FRITZ-HABER-INSTITUT

MAX-PLANCK-GESELLSCHAFT

Modern Methods in Heterogeneous Catalysis Research

TRANSPORT PHENOMENA

10/31/08

Giulio Lolli

Outline

- Part I - Theory
  - Why Transport?
  - Fundamental equations
  - Unified approach to transport phenomena
  - Boundary Layer approach
  - Dimensionless numbers
- Part II - Practice
    - Example: Methanol Synthesis

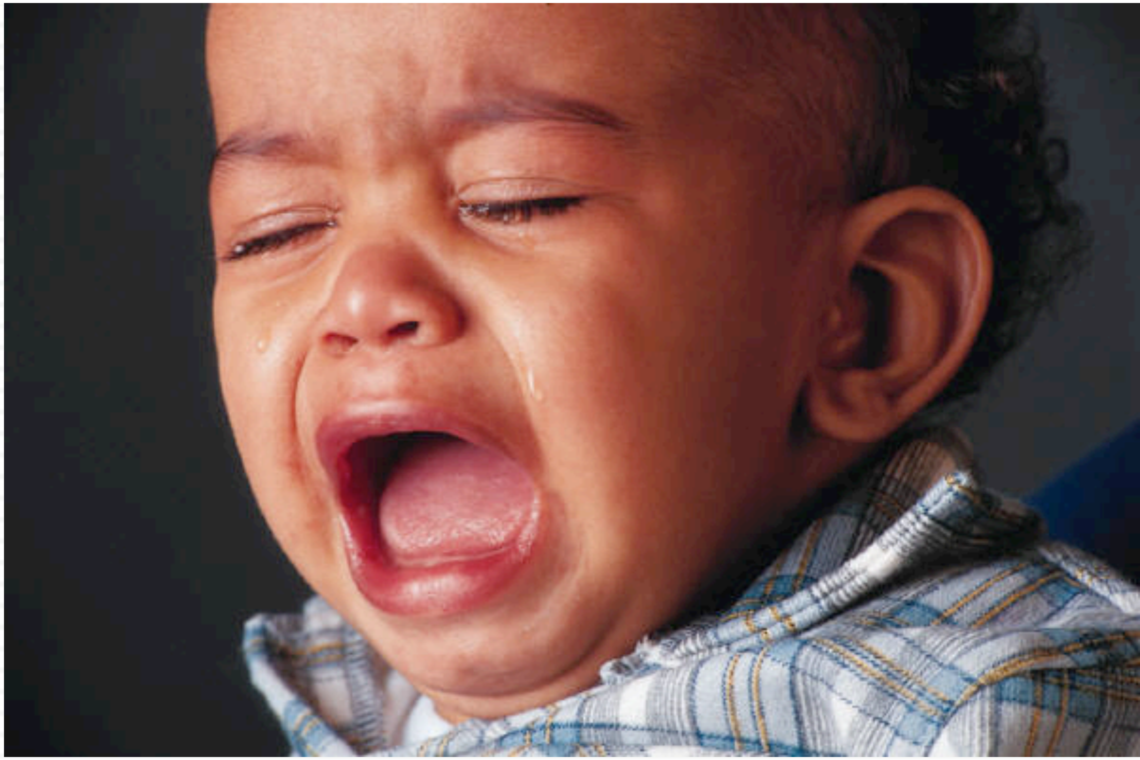
Further Reading

- Part I
  - Bird, Steward, Lightfoot
    - Transport Phenomena
  - Asano Welty

    Mass Transport Fundamentals of M,H&M Transfer
- Part II
  - Handout
    - Web: Document DB # 15375
  - Perry's Chemical Engineering Handbook

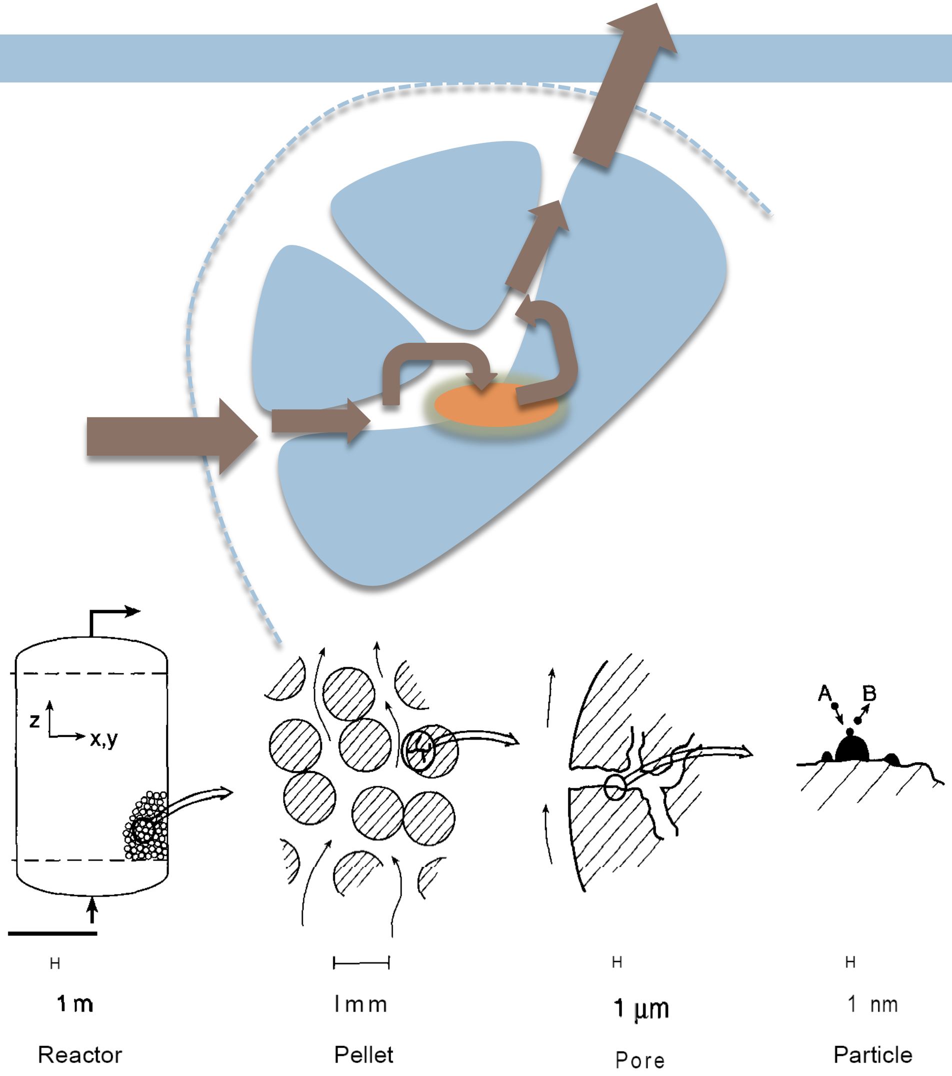
Part I

Theory



Why Transport? Catalytic Process

- Thermodynamic
  - Reaction Equilibrium
  - Phase equilibrium: adsorption/desorption
- Kinetic
  - Reaction Kinetic
- Transport
  - Reactants/Product to/from the active sites
  - Heat to/from the active site



Transport Phenomena

Type of transport	**What is transferred**
Momentum Transport $\vec{\tau}_{xy} = -\mu \frac{\partial \vec{u}_y}{\partial x}$	Kinetic **Energy** Newton's Law
Heat Transport $q_x = -k \frac{\partial T}{\partial x}$	Thermal **Energy** Fourier's Law
Mass Transport $j_{A,x} = -D_A \frac{\partial C_A}{\partial x}$	Chemical **Energy** Fick's Law

First Law of transport

$$\vec{\tau}_{xy} = -\mu \frac{\partial \vec{u}_y}{\partial x} \qquad q_x = -k\frac{\partial T}{\partial x} \qquad j_{A,x} = -D_A\frac{\partial C_A}{\partial x}$$

$$\vec{\vec{T}} = -\mu\vec{\nabla}\vec{u} \qquad \vec{q} = -k\vec{\nabla}T \qquad \vec{j}_A = -D_A\vec{\nabla}C_A$$

$$\vec{\Phi} = -\sigma\vec{\nabla}\varphi_A$$

Math 101- Gradient

$$\vec{\nabla} = \begin{bmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{bmatrix} \quad \vec{\nabla} S = \begin{bmatrix} \frac{\partial S}{\partial x} \\ \frac{\partial S}{\partial y} \\ \frac{\partial S}{\partial z} \end{bmatrix}$$

Second Law of Transport

$$\rho\frac{D\vec{u}}{Dt} = \mu\nabla^2\vec{u}+\rho\vec{g}-\vec{\nabla}p$$

- Navier-Stokes

$$\rho C_p\frac{DT}{Dt} = k\nabla^2 T+\mu\phi_u-r\Delta H_{rxn}$$

- 2nd Fourier's

$$\frac{DC_A}{Dt} = D_A\nabla^2 C_A+\nu_A r$$

- 2nd Fick

$$\frac{D\varphi}{Dt} = \sigma\nabla^2\varphi$$

Math 102 – Divergence & Laplace

$$\vec{\nabla} = \begin{bmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{bmatrix} \quad \vec{\nabla} S = \begin{bmatrix} \frac{\partial S}{\partial x} \\ \frac{\partial S}{\partial y} \\ \frac{\partial S}{\partial z} \end{bmatrix} \quad \vec{\nabla} \cdot \vec{V} = \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z}$$

$$\nabla^2 S = \vec{\nabla} \cdot \vec{\nabla} S = \frac{\partial^2 S}{\partial x^2} + \frac{\partial^2 S}{\partial y^2} + \frac{\partial^2 S}{\partial z^2}$$

Math 103 – Substantial Derivative

$$\vec{\nabla} = \begin{bmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{bmatrix} \quad \vec{\nabla} S = \begin{bmatrix} \frac{\partial S}{\partial x} \\ \frac{\partial S}{\partial y} \\ \frac{\partial S}{\partial z} \end{bmatrix} \quad \vec{\nabla} \cdot \vec{V} = \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z}$$

$$\nabla^2 S = \vec{\nabla} \cdot \vec{\nabla} S = \frac{\partial^2 S}{\partial x^2} + \frac{\partial^2 S}{\partial y^2} + \frac{\partial^2 S}{\partial z^2}$$

$$\frac{DS}{Dt} = \frac{\partial S}{\partial t} + \vec{u} \cdot \vec{\nabla} S = \frac{\partial S}{\partial t} + u_x \frac{\partial S}{\partial x} + u_y \frac{\partial S}{\partial y} + u_z \frac{\partial S}{\partial z}$$

Equations of Motion

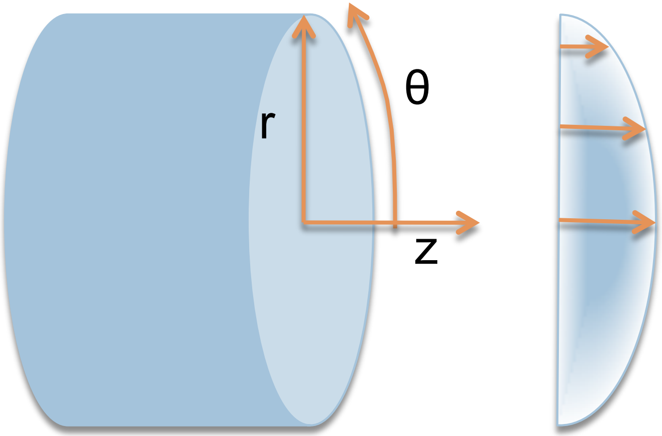
$$\rho \frac{D\vec{u}}{Dt} = \mu \nabla^2 \vec{u} + \rho \vec{g} - \vec{\nabla} p$$

$$\rho C_p \frac{DT}{Dt} = k \nabla^2 T + \mu \phi_u - r \Delta H_{rxn}$$

$$\frac{DC_A}{Dt} = D_A \nabla^2 C_A + \nu_A r$$

$$\vec{\nabla} \cdot (\rho \vec{u}) = 0$$

Example



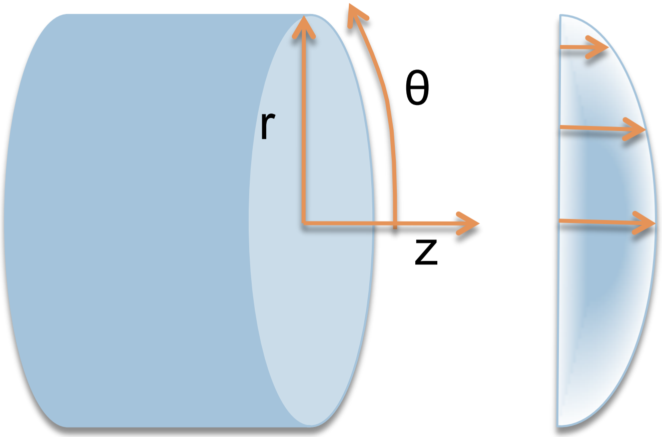
- Start-up in circular tube
  - Cylindrical coordinates
  - Only $v_z(r) \neq 0$

Example: startup in circular tube only $u_z(r) \neq 0$

$$\rho \frac{\partial u_z}{\partial t} + \cancel{u_z \frac{\partial u_z}{\partial z}} = \Delta p + \mu \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u_z}{\partial r} \right)$$

Example

$$\rho\frac{\partial u_z}{\partial t}+\cancel{u_z\frac{\partial u_z}{\partial z}}=\Delta p+\mu\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_z}{\partial r}\right)$$



In S.S. conditions $(\partial/\partial t=0)$

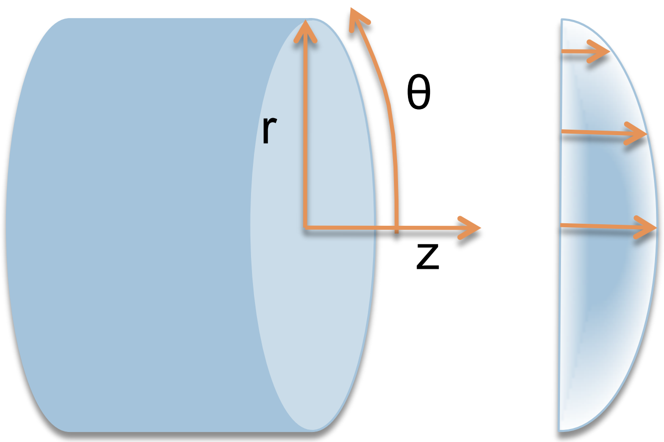
$$\frac{\partial}{\partial r}\left(r\frac{\partial u_z}{\partial r}\right)=-\frac{\Delta p}{\mu}r$$

$$\cancel{r}\frac{\partial u_z}{\partial r}=-\frac{\Delta p}{\mu}\frac{r^{\cancel{2}}}{2}+\cancel{\frac{A}{r}}\qquad B.C.\qquad \frac{\partial u_z}{\partial r}=finite\qquad r=0$$

$$u_z=-\frac{\Delta p}{\mu}\frac{r^2}{4}+B\qquad B.C.\qquad u_z=0\qquad r=R$$

$$u_z=\frac{\Delta p}{4\mu}\left(R^2-r^2\right)$$

$$\rho \frac{\partial u_z}{\partial t} + \cancel{u_z \frac{\partial u_z}{\partial z}} = \Delta p + \mu \frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial u_z}{\partial r}\right)$$



In non S.S. conditions !?!?!

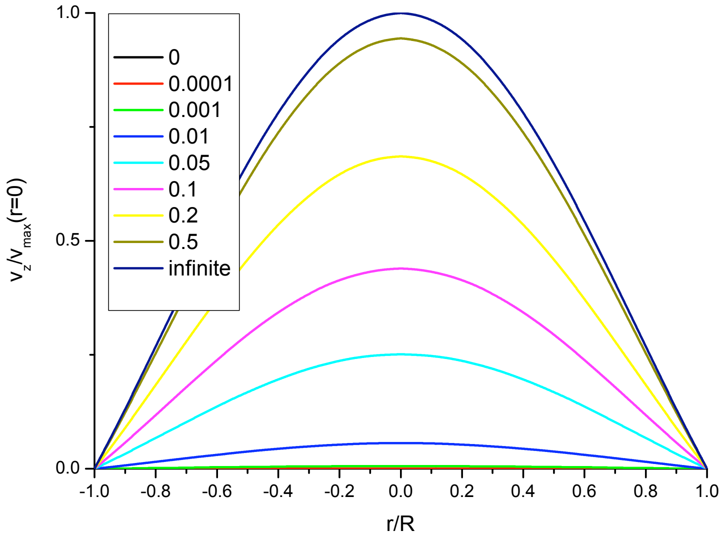
$$u_z = C_0 e^{-\alpha^2 \tau}\left(C_1 J_0(\alpha\xi) + C_2 Y_0(\alpha\xi)\right)$$

J_0 and Y_0 are Bessel functions of the first and second kind of order 0.

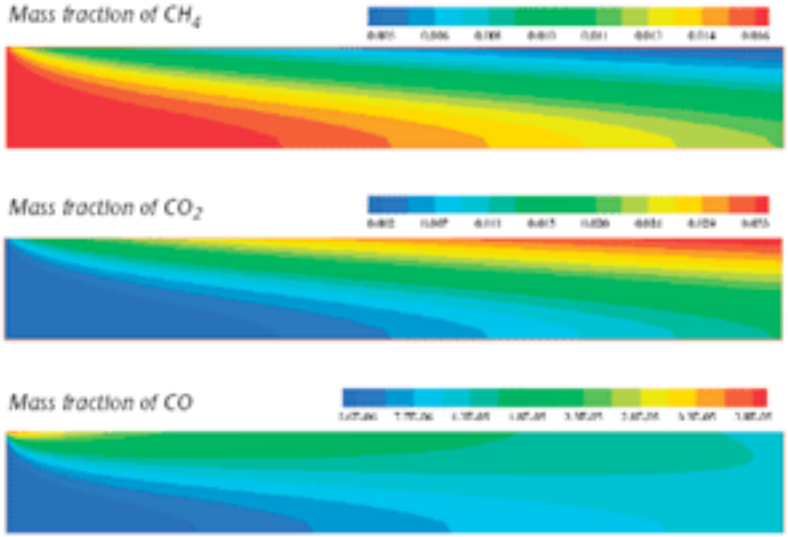
$$u_z = C_0 e^{-\alpha^2 \tau}\left(C_1 J_0(\alpha\xi) + C_2 Y_0(\alpha\xi)\right)$$

$$J_n(x) = \sum_{k=0}^{\infty} \frac{(-1)^k \left(\frac{x}{2}\right)^{n+2k}}{k!\,\Gamma(n+k+1)}$$

$$Y_n(x) = \lim_{p \to n} \frac{J_p(x)\cos(p\pi) - J_{-p}(x)}{\sin(p\pi)}$$

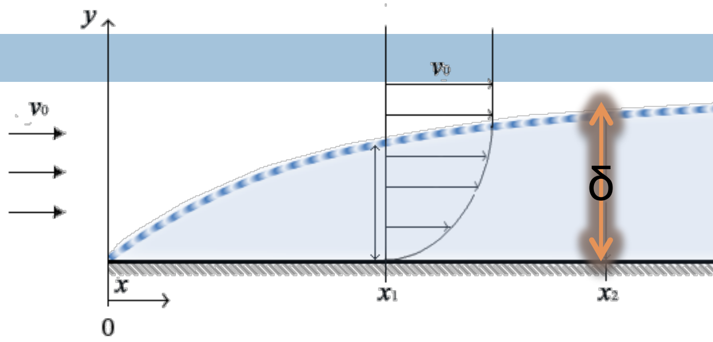


Numerical Solution



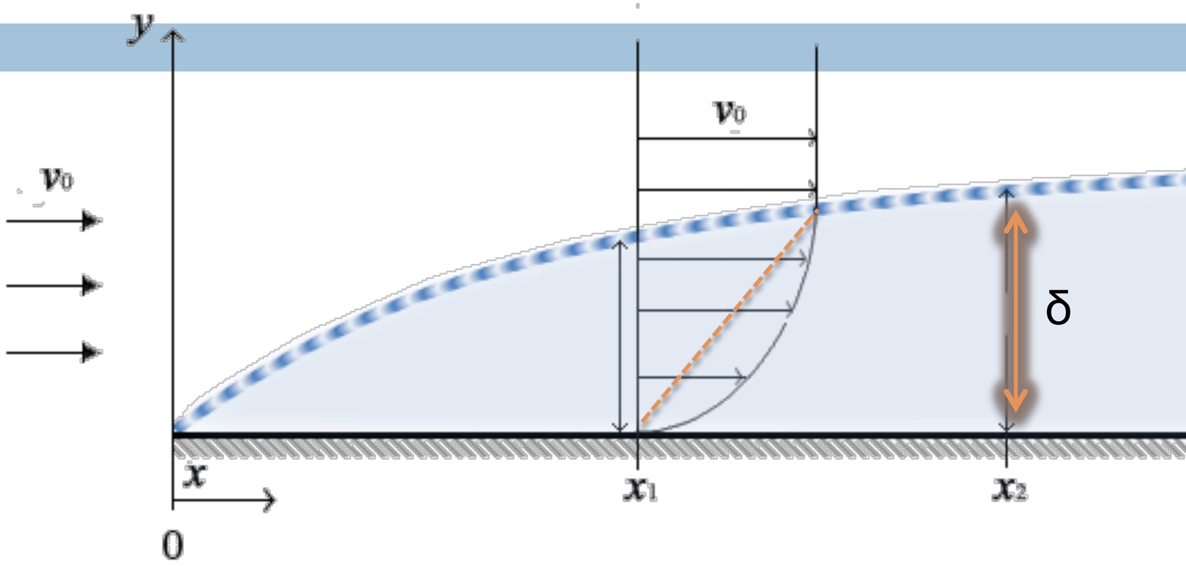
- Finite elements approach
- Software packages
  - *Fluent*
  - CFD
  - Physics
- Set up the correct problem and boundary conditions
- Many times is not necessary to know the exact T,C,v of every single point in your system

Boundary Layer



- All the phenomena happen in the boundary layer
  - Everything outside the boundary layer is in equilibrium and constant
- The boundary layer is very "thin"
  - The size of the boundary layer (δ) is smaller than the characteristic size of the system
  - Order of magnitude approach
    - Taylor series

Reynold's Number



$$\rho \frac{D\vec{u}}{Dt} = \mu \nabla^2 \vec{u}$$

$$\rho u \frac{\cancel{\Delta} u}{x} \approx \mu \frac{\cancel{\Delta} u}{\delta^2}$$

$$\left(\frac{\delta}{x}\right)^2 \approx \frac{\mu}{\rho u x} = 1/Re$$

$$Re = \frac{\rho u x}{\mu}$$

Prandtl's Number

$$u_T = u\delta_T/\delta$$

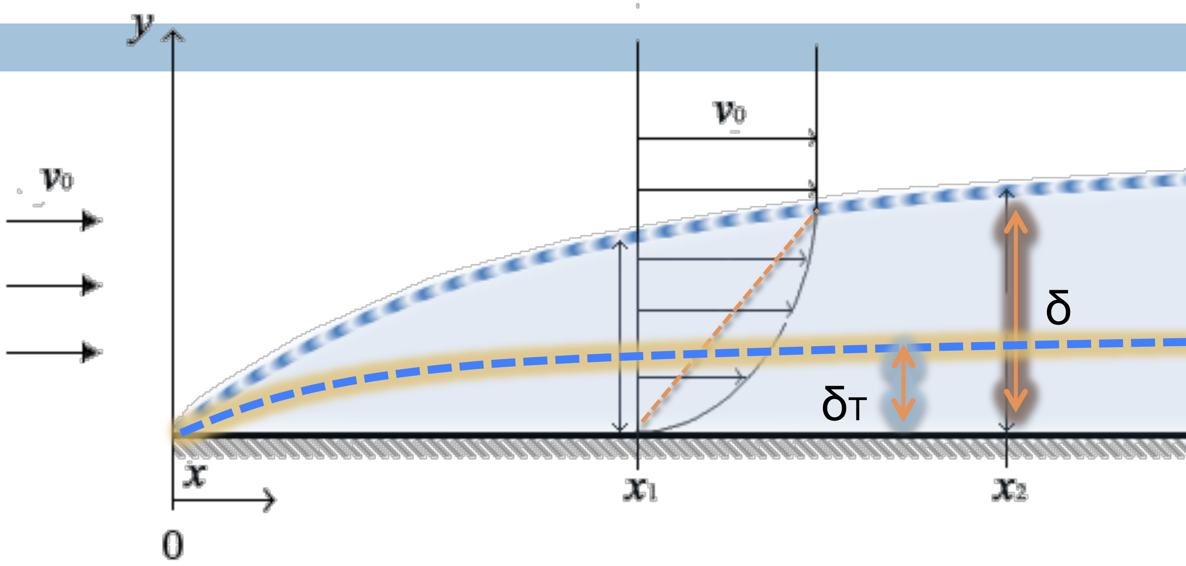
$$\rho C_p \frac{DT}{Dt} = k\nabla^2 T$$

$$\rho C_p u_T \frac{\cancel{\Delta T}}{x} \approx k\frac{\cancel{\Delta T}}{\delta_T^2}$$

$$\rho C_p u \frac{\delta_T}{\delta x} \approx \frac{k}{\delta_T^2}$$

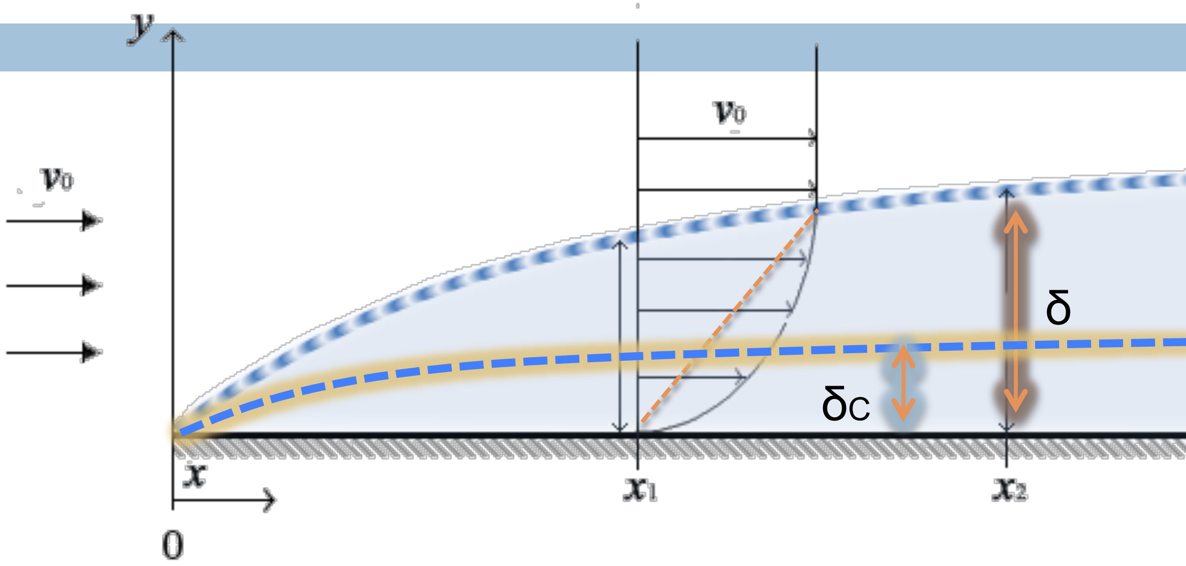
$$\left(\frac{\delta_T}{\delta}\right)^3 \approx \frac{k}{C_p\mu}$$

$$\frac{\delta_T}{\delta} \approx Pr^{-1/3}$$



$$Pr = \frac{C_p\mu}{k}$$

Schmidt's Number…

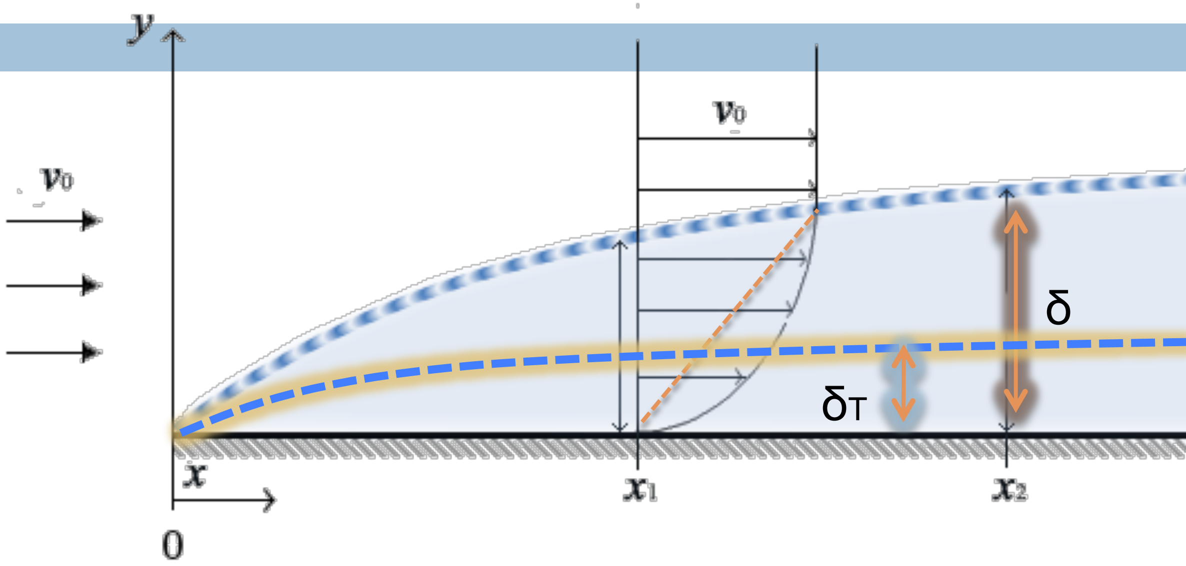


… As usual everything is the same

$$\frac{\delta_C}{\delta} \approx Sc^{-1/3}$$

$$Sc = \frac{\rho D_A}{\mu}$$

Nusselt's Number

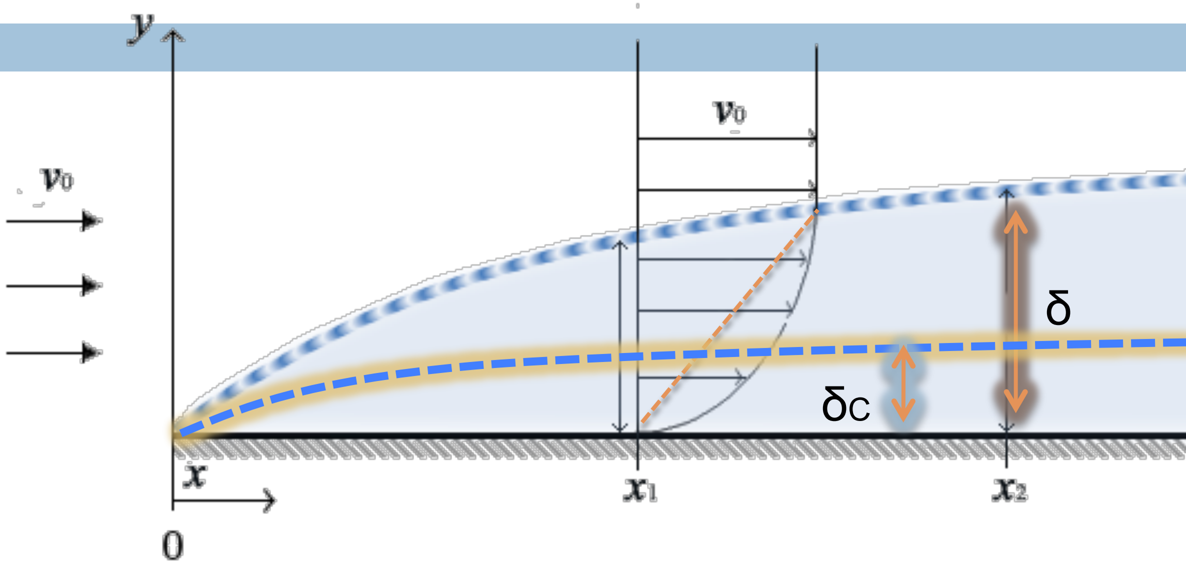


$$q = -k\frac{\partial T}{\partial x} = h\Delta T$$

$$h\cancel{\Delta T} \approx k\frac{\cancel{\Delta T}}{\delta_T}$$

$$Nu = \frac{hx}{k} \approx \underbrace{\frac{x}{\delta}}_{Re^{1/2}} \underbrace{\frac{\delta}{\delta_T}}_{Pr^{1/3}}$$

Sherwood's Number



$$q = -k\frac{\partial T}{\partial x} = h\Delta T$$

$$h\cancel{\Delta T} \approx k\frac{\cancel{\Delta T}}{\delta_T}$$

$$Nu = \frac{hx}{k} \approx \underbrace{\frac{x}{\delta}}_{Re^{1/2}} \underbrace{\frac{\delta}{\delta_T}}_{Pr^{1/3}}$$

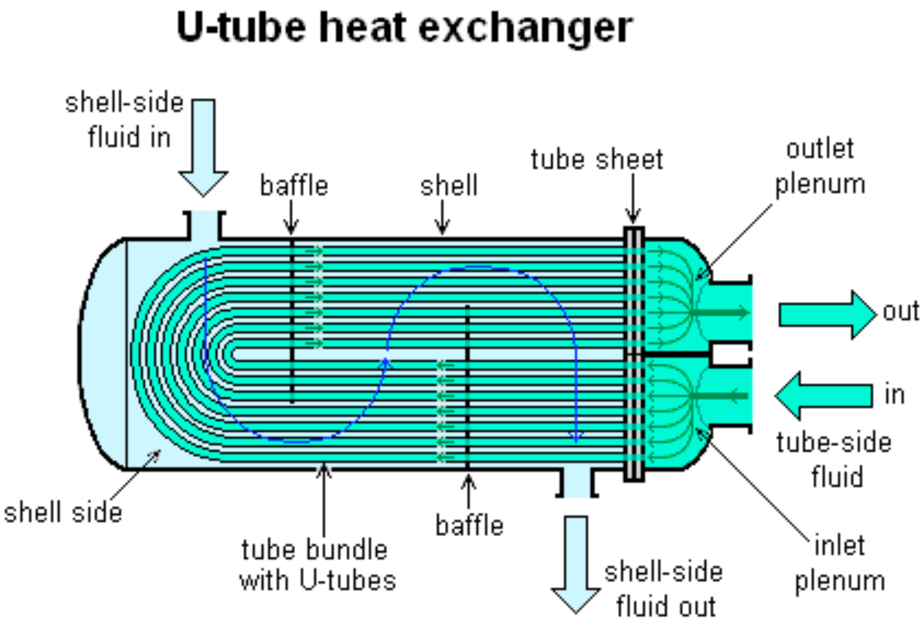
$$Sh = \frac{K_A x}{D_A} \approx \underbrace{\frac{x}{\delta}}_{Re^{1/2}} \underbrace{\frac{\delta}{\delta_C}}_{Sc^{1/3}}$$

In General…

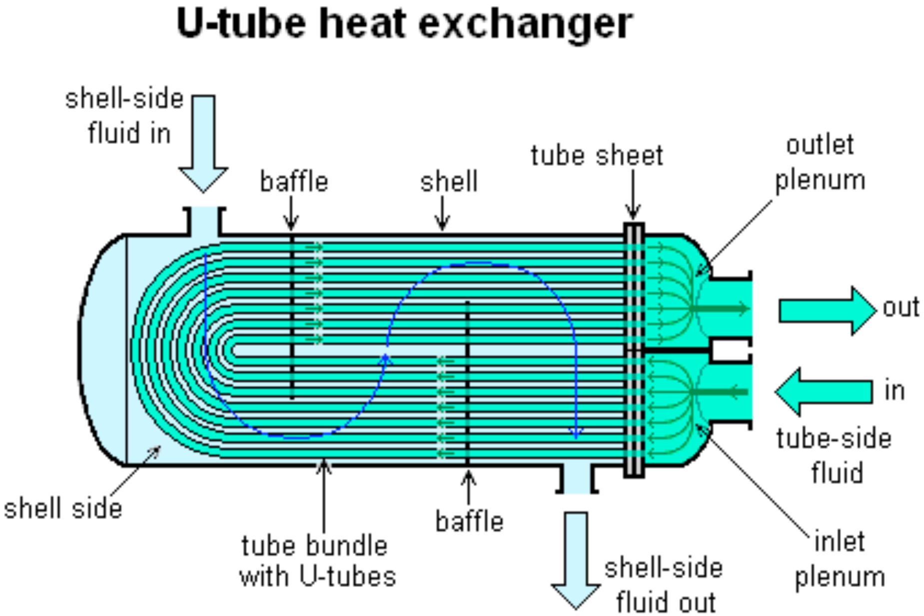
$$Nu = \frac{hx}{k} = f\left(Re\right) Pr^{1/3} \qquad Sh = \frac{K_A x}{D_A} = f\left(Re\right) Sc^{1/3}$$

$$f\left(Re\right) = \begin{cases} Re^{1/2} & \text{Plate in laminar flow} \\ 2 + Re^{1/2} & \text{Sphere in laminar flow} \\ 0.005 Re^{0.8} & \text{Packed bed in turbulent flow} \\ \ldots\ldots\ldots\ldots & \end{cases}$$

Extension to Macroscopic Balances



Overall Transfer Coefficient

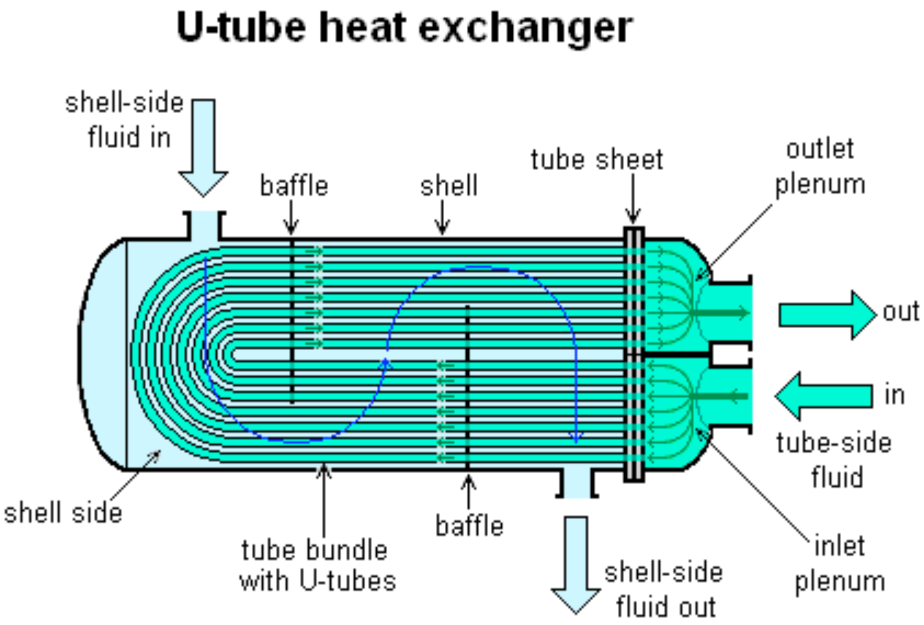


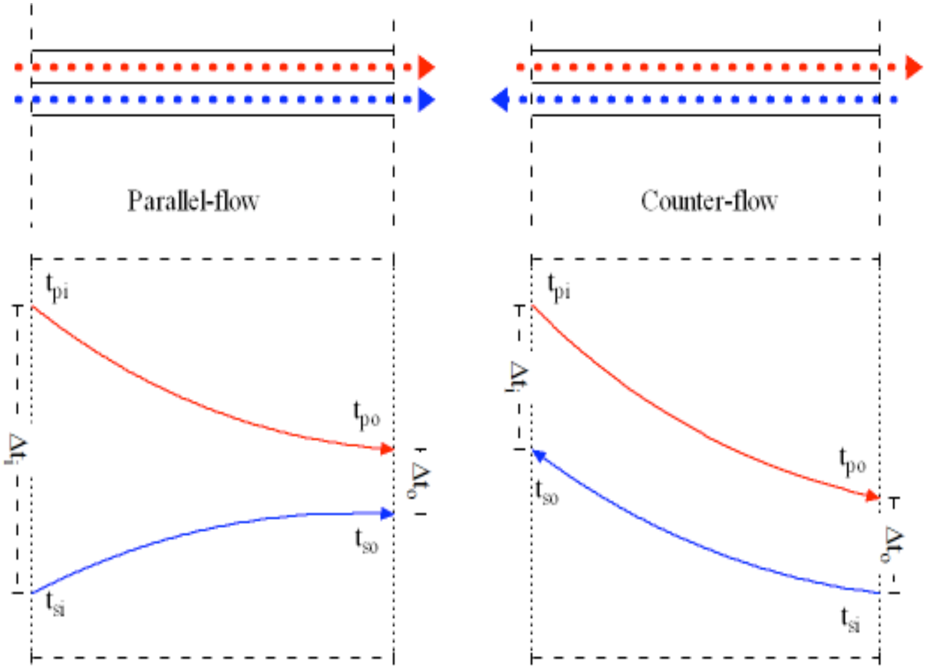
$$\dot{Q} = \int_A q\, dA = A\, U\, \Delta T$$

$$1/U = \sum 1/h_i + \sum s_i/k_i$$

$$1/U = 1/h_{int} + s/k_{metal} + 1/h_{ext}$$

Log-Mean Temperature Difference





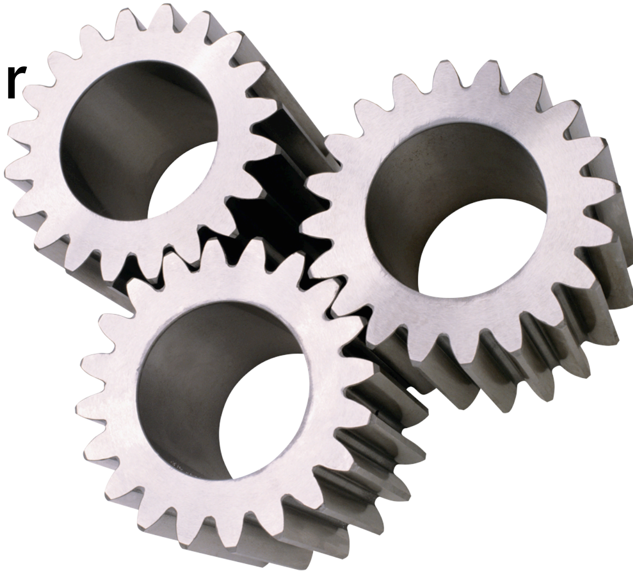
$$\dot{Q} = \int_A q\, dA = A\, U\, \Delta T$$

$$1/U = \sum 1/h_i + \sum s_i/k_i$$

$$1/U = 1/h_{int} + s/k_{metal} + 1/h_{ext}$$

$$\Delta T_{ln} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\Delta T_1/\Delta T_2\right)}$$

Conclusions



- Momentum, Heat and Mass Transfer
  - Highly inter-correlated
    - Similar physical principles
    - Similar driving force
    - Similar mathematical formulas
  - 2nd order PDE – numerical solutions
  - Highly dependent from fluid-dynamic properties
  - Simplifications
    - Boundary layer
    - Dimensionless numbers

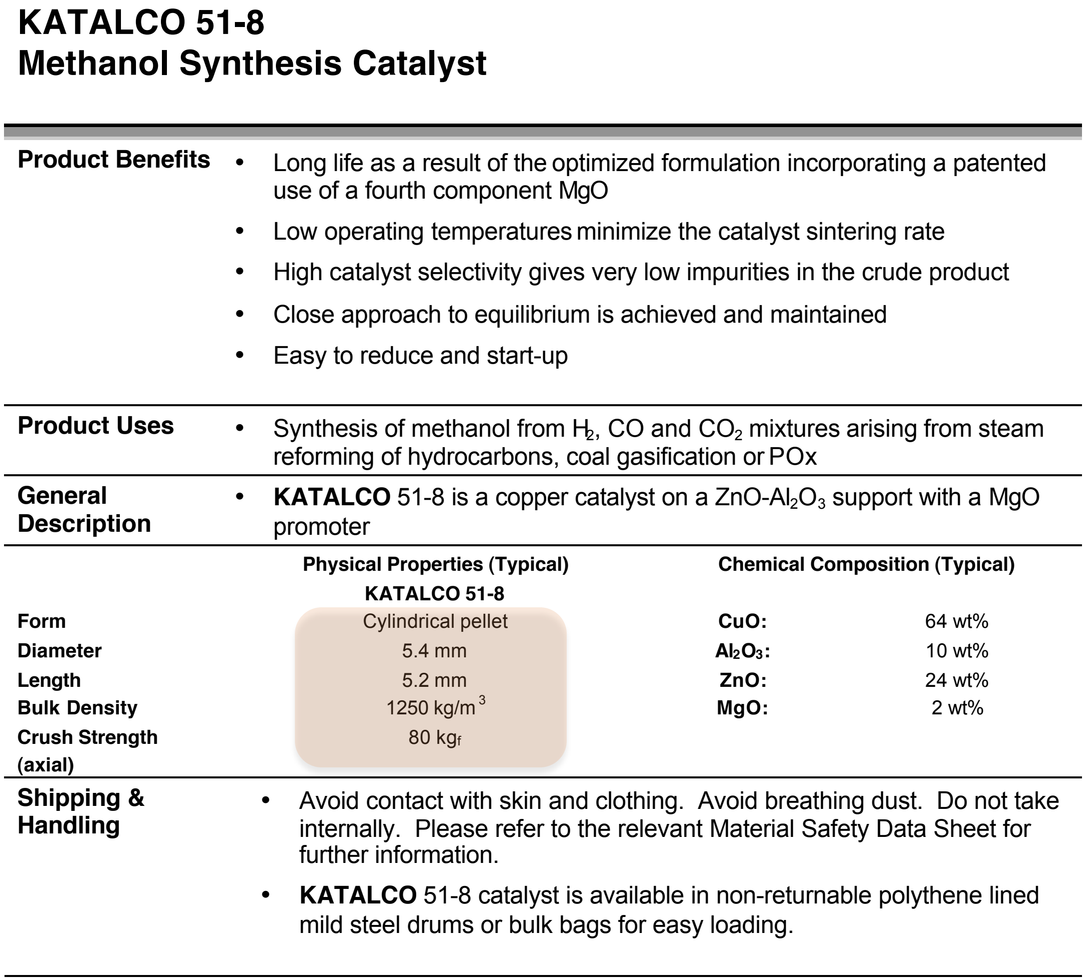
PART II

Methanol Synthesis

Methanol Production

- Produced from SynGas
  - Catalyst $Cu/ZnO\text{-}Al_2O_3$
  - Equilibrium limited
    - P = 50 – 100 bar
    - T = 200 – 300 °C
- Main Commodity
  - 20 Million ton/year
- Typical plant size is 1 Million ton/year
  - 12 m^3/s

Catalyst specs



KATALCO 51-8
Methanol Synthesis Catalyst

Product Benefits

- Long life as a result of the optimized formulation incorporating a patented use of a fourth component MgO
- Low operating temperatures minimize the catalyst sintering rate
- High catalyst selectivity gives very low impurities in the crude product
- Close approach to equilibrium is achieved and maintained
- Easy to reduce and start-up

Product Uses

- Synthesis of methanol from H_2, CO and CO_2 mixtures arising from steam reforming of hydrocarbons, coal gasification or POx

General Description

- **KATALCO** 51-8 is a copper catalyst on a ZnO-Al_2O_3 support with a MgO promoter

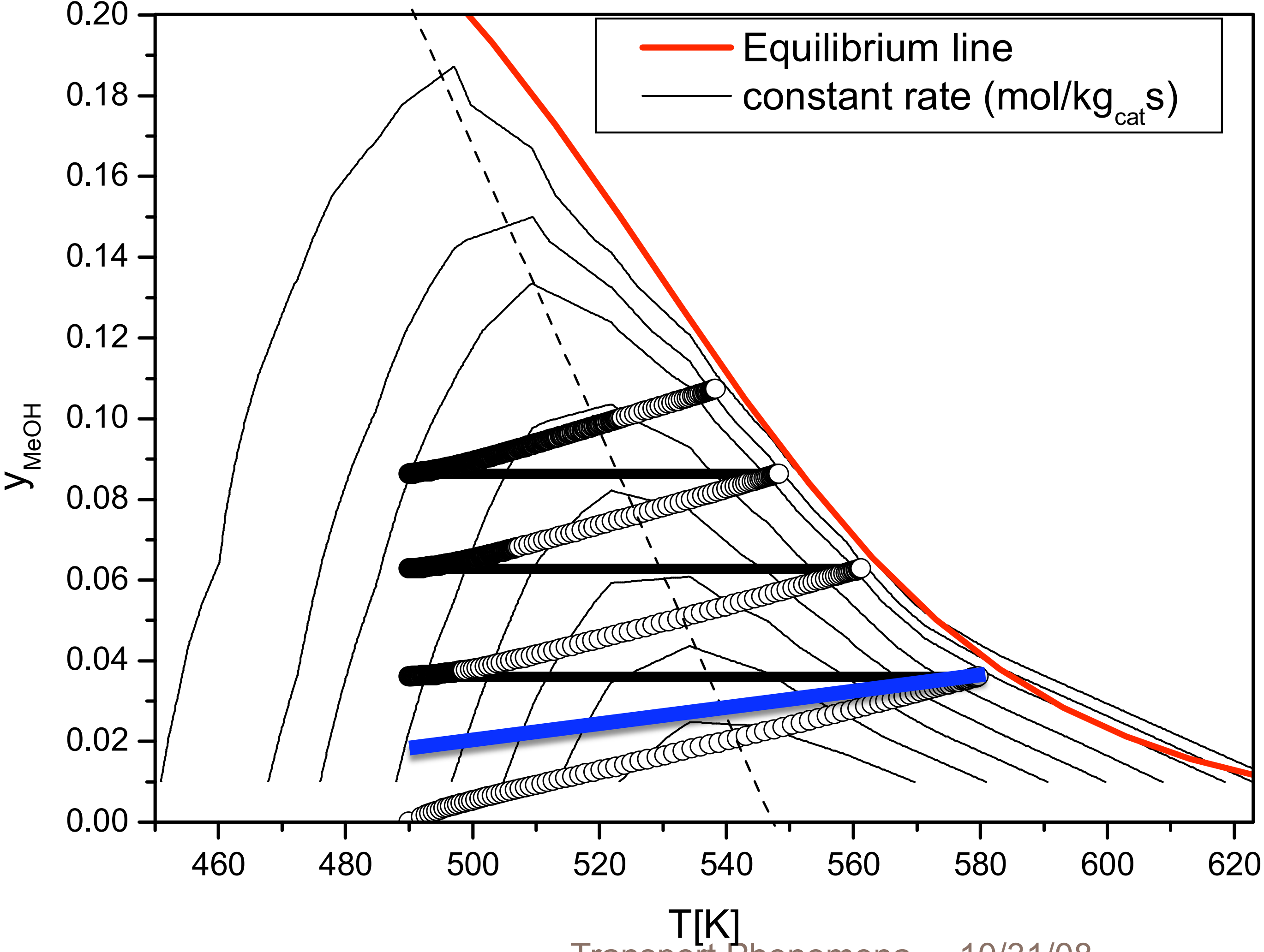
	Physical Properties (Typical) KATALCO 51-8	Chemical Composition (Typical)	
Form	Cylindrical pellet	**CuO:**	64 wt%
Diameter	5.4 mm	**Al_2O_3:**	10 wt%
Length	5.2 mm	**ZnO:**	24 wt%
Bulk Density	1250 kg/m^3	**MgO:**	2 wt%
Crush Strength (axial)	80 kg$_f$		

Shipping & Handling

- Avoid contact with skin and clothing. Avoid breathing dust. Do not take internally. Please refer to the relevant Material Safety Data Sheet for further information.
- **KATALCO** 51-8 catalyst is available in non-returnable polythene lined mild steel drums or bulk bags for easy loading.

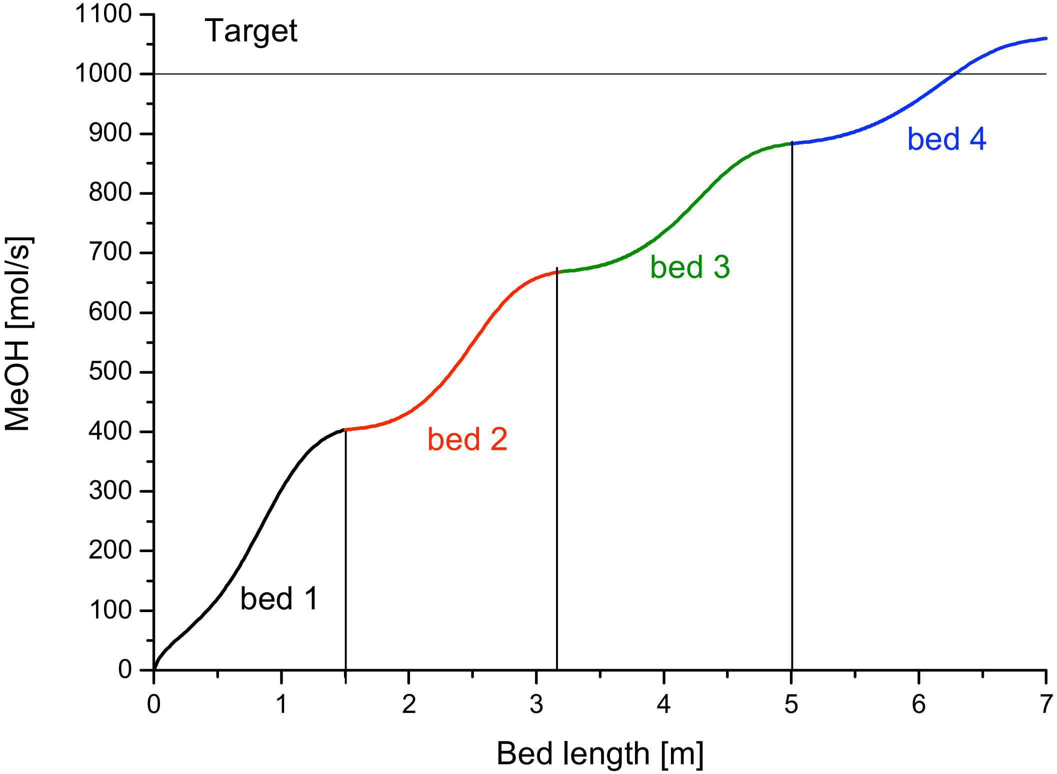
Reactor types

Multi-Bed Reactor



Reactor dimensioning

- 1 m/s wanted gas velocity
  - 12 m^2 section – approx 4 m diameter
  - Approx 7 m tall



Pressure Drop

$$\frac{P}{P_0} = \sqrt{1 - \frac{2\beta_0 L}{P_0}}$$

$$\beta_0 = \frac{G\varepsilon_b}{\rho_o D_p \left(1-\varepsilon_b\right)^3}\left(\frac{150\varepsilon_b \mu}{D_p} + 1.75G\right)$$

- To have 1 bar pressure drop D_p= 5 mm

Internal Mass Transfer Limitation

$$\phi_{\max} = R\sqrt{\frac{r_{\max}\rho_{cat}}{C_A D_{AB_{eff}}}}$$

Considering[6]:

$$r_{\max} = 0.05 \, {}^{mol}/_{kg_{cat} s}$$

$$\rho_{cat} = 1980 \, {}^{kg}/_{m^3}$$

$$C_{tot} = \frac{1}{V} = \frac{P}{RT} = 1003 \, {}^{mol}/_{m^3}$$

$$D_{CO_{eff}} = 5.67E-8 \, {}^{m^2}/_{s}$$

- At *least* 85% catalyst efficiency

$$\eta = \frac{3}{\phi^2}\left(\frac{\phi}{tgh\phi} - 1\right)$$

  - $\phi = 1.7$
  - R = 0.5 mm

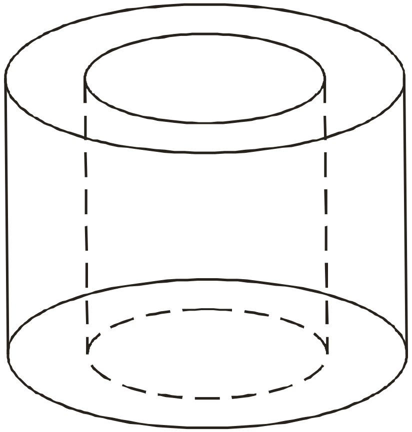
Pressure Drop

$$\frac{P}{P_0} = \sqrt{1 - \frac{2\beta_0 L}{P_0}}$$

$$\eta = \frac{3}{\phi^2}\left(\frac{\phi}{tgh\phi} - 1\right)$$

$$\beta_0 = \frac{G\varepsilon_b}{\rho_o D_p \left(1-\varepsilon_b\right)^3}\left(\frac{150\varepsilon_b \mu}{D_p} + 1.75G\right)$$

- To have 1 bar pressure drop $D_p > 5$ mm
- To have 85% cat efficiency $D_p < 1$ mm



External properties

Nusselt and Sherwood Numbers

$$\mathrm{Re} = \frac{\rho v D_p}{\mu} = 3760$$

$$\mathrm{Pr} = \frac{\mu Cp}{k} = 0.242$$

$$Sc = \frac{\mu}{\rho D_{bulk}} = 0.831$$

$$h = 725 \frac{J}{m^2 s K}$$

$$k = 13.2 \frac{mol}{m^2 s}$$

Colburn Factors

$$J_D = \frac{k_y}{v_{gas} C_{tot}} Sc^{2/3} = \frac{20.4}{\varepsilon_b} \mathrm{Re}^{-0.815}$$

$$J_H = \frac{h}{v_{gas} \rho_{gas} Cp_{gas}} \mathrm{Pr}^{2/3} = \frac{J_D}{0.95}$$

$$h = 610 \frac{J}{m^2 s K}$$

$$k = 65.6 \frac{mol}{m^2 s}$$

External Limitations

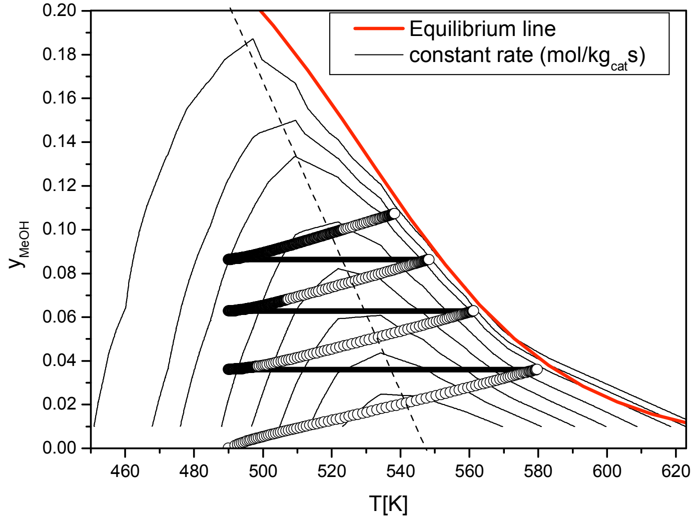
$$\Delta T_{\max} = \rho_{cat}\varepsilon_b r_{\max}\Delta H_{rx}\frac{D_p}{6h} = 3.1K$$

$$\Delta y_{\max} = \frac{D_p r_{\max}}{6k_y} = 6.35E-7$$

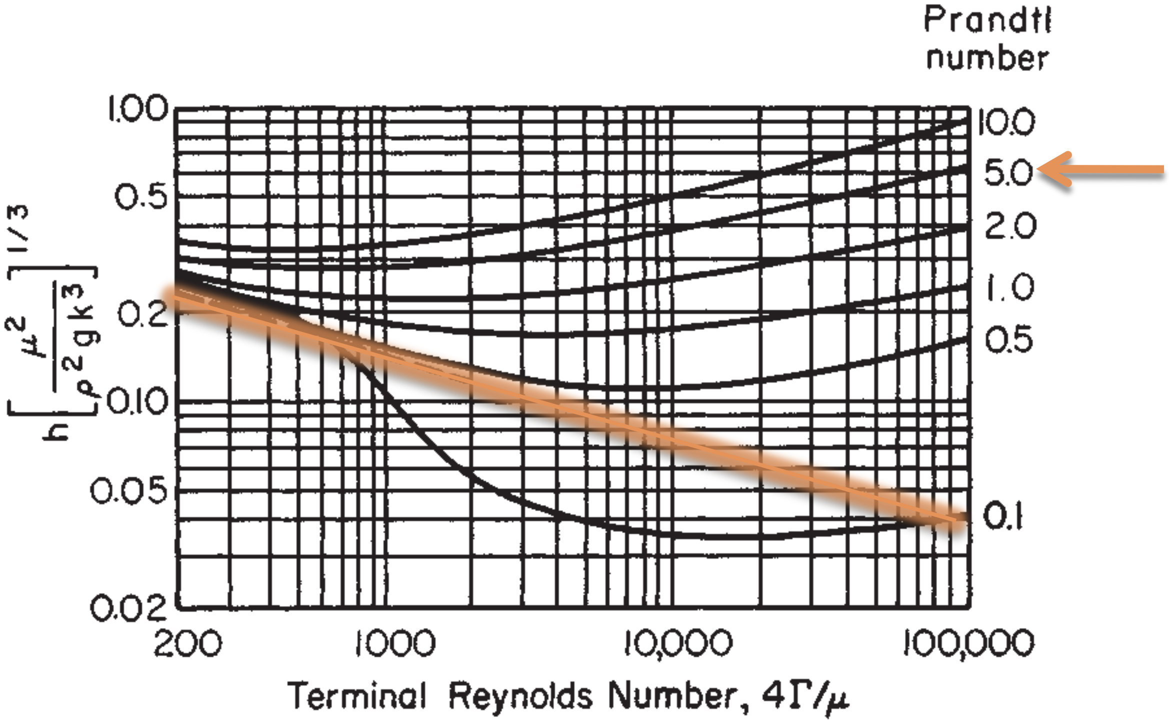
- No external limitations in terms of gas composition and temperature profile
  - Due to the turbulent flow regime

Heat Exchanger

- 1st bed 580 ➔ 490 K
  - 35 MW power to take out
  - Boiling water to produce low pressure steam
    - 16 kg/s steam produced
  - Shell tube heat exchanger: 2” (5cm) tubes
    - h_{out}=220 W/m^{2}K
    - U ≈ 200 W/m^{2}K



Evaporation/condensation



Pr water ≈ 7

FIG. 5-10 Dukler plot showing average condensing-film coefficient as a function of physical properties of the condensate film and the terminal Reynolds number. (Dotted line indicates Nusselt theory for Reynolds number < 2100.) [*Reproduced by permission from* Chem. Eng. Prog., **55,** *64 (1959).*]

Heat Exchanger

- 1st bed 580 → 490 K
  - 35 MW power to take out
  - Boiling water to produce low pressure steam
    - 16 kg/s steam produced
  - Shell tube heat exchanger: 2" (5cm) tubes
    - h_{out}=220 W/m^2K
    - U ≈ 200 W/m^2K
  - Low pressure steam 1-2 atm 120°C
    - ΔT_{ln}= 140K
    - Exchange Area 1300 m^3 (about 2000 tubes)
    - 40 banks of 50 tubes (4-5 m in size)

Further Reading

- Part I
  - Bird, Steward, Lightfoot
    - Transport Phenomena
  - Asano — Welty

    Mass Transport — Fundamentals of M,H&M Transfer
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CHE 6723
ADVANCED KINETICS

METHANOL PROJECT

GIULIO LOLLI

METHANOL SYNTHESIS

The methanol synthesis from CO and H_2 is an exothermic reaction characterized by equilibrium. To shift the equilibrium forward, high pressure and low temperature is required. The temperature is the main issue, because it depends on the catalyst. The first catalyst used (ZnO/Cr_2O_3) had high working temperature, in the range 320-450°C. To achieve acceptable conversion high pressure (250-350 bar) were necessary. In the '60s ICI introduced an improved catalyst based on $Cu/ZnO/Al_2O_3$ that can work at much lower temperatures (200-270 °C) and this allows to reduce the working pressure to 50-100 bar without loosing in conversion. This is an important economic factor in the operation cost (less energy consumption in compression) and in the reactor costs (cheaper reactor and material). It derives from the water-gas shift reaction catalyst, and this allows to possibly convert directly CO_2 in CH_3OH and H_2O. An accurate catalytic study of this system shows that 2-3% CO_2 in the stream maximize the carbon conversion balancing the oxidizing effect of CO_2 and reductive of CO and H_2 increasing the catalyst activity. This make this catalyst suitable for a direct feed from the steam reformer or methane partial oxidation reactor.

THERMODYNAMIC

The reaction involved in the methanol synthesis can be summarized as follows:

(1) $CO + 2\,H_2 \Leftrightarrow CH_3OH$ ΔH= -22.63 kcal/mol
(2) $CO_2 + 3\,H_2 \Leftrightarrow CH_3OH + H_2O$ ΔH= -12.92 kcal/mol
(3) $CO_2 + H_2 \Leftrightarrow CO + H_2O$ ΔH= +9.71 kcal/mol

Since these 3 reaction are not independent (1+3 = 2) only 2 of them should be used in the modeling. In this works we consider (1) : direct methanol synthesis and (3) : reverse water gas shift.
The equilibrium constant can be expressed as function of the fugacities as follows:

$$K^{(1)}{}_{Meth} = \frac{f_{MeOH}}{f_{CO} f^2{}_{H_2}} = \frac{p_{MeOH}}{p_{CO} p^2{}_{H_2}} \frac{\varphi_{MeOH}}{\varphi_{CO} \varphi^2{}_{H_2}} = \frac{1}{p^2} \frac{y_{MeOH}}{y_{CO} y^2{}_{H_2}} K\phi_{Meth}$$

$$K^{(3)}{}_{RWGS} = \frac{f_{CO} f_{H_2O}}{f_{CO_2} f_{H_2}} = \frac{p_{CO} p_{H_2O}}{p_{CO_2} p_{H_2}} \frac{\varphi_{CO} \varphi_{H_2O}}{\varphi_{CO_2} \varphi_{H_2}} = \frac{y_{CO} y_{H_2O}}{y_{CO_2} y_{H_2}} K\phi_{RWGS}$$

The use of fugacities instead partial pressures is necessary due to the high process pressure and relatively low temperature. These thermodynamic data can be calculated easily using RKS equation of state[1] as shown in detail in appendix A.
In figure 1 is shown the trend of $K\phi_{Meth}$ and $K\phi_{RWGS}$ in function of T and P in an interval of typical reaction condition.

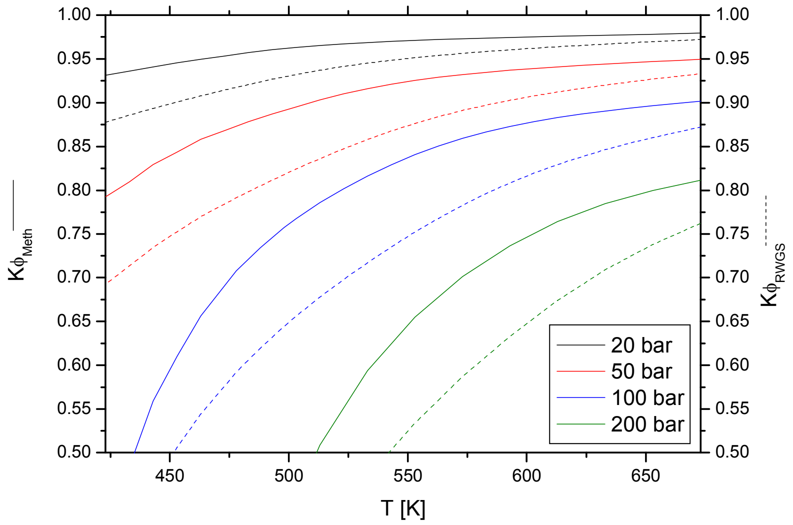


Figure 1. Kϕ in function of T and P

The thermodynamic equilibrium in function of temperature can be expressed using Arrhenius-like empirical correlations as follows[2]:

$$K_{Meth} = 9.740\times10^{-1}\exp\left[21.225+\frac{9143.6}{T}-7.492\ln T+4.076\times10^{-3}T-7.161\times10^{-8}T^{2}\right](bar^{-2})$$

$$K_{RWGS} = \exp\left[13.148-\frac{5639.5}{T}-1.077\ln T-5.44\times10^{-4}T+1.125\times10^{-7}T^{2}+\frac{49170}{T^{2}}\right]$$

It results to be quite unfavorable as shown in figure 2.

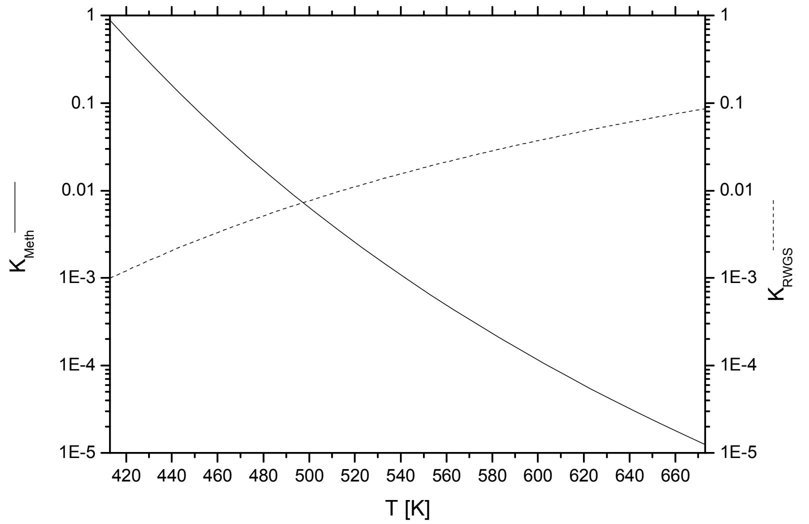


Figure 2. K in function of T

From them is possible calculate the equilibrium composition given a specific feed and conditions. A typical feed coming from a steam reformer used in the methanol synthesis, so without the shift converter, is as follows:

15%	CO
8%	CO_2
74%	H_2
3%	CH_4

In the CH_4 fractions are considered also traces of other inert that can be present in the natural gas feed.

Considering this inlet composition, the amount of methanol produced at equilibrium is plotted in figure 3.

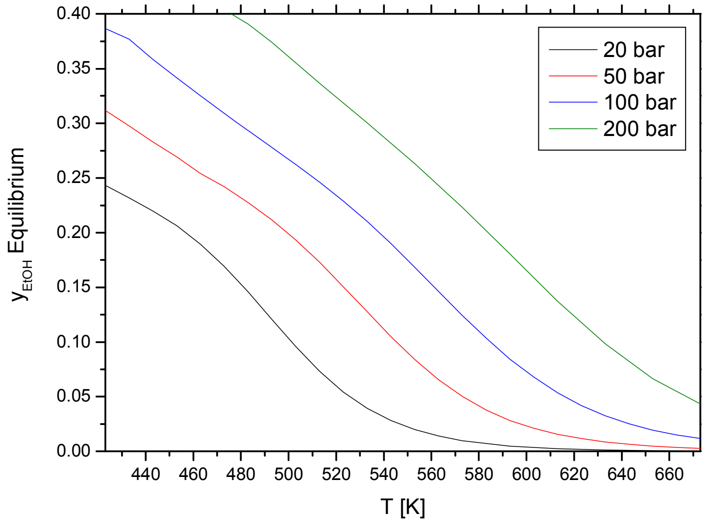


Figure 3. y_{MeOH} equilibrium in function of T and P for a feed as above

KINETIC

In the previous paragraph we have appreciated that for having a reasonable fraction of Methanol in the outlet gas, low temperature should be reached. In the past the main problem with the temperature was the activity of the catalyst. The first Methanol catalyst developed was a ZnO_2/Cr_2O_3 mixed oxide catalyst. It works in a temperature region of 320-450 °C. At this temperature very high pressures (> 100-200 bar) are necessary for having few % of MeOH in the exit.

The modern catalyst, much more active, composed of $Cu/ZnO/Al_2O_3$ and based on a redox cycle between the metallic Cu and the oxidized support (ZnO_2), can works at much lower temperature (180-300 °C) and this allows reducing sensibly the working pressure in the range 50-100 bar without loosing in conversion. Nowadays the trend is to reduce even more the pressure for minimize the energetic costs related to the compression and new processes are developed at pressures even below 50 bar.

Interesting is that if we plot Z (compressibility factor) in function of Temperature and Pressure (as shown in figure 4), in this milder conditions (50 bar) it is almost always between 0.98 and 1.02. This means that the non idealities are not so pronounced in this condition. This is explainable because the mixture is composed mainly by H_2 that has low T_c (33.3 K). When the reduced temperature T_c/T is high the non idealities given by the high pressure are reduced.

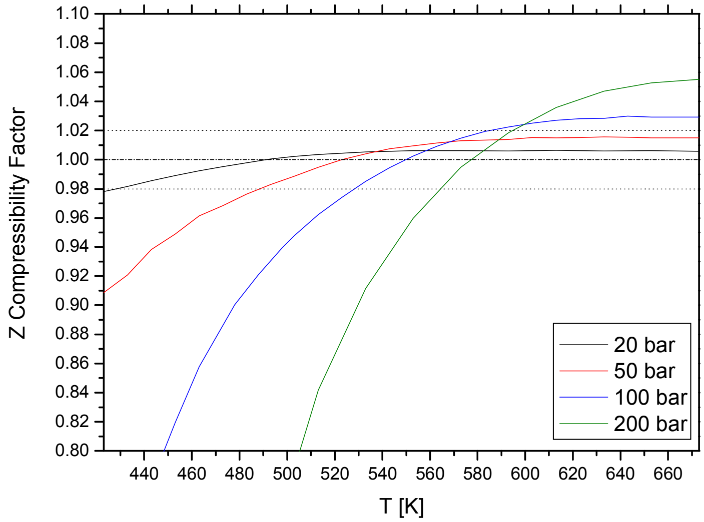


Figure 4. Z compressibility factor in function of T and P for the mixture as fed to the reactor.

Considering this, the most recent kinetic studies have repurposed the use of partial pressures instead fugacities in the kinetic expression obtaining very good fittings of the experimental data. The model proposed by Vanden Bussche and Froment[3] is based on an accurate study of the single elementary steps involved in the catalytic process using a LHHW-type kinetic. It results very complex because the different way CO_2 can absorb on the catalyst, direct absorption or bridge absorption. This makes the count of free active sites quite tedious. For a complete derivation of the kinetic see appendix B. The finals rate equations are the following:

$$r_{Meth} = \frac{C_4 p_{CO_2} p_{H_2}\left[1-\frac{1}{K_2}\frac{p_{H_2O}p_{MeOH}}{p_{H_2}^3 p_{CO_2}}\right]}{\left(1+C_3\frac{p_{H_2O}}{p_{H_2}}+C_1\sqrt{p_{H_2}}+C_2 p_{H_2O}\right)^3}\left(mol/kg_{cat}s\right)$$

$$r_{RWGS} = \frac{C_5 p_{CO_2}\left[1-\frac{1}{K_3}\frac{p_{H_2O}p_{CO}}{p_{H_2} p_{CO_2}}\right]}{\left(1+C_3\frac{p_{H_2O}}{p_{H_2}}+C_1\sqrt{p_{H_2}}+C_2 p_{H_2O}\right)}\left(mol/kg_{cat}s\right)$$

Vanden Bussche used the indirect methanol synthesis (from CO_2 instead CO) to calculate the rate of production of MeOH. Because the 3 reaction are linked together this is not important and the value of the equilibrium constant is easily calculated in the following way: $K_2=K_1K_3$

For a better result, remembering K=KpKϕ, in the rate equation is better plugging the value of Kp=K/Kϕ considering that the equation are given in partial pressures. Because Kϕ≈1 in mild condition (see figure 1), the error committed trascuring it is small.

With the values of the constants calculated in the following way[3]:

$$C_i = A_i \exp\left(-\frac{B_i}{R}\left(\frac{1}{T_{AV}} - \frac{1}{T} \right) \right)$$

		A_i	B_i (J/mol)
C_1	$\sqrt{K_{H_2}}$	30.82	17197
C_2	K_{H_2O}	558.17	124119
C_3	$K_{H_2O} / K_8 K_9 K_{H_2}$	3453.38	0
C_4	$k'_{5a} K'_2 K_3 K_4 K_{H_2O}$	7070.34	36696
C_5	k'_1	1.65	-94765

Where T_{AV} is the average temperature used as reference and is 501.57 K.

In figure 5 is reported the rate of methanol synthesis as function of temperature and methanol molar fraction. This is calculated forcing the RWGS reaction at the equilibrium. Considring that the ratio of the RWGS is generally higher than the rate of methanol synthesis, in first approximation is an hypothesis more than acceptable. The feed used for the simulation is the same described above and the pressure is fixed at 50 bar.

In figure 5 is also reported the locus of the maximum in the rate that result to be 20-40°C below the equilibrium temperature. For minimizing the reactor volume (and so the costs) is necessary following this line. Because it will be too complex and expensive a reactor with a temperature gradient along the length that follows exactly this path, the commercial process for the methanol synthesis are multi bed reactor with intermediate cooling or quenching or as in the case of Linde process a multi-tubolar isothermal reactor that work below this optimum line.

For a reactor dimensioning is sometime more useful a similar plot given versus conversion of the main reactant. This plot is shown in figure 6. In this plot the path along the reactor start at the inlet temperature and conversion 0 and increase almost linearly with a slope given by the ratio Cp/ΔH. When the line cross the locus of the maximum rate and starts to be too close to the equilibrium line, the first bed is ended and the gas is cooled down below the optimum line and start oscillating across this one till the wanted conversion is reached or no further significant progress is possible.

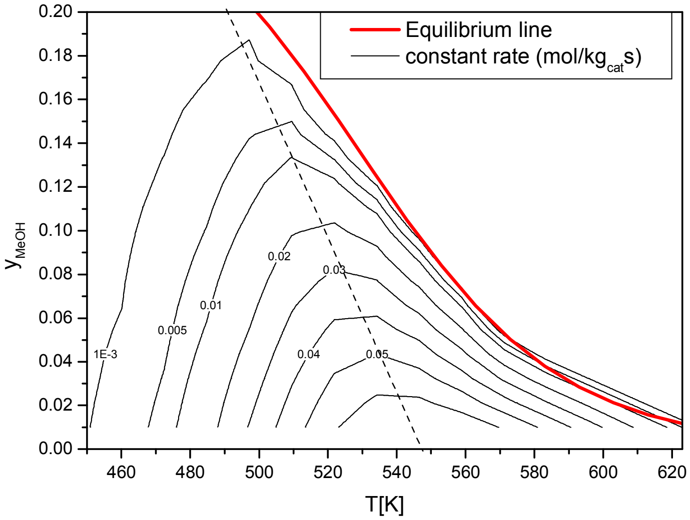


Figure 5. Reaction rate of the methanol production in function of T and composition. The RWGS was considered in equilibrium.

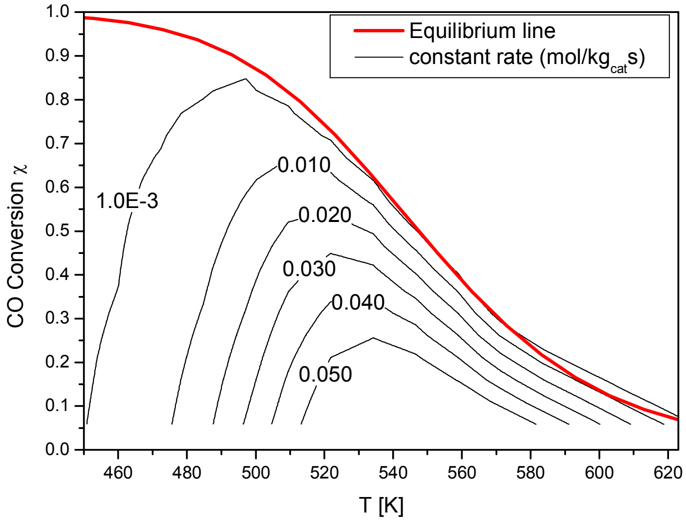


Figure 6. Reaction rate of the methanol production in function of T and CO conversion. The RWGS was considered in equilibrium.

CATALYST DESIGN

Before starting the study of the optimal catalyst configuration, in terms of pellet dimension, catalytic efficiency and eventually heat and mass transfer limitation, is a good choice to try a first very coarse simulation of the reactor. This helps in catching the order of magnitude of the project.
The methanol is one of the main commodities in organic chemistry. It's production is in the order of 15-20 millions of tons per year. It is very affected by the scale economy, so in the world there are very big methanol plants. The biggest was placed in the 2003 in Nigeria and has a nominal production of 2.48 millions of tons[4]. A more conventional plant is in the order of 0.5-1.5 millions of tons per year. In this study we will consider a plant for the production of 1 million of tons per year.

$$10^6\ ton/year \xrightarrow{8500\ h/year} 32.7\ kg/s \xrightarrow{32\ kg/kmol} 1\ kmol/s\ MeOH$$

$$\dot{F} = 12\ kmol/s \xrightarrow{1\ m^3/kmol} \dot{V} = 12\ m^3/s$$

Considering a wanted speed of 1 m/s, the reactor section should be 12 m^2 (∅=3.9 m)
For an accurate length we need to solve the differential equations for the packed bed reactor, but, if we pick an average reaction rate (from figure 5 for example) of 0.005 mol/kg s, we can estimate the length of the bed necessary to reach the wanted 1 kmol/s of methanol in exit. For a packed bed reactor with spherical pellets[5]:

$$L^2 = \frac{mv^2}{r\dot{V}\rho_c\varepsilon_b} = 12.56m^2$$

$$L = 3.54m$$

This value is highly underestimate because the reaction rate close to the exit is much lower and is calculated using a packing factor of 0.67 (spheres) that is one of the highest available. In every way it gives a reactor aspect ratio around 0.9 that is a good starting point. We can estimate that the real final length would be 2-3 times higher than this one, leading to a aspect ratio of 2-3 that is the ideal for catalytic reactors.

The methanol catalyst is Cu supported on ZnO and Al_2O_3. Even if it doesn't contain precious noble metals it's quite expensive because the purity of the catalyst is a key-role in the selectivity. Other transitions metals like Fe, Co, Mo catalyze the Fisher Tropsh reaction while traces of alkali promote higher alcohols synthesis. A good utilization of the catalyst is economically important. Moreover, being an alumina based catalyst (surface area 50-200 m^2/g), the internal diffusion limitations can be important. In presence of internal limitation the reduction of the particle size minimize these limitations but increase quadratically the pressure drop across the bed. In this case the use of a structured catalyst, even in the simple form of a Rushing ring, can increase the efficiency without increasing the pressure drop.

The catalyst efficiency is related to the Thiele modulus according to the following equation[5]:

$$\eta = \frac{3}{\phi^2}\left(\frac{\phi}{tgh\phi} - 1\right)$$

If we want a minimum efficiency (at the beginning of the reactor where the reaction rate is maximum) of 85% the maximum Thiele modulus should be 1.69. It is defined as follows[5]:

$$\phi_{\max} = R\sqrt{\frac{r_{\max}\rho_{cat}}{C_A D_{AB_{eff}}}}$$

Considering[6]:

$$r_{\max} = 0.05\, {}^{mol}\!/_{kg_{cat}s}$$

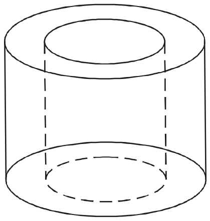
$$\rho_{cat} = 1980\, {}^{kg}\!/_{m^3}$$

$$C_{tot} = \frac{1}{V} = \frac{P}{RT} = 1003\, {}^{mol}\!/_{m^3}$$

$$D_{CO_{eff}} = 5.67E-8\, {}^{m^2}\!/_{s}$$

Results R=0.5mm

Because a spherical particle of 1 mm in diameter will not be suitable in such kind of reactor, a structured catalyst with pellet size of about 5 mm with walls of 1 mm is a good choice.



The packing factor of the bed drop down from 0.67 (packed spheres) to:

$$\varepsilon_b = 0.67\frac{V_{full}}{V_{tot}} = 0.43$$

So the overall bed density becomes:

$$\rho_b = \rho_c \varepsilon_b = 851.4\, {}^{kg}\!/_{m^3}$$

Considering this pellet conformation the pressure drop across the bed can be calculated using the following formula[5]:

$$\frac{P}{P_0} = \sqrt{1 - \frac{2\beta_0 L}{P_0}}$$

$$\beta_0 = \frac{G\varepsilon_b}{\rho_o D_p \left(1-\varepsilon_b\right)^3}\left(\frac{150\varepsilon_b \mu}{D_p} + 1.75G\right)$$

Where G is the superficial mass velocity (10 kg/m^{2}s), ε_b is the packing factor (0.43), ρ_0 is the gas mixture density (10 kg/m^3), μ is the viscosity (1.33 10^{-5} Pa s) and Dp is the catalyst pellet dimension (0.005 m).

Results that β_0= 8200 Pa/m = 0.082 bar/m

And considering 10 m length

P=49 bar with P_0= 50 bar

Using a Rushing ring the pressure drop is contained because the packing factor is low.

To evaluate the external mass and heat transport limitation we can use the Coleburn factors[6]:

$$J_D = \frac{k_y}{v_{gas} C_{tot}} Sc^{2/3} = \frac{20.4}{\varepsilon_b} \mathrm{Re}^{-0.815}$$

$$J_H = \frac{h}{v_{gas}\rho_{gas} Cp_{gas}} \mathrm{Pr}^{2/3} = \frac{J_D}{0.95}$$

Considering

$$\mathrm{Re} = \frac{\rho v D_p}{\mu} = 3760$$

$$\mathrm{Pr} = \frac{\mu Cp}{k} = 0.242$$

$$Sc = \frac{\mu}{\rho D_{bulk}} = 0.831$$

With:

$$Cp = 388.4 \, {}^{J}\!/_{kgK}$$
$$D_{bulk} = 1.6E-6 \, {}^{m^2}\!/_{s}$$
$$k = 0.16 \, {}^{J}\!/_{msK}$$

So results:

$$J_D = 0.058 \rightarrow k_y = 65.6 \, {}^{mol}\!/_{m^2 s}$$
$$J_H = 0.061 \rightarrow h = 610 \, {}^{J}\!/_{m^2 sK}$$

The maximum difference between the gas and the pellet surface is given by the formulas[6]:

$$\Delta T_{\max} = \rho_{cat} \varepsilon_b r_{\max} \Delta H_{rx} \frac{D_p}{6h} = 3.1K$$
$$\Delta y_{\max} = \frac{D_p r_{\max}}{6k_y} = 6.35E-7$$
$$with$$
$$\Delta H_{rx} = 54,000 \, {}^{J}\!/_{mol}$$
$$r_{\max} = 0.05 \, {}^{mol}\!/_{kg_{cat} s}$$

The mass transfer is not an issue, only the heat transfer starts to be significative because the high heat of reaction involved.

We can also compute the temperature gradient inside the pellet. It can be quite high because the thermal conductivity of the alumina is scarce. But we have to consider that the thickness is very thin (0.5 mm from the center to the surface) Considering it as a layer of 1 mm thikness, with planar geometry (curvature not influencing) we can express the heat flows as follows:

$$\dot{q}_{\max} = \eta r_{\max} \Delta H_{rx} \rho_{cat} dz \cancel{A} = k \frac{dT}{dz} \cancel{A}$$
$$\Delta T = \frac{\eta r_{\max} \Delta H_{rx} \rho_{cat} \Delta z^2}{2k} = 0.16K$$
$$with$$
$$k = 4.18 \, {}^{J}\!/_{msK}$$

So the internal heat transport is not an issue because the thickness is very small.

REACTOR DESIGN

The easier reactor configuration for treating highly exothermic equilibrium limited reactions is the adiabatic multi bed reactor with intermediate cooling. The cooling can be done using heat exchangers (e.g. steam production) or quenching the flow using cold feed. This second option is easier in terms of equipment but leads to lower conversions compared with the one using heat exchangers. Here for simplicity will be discussed the option with heat exchangers that leads to an higher methanol content in the output stream.

The differential constitutive equations (for a complete description refers to appendix C) results to be:

$$\frac{d\dot{n}_{CO}}{dz} = \eta_3 r_3 \rho_{cat} \varepsilon_b A$$

$$\frac{d\dot{n}_{CO_2}}{dz} = \left(-\eta_2 r_2 - \eta_3 r_3\right) \rho_{cat} \varepsilon_b A$$

$$\frac{d\dot{n}_{H_2}}{dz} = \left(-3\eta_2 r_2 - \eta_3 r_3\right) \rho_{cat} \varepsilon_b A$$

$$\frac{d\dot{n}_{H_2O}}{dz} = \left(\eta_2 r_2 + \eta_3 r_3\right) \rho_{cat} \varepsilon_b A$$

$$\frac{d\dot{n}_{MeOH}}{dz} = \eta_2 r_2 \rho_{cat} \varepsilon_b A$$

$$\frac{dT}{dz} = -\left(\eta_2 r_2 \Delta H_2 + \eta_3 r_3 \Delta H_3\right) \frac{\varepsilon_b \rho_{cat} A}{Cp \sum \dot{n}_i}$$

Where the index 2 and 3 refers to the indirect methanol synthesis and RWGS as proposed by Vanden Bussche[3]. The molar flow for CH_4 is constant. Cp is the mixture specific heat and is calculated as average of the specific heats of the components:

$$Cp = \sum_i y_i Cp_i$$

Considering a feed of 12 kmol/s with the following composition:

15%	CO
8%	CO_2
74%	H_2
3%	CH_4

And wanting 1 kmol/s of methanol in exit, the reaction path is reported in figure 7. The complete numerical solutions are reported in appendix D.

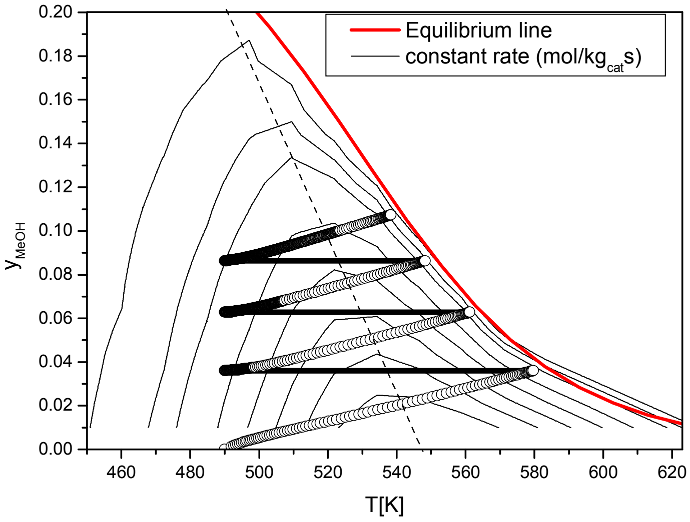


Figure 7. Reaction path in the 4 beds of the reactor.

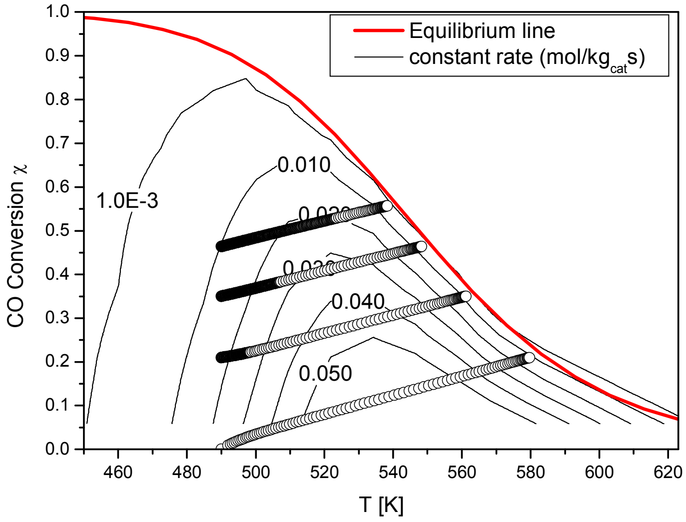


Figure 8. Reaction path in the 4 beds of the reactor

For dimensioning the reactor we need to plot a characteristic variable (as the molar flow of the wanted product) in function of the reactor length. This is shown in figure 9.

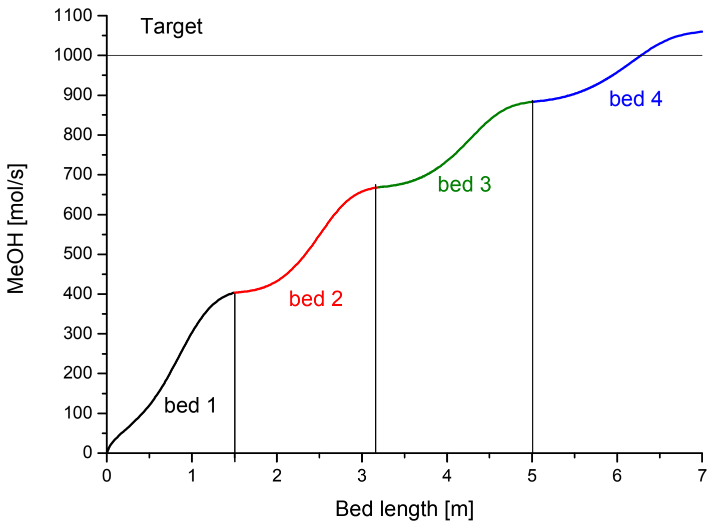


Figure 9. molar flow of methanol in function of bed depth.

The bed distribution is as follows:

	Bed Depth (m)	T_{in} (K)	T_{out} (K)	$MeOH_{out}$ (mol/s)
1st	1.5	490	580	404
2nd	1.7	490	561	669
3rd	1.8	490	548	883
4th	2	490	538	1060

This is a total of 7 m of catalytic bed. Adding 1 m between the beds for placing the heat exchangers, results a total 10 m reactor. Remembering that the diameter is 3.9 m the aspect ratio becomes 2.6 that is a good value.

Now that the reactor is dimensioned properly we can verify the pressure drop and the catalyst efficiency. For the pressure drop across the bed, before we have estimated a 10 m bed and the pressure drop was about 1 bar. The final bed is shorter, but we have to add the pressure drop across the heat exchangers, so we can suppose 1-2 bar total pressure drop for the whole reactor.
Also the efficiency of the catalyst was an issue, and for this the use of a structured catalyst like a rushing ring was chosen. We can plot in every way the efficiency for both the reaction along the reactor. It is reported in figure 10.

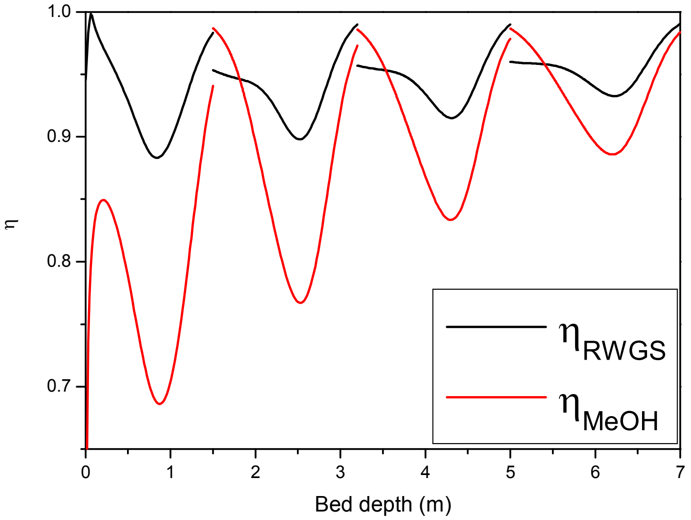


Figure 10. Catalyst efficiency in function of bed depth.

We see that for the RWGS the catalyst efficiency is never an issue, while for the methanol production in the first meter of the bed the catalyst is not properly used. In every way is never below 70%, even if the wanted value was above 85%.

EFFECT OF TEMPERATURE IN THE REACTOR DESIGN

Looking at figure 7 we can understand that the optimal design (in terms of catalyst utilization) is the one that follows the dotted line representing the locus of maximum reaction rate for a given composition. A reactor that follows exactly this line, as mentioned before, would be too expensive and engineeristically complex. The resulting is an approximation of this line with several beds that work across this optimum line. Obviously staying closer to this line means having a better catalytic efficiency but an higher number of beds to reach the same conversion. Here the economic considerations starts to be important: what is the save in catalyst compared to the extra cost associated to the new bed (frame, exchanger, ecc…)?
Here is analyzed the effect of the upper temperature limit (exit temperature from the bed) that is generally expressed as ΔT from the equilibrium line at this composition.

ΔT = 2 K	Case considered in the Reactor Design		
	Depth (m)	$T_{IN} \rightarrow T_{OUT}$ (K)	MeOH (mol/s)
Bed 1	1.5	490→580	404
Bed 2	1.7	490→561	669
Bed 3	1.8	490→548	883
Bed 4	2	490→538	1060
Total Depth	7	Efficiency (mol/ m s)	151.4

ΔT = 10 K			
	Depth (m)	$T_{IN} \rightarrow T_{OUT}$ (K)	MeOH (mol/s)
Bed 1	1.25	490→573	374
Bed 2	1.3	490→553	609
Bed 3	1.3	490→540	795
Bed 4	1.35	490→531	946
Total Depth	5.2	Efficiency (mol/ m s)	181.9

ΔT = 20 K			
	Depth (m)	$T_{IN} \rightarrow T_{OUT}$ (K)	MeOH (mol/s)
Bed 1	1.08	490→563	330
Bed 2	1.12	490→544	532
Bed 3	1.05	490→530	680
Bed 4	1.15	490→528	825
Total Depth	4.4	Efficiency (mol/ m s)	187.5

The case with 10 and 20 K have an higher efficiency, but for reaching 1 kmol/s need a fifth (or sixth) bed. Probably the optimum for this problem (willing to use 4 beds) is around 4-5 K from the equilibrium, but in this way you loose the 6% margin in production that is possible with the 7 m bed.

APPENDIX A

RKS EQUATION OF STATE

The Redlich-Kwong-Soave[1] is cubic equation of state that derives from the original Van der Walls equation of state. The implicit form is the following:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

Where b represent the co-volume and a an interaction-like term that is temperature dependent.
For pure components the parameters a and b can be expressed:

$$b = 0.08664\frac{RTc}{Pc}$$

$$a = a_c(Tc)\alpha(Tr)$$

Where

$$a_c = 0.42748\frac{R^2Tc^2}{Pc}$$

$$\alpha = \left[1 + S\left(1 - \sqrt{Tr}\right)\right]^2$$

With

$$S = 0.48 + 1.574\omega - 0.177\omega^2$$

The power of the RKS, and the reason for which is widely used is that using appropriate mixing rules is possible describe the behavior of the whole fluid, especially for complex mixtures of hydrocarbons.

The mixing rules are based on the calculation of the pure component parameter a_i and b_i using the equations presented above and adding them together in the following way.

$$b = \sum_i y_i b_i$$

$$a = b \sum_i y_i \frac{a_i}{b_i}$$

From these 2 parameters is possible calculate the overall behavior of the gas.

More interesting is that from the EOS is possible calculate the fugacity coefficient of every single component.

$$\ln \varphi_i = \frac{b_i}{b}\left(\frac{PV}{RT} - 1\right) - \ln\left(\frac{P(V-b)}{RT}\right) - \frac{a_i}{RTb_i}\ln\left(1 + \frac{b}{V}\right)$$

The only problem with cubic equation of state is that, for definition, are non linear in the volumetric term. Because generally the problem fix P and T and need to calculate V, numerical method should be used. Once the volume is determined, every property of the gas can be calculated.

Here is reported for example the calculations using RKS EOS of the mixture of in entrance to the methanol synthesis reactor discussed above. The critical parameter are taken from Elliott and Lira[7].

	CO	CO2	H2	H20	MeOH	CH4
Tc (K)	132.9	304.2	33.3	647.3	512.6	190.6
Pc (bar)	34.99	73.82	12.97	221.2	80.96	46.04
omega	0.066	0.228	-0.215	0.344	0.566	0.011

Constants		
R	0.0831	dm3 bar / K mol

Tr	3.559067	1.554898	14.2042	0.730728	0.922747	2.481637
Pr	1.42898	0.677323	3.85505	0.22604	0.617589	1.086012
aci	1.490129	3.700515	0.252387	5.591701	9.580861	2.329316
Si	0.583113	0.829671	0.133408	1.000511	1.314181	0.497293
alpha i	0.233329	0.632197	0.397673	1.311593	1.106247	0.509649
ai	0.347691	2.339455	0.100367	7.334036	10.59879	1.187133
bi	0.027346	0.029669	0.018485	0.021069	0.045586	0.029806

T	473	K
P	50	bar
Vig	0.7861	dm3/mol
V	0.8005	dm3/mol
Z	1.0183	

yi	0.15	0.08	0.74	0	0	0.03

yibi	0.004102	0.002374	0.013679	0	0	0.000894	------------>	0.021049	b
yiai/bi	1.907146	6.308121	4.017913	0	0	1.194851	------------>	0.282643	a

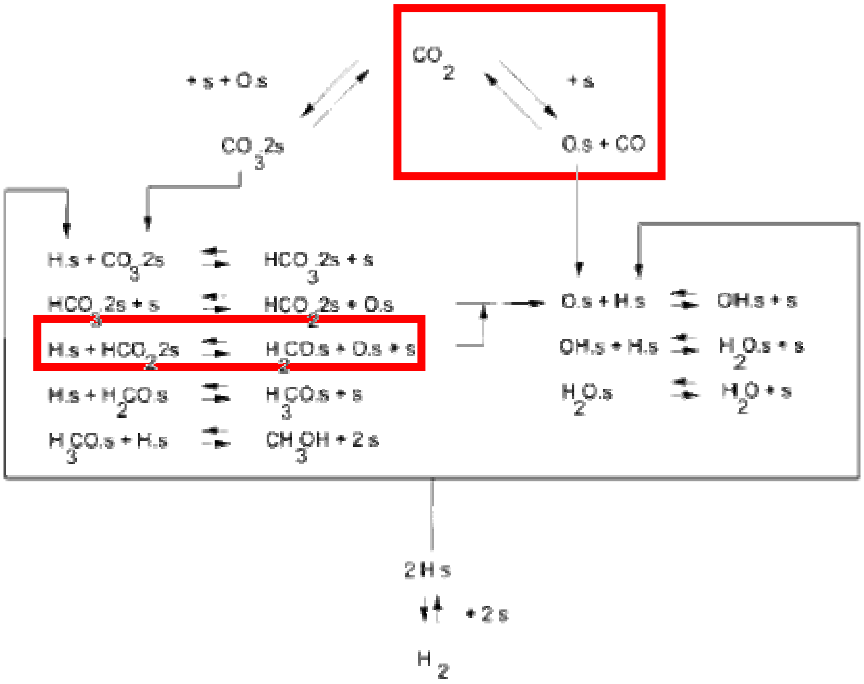
fi i	1.024166	0.982378	1.021225	0.816251	0.899933	1.008141

f i (bar)	7.681246	3.929511	37.78532	0	0	1.512211
p i (bar)	7.5	4	37	0	0	1.5

APPENDIX B

REACTION MECHANISM

The activity of the Cu based catalyst is supposed to follow a redox mechanism that involve the copper sites that are oxidized by CO_2 and reduced by CO and H_2 in a concerted mechanism that consider both the RWGS reaction both the methanol synthesis. It can be schematized as follows[3]:



Where the two RDS are highlighted in red. Considering every single step we can impose the equilibrium of the non rate determining.

Adsorption

$$H_2(g) + 2s \overset{K_{H_2}}{\rightleftarrows} 2H \cdot s$$

$$\boxed{CO_2(g) + s \underset{k_1/K_1}{\overset{k_1}{\rightleftarrows}} O \cdot s + CO(g)}\, RDS$$

$$CO_2(g) + O \cdot s + s \overset{K_2}{\rightleftarrows} CO_3 \cdot 2s$$

Surface reaction

$$CO_3 \cdot 2s + H \cdot s \overset{K_3}{\rightleftarrows} HCO_3 \cdot 2s + s$$

$$HCO_3 \cdot 2s + s \overset{K_4}{\rightleftarrows} HCO_2 \cdot 2s + O \cdot s$$

$$\boxed{HCO_2 \cdot 2s + H \cdot s \overset{k_{5a}}{\rightleftarrows} H_2CO_2 \cdot 2s + s}\, RDS$$

$$H_2CO_2 \cdot 2s \overset{K_{5b}}{\rightleftarrows} H_2CO \cdot s + O \cdot s$$

$$H_2CO \cdot s + H \cdot s \overset{K_6}{\rightleftarrows} H_3CO \cdot s + s$$

$$O \cdot s + H \cdot s \overset{K_8}{\rightleftarrows} OH \cdot s + s$$

$$OH \cdot s + H \cdot s \overset{K_9}{\rightleftarrows} H_2O \cdot s + s$$

Desorption

$$H_3CO \cdot s + H \cdot s \overset{K_7}{\rightleftarrows} CH_3OH(g) + 2s$$

$$H_2O \cdot s \overset{K_{H_2O}}{\rightleftarrows} H_2O(g) + s$$

Where K_i are the equilibrium constants, while k_i are the rate constants.

The balance of sites is the following:

$$1 = \frac{C_s}{C_t} + \frac{C_{O \cdot s}}{C_t} + \frac{C_{H_2O \cdot s}}{C_t} + \frac{C_{HCO_2 \cdot 2s}}{C_t} + \frac{C_{CO_3 \cdot 2s}}{C_t} + \frac{C_{H \cdot s}}{C_t} + \cancel{\frac{C_{HCO_3 \cdot 2s}}{C_t}} + \cancel{\frac{C_{H_2CO \cdot s}}{C_t}} + \cancel{\frac{C_{H_3CO \cdot s}}{C_t}} + \cancel{\frac{C_{H_2CO_2 \cdot 2s}}{C_t}} + \cancel{\frac{C_{OH \cdot s}}{C_t}}$$

That can be simplified for the spices that are not seen to be strongly absorbed. In the hypothesis of pseudo steady state the concentration of absorbed spices depends only from the concentration of the spices in the gas phase.

$$e.g. C_{H \cdot s} = \sqrt{K_{H_2}}\sqrt{p_{H_2}}\, C_s$$

The balance can be solved for C_s and results:

$$1 = b\frac{C_s}{C_t} + a\left(\frac{C_s}{C_t}\right)^2$$

$$a = K'_2 K_3 K_4 \sqrt{K_{H_2}}\, p_{CO_2} \sqrt{p_{H_2}} + \frac{K'_2 K_{H_2O}}{K_{H_2} K_8 K_9} \frac{p_{H_2O} p_{CO_2}}{p_{H_2}}$$

$$b = 1 + \frac{K_{H_2O}}{K_8 K_9 K_{H_2}} \frac{p_{H_2O}}{p_{H_2}} + \sqrt{K_{H_2}} \sqrt{p_{H_2}} + K_{H_2O} p_{H_2O}$$

$$K'_2 = K_2 C_t$$

The quadratic relation has 2 root, but only the positive one has a physical meaning.

$$\beta = \frac{C_s}{C_t} = \frac{\sqrt{b^2 + 4a} - b}{2a}$$

Imposing the RDS results:

$$r_{MeOH} = k'_{5a} K'_2 K_3 K_4 K_{H_2} p_{CO_2} p_{H_2} \left(1 - \frac{1}{K_2^*} \frac{p_{H_2O} p_{MeOH}}{p^3_{H_2} p_{CO_2}}\right) \beta^3$$

$$r_{RWGS} = k'_1 p_{CO_2} \left(1 - \frac{1}{K_3^*} \frac{p_{H_2O} p_{CO}}{p_{CO_2} p_{H_2}}\right) \beta$$

$$k'_{5a} = k_{5a} C_t^2$$

$$k'_1 = k_1 C_t$$

During the fitting of the experimental data to calculate the parameters the groups of costant describing the concentration of carbonates and formate results to be negligible. This allows to simplify the expression of β that becomes:

$$\beta = \frac{1}{1 + \frac{K_{H_2O}}{K_8 K_9 K_{H_2}} \frac{p_{H_2O}}{p_{H_2}} + \sqrt{K_{H_2}} \sqrt{p_{H_2}} + K_{H_2O} p_{H_2O}}$$

And so the rate expression can be written as:

$$r_{MeOH} = \frac{k'_{5a} K'_2 K_3 K_4 K_{H_2} p_{CO_2} p_{H_2} \left(1 - \frac{1}{K_2^*} \frac{p_{H_2O} p_{MeOH}}{p^3_{H_2} p_{CO_2}}\right)}{\left(1 + \frac{K_{H_2O}}{K_8 K_9 K_{H_2}} \frac{p_{H_2O}}{p_{H_2}} + \sqrt{K_{H_2}} \sqrt{p_{H_2}} + K_{H_2O} p_{H_2O}\right)^3}$$

$$r_{RWGS} = \frac{k'_1 p_{CO_2} \left(1 - \frac{1}{K_3^*} \frac{p_{H_2O} p_{CO}}{p_{CO_2} p_{H_2}}\right)}{1 + \frac{K_{H_2O}}{K_8 K_9 K_{H_2}} \frac{p_{H_2O}}{p_{H_2}} + \sqrt{K_{H_2}} \sqrt{p_{H_2}} + K_{H_2O} p_{H_2O}}$$

Or as presented previously, grouping the constant:

$$r_{Meth} = \frac{C_4 p_{CO_2} p_{H_2} \left[1 - \frac{1}{K_2} \frac{p_{H_2O} p_{MeOH}}{p^3_{H_2} p_{CO_2}}\right]}{\left(1 + C_3 \frac{p_{H_2O}}{p_{H_2}} + C_1 \sqrt{p_{H_2}} + C_2 p_{H_2O}\right)^3} \left({}^{mol}\!/\!_{kg_{cat} s} \right)$$

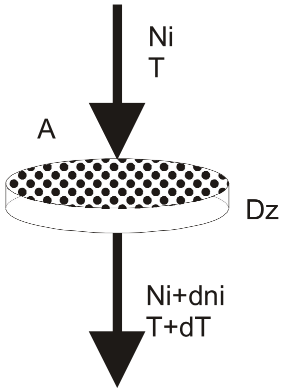
$$r_{RWGS} = \frac{C_5 p_{CO_2} \left[1 - \frac{1}{K_3} \frac{p_{H_2O} p_{CO}}{p_{H_2} p_{CO_2}}\right]}{\left(1 + C_3 \frac{p_{H_2O}}{p_{H_2}} + C_1 \sqrt{p_{H_2}} + C_2 p_{H_2O}\right)} \left({}^{mol}\!/\!_{kg_{cat} s} \right)$$

Where K_2 and K_3 are the equilibrium constants (previously K_2^* and K_3^*)

APPENDIX C

REACTOR CONSTITUTIVE EQUATIONS

The constitutive equations for a catalytic reactor are the mass and heat balance[5]. Considering a section of the reactor of thickness dz:



$$(n_i + dn_i) - (n_i) = r dm_{cat} = r \rho_{cat} \varepsilon_b dV = r \rho_{cat} \varepsilon_b A dz$$
$$Cpn_{tot}\left((T + dT) - (T)\right) = -\Delta H r dm_{cat}$$

Introducing the efficiency of both the reaction become the system of equation presented before:

$$\frac{d\dot{n}_{CO}}{dz} = \eta_3 r_3 \rho_{cat} \varepsilon_b A$$

$$\frac{d\dot{n}_{CO_2}}{dz} = \left(-\eta_2 r_2 - \eta_3 r_3\right) \rho_{cat} \varepsilon_b A$$

$$\frac{d\dot{n}_{H_2}}{dz} = \left(-3\eta_2 r_2 - \eta_3 r_3\right) \rho_{cat} \varepsilon_b A$$

$$\frac{d\dot{n}_{H_2O}}{dz} = \left(\eta_2 r_2 + \eta_3 r_3\right) \rho_{cat} \varepsilon_b A$$

$$\frac{d\dot{n}_{MeOH}}{dz} = \eta_2 r_2 \rho_{cat} \varepsilon_b A$$

$$\frac{dT}{dz} = -\left(\eta_2 r_2 \Delta H_2 + \eta_3 r_3 \Delta H_3\right) \frac{\varepsilon_b \rho_{cat} A}{Cp \sum \dot{n}_i}$$

For a proper calculation the Cp and the efficiency should be updated for changing in composition and temperature:

$$Cp_i = A + BT + CT^2 + DT^3 \left({}^{J}\!/\!{}_{molK} \right)$$

$$Cp = \sum_i y_i Cp_i$$

Where the values of the parameter are[7]:

	A	B	C	D
CO	30.87	-1.285E-2	2.789E-5	-1.272E-8
CO_2	19.80	7.344E-2	-5.602E-5	1.715E-8
H_2	27.14	9.274E-3	-1.381E-5	7.645E-9
H_2O	32.24	1.924E-3	1.055E-5	-3.596E-9
MeOH	21.15	7.092E-2	2.587E-5	-2.852E-8
CH_4	19.25	5.213E-2	1.197E-5	-1.132E-8

$$\eta_i = \frac{3}{\phi_i^2}\left(\frac{\phi_i}{\tanh(\phi_i)} - 1\right)$$

$$\phi_2 = S\sqrt{\frac{|r_2|\rho_{cat}}{\frac{RT}{P} y_{CO_2} D_{CO_2 eff}}}$$

$$\phi_3 = S\sqrt{\frac{|r_3|\rho_{cat}}{\frac{RT}{P} y_{CO} D_{CO eff}}}$$

Where the production of methanol is considered limited by availability of CO_2 while the RWGS by CO[3].

The value of the effective diffusion coefficient are[6]:

$$D_{CO_2 eff} = 4.11E-8\left(m^2/s\right)$$

$$D_{COeff} = 5.67E-8\left(m^2/s\right)$$

The rate expression are taken according with Vanden Busche[3]:

$$r_2 = \frac{C_4 p_{CO_2} p_{H_2}\left[1-\frac{1}{K_2}\frac{p_{H_2O}p_{MeOH}}{p_{H_2}^3 p_{CO_2}}\right]}{\left(1+C_3\frac{p_{H_2O}}{p_{H_2}}+C_1\sqrt{p_{H_2}}+C_2 p_{H_2O}\right)^3}\left(mol/kg_{cat}s\right)$$

$$r_3 = \frac{C_5 p_{CO_2}\left[1-\frac{1}{K_3}\frac{p_{H_2O}p_{CO}}{p_{H_2} p_{CO_2}}\right]}{\left(1+C_3\frac{p_{H_2O}}{p_{H_2}}+C_1\sqrt{p_{H_2}}+C_2 p_{H_2O}\right)}\left(mol/kg_{cat}s\right)$$

Where the parameters:

$$C_i = A_i \exp\left(-\frac{B_i}{R}\left(\frac{1}{T_{AV}}-\frac{1}{T}\right)\right)$$

		A_i	B_i (J/mol)
C_1	$\sqrt{K_{H_2}}$	30.82	17197
C_2	K_{H_2O}	558.17	124119
C_3	$K_{H_2O}/K_8K_9K_{H_2}$	3453.38	0
C_4	$k'_{5a}K'_2K_3K_4K_{H_2O}$	7070.34	36696
C_5	k'_1	1.65	-94765

And the equilibrium constants[2]:

$$K_1 = 9.740\times10^{-1}\exp\left[21.225+\frac{9143.6}{T}-7.492\ln T+4.076\times10^{-3}T-7.161\times10^{-8}T^2\right](bar^{-2})$$

$$K_3 = \exp\left[13.148 - \frac{5639.5}{T} - 1.077\ln T - 5.44\times10^{-4}T + 1.125\times10^{-7}T^2 + \frac{49170}{T^2}\right]$$
$$K_2 = K_1K_3\left(bar^{-2}\right)$$

Because the rate expression are given in partial pressures and the balance is in total molar flow, using the definition of molar fraction we can write:

$$y_i = \frac{n_i}{\sum n_i}$$

Using the proper value for the enthalpy of reaction[2]:

$$\Delta H_2 = -54000\left(J/_{mol}\right)$$
$$\Delta H_3 = 40600\left(J/_{mol}\right)$$

Giving initial conditions we can compute the temperature and composition profile in the reactor as shown in appendix D.

APPENDIX D

NUMERICAL SIMULATION OF THE REACTOR

We can insert the equations presented in appendix C in a simultaneous differential equation solver and giving the proper boundary condition computing everything that is of interest.

ODE Report (STIFF)

```
Differential equations as entered by the user
 [1]  d(n1)/d(z) = eta3*r3*rhocat*eb*A
 [2]  d(n2)/d(z) = (-eta2*r2-eta3*r3)*rhocat*eb*A
 [3]  d(n3)/d(z) = (-3*eta2*r2-eta3*r3)*rhocat*eb*A
 [4]  d(n4)/d(z) = (eta2*r2+eta3*r3)*rhocat*eb*A
 [5]  d(n5)/d(z) = eta2*r2*rhocat*eb*A
 [6]  d(T)/d(z) = (eta2*DH2*r2+eta3*DH3*r3)*eb*rhocat*A/(Cp*(n1+n2+n3+n4+n5+n6))

Explicit equations as entered by the user
 [1]  n6 = 360
 [2]  y1 = n1/(n1+n2+n3+n4+n5+n6)
 [3]  y2 = n2/(n1+n2+n3+n4+n5+n6)
 [4]  y3 = n3/(n1+n2+n3+n4+n5+n6)
 [5]  y4 = n4/(n1+n2+n3+n4+n5+n6)
 [6]  y5 = n5/(n1+n2+n3+n4+n5+n6)
 [7]  y6 = n6/(n1+n2+n3+n4+n5+n6)
 [8]  K1 = 0.974*exp(21.225+9143.6/T-7.492*ln(T)+4.076*10^(-3)*T-7.161*10^(-8)*T^2)
 [9]  K3 = exp(13.148-5639.5/T-1.077*ln(T)-5.44*10^(-4)*T+1.125*10^(-7)*T^2+49170/T^2)
 [10]  K2 = K1*K3
 [11]  a4 = 7070.34
 [12]  P = 50
 [13]  b1 = 17197
 [14]  b2 = 124119
 [15]  b3 = 0
 [16]  b4 = 36696
 [17]  Tav = 501.57
 [18]  a1 = 30.82
 [19]  a2 = 558.17
 [20]  a3 = 3453.38
```

```
C4 = a4*exp(-b4/8.31*(1/Tav-1/T))
a5 = 1.65
C1 = a1*exp(-b1/8.31*(1/Tav-1/T))
C2 = a2*exp(-b2/8.31*(1/Tav-1/T))
C3 = a3*exp(-b3/8.31*(1/Tav-1/T))
r2 = (C4*P^2*y2*y3*(1-(y4*y5/(P^2*K2*y3^3*y2))))/((1+C3*y4/y3+C1*P^0.5*y3^0.5+C2*P*y4)^3)
b5 = -94765
C5 = a5*exp(-b5/8.31*(1/Tav-1/T))
E1 = -1.272*10^(-8)
E2 = 1.715*10^(-8)
E3 = 7.645*10^(-9)
E4 = -3.596*10^(-9)
E5 = -2.852*10^(-8)
E6 = -1.132*10^(-8)
D6 = 1.197*10^(-5)
r3 = (C5*P*y2*(1-(y4*y1/(K3*y3*y2))))/(1+C3*y4/y3+C1*P^0.5*y3^0.5+C2*P*y4)
Deff2 = 4.11*10^(-8)
Deff1 = 5.67*10^(-8)
rhocat = 1980
S = 0.0005
TM2 = S*(((r2^2)^0.5)*rhocat*0.0000831*T/P/y2/Deff2)^0.5
eb = 0.43
A = 12
TM3 = S*(((r3^2)^0.5)*rhocat*0.0000831*T/P/y1/Deff1)^0.5
eta3 = (3/(TM3^2))*((TM3/tanh(TM3))-1)
eta2 = (3/(TM2^2))*((TM2/tanh(TM2))-1)
DH2 = 54000
DH3 = -40600
A1 = 30.87
A2 = 19.8
A3 = 27.14
A4 = 32.24
A5 = 21.15
A6 = 19.25
B1 = -1.285*10^(-2)
B2 = 7.334*10^(-2)
B3 = 9.274*10^(-3)
B4 = 1.924*10^(-3)
B5 = 7.092*10^(-2)
B6 = 5.213*10^(-2)
D1 = 2.789*10^(-5)
D2 = -5.602*10^(-5)
D3 = -1.381*10^(-5)
D4 = 1.055*10^(-5)
D5 = 2.587*10^(-5)
Cp6 = A6+B6*T+D6*T^2+E6*T^3
Cp1 = A1+B1*T+D1*T^2+E1*T^3
Cp2 = A2+B2*T+D2*T^2+E2*T^3
Cp3 = A3+B3*T+D3*T^2+E3*T^3
Cp4 = A4+B4*T+D4*T^2+E4*T^3
Cp5 = A5+B5*T+D5*T^2+E5*T^3
Cp = y1*Cp1+y2*Cp2+y3*Cp3+y4*Cp4+y5*Cp5+y6*Cp6
```

Considering an initial composition of:

15%	CO
8%	CO_2
74%	H_2
3%	CH_4

And a feed of 12 Kmol/s (about 12 m^3/s in the conditions of the feed) at 490 K.
The results are reported in the next pages.

z [m]	n1 [mol/s]	n2 [mol/s]	n3 [mol/s]	n4 [mol/s]	n5 [mol/s]	T [K]	n6 [mol/s]	y1	y2	y3	y4	y5	y6
0	1800	960	8880	0	0	490	360	0.15	0.08	0.74	0	0	0.03
0.030042	1803.088	941.2347	8829.881	18.76531	15.67712	491.9363	360	0.150651	0.078642	0.737751	0.001568	0.00131	0.030079
0.045509	1803.699	935.3345	8813.401	24.66547	20.96692	492.6373	360	0.150835	0.078218	0.737026	0.002063	0.001753	0.030105
0.060614	1803.929	930.6795	8799.897	29.32053	25.39141	493.2544	360	0.150966	0.077886	0.736441	0.002454	0.002125	0.030128
0.075022	1803.888	926.9391	8788.594	33.06095	29.17276	493.8079	360	0.151059	0.077622	0.735961	0.002769	0.002443	0.030147
0.090066	1803.624	923.5698	8777.958	36.43023	32.80611	494.3645	360	0.151128	0.077387	0.735518	0.003053	0.002749	0.030165
0.105966	1803.138	920.4645	8767.67	39.5355	36.39729	494.9393	360	0.151179	0.077174	0.735098	0.003315	0.003052	0.030183
0.122165	1802.454	917.6798	8757.948	42.32025	39.86614	495.5181	360	0.151209	0.076985	0.734711	0.00355	0.003344	0.030201
0.135505	1801.763	915.6198	8750.385	44.38021	42.61728	495.9935	360	0.151221	0.076848	0.734415	0.003725	0.003577	0.030215
0.151251	1800.812	913.4135	8741.864	46.58652	45.77482	496.5565	360	0.151221	0.076703	0.734089	0.003912	0.003844	0.030231
1.350581	1530.247	839.7158	7979.641	120.2842	390.0373	576.6057	360	0.136387	0.074842	0.711203	0.010721	0.034763	0.032086
1.366717	1528.831	839.1299	7975.051	120.8701	392.0395	577.0556	360	0.136309	0.074816	0.711047	0.010777	0.034954	0.032097
1.38157	1527.621	838.6267	7971.121	121.3733	393.7527	577.4405	360	0.136243	0.074794	0.710914	0.010825	0.035117	0.032107
1.395001	1526.6	838.2005	7967.802	121.7995	395.1995	577.7653	360	0.136187	0.074775	0.710802	0.010866	0.035255	0.032115
1.410896	1525.478	837.7299	7964.145	122.2701	396.7923	578.1228	360	0.136125	0.074755	0.710677	0.010911	0.035408	0.032125
1.425329	1524.535	837.333	7961.069	122.667	398.1318	578.4233	360	0.136074	0.074737	0.710573	0.010949	0.035536	0.032132
1.4403	1523.63	836.9505	7958.111	123.0495	399.42	578.7122	360	0.136024	0.07472	0.710472	0.010985	0.035659	0.03214
1.455861	1522.762	836.5827	7955.272	123.4173	400.6556	578.9893	360	0.135977	0.074704	0.710375	0.011021	0.035777	0.032147
1.47207	1521.932	836.2301	7952.555	123.7699	401.8377	579.2543	360	0.135931	0.074688	0.710283	0.011055	0.03589	0.032153
1.486526	1521.252	835.9404	7950.326	124.0596	402.8074	579.4716	360	0.135894	0.074675	0.710207	0.011082	0.035983	0.032159
1.5	1520.666	835.6901	7948.402	124.3099	403.644	579.659	360	0.135863	0.074664	0.710143	0.011106	0.036061	0.032164

K1 [bar-2]	K3	K2 [bar-2]	P bar	r2 [mol/kgs]	r3 [mol/kgs]	TM2	TM3	eta3	eta2	Cp [J/molK]
0.010364	0.006299	6.53E-05	50	0.143869	0.01858	4.199844	0.938438	0.945815	0.544553	31.05865
0.009423	0.006547	6.17E-05	50	0.050107	0.005427	2.504811	0.50706	0.983269	0.73563	31.09944
0.009105	0.006639	6.05E-05	50	0.039681	0.00257	2.236665	0.348962	0.991975	0.772562	31.1139
0.008835	0.00672	5.94E-05	50	0.033866	5.24E-04	2.07198	0.157581	0.998349	0.795762	31.12641
0.0086	0.006794	5.84E-05	50	0.030291	-0.001031	1.963978	0.221108	0.996756	0.81109	31.13747
0.00837	0.006869	5.75E-05	50	0.027728	-0.002388	1.882986	0.336689	0.992523	0.822601	31.14843
0.00814	0.006947	5.66E-05	50	0.025831	-0.003623	1.820996	0.41486	0.988711	0.831402	31.1596
0.007915	0.007026	5.56E-05	50	0.024464	-0.004733	1.775369	0.474377	0.985312	0.837866	31.17071
0.007735	0.007092	5.49E-05	50	0.023642	-0.005564	1.747681	0.514597	0.98278	0.841779	31.17976
0.007528	0.00717	5.40E-05	50	0.022934	-0.006475	1.723904	0.555411	0.980021	0.845133	31.19038
2.63E-04	0.027118	7.12E-06	50	0.014358	-0.009256	1.488014	0.753521	0.964084	0.877882	32.80636
2.58E-04	0.027291	7.05E-06	50	0.013196	-0.00855	1.427367	0.724679	0.966653	0.886076	32.81688
2.55E-04	0.02744	6.99E-06	50	0.012193	-0.007934	1.372666	0.698523	0.968912	0.893359	32.82589
2.52E-04	0.027566	6.94E-06	50	0.011338	-0.007407	1.324203	0.675234	0.970866	0.899713	32.8335
2.48E-04	0.027706	6.88E-06	50	0.010389	-0.006818	1.268153	0.648158	0.973068	0.906935	32.84189
2.46E-04	0.027823	6.84E-06	50	0.009585	-0.006315	1.218548	0.624068	0.974963	0.913201	32.84896
2.43E-04	0.027936	6.79E-06	50	0.008806	-0.005824	1.168442	0.599613	0.976823	0.919397	32.85575
2.41E-04	0.028045	6.75E-06	50	0.008055	-0.005348	1.117863	0.574801	0.978645	0.925507	32.86228
2.38E-04	0.02815	6.71E-06	50	0.007332	-0.004886	1.066846	0.549647	0.980422	0.931508	32.86853
2.37E-04	0.028236	6.68E-06	50	0.006735	-0.004503	1.022803	0.527827	0.981906	0.936549	32.87365
2.35E-04	0.028308	6.65E-06	50	0.006233	-0.004179	0.984161	0.508605	0.983169	0.940859	32.87795

Tab. D.1. Results for the first bed (0→1.5m)

z [m]	n1 [mol/s]	n2 [mol/s]	n3 [mol/s]	n4 [mol/s]	n5 [mol/s]	T [K]	n6 [mol/s]	y1	y2	y3	y4	y5	y6
1.5	1520.666	835.6901	7948.402	124.3099	403.644	490	360	0.135862	0.074664	0.710141	0.011106	0.036063	0.032164
1.5	1520.666	835.6901	7948.402	124.3099	403.644	490	360	0.135862	0.074664	0.710141	0.011106	0.036063	0.032164
1.5001	1520.652	835.7025	7948.412	124.2975	403.6455	490.0018	360	0.135861	0.074665	0.710142	0.011105	0.036063	0.032164
1.50025	1520.631	835.7212	7948.426	124.2789	403.6478	490.0045	360	0.135859	0.074667	0.710143	0.011104	0.036064	0.032164
1.500475	1520.6	835.7491	7948.447	124.2509	403.6513	490.0086	360	0.135856	0.074669	0.710146	0.011101	0.036064	0.032164
1.500813	1520.552	835.7911	7948.478	124.2089	403.6565	490.0147	360	0.135852	0.074673	0.710149	0.011097	0.036064	0.032164
1.501319	1520.482	835.854	7948.526	124.146	403.6643	490.0238	360	0.135846	0.074679	0.710155	0.011092	0.036065	0.032164
1.502078	1520.376	835.9484	7948.597	124.0516	403.676	490.0376	360	0.135837	0.074687	0.710162	0.011083	0.036066	0.032164
1.503217	1520.216	836.09	7948.703	123.91	403.6936	490.0582	360	0.135823	0.0747	0.710174	0.011071	0.036068	0.032164
1.504926	1519.977	836.3024	7948.862	123.6976	403.7203	490.0892	360	0.135803	0.07472	0.710192	0.011052	0.03607	0.032164
3.045573	1247.36	851.2509	7448.473	108.7491	661.3889	559.4436	360	0.116824	0.079726	0.697604	0.010185	0.061944	0.033717
3.061549	1246.546	850.9723	7446.008	109.0277	662.4823	559.6996	360	0.116772	0.079716	0.697516	0.010213	0.062059	0.033724
3.07809	1245.773	850.7069	7443.667	109.2931	663.52	559.9424	360	0.116722	0.079707	0.697432	0.01024	0.062168	0.03373
3.095241	1245.043	850.4552	7441.452	109.5448	664.5017	560.1721	360	0.116675	0.079698	0.697353	0.010266	0.062272	0.033736
3.113051	1244.356	850.2172	7439.363	109.7828	665.427	560.3885	360	0.116631	0.079689	0.697278	0.01029	0.062369	0.033742
3.128433	1243.816	850.0297	7437.72	109.9703	666.1547	560.5586	360	0.116597	0.079683	0.697219	0.010309	0.062446	0.033747
3.14744	1243.211	849.8192	7435.879	110.1808	666.9699	560.7491	360	0.116558	0.079675	0.697153	0.01033	0.062532	0.033752
3.163389	1242.753	849.6593	7434.483	110.3407	667.588	560.8936	360	0.116528	0.079669	0.697103	0.010346	0.062597	0.033756
3.179457	1242.333	849.5124	7433.203	110.4876	668.1548	561.026	360	0.116501	0.079664	0.697057	0.010361	0.062657	0.033759
3.198959	1241.874	849.3517	7431.804	110.6483	668.774	561.1706	360	0.116472	0.079658	0.697007	0.010377	0.062722	0.033763
3.2	1241.851	849.3436	7431.734	110.6564	668.8051	561.1779	360	0.116471	0.079658	0.697006	0.010378	0.062724	0.033764

K1 [bar-2]	K3	K2 [bar-2]	P bar	r2 [mol/kgs]	r3 [mol/kgs]	TM2	TM3	eta3	eta2	Cp [J/molK]
0.010364	0.006299	6.53E-05	50	0.001519	-0.014336	0.446697	0.866137	0.953311	0.986945	32.13857
0.010364	0.006299	6.53E-05	50	0.001519	-0.014336	0.446697	0.866137	0.953311	0.986945	32.13857
0.010364	0.0063	6.53E-05	50	0.00152	-0.014337	0.446799	0.866166	0.953308	0.986939	32.1386
0.010362	0.0063	6.53E-05	50	0.001521	-0.014338	0.446953	0.866209	0.953304	0.986931	32.13865
0.01036	0.0063	6.53E-05	50	0.001522	-0.01434	0.447183	0.866273	0.953298	0.986917	32.13871
0.010357	0.006301	6.53E-05	50	0.001525	-0.014342	0.447529	0.86637	0.953288	0.986898	32.13881
0.010352	0.006302	6.52E-05	50	0.001528	-0.014346	0.448048	0.866515	0.953273	0.986868	32.13896
0.010345	0.006304	6.52E-05	50	0.001534	-0.014352	0.448828	0.866732	0.953251	0.986823	32.13919
0.010335	0.006307	6.52E-05	50	0.001542	-0.01436	0.450001	0.867057	0.953219	0.986755	32.13953
0.010319	0.006311	6.51E-05	50	0.001555	-0.014374	0.451768	0.867544	0.95317	0.986653	32.14004
5.00E-04	0.021096	1.06E-05	50	0.007459	-0.005335	1.023547	0.608827	0.97613	0.936465	33.7067
4.95E-04	0.021177	1.05E-05	50	0.006817	-0.004887	0.978832	0.582969	0.978052	0.941445	33.71338
4.91E-04	0.021255	1.04E-05	50	0.006203	-0.004456	0.93395	0.556934	0.979914	0.946293	33.71972
4.86E-04	0.021329	1.04E-05	50	0.005617	-0.004044	0.888974	0.530763	0.98171	0.95099	33.72573
4.82E-04	0.021398	1.03E-05	50	0.00506	-0.003651	0.843987	0.504504	0.983433	0.95552	33.73139
4.79E-04	0.021453	1.03E-05	50	0.00462	-0.003339	0.806554	0.482594	0.98481	0.959154	33.73585
4.76E-04	0.021515	1.02E-05	50	0.004123	-0.002986	0.762126	0.456517	0.986376	0.963302	33.74084
4.73E-04	0.021562	1.02E-05	50	0.003744	-0.002716	0.726398	0.435491	0.987581	0.966502	33.74462
4.71E-04	0.021605	1.02E-05	50	0.003395	-0.002466	0.691823	0.415097	0.988698	0.96948	33.7481
4.68E-04	0.021652	1.01E-05	50	0.003012	-0.002191	0.651745	0.391401	0.989934	0.972781	33.75189
4.68E-04	0.021653	1.01E-05	50	0.003001	-0.002183	0.650494	0.390661	0.989971	0.972881	33.75201

Tab. D.2. Results for the second bed (1.5→3.2m)

z [m]	n1 [mol/s]	n2 [mol/s]	n3 [mol/s]	n4 [mol/s]	n5 [mol/s]	T [K]	n6 [mol/s]	y1	y2	y3	y4	y5	y6
3.2	1241.851	849.3436	7431.734	110.6564	668.8051	490	360	0.11647	0.079658	0.697005	0.010378	0.062726	0.033764
3.2	1241.851	849.3436	7431.734	110.6564	668.8051	490	360	0.11647	0.079658	0.697005	0.010378	0.062726	0.033764
3.2001	1241.84	849.3529	7431.739	110.6471	668.8068	490.0015	360	0.116469	0.079659	0.697005	0.010377	0.062726	0.033764
3.20025	1241.824	849.3668	7431.748	110.6333	668.8095	490.0039	360	0.116468	0.07966	0.697006	0.010376	0.062726	0.033764
3.200475	1241.799	849.3876	7431.761	110.6125	668.8135	490.0073	360	0.116466	0.079662	0.697008	0.010374	0.062727	0.033764
3.200813	1241.762	849.4188	7431.78	110.5813	668.8194	490.0125	360	0.116462	0.079665	0.697011	0.010371	0.062727	0.033764
3.201319	1241.706	849.4655	7431.809	110.5345	668.8284	490.0203	360	0.116457	0.07967	0.697015	0.010367	0.062728	0.033764
3.202078	1241.623	849.5357	7431.852	110.4643	668.8418	490.032	360	0.11645	0.079677	0.69702	0.01036	0.06273	0.033764
3.203217	1241.497	849.6409	7431.917	110.3591	668.8621	490.0496	360	0.116438	0.079687	0.697029	0.01035	0.062732	0.033764
3.204926	1241.309	849.7986	7432.013	110.2014	668.8927	490.076	360	0.116421	0.079702	0.697042	0.010336	0.062735	0.033764
4.82504	1026.968	856.6615	7023.92	103.3385	876.371	546.5003	360	0.100219	0.083599	0.685444	0.010085	0.085523	0.035131
4.844214	1026.099	856.4172	7021.45	103.5828	877.4838	546.7704	360	0.100156	0.083593	0.685352	0.010111	0.08565	0.035139
4.860652	1025.416	856.2239	7019.503	103.7761	878.3605	546.9831	360	0.100106	0.083589	0.685279	0.010131	0.08575	0.035145
4.880976	1024.643	856.0043	7017.3	103.9958	879.3523	547.2237	360	0.10005	0.083584	0.685197	0.010155	0.085863	0.035152
4.898189	1024.048	855.8341	7015.598	104.166	880.118	547.4093	360	0.100007	0.08358	0.685133	0.010173	0.085951	0.035157
4.915461	1023.501	855.6769	7014.032	104.3231	880.8226	547.58	360	0.099967	0.083576	0.685074	0.010189	0.086032	0.035162
4.932843	1022.996	855.5317	7012.588	104.4683	881.472	547.7373	360	0.099931	0.083572	0.68502	0.010205	0.086106	0.035166
4.950379	1022.532	855.3975	7011.256	104.6025	882.0706	547.8823	360	0.099897	0.083569	0.68497	0.010219	0.086175	0.035171
4.968109	1022.104	855.2734	7010.028	104.7266	882.6227	548.016	360	0.099866	0.083566	0.684924	0.010232	0.086238	0.035174
4.986072	1021.71	855.1588	7008.895	104.8412	883.1317	548.1392	360	0.099837	0.083563	0.684881	0.010245	0.086296	0.035178
5	1021.429	855.077	7008.089	104.923	883.4941	548.2269	360	0.099819	0.083561	0.684854	0.010253	0.086334	0.03518

K1 [bar-2]	K3	K2 [bar-2]	P bar	r2 [mol/kgs]	r3 [mol/kgs]	TM2	TM3	eta3	eta2	Cp [J/molK]
0.010364	0.006299	6.53E-05	50	0.001749	-0.011259	0.464059	0.82901	0.956989	0.985932	33.01303
0.010364	0.006299	6.53E-05	50	0.001749	-0.011259	0.464059	0.82901	0.956989	0.985932	33.01303
0.010364	0.0063	6.53E-05	50	0.00175	-0.011259	0.464148	0.829026	0.956987	0.985926	33.01306
0.010363	0.0063	6.53E-05	50	0.001751	-0.011259	0.464282	0.82905	0.956985	0.985918	33.0131
0.010361	0.0063	6.53E-05	50	0.001752	-0.01126	0.464482	0.829087	0.956982	0.985906	33.01317
0.010358	0.006301	6.53E-05	50	0.001755	-0.011261	0.464783	0.829142	0.956976	0.985889	33.01327
0.010354	0.006302	6.53E-05	50	0.001758	-0.011263	0.465236	0.829225	0.956968	0.985862	33.01342
0.010348	0.006303	6.52E-05	50	0.001763	-0.011265	0.465915	0.829348	0.956956	0.985821	33.01365
0.010339	0.006306	6.52E-05	50	0.001771	-0.011269	0.466936	0.829533	0.956938	0.98576	33.01399
0.010326	0.006309	6.51E-05	50	0.001783	-0.011274	0.468472	0.82981	0.956911	0.985668	33.0145
8.33E-04	0.017262	1.44E-05	50	0.006256	-0.004754	0.904773	0.613286	0.975791	0.949359	34.44859
8.24E-04	0.017336	1.43E-05	50	0.005692	-0.004329	0.86327	0.585583	0.977861	0.9536	34.45629
8.17E-04	0.017394	1.42E-05	50	0.005242	-0.00399	0.828622	0.562421	0.979528	0.957027	34.46235
8.09E-04	0.017461	1.41E-05	50	0.004727	-0.003601	0.787048	0.534587	0.981452	0.960998	34.46921
8.03E-04	0.017512	1.41E-05	50	0.004325	-0.003297	0.752974	0.511739	0.982966	0.964134	34.47451
7.98E-04	0.01756	1.40E-05	50	0.003951	-0.003015	0.719859	0.489503	0.984382	0.967075	34.47939
7.93E-04	0.017603	1.40E-05	50	0.003604	-0.002752	0.687642	0.46784	0.985706	0.969832	34.48389
7.88E-04	0.017644	1.39E-05	50	0.003282	-0.002508	0.656276	0.446723	0.986944	0.972416	34.48804
7.84E-04	0.017681	1.39E-05	50	0.002983	-0.002281	0.625726	0.426129	0.9881	0.974834	34.49186
7.80E-04	0.017716	1.38E-05	50	0.002705	-0.00207	0.595966	0.406042	0.989178	0.977095	34.49539
7.78E-04	0.017738	1.38E-05	50	0.002523	-0.001931	0.575614	0.392292	0.989889	0.978586	34.4977

Tab. D.3. Results for the third bed (3.2→5m)

z [m]	n1 [mol/s]	n2 [mol/s]	n3 [mol/s]	n4 [mol/s]	n5 [mol/s]	T [K]	n6 [mol/s]	y1	y2	y3	y4	y5	y6
5	1021.429	855.077	7008.089	104.923	883.4941	490	360	0.099817	0.083561	0.684851	0.010253	0.086338	0.03518
5	1021.429	855.077	7008.089	104.923	883.4941	490	360	0.099817	0.083561	0.684851	0.010253	0.086338	0.03518
5.0001	1021.42	855.084	7008.092	104.916	883.4959	490.0013	360	0.099816	0.083561	0.684852	0.010253	0.086338	0.03518
5.00025	1021.407	855.0946	7008.098	104.9055	883.4985	490.0033	360	0.099815	0.083562	0.684853	0.010252	0.086338	0.03518
5.000475	1021.387	855.1103	7008.105	104.8897	883.5025	490.0062	360	0.099813	0.083564	0.684854	0.01025	0.086339	0.03518
5.000813	1021.358	855.134	7008.117	104.866	883.5084	490.0106	360	0.09981	0.083566	0.684856	0.010248	0.086339	0.03518
5.001319	1021.313	855.1694	7008.135	104.8306	883.5173	490.0172	360	0.099806	0.08357	0.684859	0.010244	0.08634	0.03518
5.002078	1021.247	855.2226	7008.161	104.7774	883.5307	490.0271	360	0.0998	0.083576	0.684863	0.010239	0.086342	0.035181
5.003217	1021.147	855.3023	7008.201	104.6978	883.5509	490.042	360	0.099791	0.083584	0.68487	0.010232	0.086344	0.035181
5.004926	1020.997	855.4217	7008.259	104.5783	883.5812	490.0643	360	0.099777	0.083596	0.684879	0.01022	0.086348	0.035181
5.007489	1020.773	855.6005	7008.346	104.3995	883.6271	490.0979	360	0.099756	0.083614	0.684894	0.010203	0.086353	0.035181
6.800922	848.6825	857.9891	6671.332	102.0109	1053.329	536.6885	360	0.085783	0.086724	0.674325	0.010311	0.106468	0.036388
6.820659	847.9768	857.8174	6669.406	102.1826	1054.206	536.9075	360	0.085727	0.086722	0.67425	0.01033	0.106576	0.036395
6.840491	847.3212	857.6571	6667.614	102.3429	1055.022	537.1111	360	0.085675	0.08672	0.67418	0.010348	0.106676	0.036401
6.860455	846.7122	857.5075	6665.947	102.4925	1055.78	537.3003	360	0.085627	0.086718	0.674115	0.010365	0.106769	0.036406
6.880588	846.1466	857.3679	6664.397	102.6321	1056.486	537.4762	360	0.085582	0.086716	0.674055	0.010381	0.106856	0.036411
6.900923	845.6215	857.2378	6662.956	102.7622	1057.141	537.6395	360	0.08554	0.086715	0.673998	0.010395	0.106936	0.036416
6.921496	845.1344	857.1167	6661.619	102.8833	1057.749	537.7911	360	0.085501	0.086713	0.673946	0.010409	0.107011	0.036421
6.942341	844.6829	857.004	6660.378	102.996	1058.313	537.9317	360	0.085465	0.086712	0.673897	0.010421	0.10708	0.036425
6.963493	844.2647	856.8992	6659.227	103.1008	1058.836	538.0619	360	0.085432	0.08671	0.673852	0.010433	0.107144	0.036429
6.980657	843.9528	856.8209	6658.368	103.1791	1059.226	538.1591	360	0.085407	0.086709	0.673818	0.010442	0.107192	0.036432
7	843.6286	856.7393	6657.475	103.2607	1059.632	538.2601	360	0.085382	0.086708	0.673785	0.01045	0.10724	0.036434

*

K1 [bar-2]	K3	K2 [bar-2]	P bar	r2 [mol/kgs]	r3 [mol/kgs]	TM2	TM3	eta3	eta2	Cp [J/molK]
0.010364	0.006299	6.53E-05	50	0.001741	-0.008934	0.45199	0.797723	0.959993	0.98664	33.78301
0.010364	0.006299	6.53E-05	50	0.001741	-0.008934	0.45199	0.797723	0.959993	0.98664	33.78301
0.010364	0.0063	6.53E-05	50	0.001741	-0.008934	0.452062	0.797731	0.959993	0.986636	33.78304
0.010363	0.0063	6.53E-05	50	0.001742	-0.008935	0.45217	0.797744	0.959991	0.98663	33.78309
0.010361	0.0063	6.53E-05	50	0.001743	-0.008935	0.452331	0.797762	0.95999	0.98662	33.78315
0.010359	0.006301	6.53E-05	50	0.001745	-0.008935	0.452574	0.79779	0.959987	0.986606	33.78325
0.010356	0.006302	6.53E-05	50	0.001748	-0.008935	0.452938	0.797832	0.959983	0.986585	33.78339
0.010351	0.006303	6.52E-05	50	0.001752	-0.008936	0.453484	0.797895	0.959977	0.986553	33.78361
0.010343	0.006305	6.52E-05	50	0.001759	-0.008937	0.454305	0.797989	0.959968	0.986505	33.78394
0.010332	0.006307	6.52E-05	50	0.001768	-0.008939	0.45554	0.798129	0.959955	0.986433	33.78443
0.010315	0.006312	6.51E-05	50	0.001783	-0.008941	0.457397	0.798338	0.959935	0.986325	33.78517
0.001246	0.014725	1.84E-05	50	0.004691	-0.003717	0.762286	0.580909	0.978202	0.963288	35.08741
0.001235	0.014779	1.83E-05	50	0.004334	-0.003435	0.732853	0.558681	0.979792	0.965933	35.09413
0.001224	0.014828	1.82E-05	50	0.003997	-0.003168	0.703906	0.536798	0.981302	0.968453	35.10037
0.001215	0.014875	1.81E-05	50	0.003679	-0.002916	0.675452	0.515268	0.982736	0.970848	35.10618
0.001206	0.014918	1.80E-05	50	0.003379	-0.002679	0.647497	0.494096	0.984094	0.973121	35.11158
0.001198	0.014958	1.79E-05	50	0.003098	-0.002456	0.62005	0.47329	0.985378	0.975273	35.1166
0.00119	0.014995	1.79E-05	50	0.002834	-0.002247	0.593116	0.452858	0.98659	0.977307	35.12127
0.001183	0.01503	1.78E-05	50	0.002586	-0.002051	0.566704	0.432805	0.987731	0.979224	35.12559
0.001177	0.015062	1.77E-05	50	0.002355	-0.001868	0.54082	0.41314	0.988803	0.981029	35.1296
0.001172	0.015086	1.77E-05	50	0.002181	-0.00173	0.520498	0.397691	0.989613	0.982393	35.13259
0.001168	0.01511	1.76E-05	50	0.002006	-0.001591	0.499208	0.381497	0.99043	0.983771	35.13559

Tab. D.4. Results for the forth bed (5→7m)

BIBLIOGRAPHY

1. G. Soave, *Chem. Eng. Sci.*, 1972. **27**: p. 1197.
2. H.F. Rase, *Handbook of commercial Catalysts*. 2000: CRC press.
3. K.M. Vanden-Bussche and G.F. Froment, *J. Catal.*, 1996. **161**(1): p. 1-10.
4. H. Topsoe, http://www.haldortopsoe.com. 2003.
5. H.S. Folger, *Elements of chemical reaction engineering*. 3rd ed. 1999: Prentice Hall.
6. P. Villa, et al., *Ind. Eng. Chem. Process*, 1985. **24**: p. 12-19.
7. J.R. Elliott and C.T. Lira, *Introductory Chemical Engineering Thermodynamics*. 1999: Prentice Hall.