



# METHANOL SYNTHESIS FROM CO<sub>2</sub> FOR MODELLING PURPOSES

Researcher's Seminar



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ENERGY**

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# INTRODUCTION



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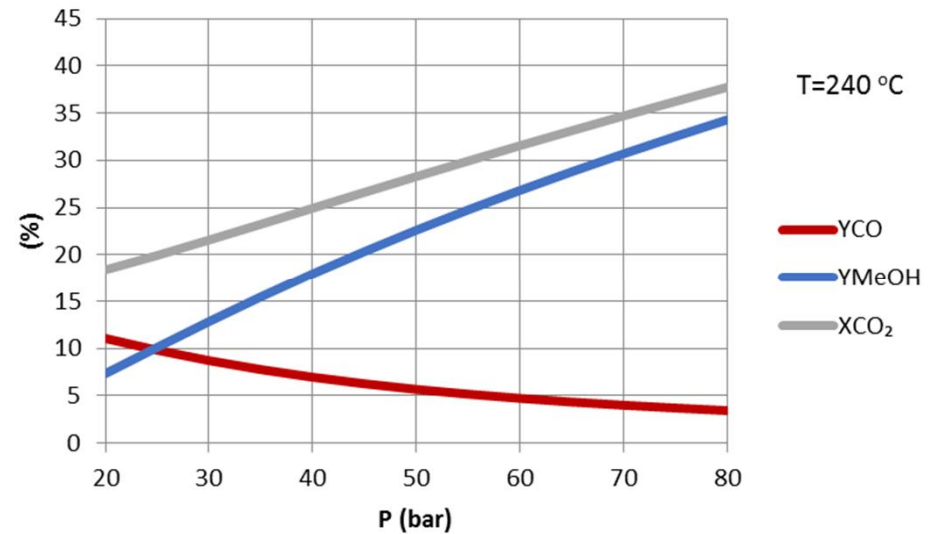
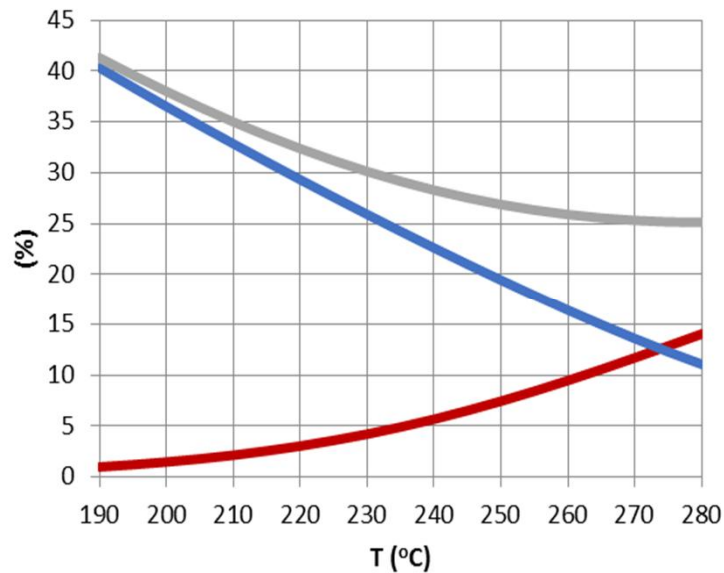


# Methanol synthesis from CO<sub>2</sub>

- CO<sub>2</sub> hydrogenation:  $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H = -49.5 \frac{\text{kJ}}{\text{mol}}$ 
  - Reverse water-gas-shift (rWGS):  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H = 41 \frac{\text{kJ}}{\text{mol}}$
- Cu/ZnO or Pd based catalysts, T = 200 – 300 °C and P = 30 – 100 bar  
Industrially always Cu based catalyst: price↔performance
- Methanol yield lower than using syngas (CO+H<sub>2</sub>)



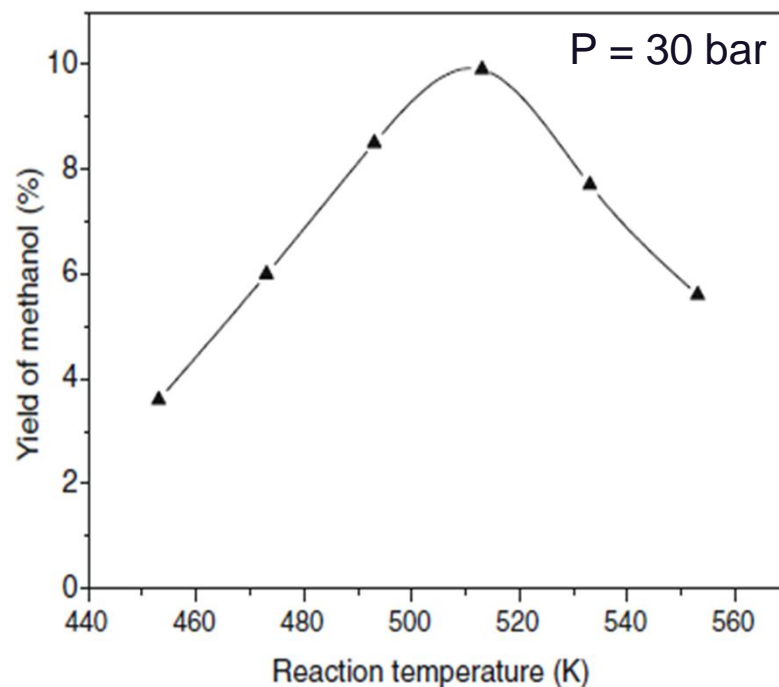
# CO<sub>2</sub> hydrogenation: Equilibrium yields



- Favoured conditions are lower T and higher P, here thermodynamically MeOH production most favoured and CO production least favoured.
- Catalyst activation however at min. 200 °C!



# Copper-based catalysts: Experimental results in literature



Guo et al. (2010)

- CO<sub>2</sub> conversion increases with increasing temperature, however selectivity to MeOH decreases → Maximum MeOH yield typically at 230 - 250 °C (at 30 – 80 bar)



# Kinetic models

- Several models for conventional methanol synthesis have been developed
- Kinetic model developed by Graaf et al. (1988 and 1990) considers 3 reactions, experiments with CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst
- The vanden Bussche and Froment (1996) model considers 2 reactions, experiments on industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at 15 – 51 bar and 180 - 280 °C

vanden Bussche and Froment:

$$r'_{MeOH} = \frac{k_1 p_{CO_2} p_{H_2} \left( 1 - \left( \frac{1}{K_4^{eq}} \right) \left( \frac{p_{H_2O} p_{CH_3OH}}{p_{H_2}^3 p_{CO_2}} \right) \right)}{\left( 1 + k_2 \left( \frac{p_{H_2O}}{p_{H_2}} \right) + k_3 p_{H_2}^{0.5} + k_4 p_{H_2O} \right)^3} \left[ \frac{mol}{kg_{cat} * s} \right]$$

$$r'_{rWGS} = \frac{k_5 p_{CO_2} \left( 1 - K_5^{eq} \left( \frac{p_{H_2O} p_{CO}}{p_{CO_2} p_{H_2}} \right) \right)}{1 + k_2 \left( \frac{p_{H_2O}}{p_{H_2}} \right) + k_3 p_{H_2}^{0.5} + k_4 p_{H_2O}} \left[ \frac{mol}{kg_{cat} * s} \right]$$



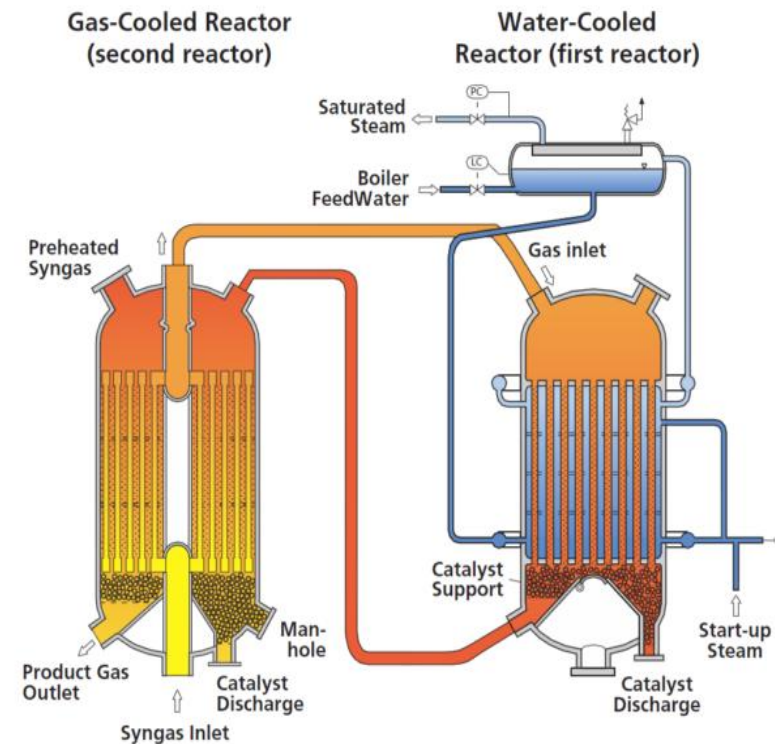
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# Reactors: Packed beds



## Lurgi MegaMethanol

- Industrial-scale methanol production is carried out in tubular packed bed reactors.
- MeOH production in industry is typically equilibrium limited
- Modelling of these reactors typically pseudo-homog. or heterog. 1D/2D
  - Mass transfer limitations are modelled with various approaches, eg. Thiele modulus with pseudo-first rate kinetics
  - Pressure drop due to the catalytic bed calculated with the Ergun equation



Peter, M. (2012)



# EXPERIMENTAL WORK

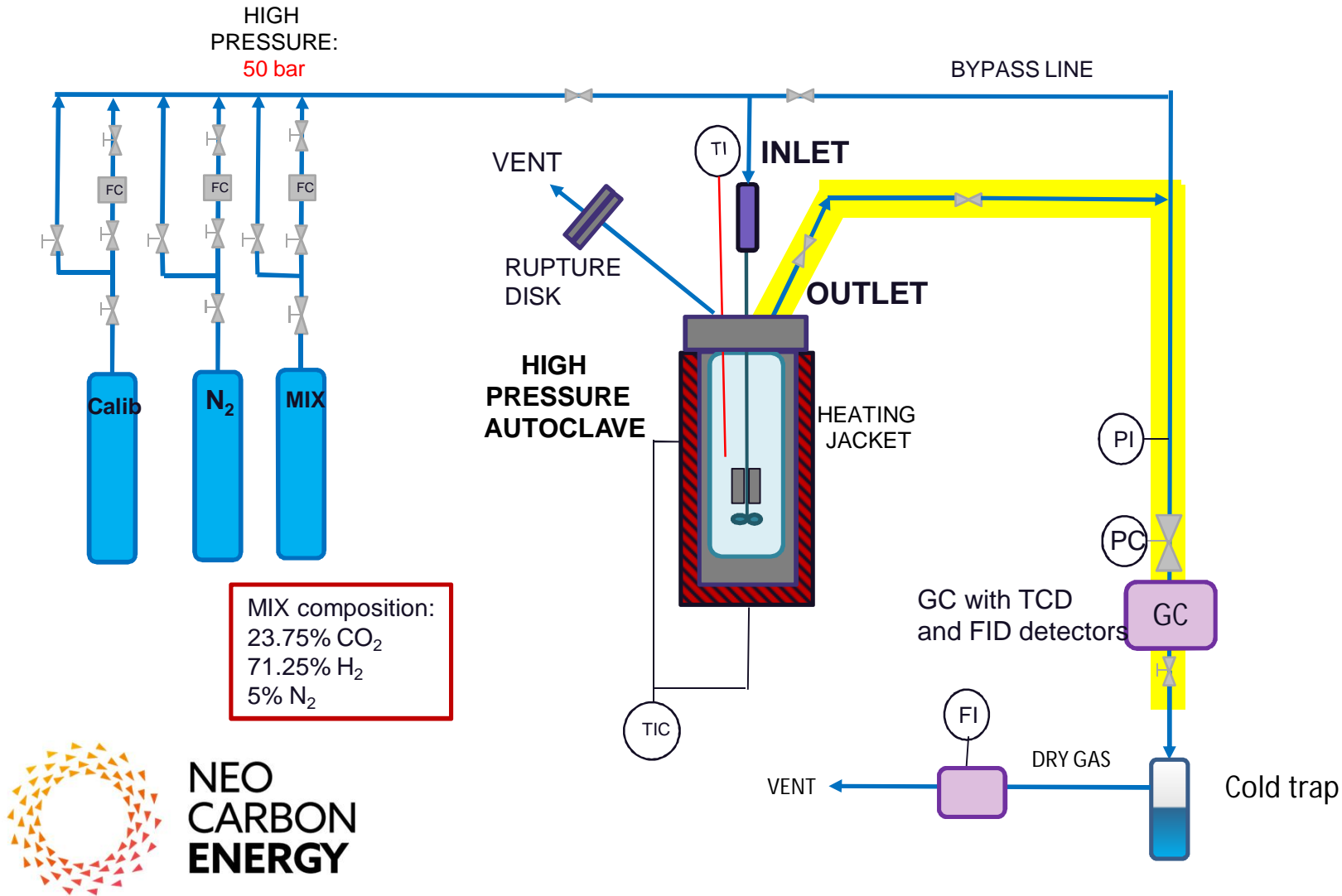


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# Experimental work

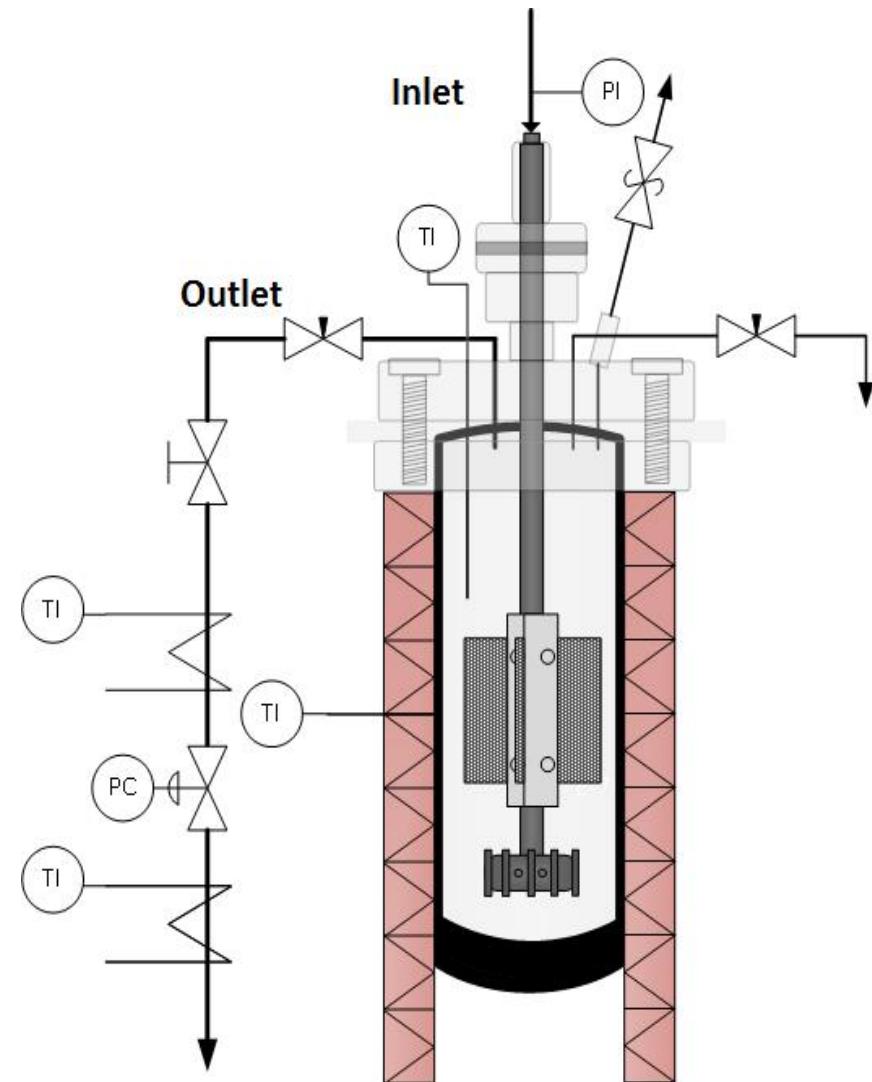
- Christian Frilund master thesis' experiments in continuously stirred tank reactor:
  - Catalyst screening
    - Room of improvement in catalyst development
    - Find out which is the best performing catalyst
  - Operating window tests with a BASF commercial catalyst → Kinetic model assessments.
- Experimental work in tubular reactor (Mari-Leena Koskinen-Soivi):
  - Operating window tests with commercial catalysts → Parameter estimation of the kinetic models found in literature

# Experimental set up: CSTR



# Experimental set up: CSTR

- CSTR not commonly used for gas/solid reactions → Unique test setup for VTT
- 200 ml autoclave with heating jacket and effectively isothermal operation
- Reacting gases enter autoclave through the hollow stirrer and exit from the top
- Catalyst basket or mesh attached to rotating stirrer



# Experiments in CSTR



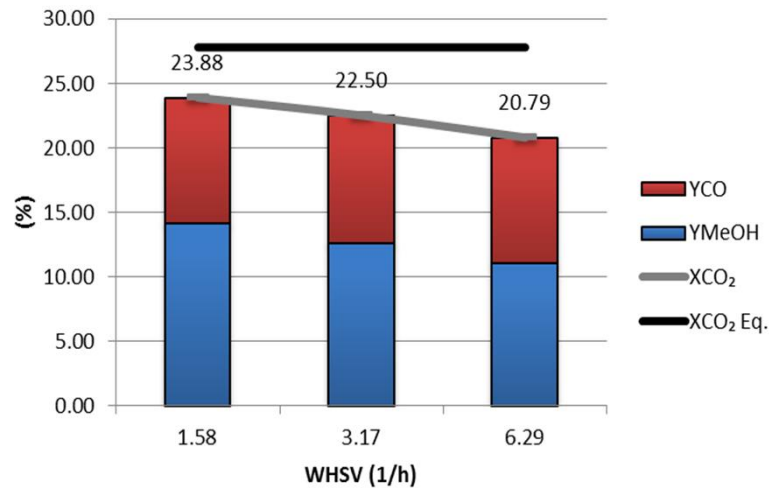
	Catalyst activity comparison (particulate and mesh)		Operating conditions tests				Step input experiment
Catalyst	All		Particulate BASF				-
Catalyst particle size ( $\mu\text{m}$ )	200 - 300		200 - 300				-
Set $T_R$ ( $^{\circ}\text{C}$ )	240		200	220	240	250	240
Set $P_R$ (bar,g)	50		30		50		50
Set WHSV (1/h)	<u>Particulate catalysts:</u> 3.17	<u>Mesh catalyst:</u> Not set	1.58	3.17	6.34		- (0.134 $\frac{\text{dm}^3}{\text{min}}$ at STP)
Set stirrer speed (rpm)	400 - 430		400				430

27 catalysts

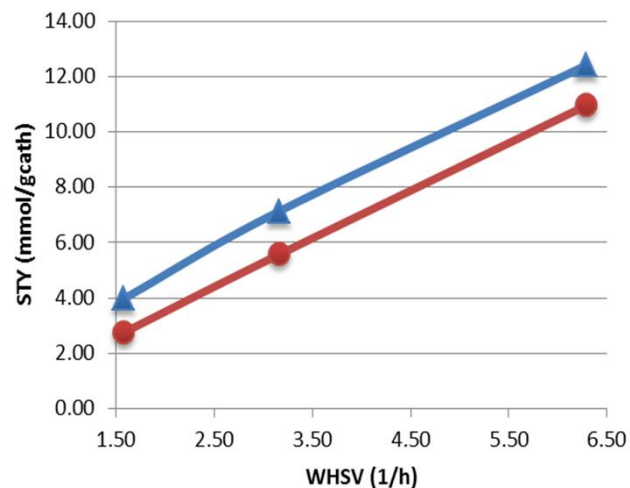


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# Operating conditions tests: Space velocity



T = 240 °C  
P = 50 bar,g



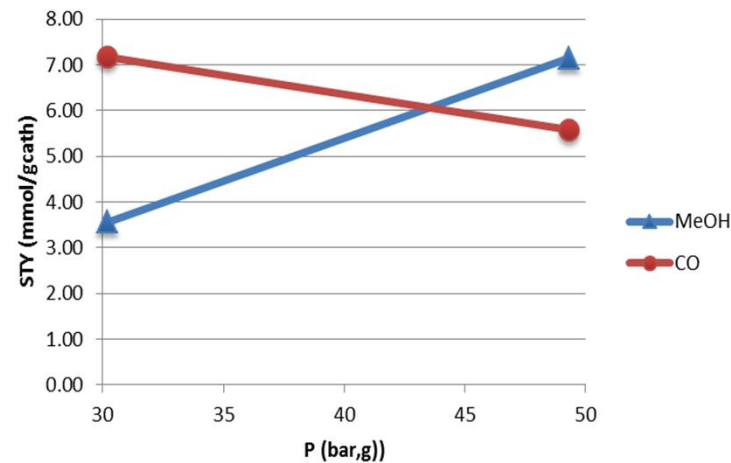
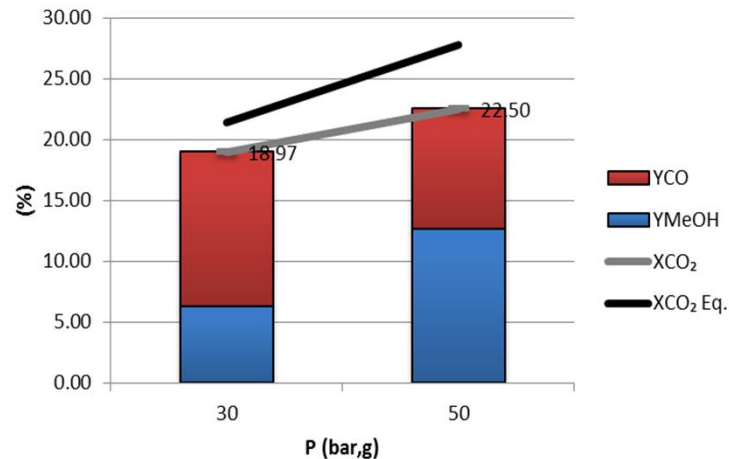
## Conclusion:

- Higher space velocity decreases product yields, but increases product STY
- Results indicate mass transfer limitations

# Condition test: Pressure



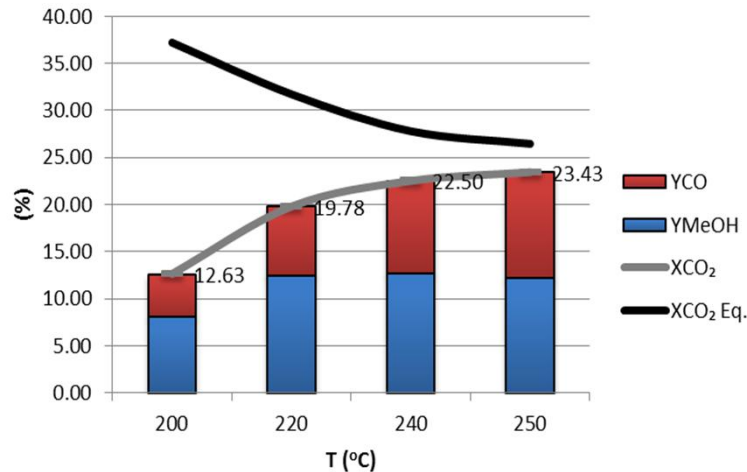
T = 240 °C  
WHSV = 3.17 1/h



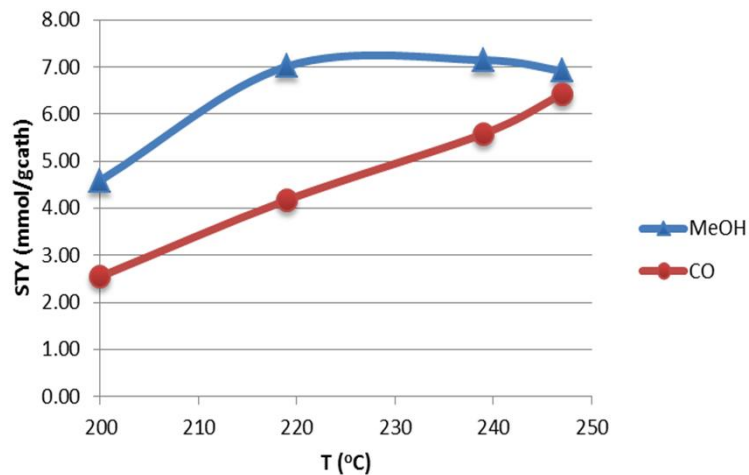
## Conclusion:

- Results as predicted by equilibrium calculations:
  - CO<sub>2</sub> hydrogenation benefits from pressure increase
  - rWGS rate decreases with increasing pressure

# Condition test: Temperature



P = 50 bar,g  
WHSV = 3.17 1/h



## Conclusion:

- MeOH formation increases up to 240 °C, after which it drops. Increasingly equilibrium limited at higher temperatures
- CO formation increases with temperature

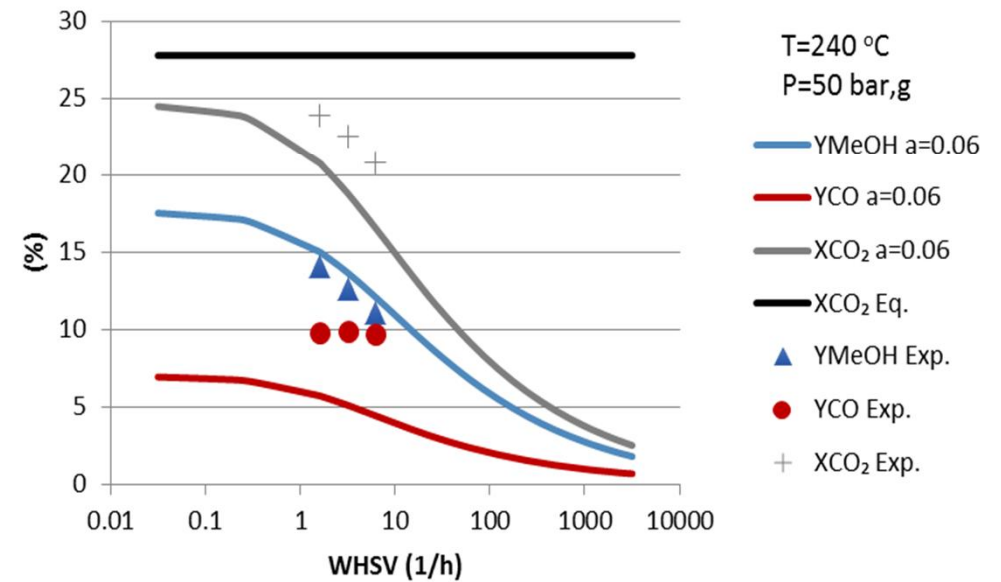
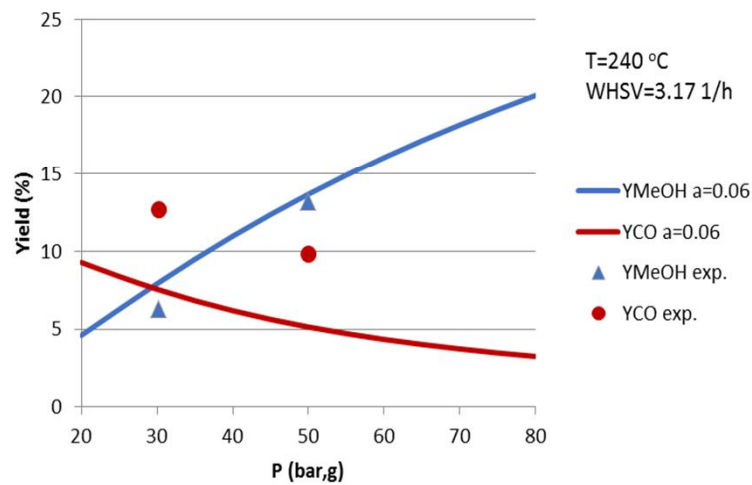
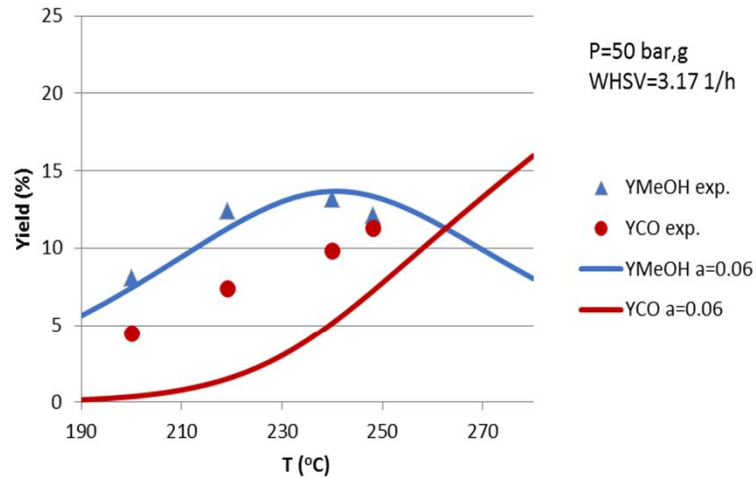


# RESULTS AND COMPARISON WITH KINETIC MODELS FROM LITERATURE

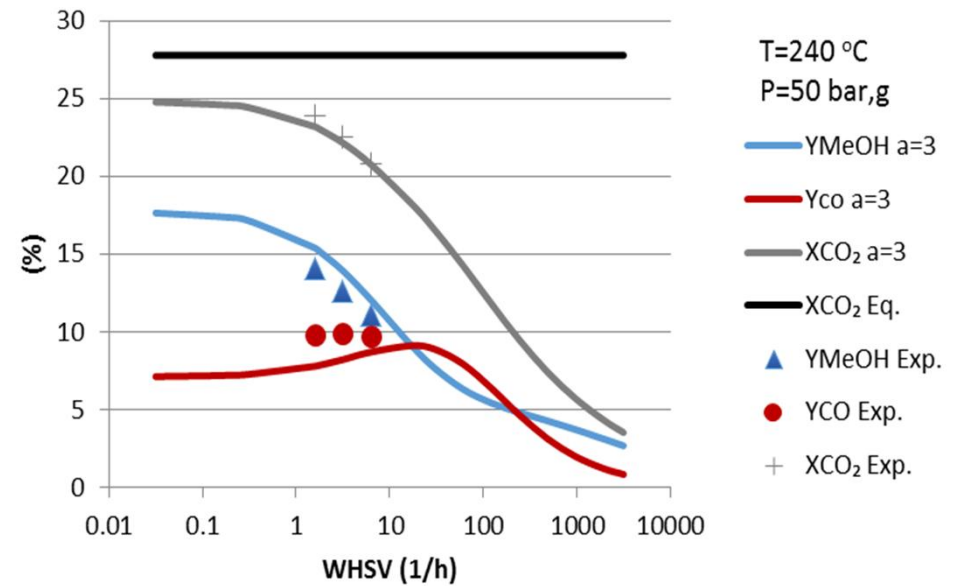
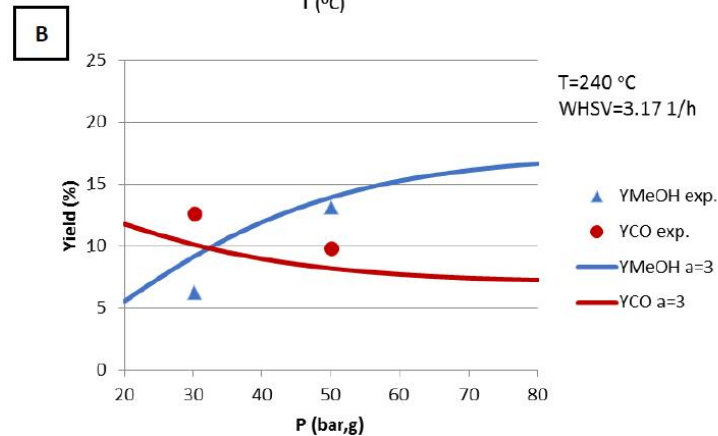
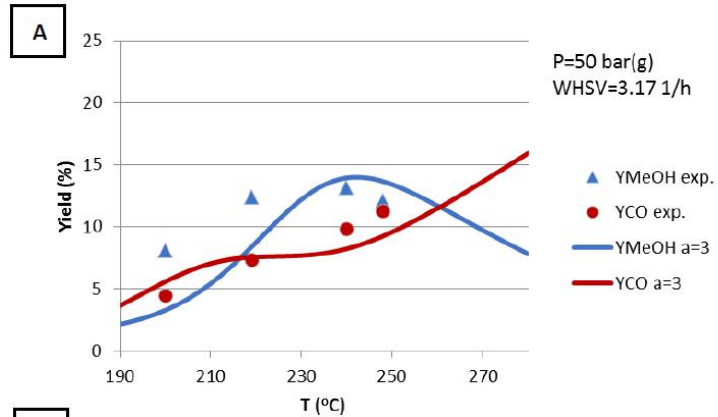


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# Simulated results: Graaf et al. model with parameters from An et al. (2009), $a = 0.06$



# Simulated results: vanden Bussche (1996) model, $a = 3$



# Experimental work in tubular reactor



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# Experiments in tubular reactor

	Operating conditions tests			
Catalyst	Particulate BASF			
Particle size ( $\mu\text{m}$ )	200 - 300			
Set $T_R$ ( $^{\circ}\text{C}$ )	200	220	240	250
Set $P_R$ (bar,g)	30		50	
Set WHSV (1/h)	1.58	3.17	6.34 (and 2 more)	
Set stirrer speed (rpm)	400			



Same operating points than in CSTR but in plug-flow tubular reactor.

# CONCLUSIONS

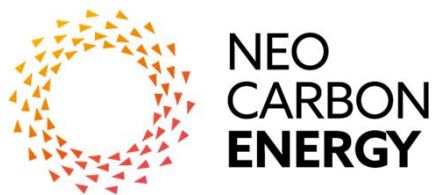


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# Conclusions



- After readjusting the activity parameter, simulation of two commonly used MeOH synthesis kinetic models showed that MeOH formation fits better with the Graaf model and that vanden Bussche model describes fairly well the behavior of the BASF catalyst for both CO and MeOH formation.
- However, both models would need readjustment of some of the kinetic model parameters to fit better the experimental results.
- Tubular reactor experiments will allow to fit 2 or 3 parameters of these models to the experimental data. This will improve the representation of the kinetics of the commercial BASF catalyst.



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NEO-CARBON ENERGY project is one of the Tekes strategic research openings and the project is carried out in cooperation with Technical Research Centre of Finland VTT Ltd, Lappeenranta University of Technology LUT and University of Turku, Finland Futures Research Centre FFRC.

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