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The production of methanol from glycerol derived syngas

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UHDE High Pressure Technologies
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SUPERMETHANOL The GtM Concept
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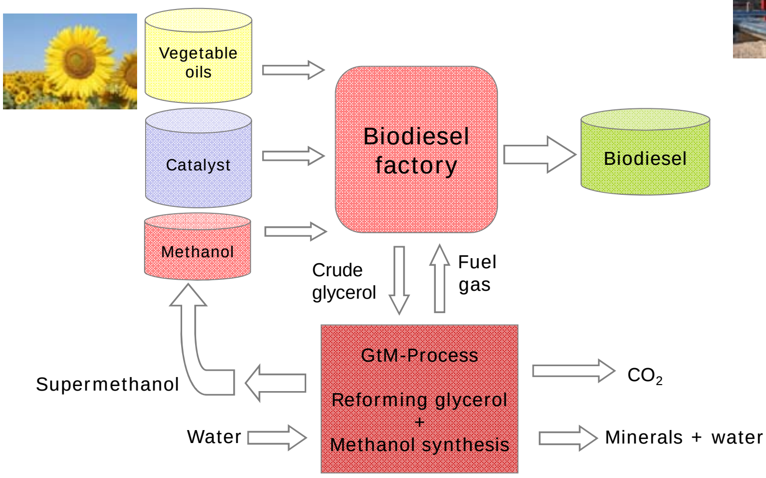
Scope of the project



Objectives (overall)

- Glycerol ⇨ syngas ⇨ methanol
- Glycerol decomposition (products, no stoichiometry):

$$C_3H_8O_3$$

$$\Downarrow$$

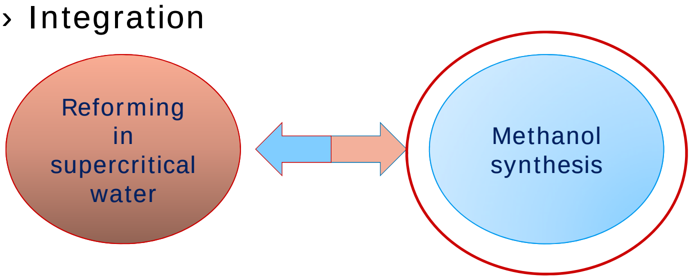
$$H_2 + CO + CO_2 + C_xH_y$$

$$\Downarrow$$

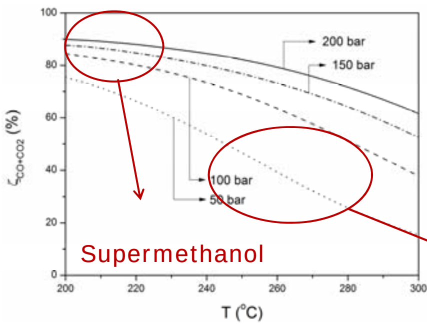
$$CH_3OH + H_2 + CO + CO_2 + C_xH_y$$

Integration of two processes

› Why is it this combination a clever one?
› Interaction between the two processes
› Separate investigation of the two processes
› Integration



Methanol synthesis



Reactions:
- $CO + 2 H_2 \rightleftarrows CH_3OH$
- $CO + H_2O \rightleftarrows CO_2 + H_2$
- $CO_2 + 3 H_2 \rightleftarrows CH_3OH + H_2O$

H_2 (65%), CO (25%), CO_2 (5%) CH_4 (5%)

Conventional methanol synthesis

› High pressure methanol synthesis
› Operation in a once-through-mode

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Content methanol research

› Fundamental studies; view cell
› Thermodynamics/kinetics; packed bed reactor
› Modelling equilibria in methanol synthesis

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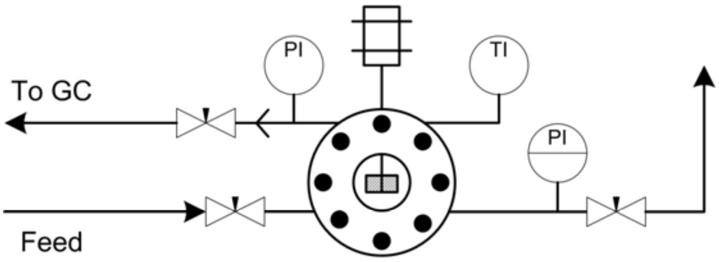
Methanol synthesis in a view cell (1)



View cell 32-64 ml
max 700 bar
max 200°C

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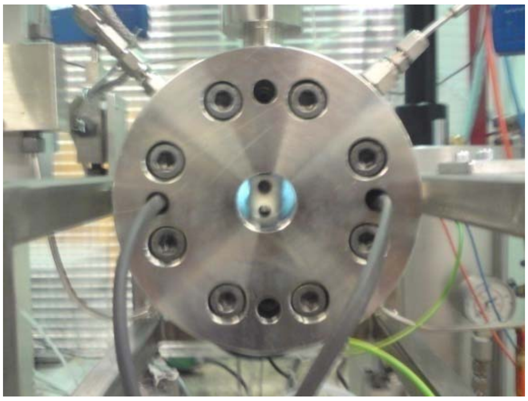
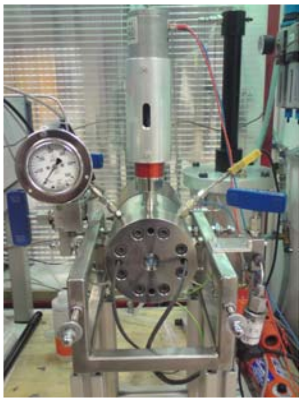
Methanol synthesis in a view cell (2)





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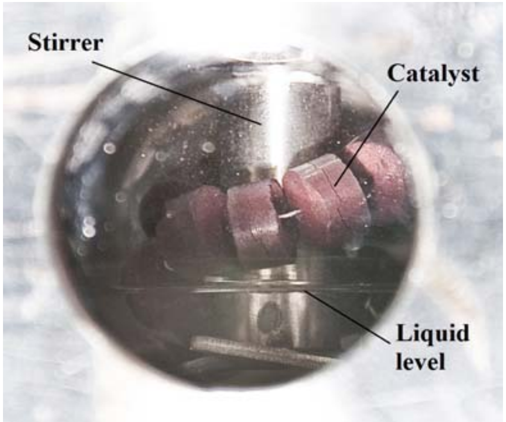
Supermethanol pictures



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Main result and consequences

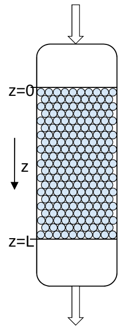
› **Liquid** methanol is produced at high pressure!
› A higher driving force towards methanol will be obtained
› Catalyst bed can be used (much) more efficiently

Methanol synthesis beyond the chemical equilibrium!!

Methanol synthesis in a packed bed

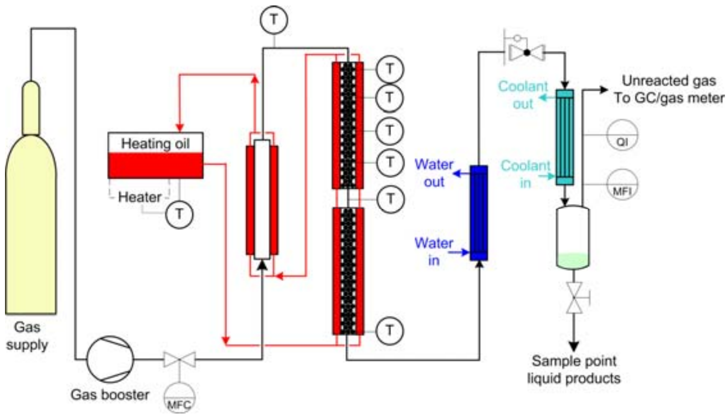
- Feed
  - Artificial gas
- Process conditions
  - T = 200 – 275 ºC
  - P = 75 - 200 bar

Syngas



Methanol
Non-converted
reactants
Inert gas

Methanol synthesis set up



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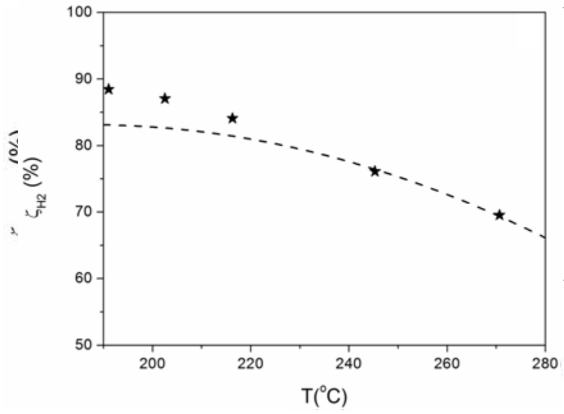
Conversions obtained in a packed bed



- Gas composition:
  - H_2 (67 %)
  - CO (24 %)
  - CO_2 (4 %)
  - CH_4 (5 %)
- P = 200 bar
- T = 200-275 ºC

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Liquid composition

- Gas composition: H_2 (67 %), CO (24 %), CO_2 (4 %), CH_4 (5 %)
- P = 200 bar

T(ºC)	MeOH	EtOH	1-Prop	1-but	2-but	1-pent	2-m-1-prop	H_2O	MeOH purity
195	91.9	0.3	0.1	0.037	0.070	0.018	0.047	8.8	99.3
210	89.7	0.5	0.2	0.063	0.109	0.031	0.095	8.3	98.9
221	91.4	0.6	0.3	0.097	0.123	0.049	0.132	7.8	98.6
242	91.4	1.0	0.4	0.134	0.207	0.065	0.292	6.7	97.8
273	91.3	1.5	0.8	0.227	0.281	0.121	0.626	6.1	96.3

All concentrations are in wt%, MeOH purity is in %

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Experimental studies with a typical composition similar to gas from biomass

$[H_2]$	[CO]	$[CO_2]$	[Inert]
54	30	10	6

Concentrations in vol%

› Influence of pressure and temperature
  - P = 75, 150, 200 bar
  - T = 200, 225, 250, 275 ºC

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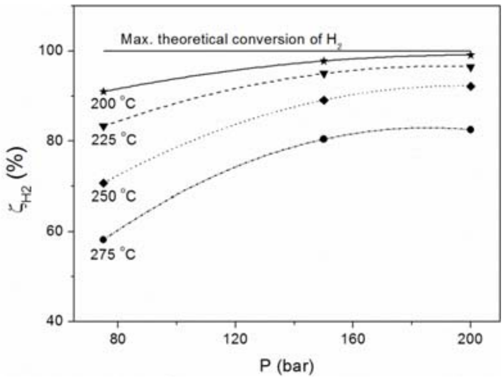
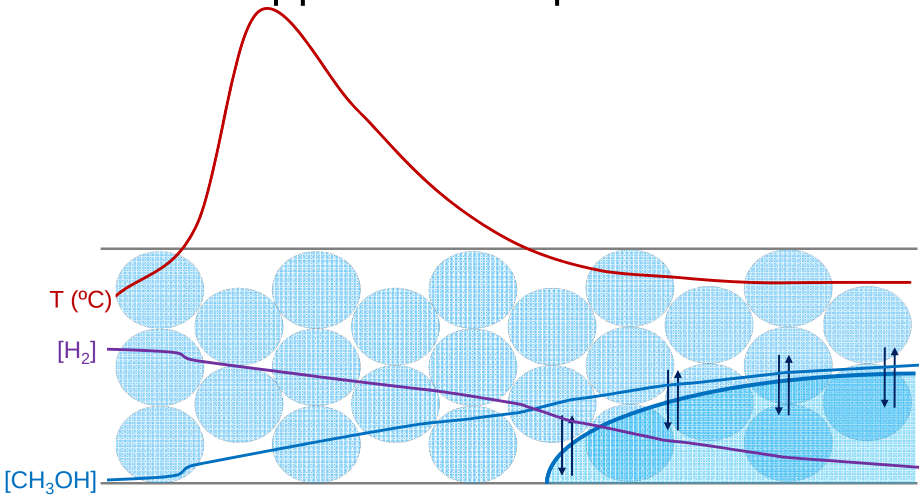
Influence of pressure and temperature in a packed bed reactor



- Gas composition:
  - H_2 (54 %)
  - CO (30 %)
  - CO_2 (10 %)
  - CH_4 (6 %)

What happens in the packed bed?

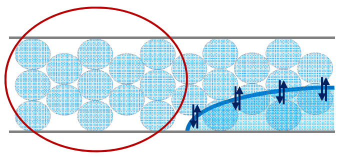


Development of an equilibrium model (1)

1 $$R_{CH_3OH,eq.1} = \frac{k'_{ps1} K_{CO}\left(f_{CO} f_{H_2}^{\frac{3}{2}} - \frac{f_{CH_3OH}}{(f_{H_2}^{\frac{1}{2}} K_{P_1^0})}\right)}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2})\left(f_{H_2}^{\frac{1}{2}} + \left(\frac{K_{H_2O}}{K_{H_2}^{\frac{1}{2}}}\right) f_{H_2O}\right)}$$

2 $f_{i,G} = f_{i,L}$
$T_{reac} > T_{dew}$

3 $f_{i,G} = f_{i,L}$
$T_{reac} = T_{dew}$

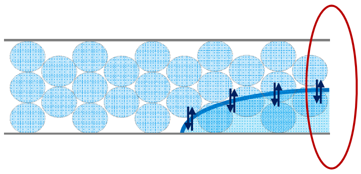


Fugacities were calculated using a modified SRK equation of state

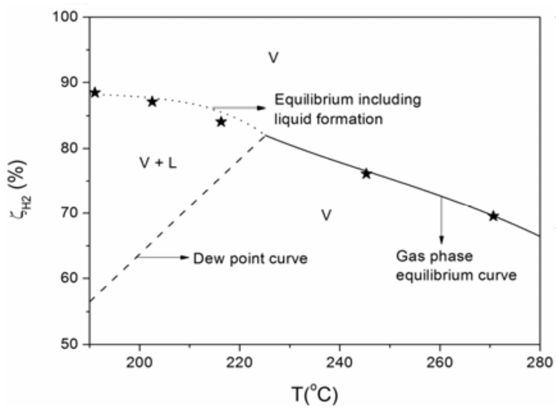
Development of an equilibrium model (2)

Equations to be solved:

- $f_{i,Liq} = f_{i,Gas}$ (6)
- $K_{f,1} = K_{theo,1}$ (1)
- $K_{f,2} = K_{theo,2}$ (1)
- $F_{C,in} = F_{C,Gas} + F_{C,Liq}$ (1)
- $F_{H,in} = F_{H,Gas} + F_{H,Liq}$ (1)
- $F_{O,in} = F_{O,Gas} + F_{O,Liq}$ (1)
- $F_{CH4,in} = F_{CH4,Gas} + F_{CH4,Liq}$ (1)

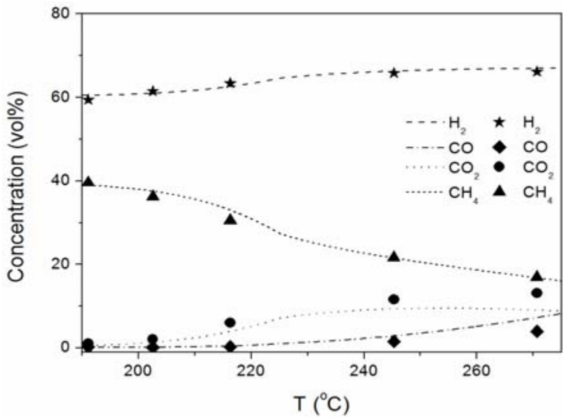


Equilibria in methanol synthesis (1)



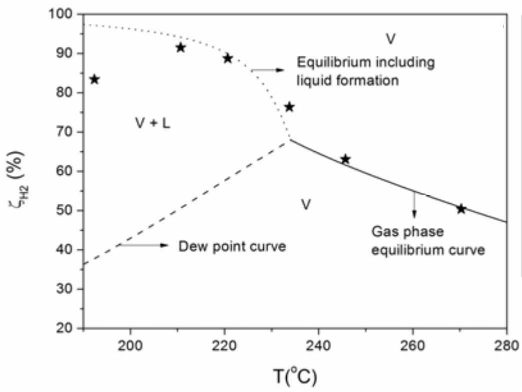
- Gas composition:
  - H_2 (67 %)
  - CO (24 %)
  - CO_2 (4 %)
  - CH_4 (5 %)
- P = 200 bar
- T = 200-275 ºC

Equilibria in methanol synthesis (2)



- Gas composition:
  - H_2 (67 %)
  - CO (24 %)
  - CO_2 (4 %)
  - CH_4 (5 %)
- P = 200 bar
- T = 200-275 ºC

Methanol from CO_2 (1)



- Gas composition:
  - H_2 (70 %)
  - CO (5 %)
  - CO_2 (20 %)
  - CH_4 (5 %)
- P = 200 bar
- T = 200-275 ºC

Methanol from CO_2 (2)

› The presence of a dew point has a stronger influence on the conversion than for a CO-rich gas
› Methanol synthesis is slower than for a CO-rich gas

T(ºC)	MeOH	EtOH	1-Prop	H_2O	MeOH purity
192	71.2	0.006	0.002	26.9	99.9
211	68.4	0.000	0.000	28.5	99.9
221	67.8	0.000	0.000	31.4	99.9
234	68.7	0.000	0.000	30.4	99.9
246	68.5	0.000	0.000	32.0	99.9
270	68.8	0.030	0.010	31.9	99.9

All concentrations are in wt%, MeOH purity is in %

- Gas composition:
  - H_2 (70 %)
  - CO (5 %)
  - CO_2 (20 %)
  - CH_4 (5 %)
- P = 200 bar
- T = 200-275 ºC

Conclusion

› High pressures are favorable for methanol synthesis
› **Liquid** methanol is produced
› Almost full conversion of the limiting gas components is obtained
› Equilibria in high pressure methanol synthesis can be predicted accurately with a model including liquid formation
› Methanol can also be synthesized from CO_2 with high purity

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Thank you for your attention!