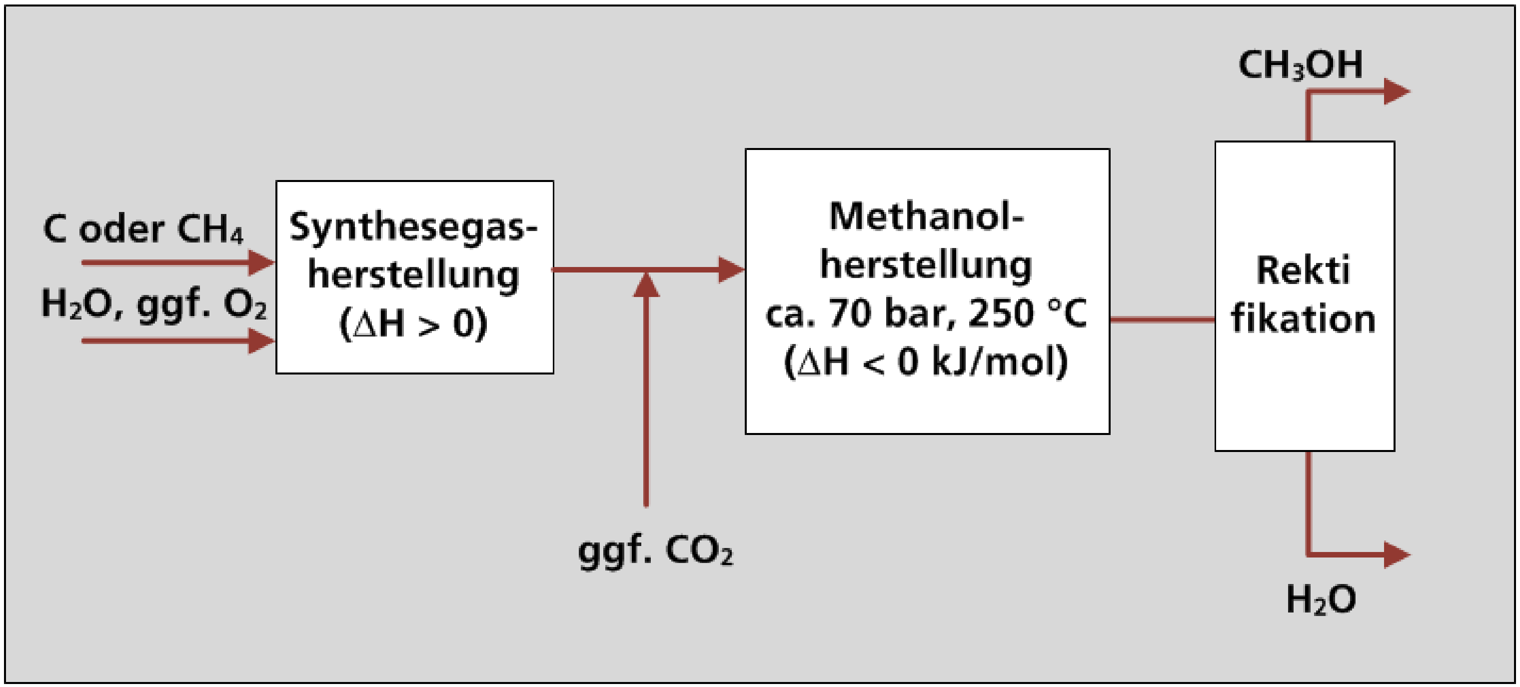
Conventional Methanol Synthesis

- Synthesis gas production accounts for approx. 40-50 % of the capital investment (Rectification approx. 10 %)



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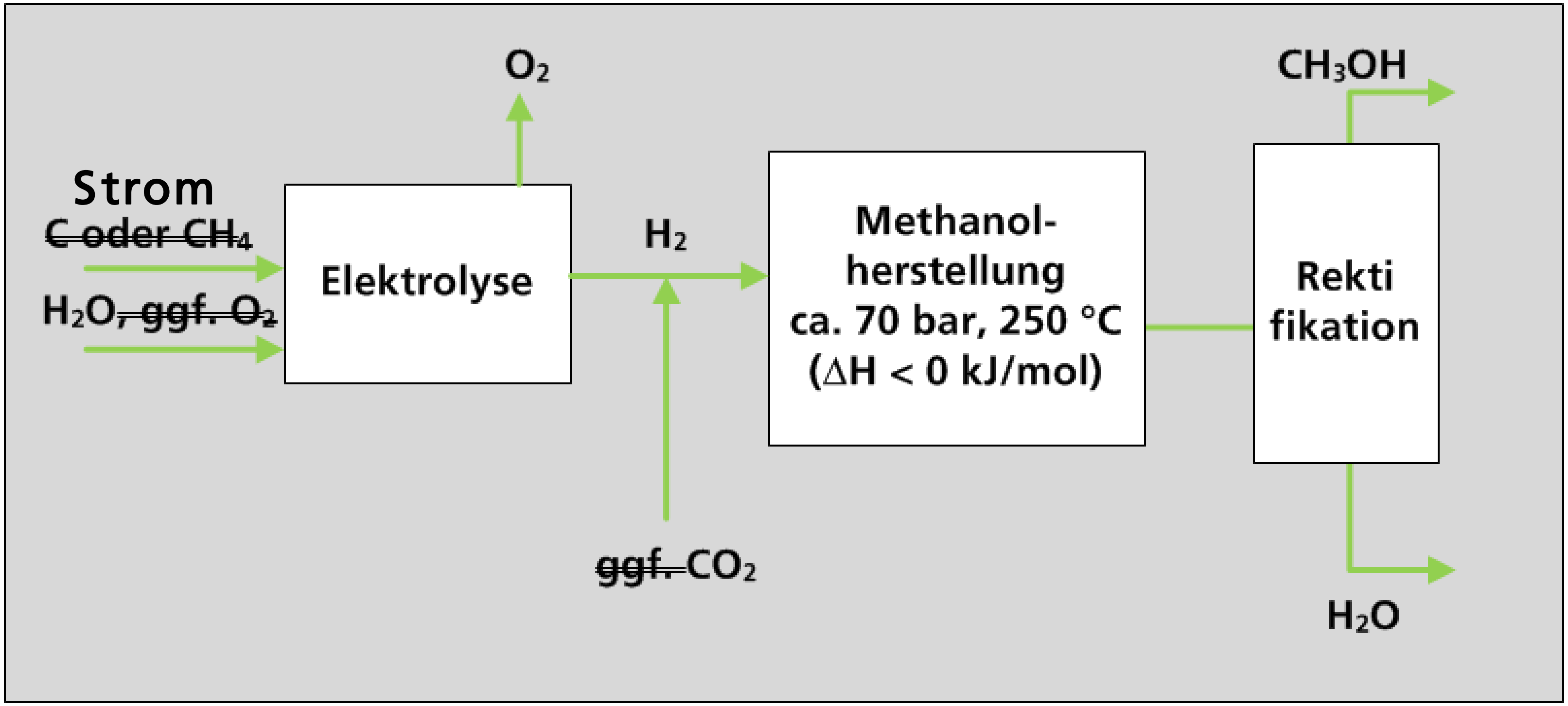
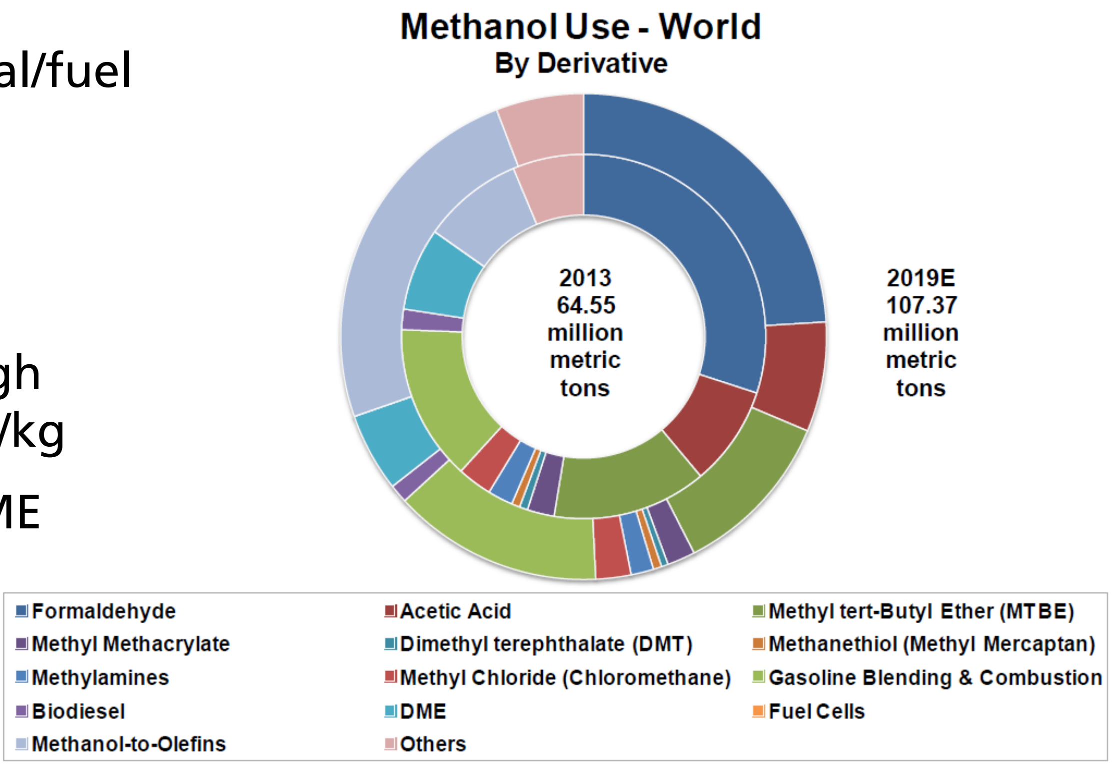
PtL as example Methanol: Future approach?



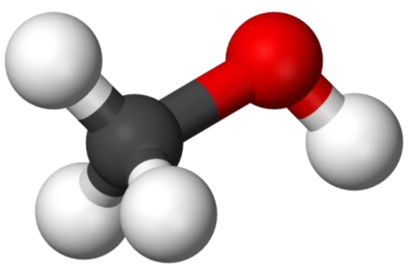
- We are evaluating the following aspects at ISE
  - Technological
  - Ecological
  - Economical

Why Methanol from CO_2?

- Why Methanol?
  - Important bulk chemical/fuel (additive)
  - Increasing demand
  - Existing infrastructure
  - Liquid: easy storage/high energy density 19,5 MJ/kg
  - Easily conversion to DME



Source: M.Berggren, MMSA for MPTC December 2014 ©



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Thermochemical Processes – Group Activities

- Process development with focus on heterogeneous catalytic conversion processes
  - Gas phase till 1 000 °C and 60 bar
  - Liquid Phase till 250 °C and 60 bar

Thermochemical Hydrogen Production

Catalytic Evaporation Processes

Biomass Use

Power-to-Liquid

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Electrochemical Hydrogen Production and Storage: New PEM Electrolysis Center

- Approx. 750 m² laboratories area for electrolyser
- Cell and Stack development
  - **Test stand till 1 MVA**
    (50 bar - 250 V - 4.000 A)
  - Stack tests (Durability- and Stress tests)
- Power-to-Gas-Plant
  - H_2-Feeding in local pipeline
  - Components development
  - Plant operation and control
  - Economical Evaluation

Hydrogen Filling Station at Fraunhofer ISE

WASSERSTOFF-ENERGIEKETTE
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- Main components of the filing station:
  - (Pressure) electrolyser
    (30 bar / 6 Nm³/h)
  - Mechanical compressor
  - Storage tanks
  - Dispenser units (200/350/700bar)
  - Filling according to SAE J2600
- Integrated container solution
- Publicly accessible filling station
- Located at premises of Fraunhofer ISE
- Coupled with renewable energies:
  - Photovoltaic modules (roof)
  - Certified green electricity

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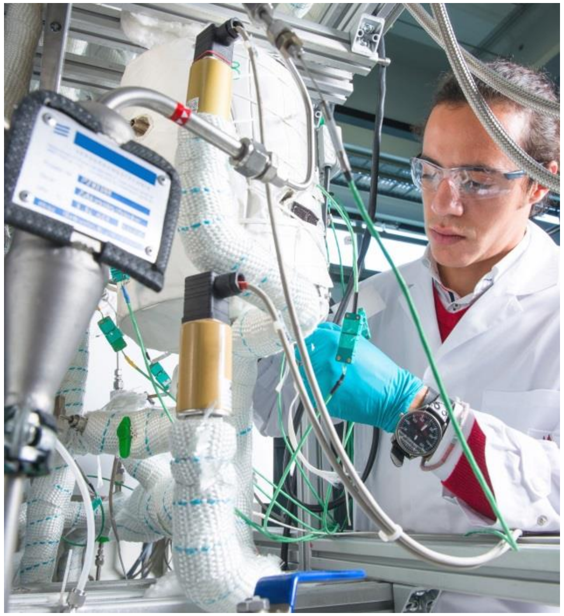
MethaKats-Project: We Operate a Mini plant to Produce Methanol/DME from CO_2 and H_2

- 1. Goal: Design Miniplant incl. Recycling
  Reactor→ adiabat
  Method: Prozess-Simulationen (CHEMCAD)
- 2. Goal: Developing novel, more aktive Cu-cats
  Provision through Uni Freiburg
- Miniplant :
  - Capacity 1 l Methanol/h:
    → Product analysis: high Methanol purity
  - Two steps → Process optimization
  - High Space velocity-Selectivity
    > 0,4 g MeOH/g cat h @ 45 bar, GHSV 11.000 h^{-1}
  - Gas- und Liquid analysis
  - Axial und radial Temperature measurements
  - Downstream: Reactor for DME-Synthesis



ISE-Methanolsynthese, 2013

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Distillation Simulation und Product analysis

Table 1. Raw product composition

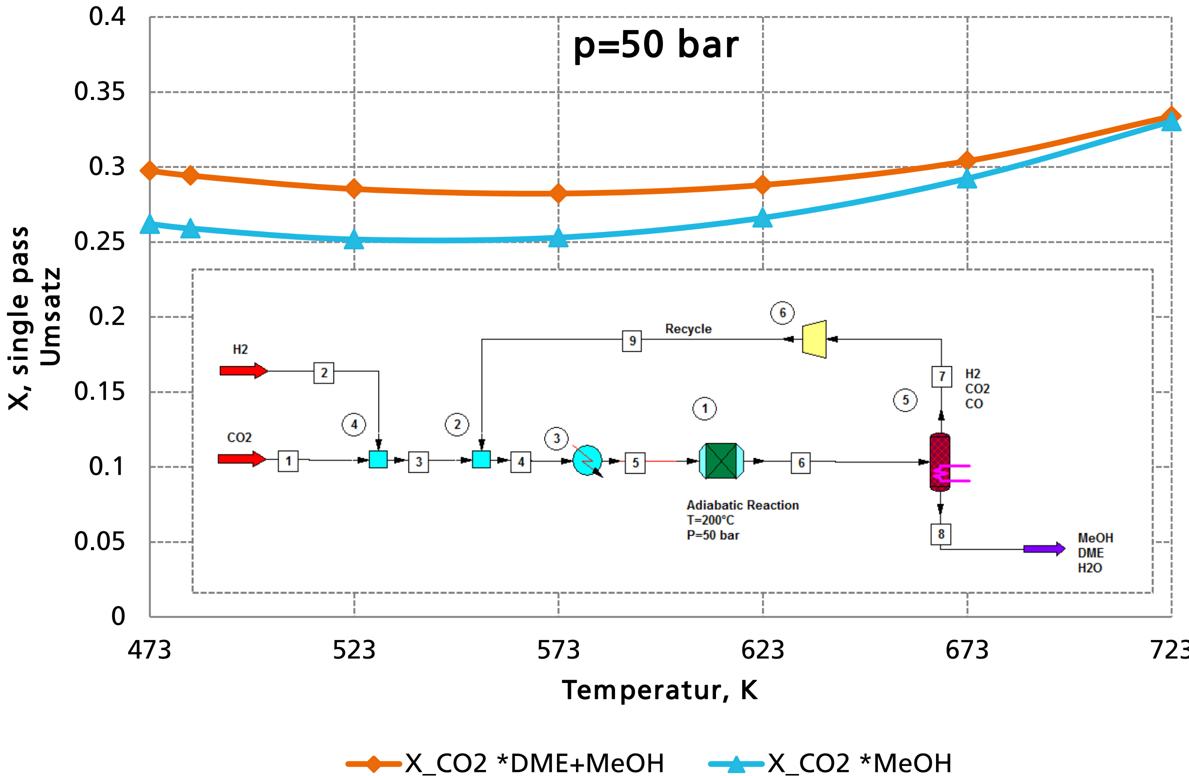
		$CO_2 + H_2$			Syngas
Temperature, °C		250.2	255.0	260.1	250.0
Main components, wt%					
Methanol		63.7	63.7	63.7	84.5
Water		36.2	36.3	36.3	15.4
Impurities, wt ppm					
n-Paraffins:	C4	0	0	0	10
	C5	0	0	0	13
	C6	0	0	0	13
	C7	0	0	0	13
	C8	0	0	0	9
	C9	0	0	0	6
	C10	0	0	0	5
	C11	0	0	0	4
	C12	0	0	0	5
	Total	**0**	**0**	**0**	**78**
Higher alcohols	C2	39	46	68	289
	n-C3	12	16	24	87
	i-C3	8	9	13	40
	n-C4	7	7	9	27
	i-C4	3	3	5	33
	s-C4	12	15	20	96
	C5+	8	9	9	54
	Total	**89**	**105**	**148**	**626**
Esters	Methyl formate	145	140	129	580
	Methyl acetate	0	0	0	1
	Methyl propionate	0	0	0	1
	Total	**145**	**140**	**129**	**582**
Ketones	Acetone	0	0	0	14
	Methyl ethylketone	0	0	0	8
	Methyl propylketone	0	0	0	2
	Total	**0**	**0**	**0**	**24**
Ethers	Dimethyl ether	14	18	24	61
Total impurities		**248**	**263**	**301**	**1371**

Source: Göhna & König (1994)

- Göhna & König (Lurgi AG):
  - Higher methanol purity
  - approx. 20 % less energy demand for distillation
- Own Simulation (CHEMCAD®): theoretical distillation load Reduction till around 28 % possible
- Produkt analysis (NMR, GC, ICP) confirmed that only methanol and water exists in liquid product

Methanol und DME Co-Production

CHEMCAD®-Equilibrium investigation



T = 200 °C, p = 50 bar	MeOH	MeOH/DME
Recycle Ratio	5	4
Conversion per pass, %	26	30
$T_{adiab.}$, °C	275	304

- Developing the Miniplant:
  - Reactor Dimethylether (DME)

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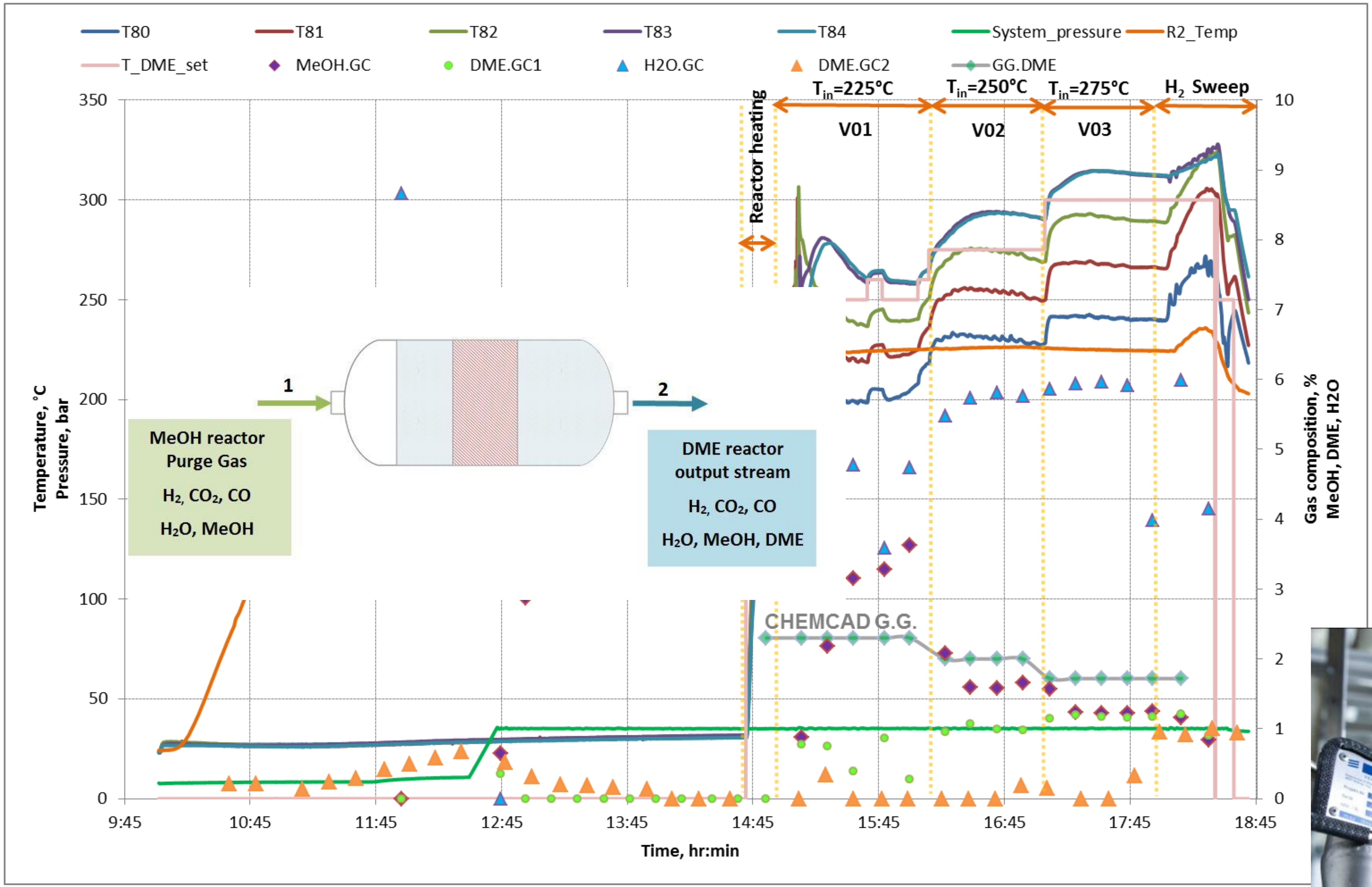
Successful Test Operation: DME- und MeOH-Herstellung



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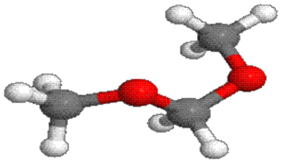
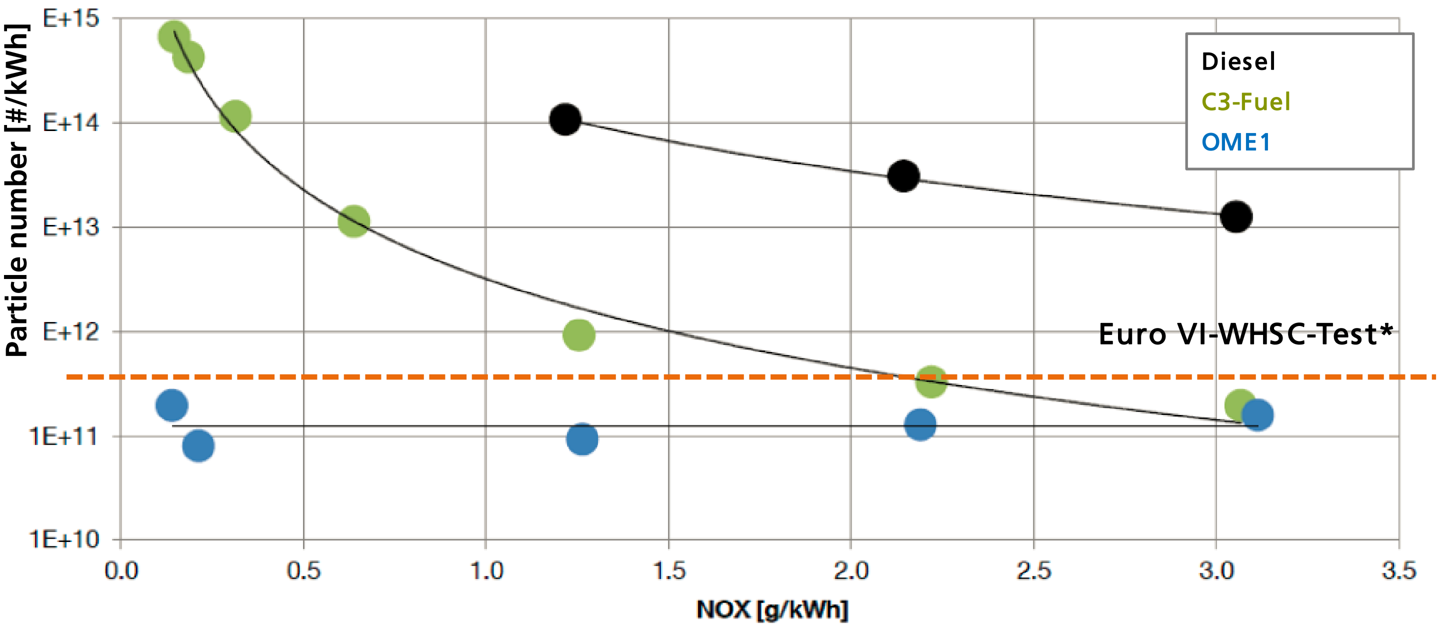
$HyCO_2$: Efficient/Economical production of DME und OMEs from Methanol

$CH_3O\text{-}(CH_2O)_n\text{-}CH_3$, n = 1, 2, 3,… → n = 0: Dimethylether (DME)

n = 1 → Oxymethylenether (OME1)



keine C-C-Bindung

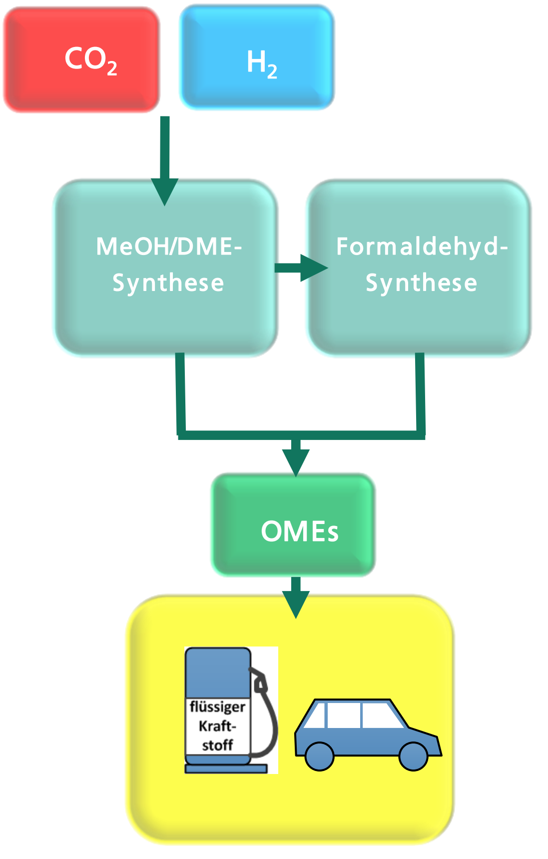


*The World Harmonized Stationary Cycle test

Maus, et al. (2014) 35. Internat. Wiener Motorensymposium, Fortschritt-Berichte VDI Reihe 12, Nr. 777, Bd.1, 325-347.

Objective

- Development and evaluation Production process for sustainable liquid energy carriers synthesis :
  - Conception
  - Simulation
  - Teststand development
  - Testing Catalysts
  - Products analysis



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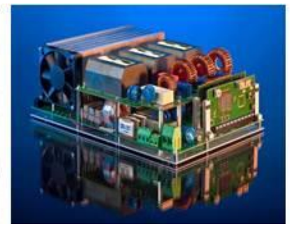
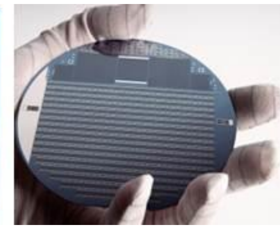
Summary

- Methanol: Two steps synthesis with recycling was designed and optimized using CHEMCAD®
- Methanol and DME was successfully produced in Miniplant at ISE
- Methanol produced from CO_2 and H_2: Purity was confirmed, distillation energy demand and equipment size ist significantly lower as conventional synthesis process
- Co-production of Methanol and DME with bi-functional catalysts will be investigated in the Miniplant at ISE
- OMEs are very promising and futuristic fuels
- A novel process concept to produce OMEs starting from CO_2 and H_2 and passing through methanol is under develoment during this Ph. D. activity
- Equilibrium model for OMEs synthesis process simulation is under development in the vicinity of this work
- PtL technology is imperative to operate our future energy systems in sustainable and reliable manner.

Thank you for your attention!

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