A PROCESS NETWORK TOWARDS A FUTURE METHANOL ECONOMY

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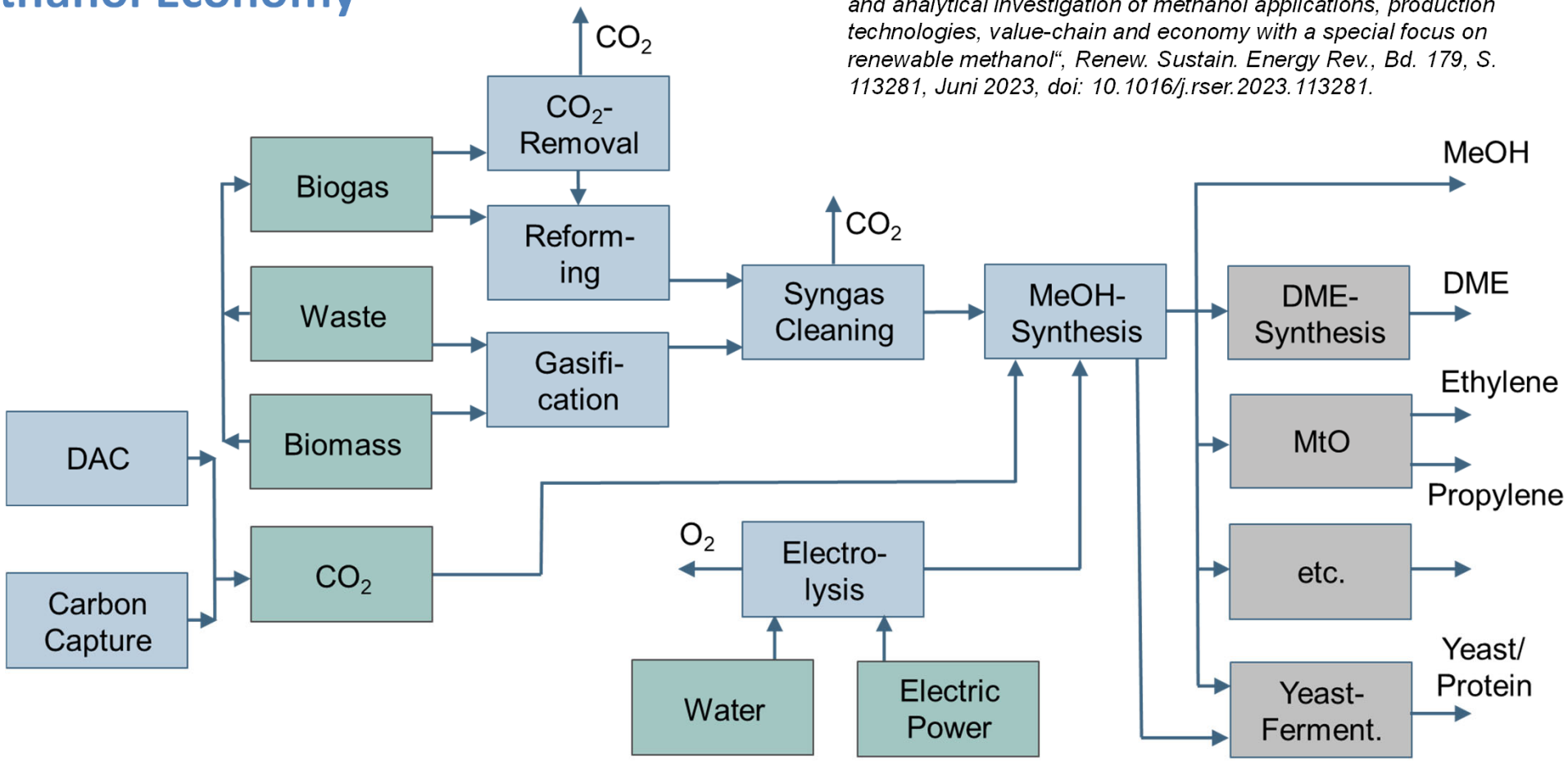
Why “Methanol Economy”

- **Alternative to proposed “Hydrogen Economy”**
- **Disadvantage Hydrogen**
  - Energy demand for production
  - Transport and storage
- **Advantage Methanol**
  - Use as a fuel and platform chemical
  - Blending with conventional fuels
  - Use of available infrastructure for transport and storage
  - Real (re)use of CO_2
- **Motivation**
  - Consistent mass and energy balances
  - Flexible process design
  - Basis for LCA and technoeconomic evaluation

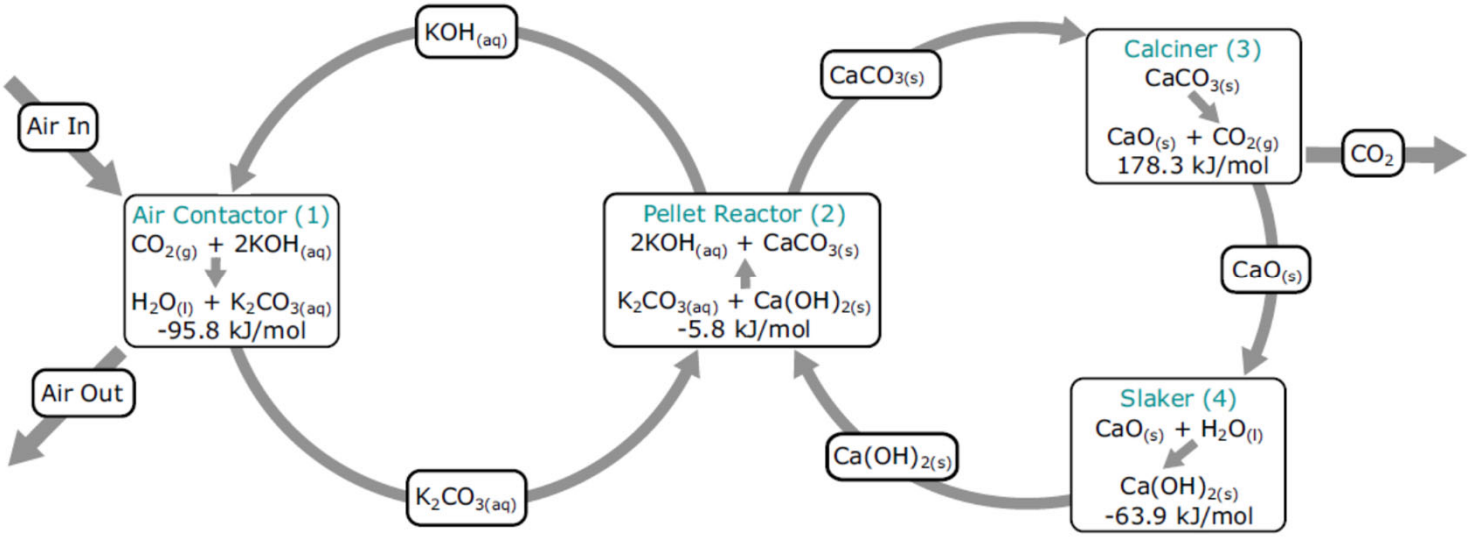
Methanol Economy

Modified based on: S. S. Tabibian und M. Sharifzadeh, „Statistical and analytical investigation of methanol applications, production technologies, value-chain and economy with a special focus on renewable methanol“, Renew. Sustain. Energy Rev., Bd. 179, S. 113281, Juni 2023, doi: 10.1016/j.rser.2023.113281.



Carbon Capture / DAC

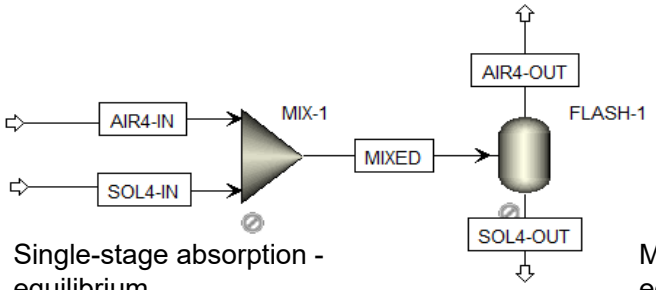
- Processes
  - Absorption
  - Adsorption
  - Membrane separation
- Point source
  - Solvents/Adsorbents
  - Upstreaming
    - Particles
    - Sulfur
    - Tar
- Diffuse source (DAC)
  - Air capture unit
  - Process integration



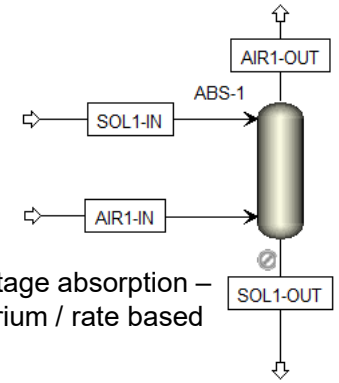
David W. Keith, Geoffrey Holmes, David St. Angelo, Kenton Heidel (2018). A Process for Capturing CO2 from the Atmosphere, Joule 2, 1573–1594; https://doi.org/10.1016/j.joule.2018.05.006.

Challenge: Modeling/simulation of Air Contactor in DAC
→ contactor design/size and mass transfer

Capturing CO_2 - DAC



Single-stage absorption - equilibrium



Multi-stage absorption – equilibrium / rate based

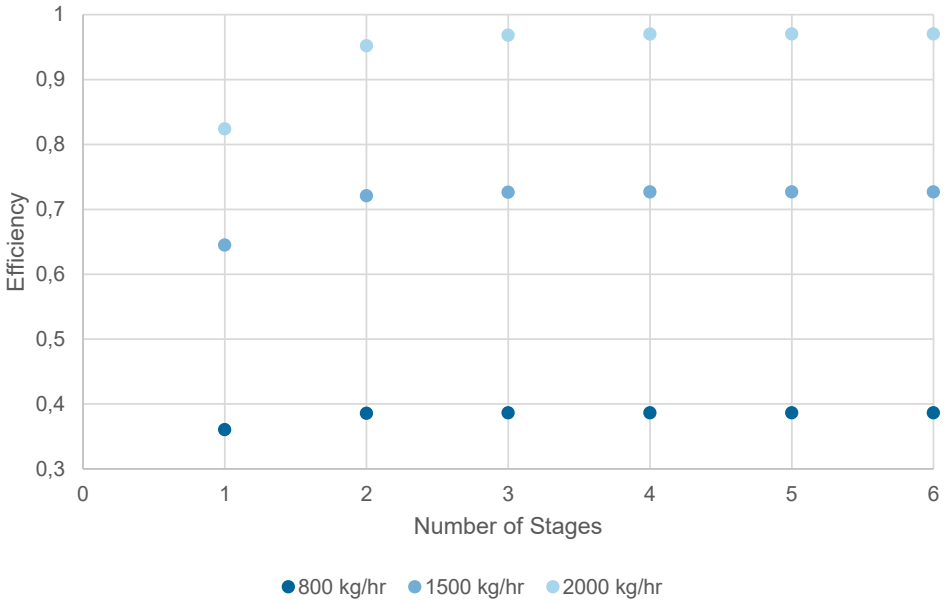
Equilibrium	H2O + HCO3- <--> CO3-- + H3O+
Equilibrium	2 H2O + CO2 <--> HCO3- + H3O+
Equilibrium	2 H2O <--> OH- + H3O+
Salt	CALCI(S) <--> CAOH+ + OH-
Salt	CACO3(S) <--> CO3-- + CA++
Dissociation	K2CO3 --> CO3-- + 2 K+
Dissociation	CACO3 --> CO3-- + CA++
Dissociation	KOH --> OH- + K+
Dissociation	CA(OH)2 --> CAOH+ + OH-

Operation: 25 °C; 1 bar

Air: 100000 kg/hr

Solvent: 1890 kg/hr

1.1 mol/l KOH; 0.45 mol/l K_2CO_3



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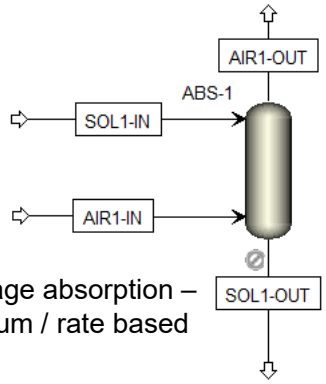
Capturing CO_2 - DAC



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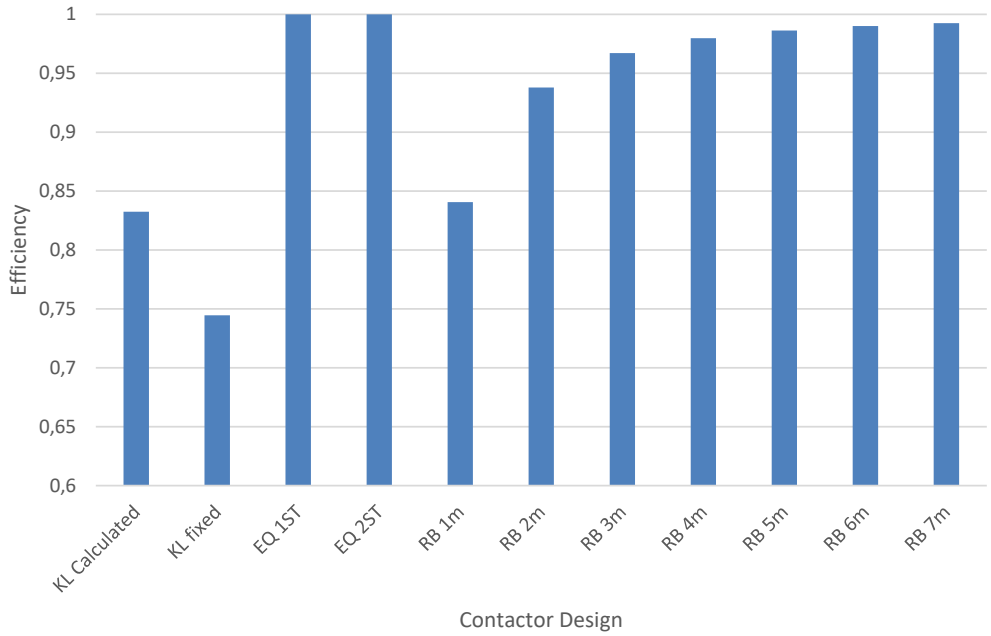
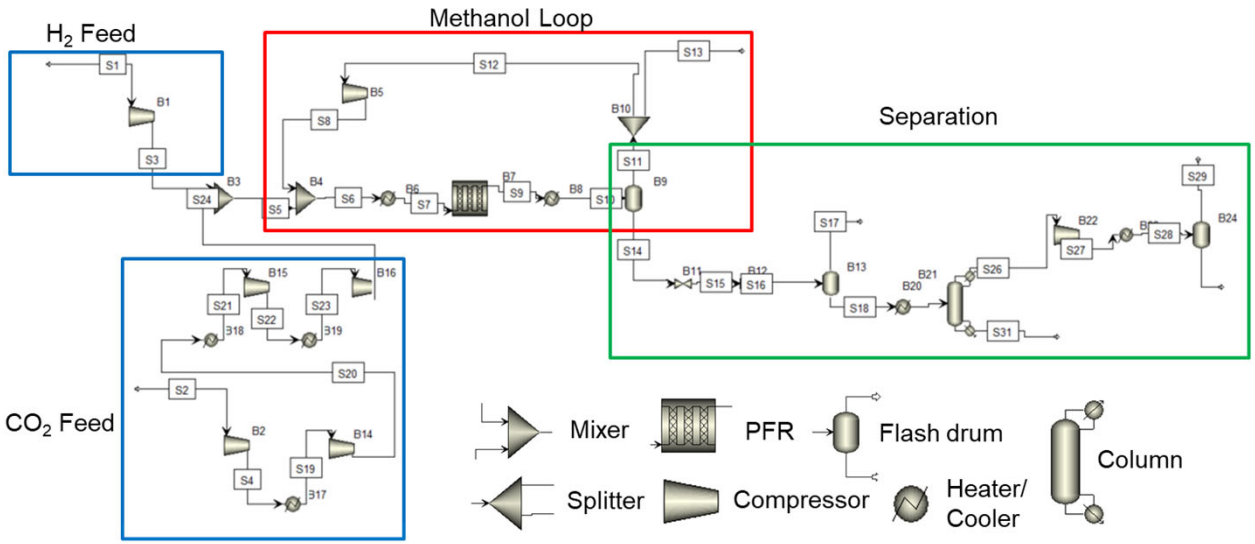
- Assumptions Air Contactor Sub-Unit
  - Sulzer Mellapak
  - Cross Flow (“Cooling Tower”)
  - Semi-empirical correlation for mass transfer coefficent
  - Packing diameter: corresponding 4.4 m (inlet cross section = 3x5 m)
  - Packing depth: 3 m

- Single stage mass transfer not possible in column model
- Challenging mass transfer calculations
- Phyton model for single stage
- To be implemented in ACM



Methanol Synthesis - Process



Catalytic reaction – LHHW*) kinetics
$Cu/ZnO/Al_2O_3$ catalysts
Multi-pass Plug-Flow-Reactor

T = 210-250°C, p = 50-100 bar
CO_2:H_2 = 1:3, Feed:Recycle = 1:5
Purge fraction about 0.01

*) LHHW = Langmuir–Hinshelwood–Hougen–Watson

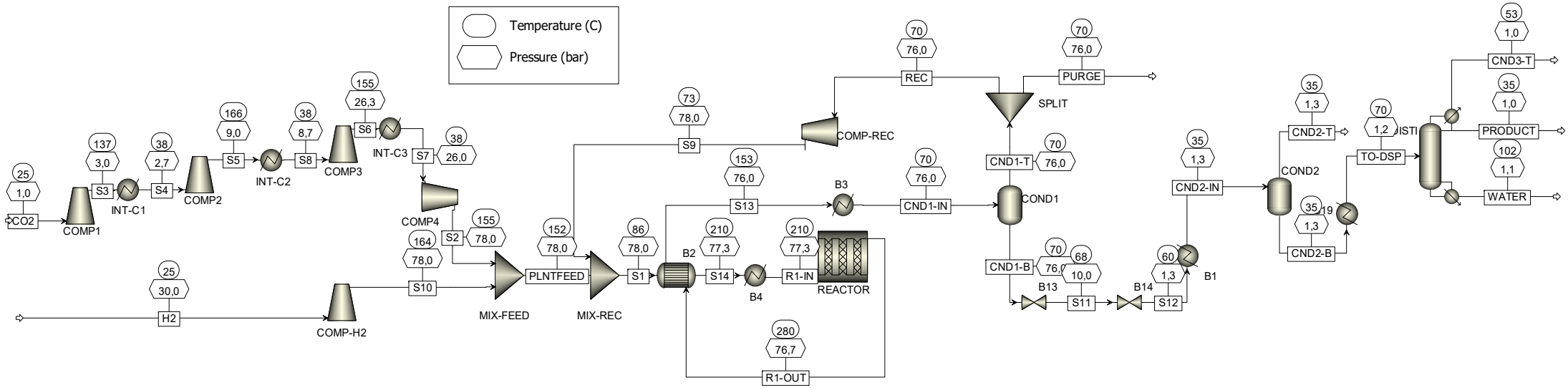
- **Process scale and boundaries**
- **Process Conditions**
- **Kinetics and Mechanism**
  - Used kinetics based on CO_2-conversion
  - Contribution of CO
  - Same mechanism for different catalysts
  - Missing side reactions (methane, etc.)
- **Reactor Design**
  - Isothermal / Adiabatic
  - Tube / fixed bed / suspension
  - Dimensions – length, diameter, tube number
  - Void fraction, particle size
- **Simulation**
  - Stoichiometric / Equilibrium / Kinetic
  - Reactor design
  - Missing / insufficient model validation

Methanol Synthesis - Example

- Capacity
  - 277 kt/a methanol
  - 54.4 kt/a H_2 input
  - 417 kt/a CO_2 input
- Standard Cu catalyst
- Adiabatic operation 210-279°C

- Recycle to feed-ratio ~6.4
- H_2 conversion of 97.6 %
  - 1.18kt/a H_2 lost in purge
  - 0.14kt/a H_2 lost in flash

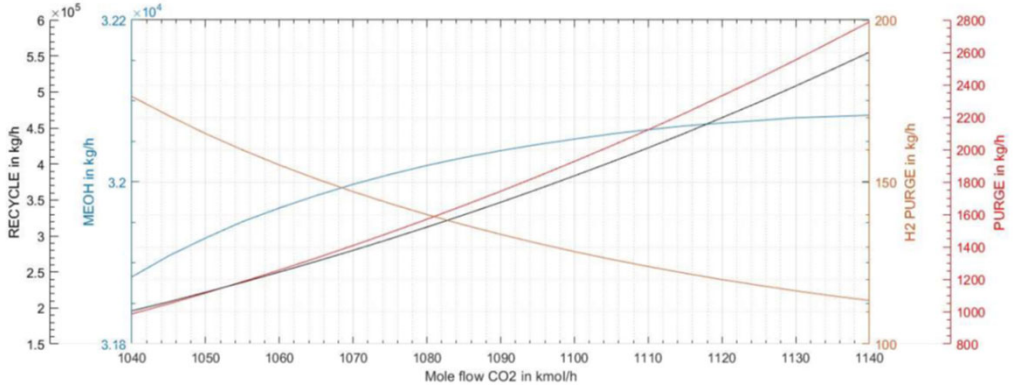
- MeOH-separation
  - Partial condensation
  - 23 stages
  - Feed @ stage 17
  - RR = 1.5



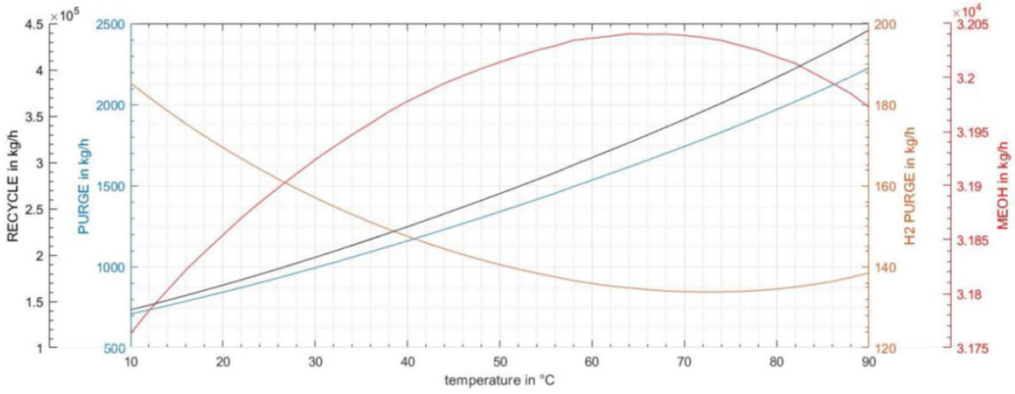
Methanol Synthesis – Case Study

		Case 1	Case 2	Case 3	Literature
Capacity	[t/h]	31,9	5,9	5,9	12,5-55
Operation		Adiabatic	Isothermal	Isothermal	
CO2:H2		1 : 2,87	1 : 3,1	1 : 3,1	1 : 3
Catalyst		Standard	Standard	Zr enhanced	
Temperature	[°C]	210-279	250	250	210-290
Pressure	[bar]	76-78	50	50	50-78
Feed:Recycle		1 : 6,4	1 : 2,6	1 : 3,2	
Purge fraction		0,005	0,01	0,01	
CO2 conversion (MeOH)	[%]	91,4	95,2	95,9	94-100
H2 conversion (MeOH)	[%]	63,4	61,3	61,8	
H2 conversion (total)	[%]	96,2	92,2	92,8	
CO2 losses	[%]	8,6	4,8	4,1	
H2 losses	[%]	3,8	7,8	7,2	
Spec. heat demand	[MJ/kg]	6,66	7,6	7,1	

Methanol Synthesis – Process Optimization



Optimization of CO_2 Feed



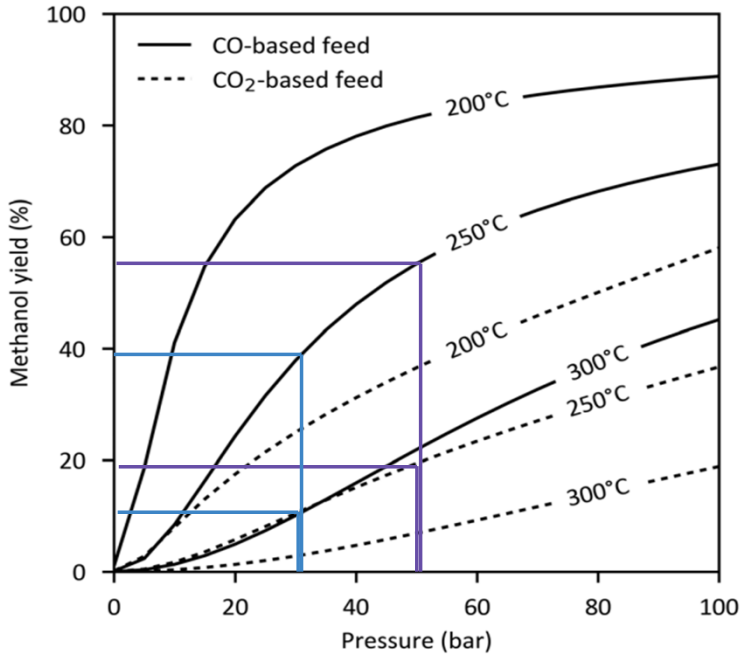
Optimization of the HPC Operating Temperature

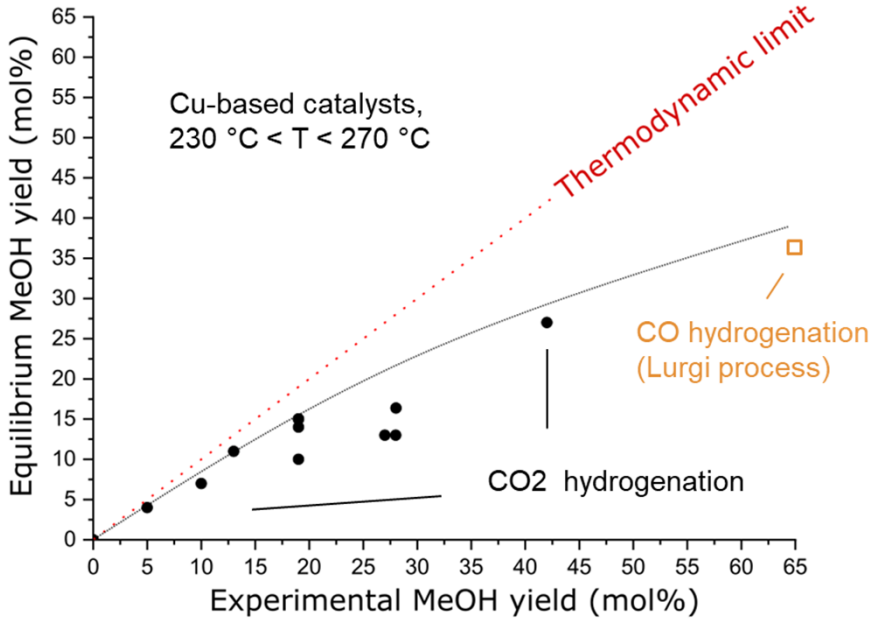
		HP Steam	LP Steam	Cooling Water	Total
Baseline	kJ/sec	30 024	28 786	102 926	
Theoretical target	kJ/sec	-	1 835	45 940	
Saving Potential	kJ/sec	30 024	26 949	56 986	
	%	100,0	93,6	55,4	
Optimized demand	kJ/sec	-	28 786	73 429	
Saved by optimization	kJ/sec	30 024	-	29 497	
	%	100,0	0,0	28,7	
Cost Baseline	€/yr	2 352 409	1 714 050	683 802	4 750 261
Theoretical cost minimum	€/yr	-	109 370	305 209	414 580
Cost optimized	€/yr	-	1 714 050	487 835	2 201 885
Additional CAPEX by optimization	€	540 000			540 000

Overview of utility demand and optimization savings

- Room for improvement
  - Recycle of offgas streams
  - HPC operating conditions
  - Reactor design

Methanol Synthesis – Syngas versus CO_2





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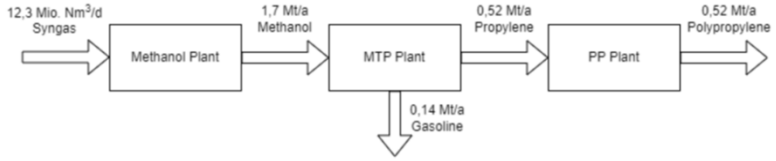
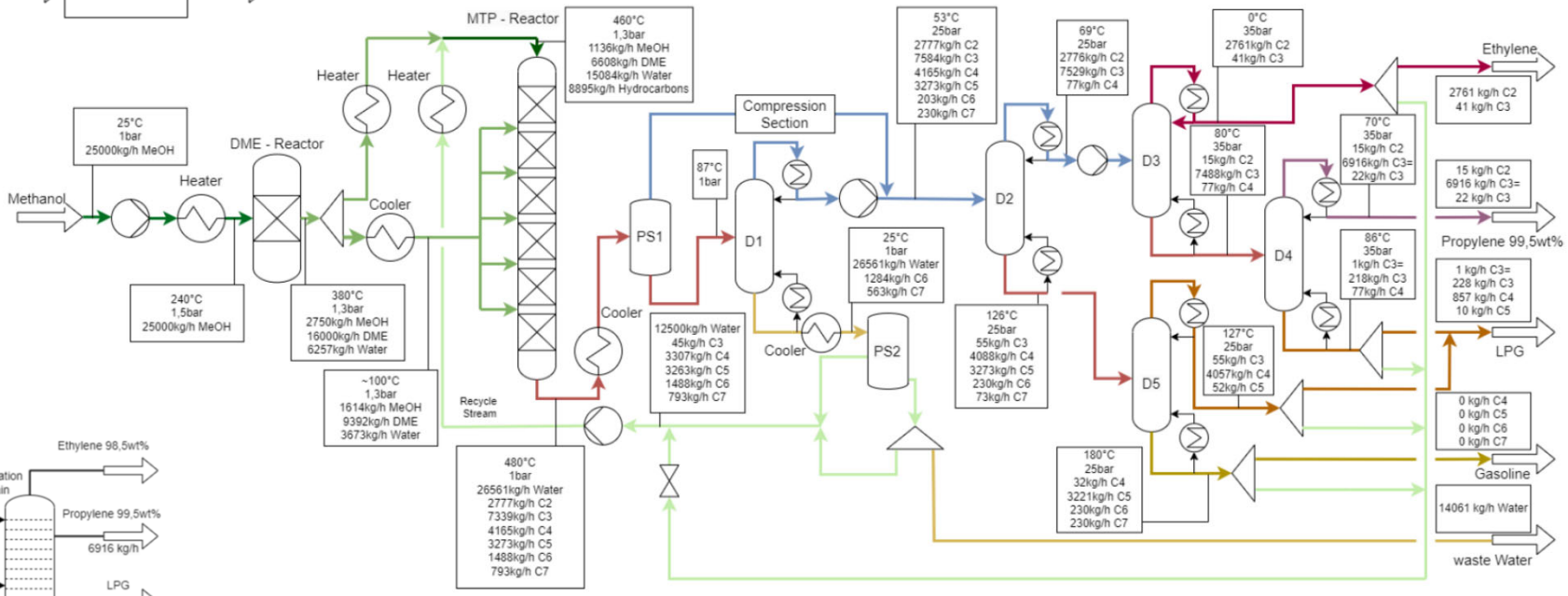
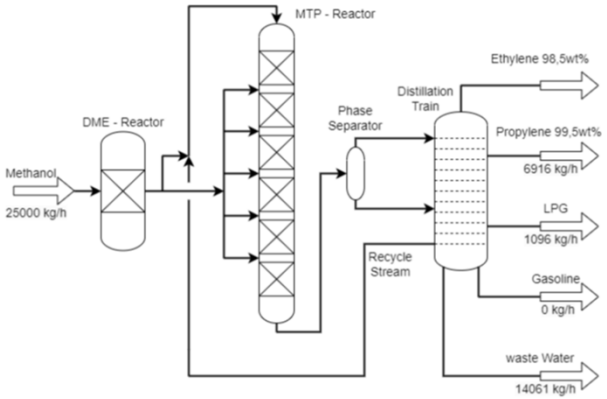
Challenge: Selection of proper kinetics! Usually CO_2-based!

Methanol to Propylene – Preliminary Design



W. Liebner, M. Rothaemel, und J. Wagner, „Methanol-To-Propylene (MTP®): An Economical Route For Creating Value From Stranded Natural Gas“, Lurgi Oel·Gas·Chemie GmbH, Germany, 2003.





H. Koempel und W. Liebner, „Lurgi's Methanol To Propylene (MTP®) Report on a successful commercialisation“, in Studies in Surface Science and Catalysis, Bd. 167, Elsevier, 2007, S. 261–267. doi: 10.1016/S0167-2991(07)80142-X.

Summary and Outlook

- Large variety of process chain options and settings of process steps hinders effective comparison
- Consistent model library in process simulation tool enables:
  - Flexible analysis of process options
  - Consistent mass and energy balances
  - Proper process and heat integration for efficient processes
  - Solid basis for process/heat integration and LCA
- Crucial for effective process chains
  - Careful implementation of new catalysts (mechanism + kinetic parameters)
  - Efficient production of hydrogen
  - Reliable design of core steps (mass transfer, dimensions, scale, etc.)
- Next steps:
  - Setup methanol routes based on syngas/gasifier gas
  - Collection/implementation/validation of kinetic models and parameters

Acknowledgement

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