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Kinetics and Reactor Modeling of Methanol Synthesis from Synthesis Gas

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History of MeOH synthesis at a glance:

- *Started from 1661, developed in 1800s*
- *First time commercial production: from wood (1830-1920)*
- *1923: BASF introduced coal based HP MeOH*
- *Late 1960s: MP & LP procesess, Copper based catalyst*

Methanol is an important final and intermediate chemical product

Reactions of MeOH Synthesis

1. $CO+2H_2 = CH_3OH$ (DH=-21.66 kcal/mol)
2. $CO_2+3H_2 = CH_3OH + H_2O$ (DH=-11.83 kcal/mol)
3. $CO_2+H_2 = CO + H_2O$ (R.WGS) (DH=+9.84 kcal/mol)

- Both exothermic and exhibit reduction in volume
- Therefore: High P and Low T is in favour of synthesis
- Reactions 1 and 3 are independent and limited by thermodynamic equilibrium

Typical Commercial Catalyst Composition

- *Copper oxide: 60-70%*
- *Zinc oxide: 20-30%*
- *Alumina:5-15%*

- Copper, an extremely selective catalyst, high yield,99.5% of converted CO+CO2 is MeOH
- Shape: Tablet form, cylinders:5.5 into 3.5 mm or 5 into 5 mm
- Reduction:1% H2 in N2 or Methane at max. 230 ∘ C
- Catalyst poisoning: Sulfide and Chlorine

Highlights of MeOH Synthesis

- Exothermic Rection, Heat integration and Recovery are important feature

- Current Technologies: Heat Transfer based:
    1. ICI: Quench Reactor
    2. Lurgi: Tubular
    3. Mitsubishi: Double-Tube Heat Exchange reactor

- Trends in technology improvement: Larger capacity, improved energy efficiency

- Suitable Syngas Technology (Topsøe, Lurgi, Mitsubishi): Two step Reforming,Primary SR plus ATR

- 32 to 44 % of the energy is used for the production of MeOH

Tube cooled: Catalyst bed + heat exchangers in one vessel

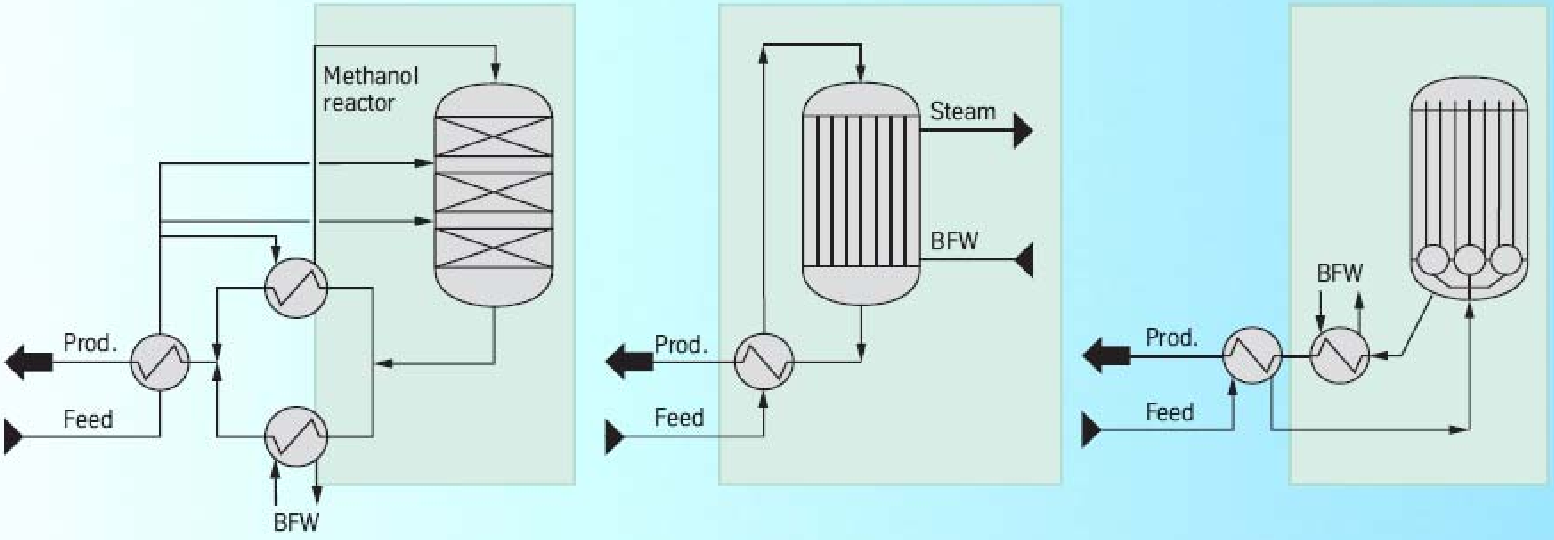
Relatively lower cat. Vo

Better heat recovery

7 commercial units operating now

Fig. 6-3
Methanol synthesis loop – different reactor types

Type	Adiabatic quench (ARC-multibed)	Isothermal tubular	Tube cooled
Gas flow	Axial (Quenchgas : Radial)	Axial	Axial
Heat recovery	BFW preheat	MP steam	BFW preheat
Single train capacity	Up to 3,000 mtpd	Up to 1,500 mtpd	Up to 2,000 mtpd
Cost factor, reactor only	Low cost	High cost	Low cost



Microstructured reactors, Velocys, Heatric…?

Challenges in Conventional MeOH Technology

1. ***Heat Management,***
   - Non-isothermal behaviour,
   - Trend: leading to different reactor configurations

2. ***Conversion per pass***:
   – Higher T, lower Conversion,Nature of the reaction (Eq. Limitation),
   – Trend: leading to development of low temp. active catalysts

Project Scope

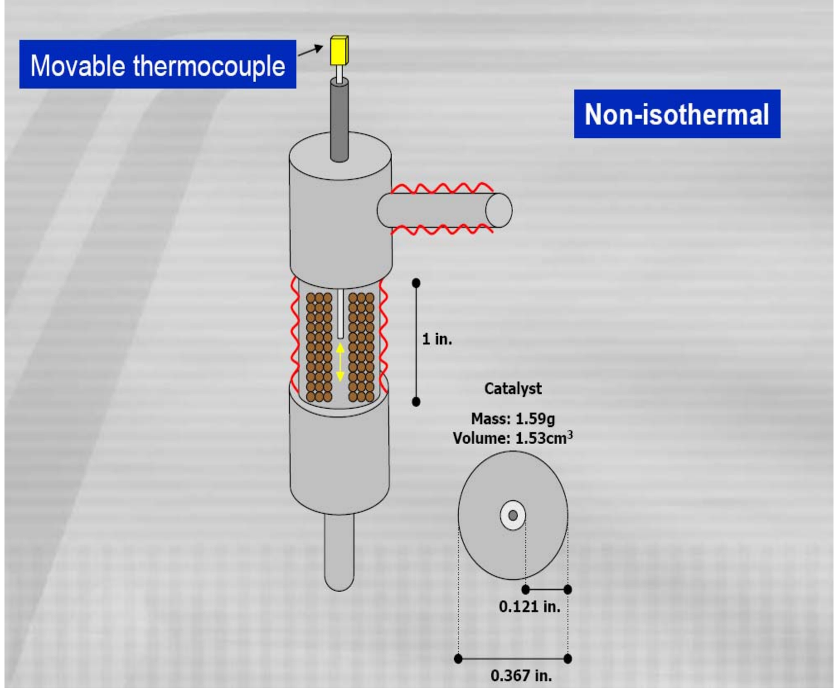
Offshore conversion of remote gas to methanol

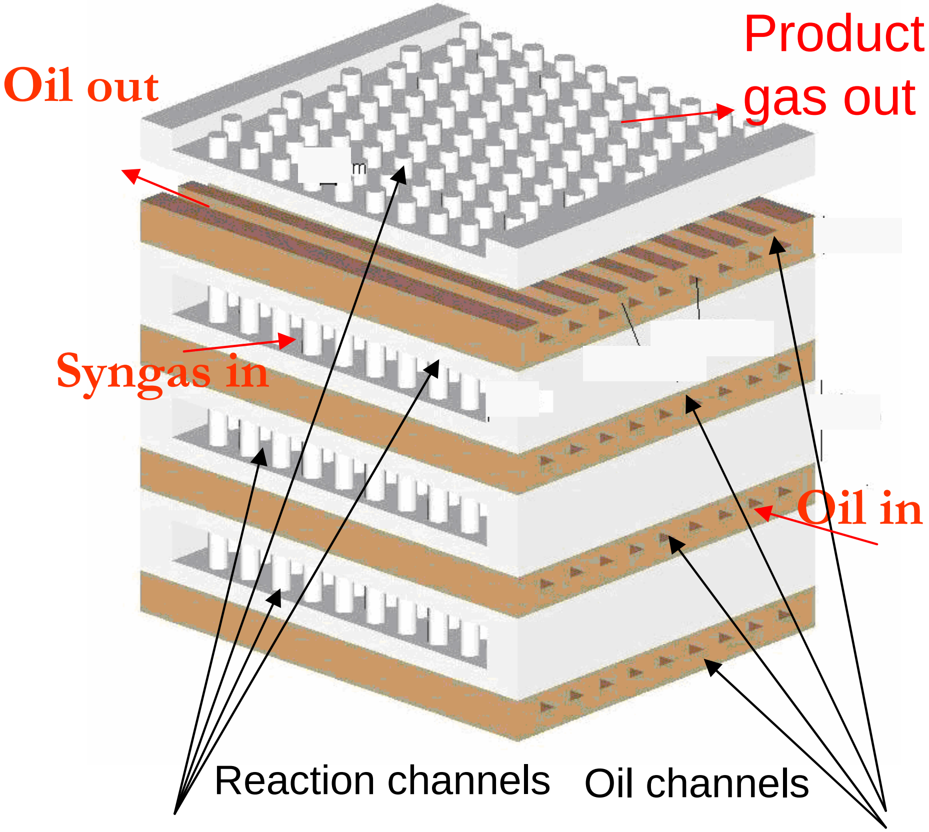
Statoil

Future Solution for Stranded Gas Fields?

Comparative study of two reactors

- Non isothermal packed bed reactor
- Micro-Packed Bed Reactor-Heat Exchanger





Fixed Bed Reactor Model

- ***Objectives of model development:***

1. To develop a model and predict the experimental data on a laboratory scale fixed bed reactor for methanol synthesis
2. Comparative performance study of fixed bed reactor and a microstructured reactor via developed models (next phase of the project)
3. COMSOL Multiphysics software package (MATLAB based) was used in this study

Fixed Bed Reactor Model

- ***Model assumptions:***

1. Pseudo-homogeneous,

   Cg = Cs and Tg = Ts

   No T and C gradinet within particles

2. 2D model: no radial velocity is considered, but dispersion and heat transfer exists in both radial and axial directions

Kinetic Rate Equations

$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ (ΔH = -11.83 kcal/mol) (2)

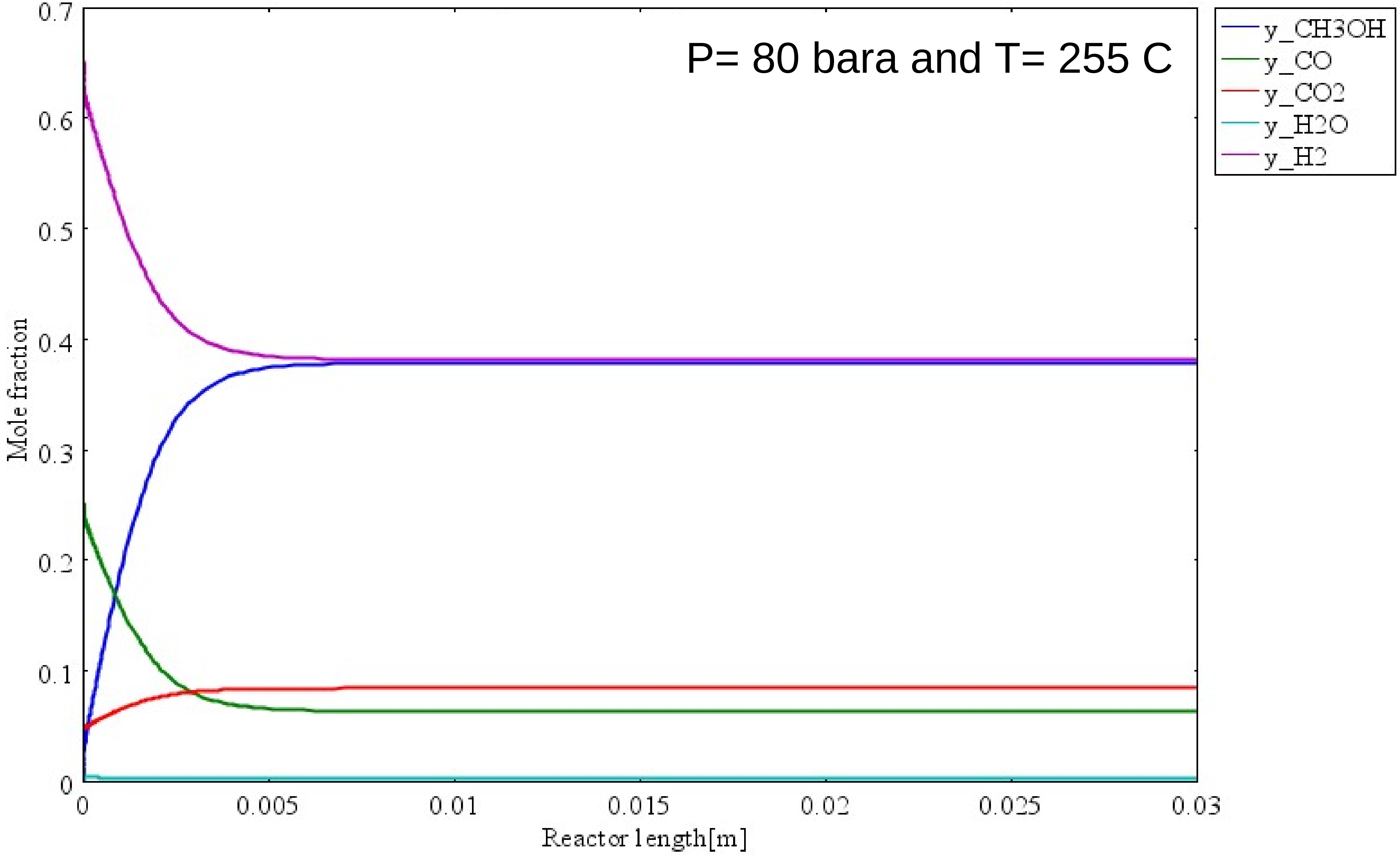
$CO_2 + H_2 \leftrightarrow CO + H_2O$ (ΔH = +9.84 kcal/mol) (3)

$$r_{MeOH} = \frac{k_d . p_{CO_2} . p_{H_2} . \left(\left(1 - \left(p_{H_2O} . p_{CH_3OH} / \left(\left(p_{H_2} \right)^3 . p_{CO_2} . K_{eq1} \right) \right) \right. \right.}{\left(\left(1 + k_c . p_{H_2O} / p_{H_2} + \sqrt{(p_{H_2}).k_a} + k_b . p_{H_2O} \right)^3 \right)}$$

$$r_{RWGS} = \frac{k_e . p_{CO_2} . \left(1 - K_{eq2} . p_{H_2O} . p_{CO} / p_{CO_2} . p_{H_2} \right)}{\left(1 + k_c . p_{H_2O} / p_{H_2} + \sqrt{(p_{H_2}).k_a} + k_b . p_{H_2O} \right)}$$

Chemical Reaction Engineering Lab

Mole fraction pofiles of reactants and products from CREL, Adiabatic Plug Flow Reactor



Kinetic model is in a good agreement with literature, Jakobsen et al., Computers and Chem. Eng., 26, 2002

Governing Equations, Boundary Conditions

- ***Mass Balance***

$$\frac{\partial c_i}{\partial t}+D_{er}\left(\frac{\partial^2 C_i}{\partial r^2}+\frac{1}{2}.\frac{\partial C_i}{\partial r}\right)+D_{ea}\frac{\partial^2 C_i}{\partial z^2}=u_s.\frac{\partial C_i}{\partial z}-\rho_B.r_i$$

- ***Energy Balance:***

$$\frac{\partial T}{\partial t}+\lambda_{er}\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{2}.\frac{\partial T}{\partial r}\right)+\lambda_{ea}\frac{\partial^2 T}{\partial z^2}=u_s.\rho_f.c_p\frac{\partial T}{\partial z}-\rho_B.(\Delta H).r_i$$

- ***Initial Conditions:***

$C_i = C_0$ at all r and z

$T = T_0$

- ***Boundary Conditions (t>0):***

$\frac{\partial C}{\partial r}=0$ at $r=0$ and r=R all z

$\frac{\partial T}{\partial z}=-\frac{U}{\lambda_{er}}\left(T-T_a\right)$ at r=R all z

$C_i = C_0$, $T = T_0$ at $z=0$ $0 \le \text{r} \le \text{R}$

$\frac{\partial C}{\partial z}=\frac{\partial T}{\partial z}=0$ at $z=L$ $0 \le \text{r} \le \text{R}$

Fixed wall T, convective flux at the exit, constant velocity along the bed (laminar)

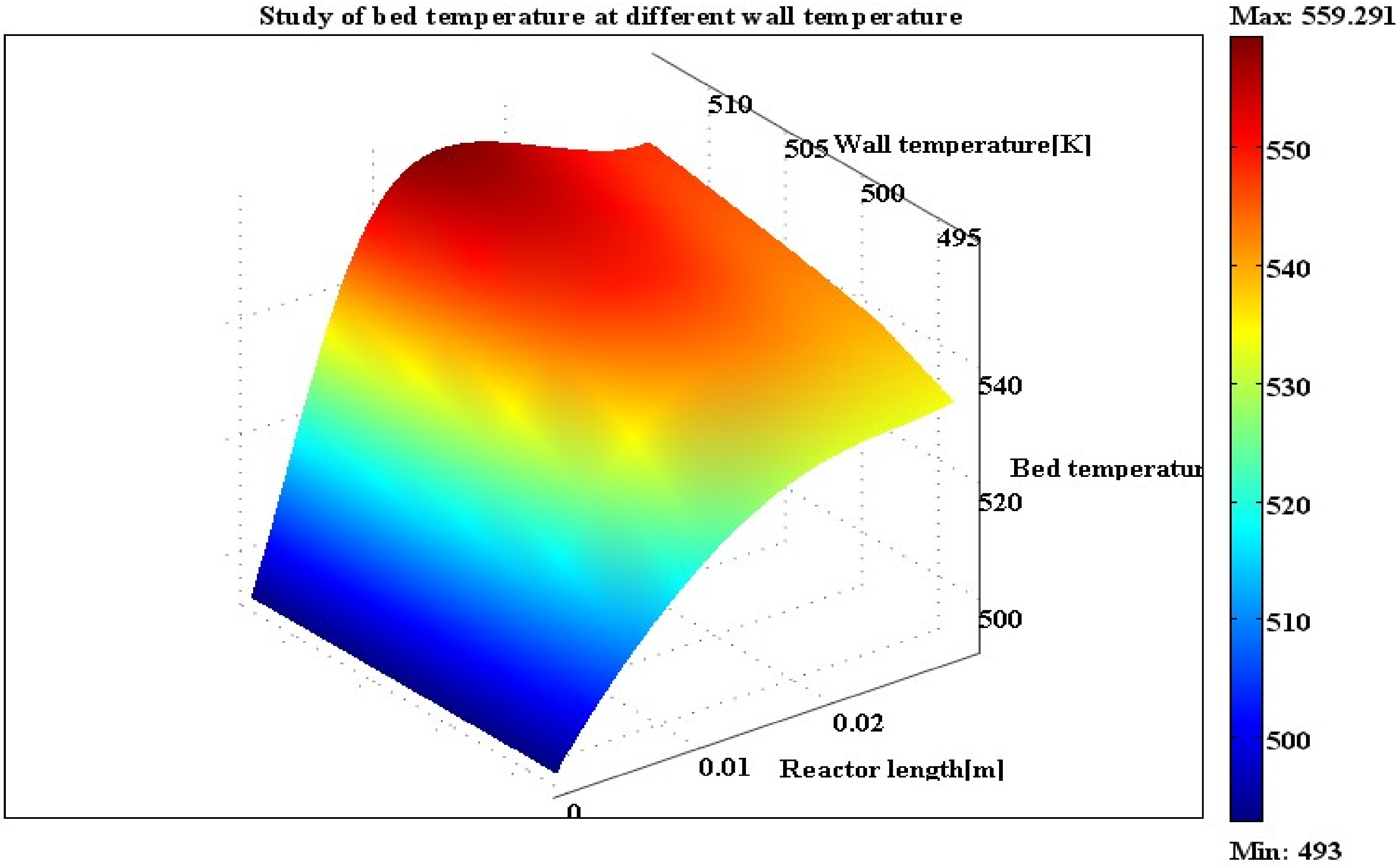
Model Coefficients, Reactor & Catalyst Data

Reactor& Catalyst Data:	
Inner Tube Diameter (m)	0.00914
Outer Tube Diameter (m)	0.0127
Tube Length (m)	0.03
Shell Temperature (K)	493 - 513
Catalyst System	$CuO/ZnO/Al_2O_3$
Pellet size	50-200 µm
Catalyst Density	1250 Kg m^{-3}
Bulk Void Fraction	0.5

Synthesis gas composition (vol%):	
H2	0.65
CO	0.25
CO2	0.05
N2	0.05

Model Coefficients	
Axial Dispersion	Wen & Fan, 1975
Radial Dispersion	De Ligny et al., 1970
Axial Gas Thermal Conductivity	Yagi et al., 1960
Radial Gas Thermal Conductivity	Froment & Bischoff, 1979
Overall Heat Coefficient	Froment & Bischoff, 1979

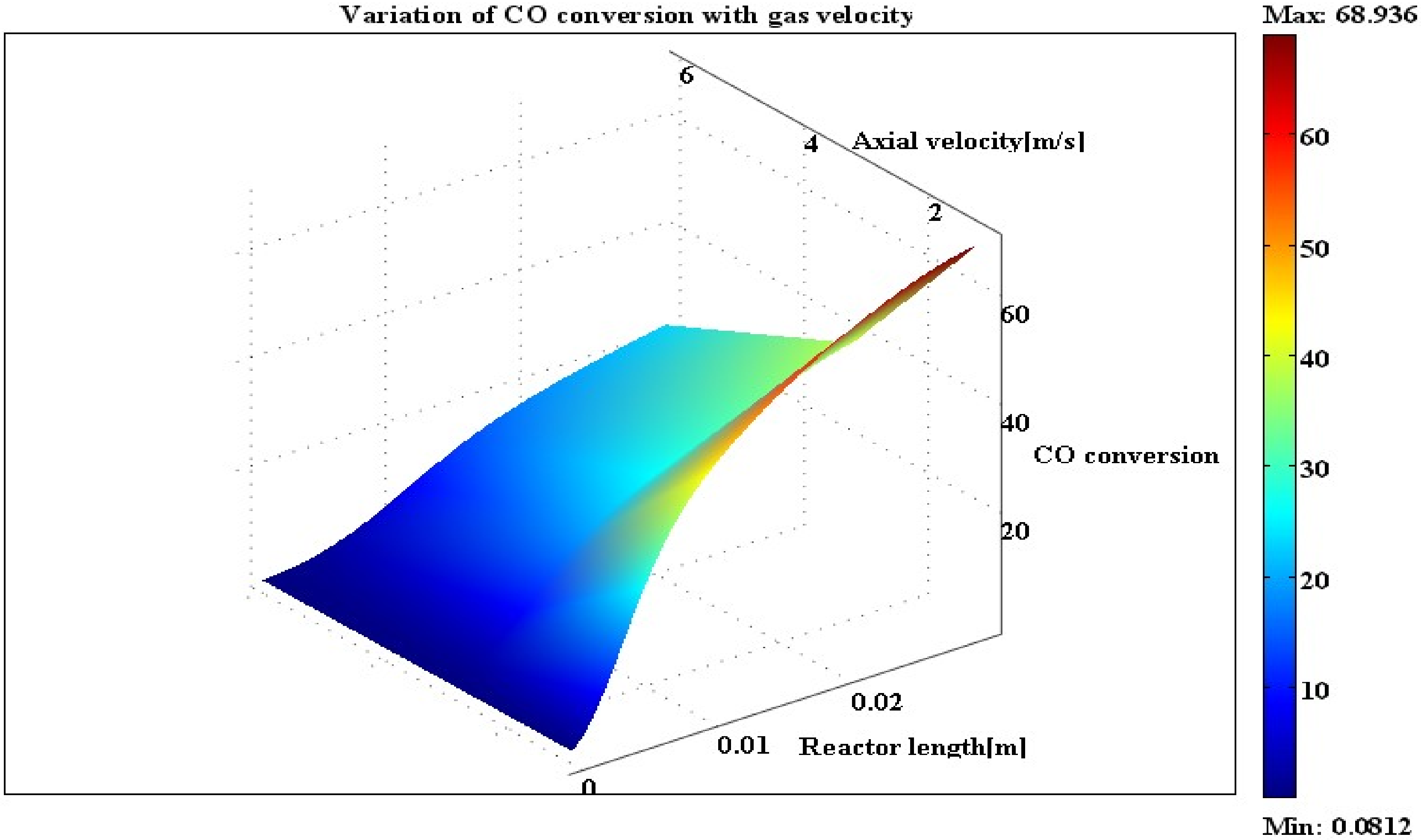
2D Simulation of the reactor



P=80 bars, syngas flow= 250 nml/min

The wall temp. strongly affects bed temperature distribution

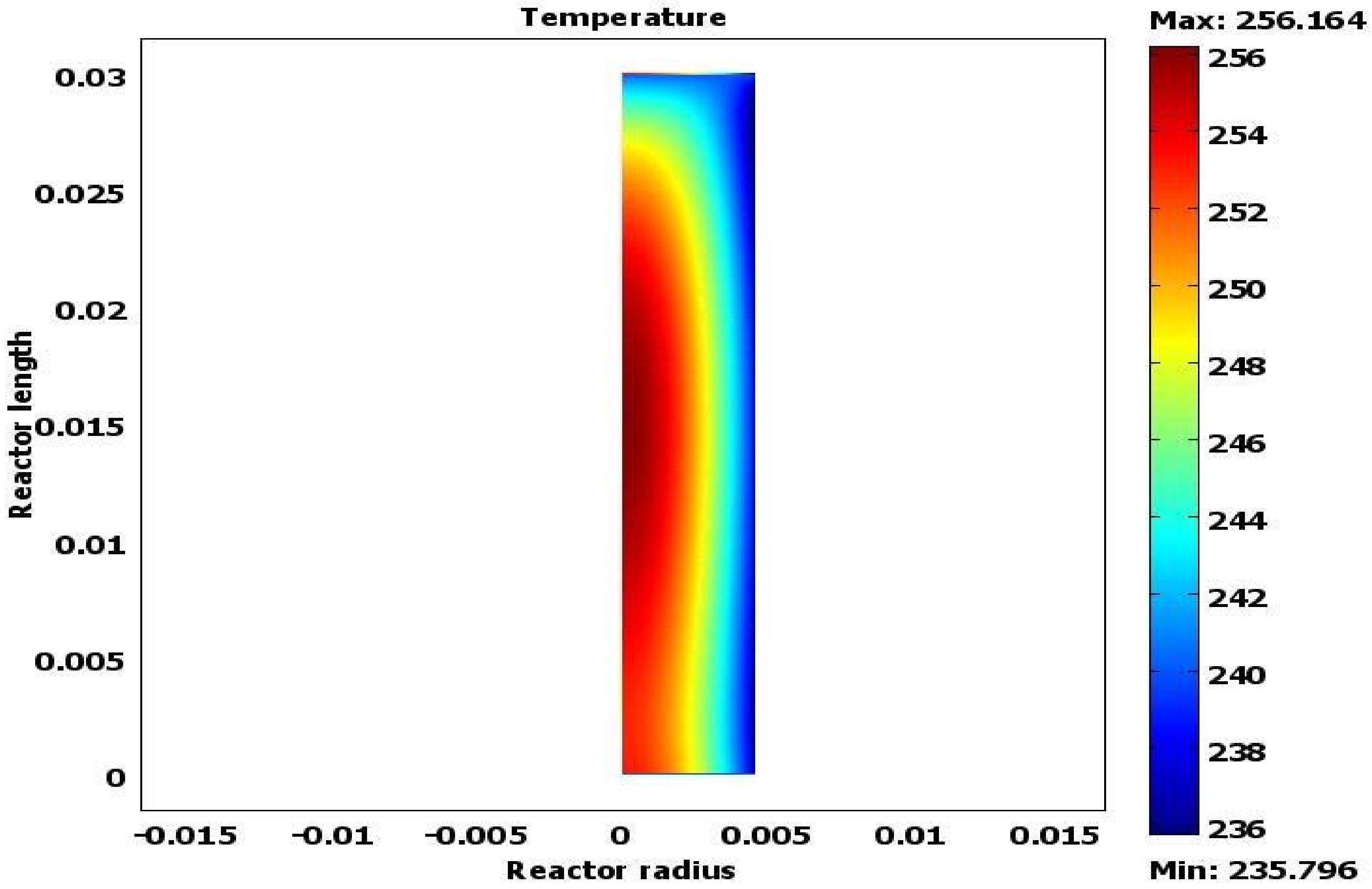
2D Simulation of the reactor



P=80 bars, T max= 255 C

2D Simulation of the reactor

The non-isothermal behaviour in Fixed Bed Reactor for exothermic reaction

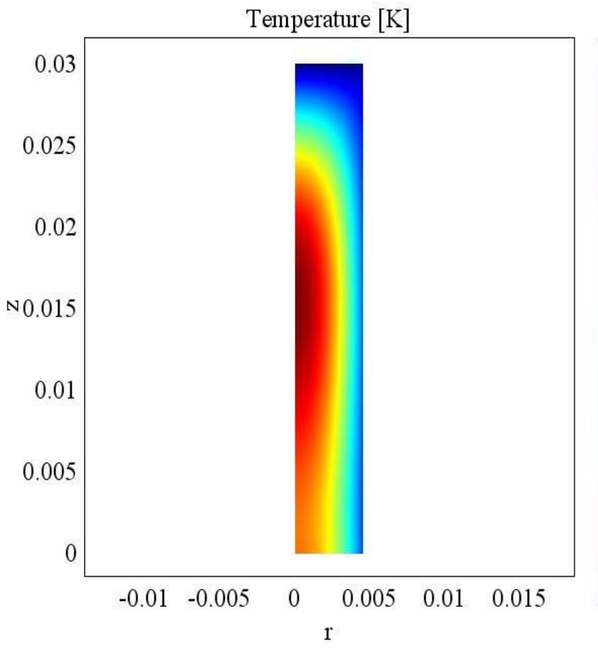


P=80 bars, T max= 255 C, Flow= 250 nml/min

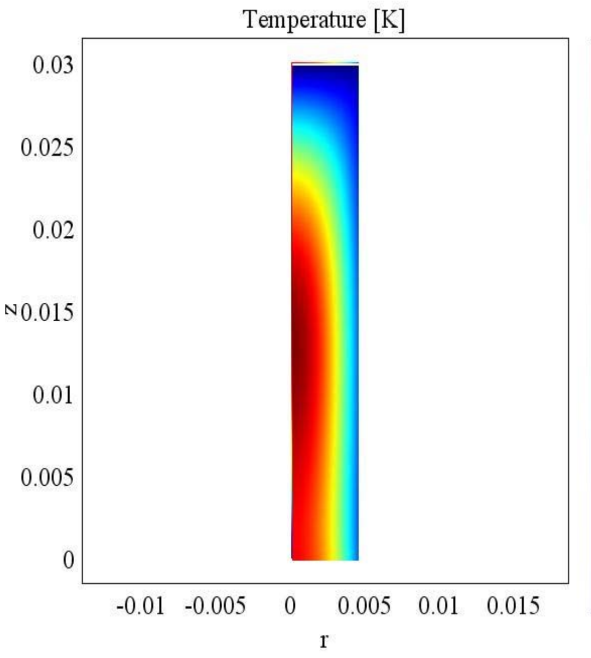
2D Simulation of the reactor

- Hot spot moves down the reactor length with increasng the flow

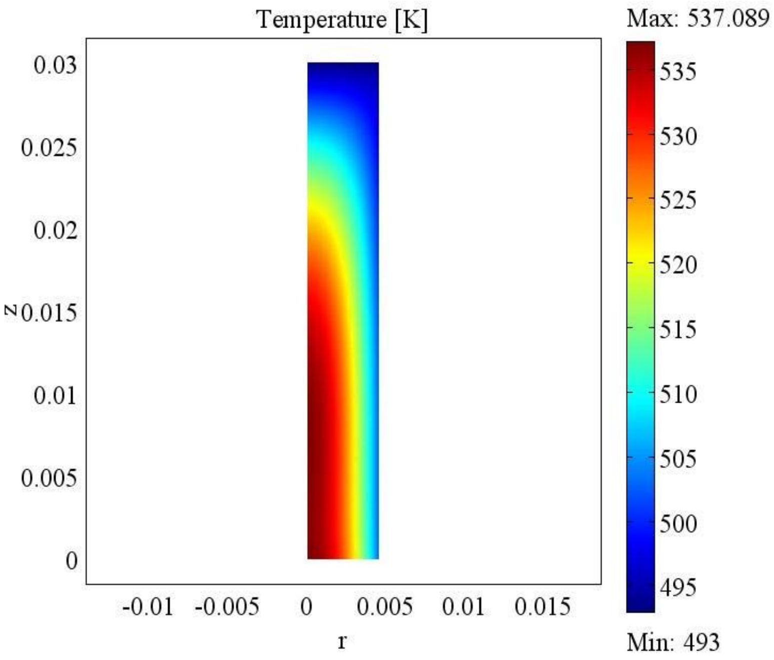
- Temperature distribution heavily affects the reactor performance



Syngas Flow= 250 nml/min



Syngas Flow= 500 nml/min



Syngas Flow= 750 nml/min

Conclusion

- The kinetic model is in a good agreement with similar published work2
- The 2D model considers both axial and radial dispersion of heat and mass and consequently provides a good tool for lab sacle studies
- With increasing gas velocity, CO conversion decreases and hot spot moves dwon the reactor
- The well knwon thermal behaviuor of exothermic reactions in fixed bed reactors could be predicted by this model
- Based on the knowledge gained in this work, the next step of this research is to build up a model for methanol synthesis in a microstructured heat exchanger - packed bed reactor

Thanks for your kind attention!