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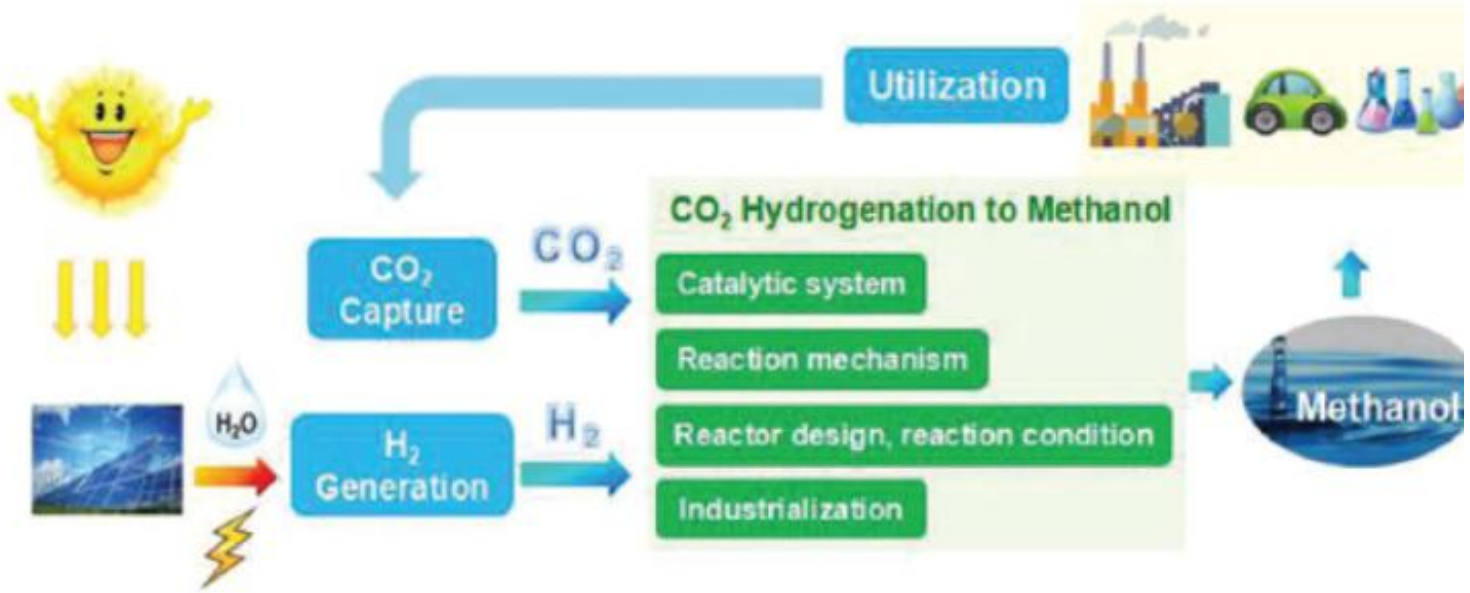


Department of Chemical and Biomolecular Engineering

Methanol Synthesis using $Cu/ZnO/Al_2O_3$ catalyst

Shannon Fernandes

Background Information

- George A Olah- Nobel prize winner in chemistry (1994) for a solution was found to deal with carbon dioxide emissions which was to convert it to methanol.
- Currently, a four-step process is used to obtain methanol.

(1) Desulphurization as Sulphur is a poison for the catalyst when present in the feed stream of the process

(2) Conversion of methane and steam to syngas

(3) Converting syngas to methanol and water which is methanol synthesis

(4) Storage and purification of the process[1].

Formation of methanol occurs by CO and CO_2 hydrogenation and it is an exothermic process.

- $CO_2 + 3H_2 <-> CH_3OH + H_2O$ $\Delta H_1^{rxn}(298\ K) = -49.5\ kJ/mol$ {1}
- $CO_2 + H_2 <-> CO + H_2O$ $\Delta H_2^{rxn}(298\ K) = 41.2\ kJ/mol$ {2}
- $CO + 2H_2 <-> CH_3OH$ $\Delta H_3^{rxn}(298\ K) = -90.7\ kJ/mol$ {3}

Some side-reactions

- Ethanol: $2CH_2OH + H_2 <-> CH_3\ CH_2OH + H_2O$
- Acetone: $CH_3CHOHCH_3 + H_2 <-> CH_3COCH_3 + H_2$
- Di-methyl ether $2CH_3OH <-> CH_3OCH_3 + H_2O$
- Methane: $CO + 3H_2 <-> CH_4 + H_2O$

Catalyst Preparation

The Cu/ZnO is generally prepared using a three-step process:

(1) Hydroxycarbonate precursor is synthesized using a coprecipitation process. In this process aqueous solution of copper, zinc and aluminum nitrates along with a solution of sodium carbonate is poured into a precipitation vessel where it is continuous being stirred. Temperatures of about 343 K and pH of 7 is maintained. The precipitates are then aged, filtered, washed and dried at 353 K.

(2) Calcination which is a process by using thermal energy to decompose the precursor into the oxide form

(3) Copper oxide is finally reduced to the active catalyst form[3].

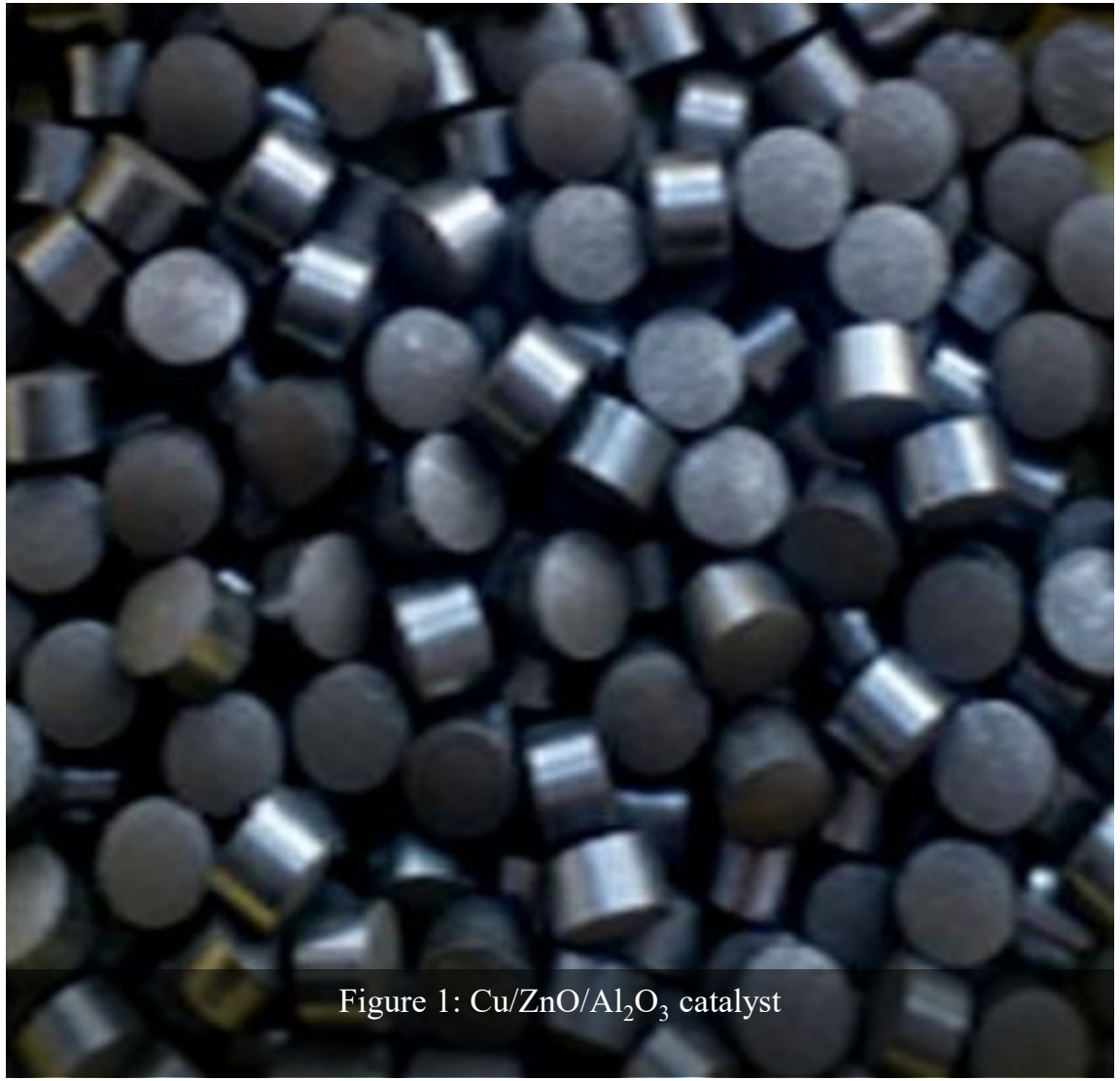


Figure 1: $Cu/ZnO/Al_2O_3$ catalyst

Characteristics

TMC-3/1 industrial ZA Tarnow

- Chemical composition: 55 % Cu, 30 % ZnO and 15 % Al_2O_3.
- Specific surface area: 75-80 m^2g
- Active Cu area: 7-7.5 m^2g
- Pore volume: 0.20-0.25 cm^3g
- Density: 1.30 kg/dm^3
- Crushing strength: 400-500 daN/cm^3 [4].

Active Sites

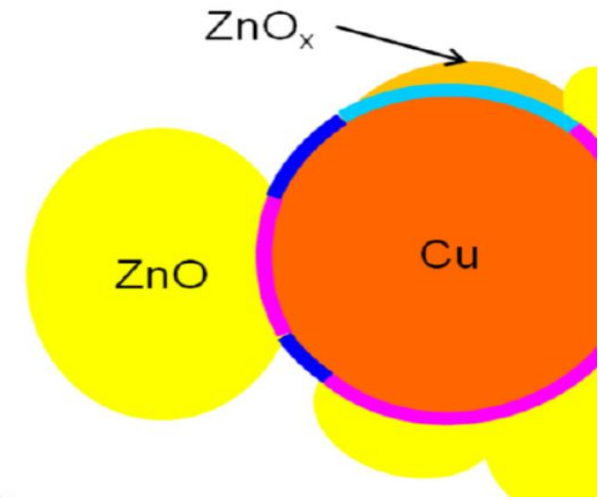
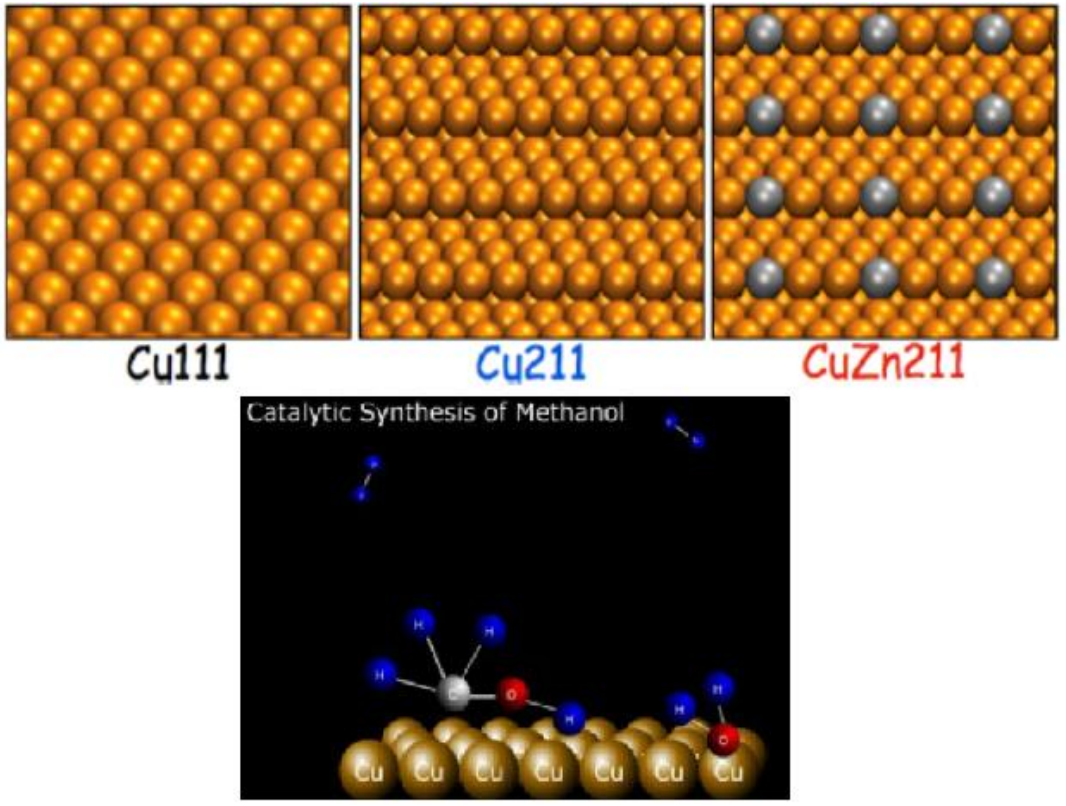


Figure 2: Schematic representation of Cu-ZnO based catalyst[5]

- The formation of methanol from carbon dioxide and the reverse water gas shift reaction progresses on the catalyst with the **copper phase**[6].
- Under typical industrial conditions, **zinc oxide is limited only to structural promotion**[7].
- Addition of small amounts of aluminum also promotes catalyst activity[5], but generally 50-70 % of the catalyst contains copper.
- The adsorption dissociative behavior of H_2 and CO_2 occur only on the copper surface.
- Traces of alkaline species or surface oxygen promotes the oxidizing adsorption of carbon dioxide on metallic copper.
- Carbonate structures are then formed due to the further adsorption of carbon dioxide on the oxidized copper surface.
- The carbonates are then hydrogenated to bicarbonate structures where it proceeds under a series of elementary steps to finally form methanol[8-15].

Active Site



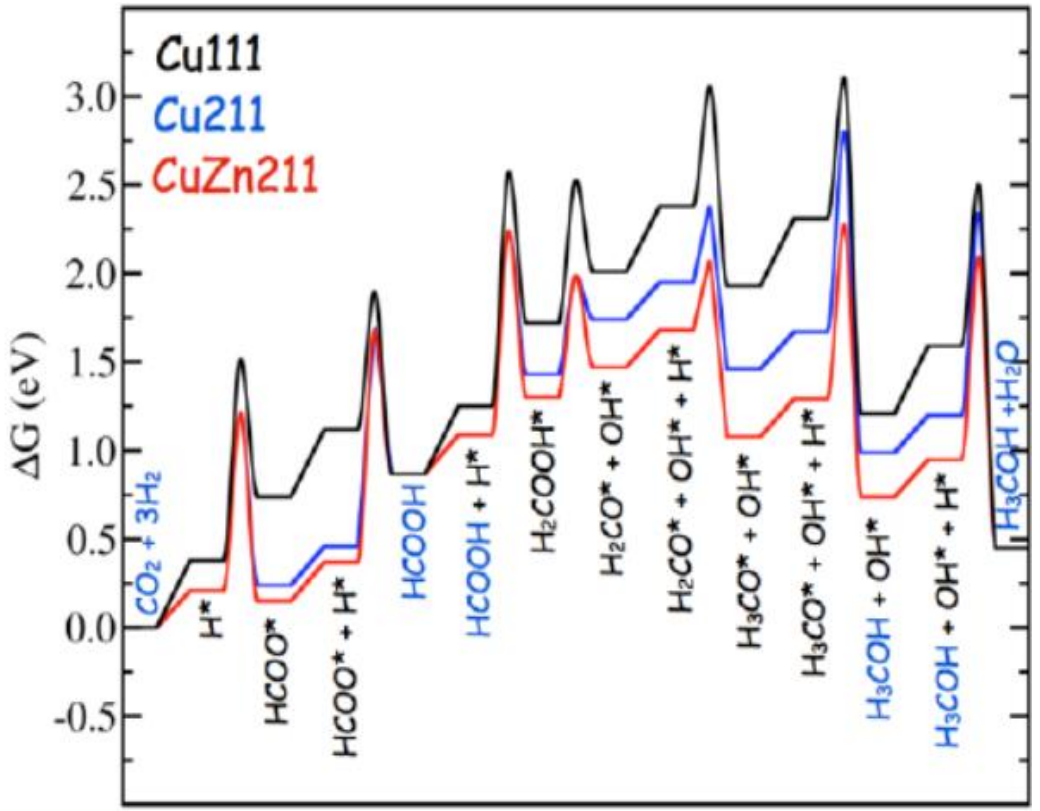
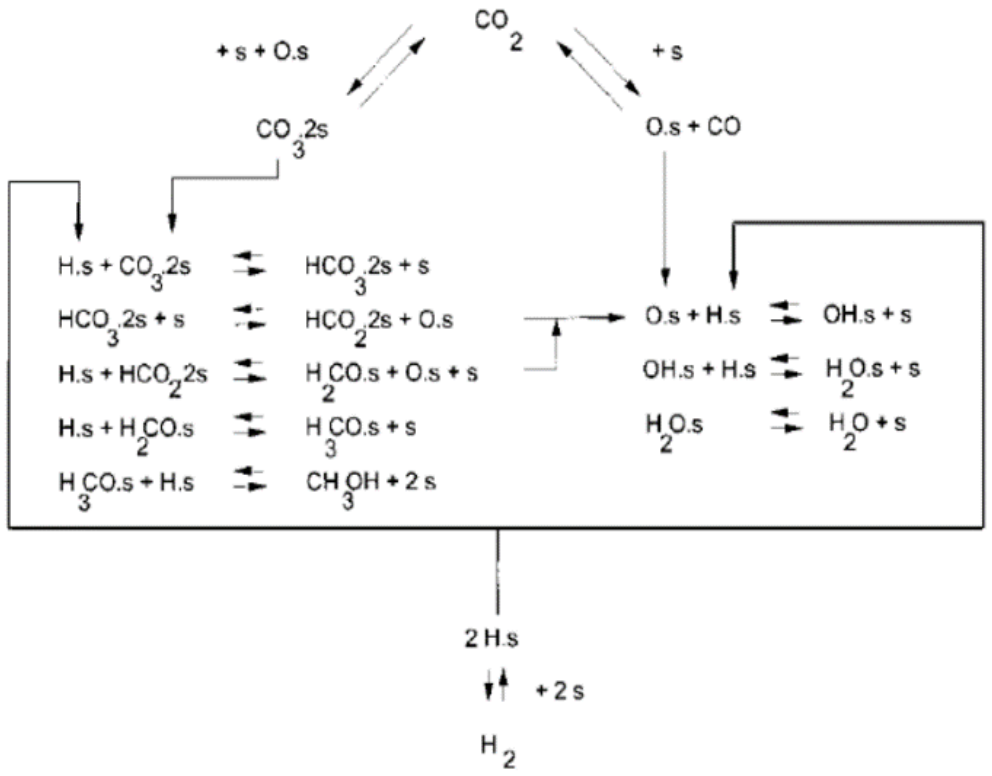


Figure 3: Gibbs energy for Cu(111) and Cu(211) surface[16]

Kinetic model by Vanden Bussche and Froment[14], 1996

$$CO_2 + 3H_2 <-> CH_3OH + H_2O \quad \{1\}$$

$$CO_2 + H_2 <-> CO + H_2O \quad \{2\}$$



$H_2(g) + 2s$	⇌	$2\ H.s$	(K_{H2})	
$CO_2(g) + s$	⇌	$O.s + CO(g)$	(k_1, K_1)	(rds)
$CO_2(g) + O.s + s$	⇌	$CO_3.2s$	(K_2)	
$CO_3.2s + H.s$	⇌	$HCO_3.2s + s$	(K_3)	
$HCO_3.2s + s$	⇌	$HCO_2.2s + O.s$	(K_4)	
$HCO_2.2s + H.s$	⇌	$H_2CO_2.2s + s$	(k_{5a})	(rds)
$H_2CO_2.2s$	⇌	$H_2CO.s + O.s$	(K_{5b})	
$H_2CO.s + H.s$	⇌	$H_3CO.s + s$	(K_6)	
$H_3CO.s + H.s$	⇌	$CH_3OH(g) + 2s$	(K_7)	
$O.s + H.s$	⇌	$OH.s + s$	(K_8)	
$OH.s + H.s$	⇌	$H_2O.s + s$	(K_9)	
$H_2O.s$	⇌	$H_2O(g) + s$	(K_{H2O})	

Figure 4: The reaction mechanism for methanol synthesis and reverse water gas shift reaction (RWGS) with the rate determining step (rds)

- CO_2 was the main source for methanol production.
- Reactive intermediate: H.s, O.s, CO_3.2s, HCO_3.2s, HCO_2.2s, H_2CO_2.2s, H_2CO.s, H_3CO.s, OH.s and H_2O.s.
- However, the free active sites concentration c_s can be achieved by eliminating the surface intermediates and performing a balance over the total number of sites c_t $1 = \frac{c_s}{c_t} + \frac{c_{O.s}}{c_t} + \frac{c_{H2O.s}}{c_t} + \frac{c_{HCO2.2s}}{c_t} + \frac{c_{CO3.2s}}{c_t} + \frac{c_{H.s}}{c_t}$;
- Concentrations of adsorbed methoxy, methanol, bicarbonate, formaldehyde, and hydroxyl species can be ignored as the concentrations are negligible under these reactive conditions.

Rate Equations

RDS

- (1) The first rate determining step (rds) is the **dissociative adsorption of carbon dioxide as there a breakage of carbon oxygen bond**, and several studies[17,18,19] have proved it to be a rds.
- (2) The second rds if the formate hydrogenation as studies have shown[20,21,22] that it is the **longest living reactive intermediate on copper** in methanol synthesis, and also HCO_2.2s is **the most abundant reactive intermediate (mari)**[23].

$$r_1 = \frac{k_{MeOH} p_{CO2} p_{H2} \cdot \left(1 - \frac{p_{CH3OH} p_{H2O}}{K_{eq1} p_{H2}^3 p_{CO2}}\right)}{\left(1 + k_c \frac{p_{H2O}}{p_{H2}} + k_a \sqrt{p_{H2}} + k_b p_{H2O}\right)^3}$$

$$r_2 = \frac{k_{RWGS} p_{CO2} \cdot \left(1 - \frac{p_{CO} p_{H2O}}{K_{eq2} p_{H2} p_{CO2}}\right)}{\left(1 + k_c \frac{p_{H2O}}{p_{H2}} + k_a \sqrt{p_{H2}} + k_b p_{H2O}\right)}$$

Table 1: Values of the reaction constants

Reaction constant	A	B
k_a	0.499	17197
k_b	$6.62*10^{-11}$	124119
k_c	3453.38	-
k_{MeOH}	1.07	36696
k_{RWGS}	$1.22*10^{10}$	94765

The reaction constants can be expressed as $k_i = Ae^{(\frac{B}{RT})}$ where R is the universal gas constant (J/molK) and the values in the below table.

- Equilibrium constants K_{eq1} and K_{eq2} can be calculated using equations: $\log_{10}K_{eq1}$ = (3066/T) - 10592 and $\log_{10}K_{eq2}$ = (-2073/T) +2029.
- Based on [15,24], this model has no diffusion limitations so the effectiveness factors can be assumed to be 1.

Methanol Synthesis Reactor

- Syngas is used to obtain methanol where chemical equilibrium limits the reaction, so recycling is carried out for the unreacted gas.
- A common catalyst used in this process is $Cu/ZnO/Al_2O_3$ and the process is called Lurgi.
- Commercially this process is carried out at temperatures and pressures between 493-543 K and 15-100 bar
- The life cycle of this catalyst is two years where Sulphur is not considered in the feed as Sulphur damages the catalyst.
- A multi-tubular reactor is used with a cooling water jacket and the catalytic pallets are placed inside the tubes
- The reactor design closely resembles a shell and tube heat exchanger[24].

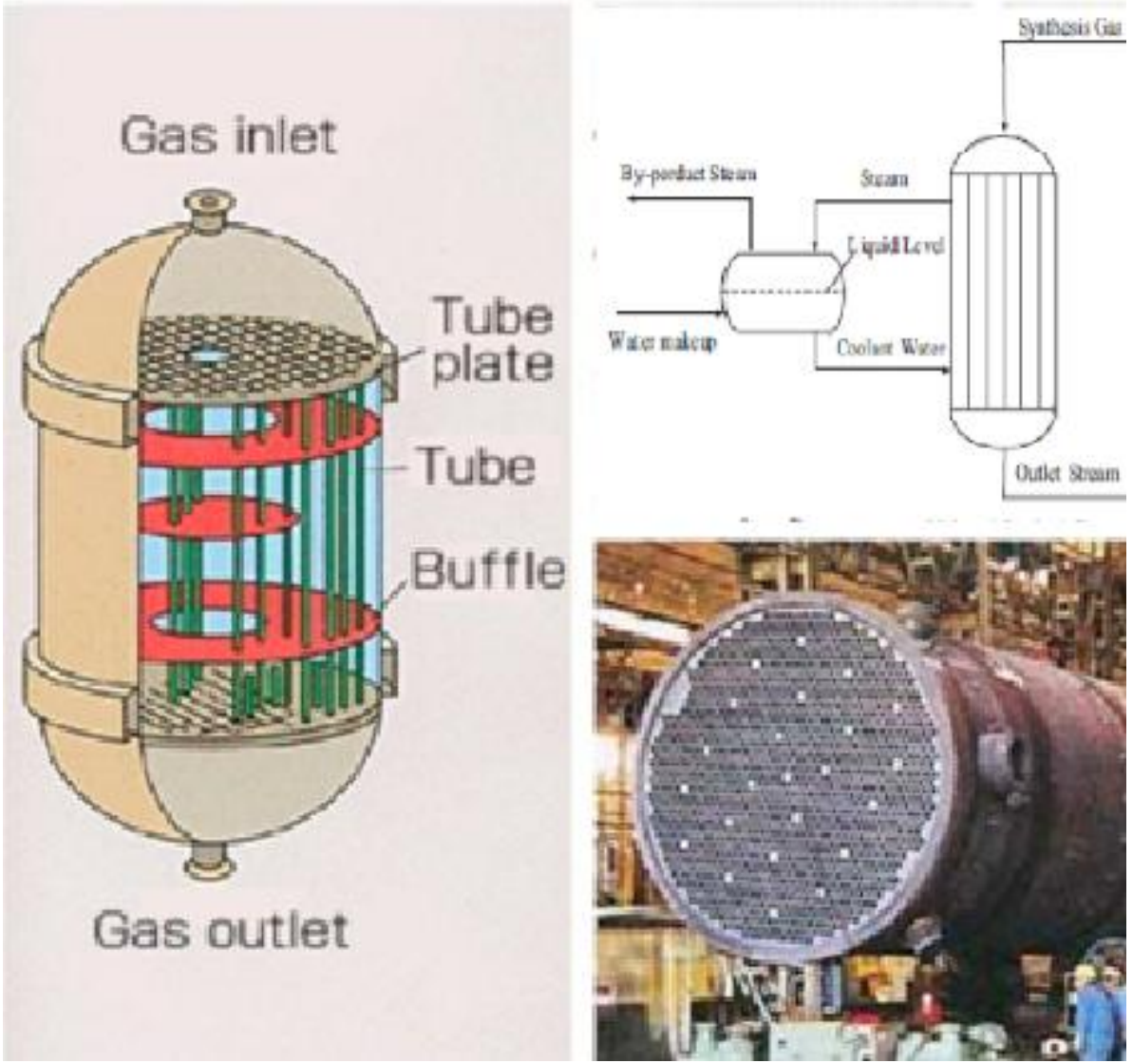


Figure 5: Multi-tubular reactor

Assumptions

- A **one-dimension pseudo-homogenous model** is considered
- **Axial diffusion** can be **neglected** because of the high gas velocity
- **Radial effects** can be **neglected** because the ratio of the reactor diameter to the reactor length is small so the velocity, concentration and temperature profiled can be assumed as constant.
- Due to the small pallet size, the pressure and temperature gradient inside the pallet can be neglected which results to a **homogenous catalytic particle** (merging the equations of solid and gas phase) instead of a heterogenous catalytic particle.
- Methanation reactions occur at temperatures run above 570 K which would lead to reactor instabilities and thermal runaway, so this may lead to drop in efficiency of the process[1].
- The deactivation of the catalyst can also be neglected as there is **no Sulphur** in the inlet stream and the process is carried out at temperatures **below 570 K**, thus ignoring sintering phenomena.
- The side reactions can be ignored because of **high catalyst selectivity**[1,26,27].

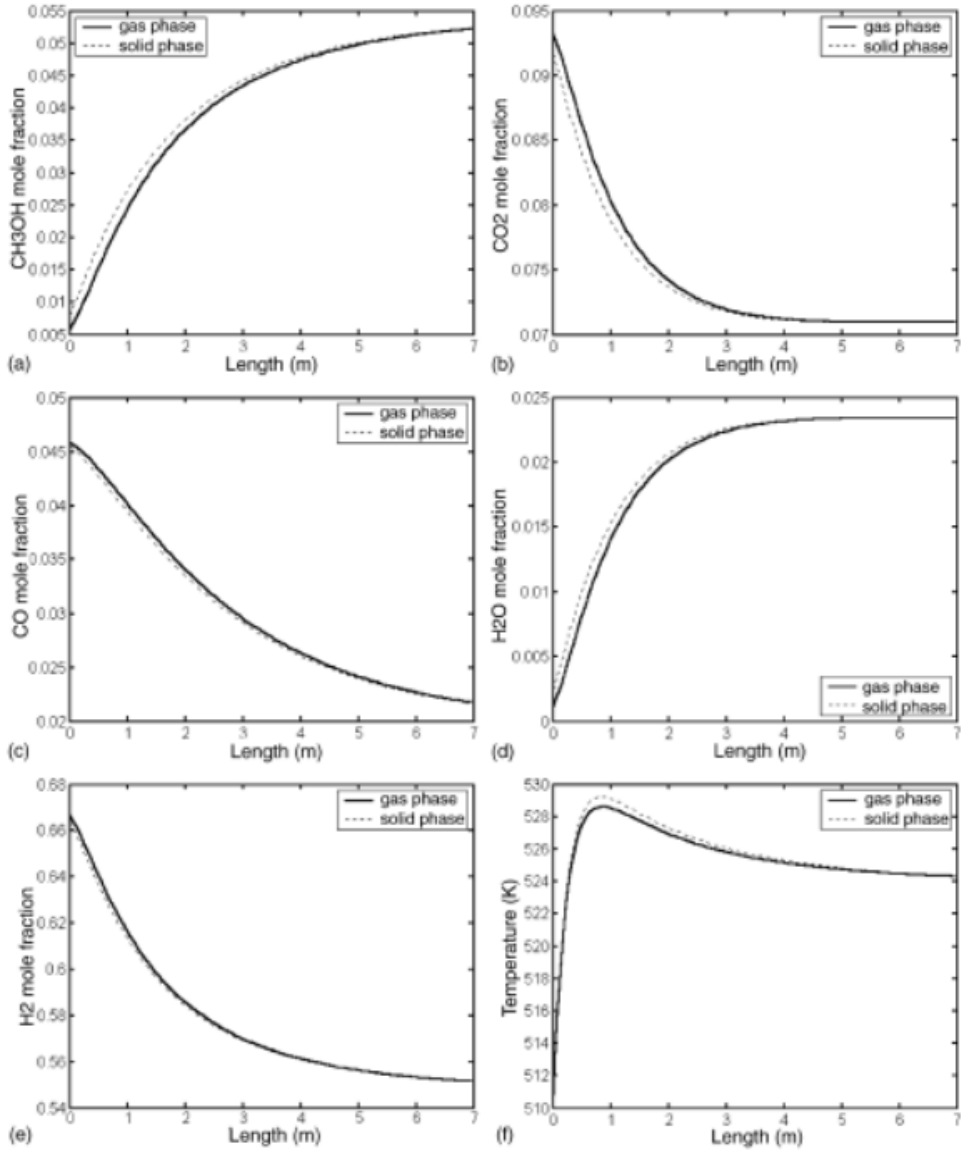


Figure 6: Comparison of solid and gas phase in the catalyst[25]

Equations

- Mass Balance
- $\frac{dF_i}{dw} = r_i$
- Energy Balance
- $\frac{dT}{dw} = \frac{Ua(T_j - T)}{FC_{pm}} - \frac{\Delta H_j^{rxn} r_j \eta_j}{FC_{pm}}$
- Pressure Drop (Ergun's Equation)
- $\frac{dP}{dw} = -\frac{G}{\rho g_c d_p}\left(\frac{1-\emptyset}{\emptyset^3}\right)\left[\frac{150(1-\emptyset)\mu}{d_p} + 1.75G\right]\frac{z}{w}$
- The global heat exchange coefficient is given by:
- $U = \left(\frac{1}{h_i} + \frac{A_i \ln\left(\frac{D_o}{D_i}\right)}{2\pi Lk} + \frac{A_i}{A_o h_o}\right)$

No Diffusion limitations so effectiveness factor is 1

Industrial methanol reactor design

Table 2: Industrial methanol reactor design

Internal diameter of tube	44.5	mm
External diameter of tube	48.5	mm
Number of tubes	4801	
Tube length	7260	mm
Tube inlet temperature	500	K
Shell steam temperature	523	K
Catalyst diameter	6	mm
Bed porosity	0.4	
Catalyst density	1100	kg/m^3
Inlet pressure	82	bar

Results

- The industrial reactor used produces **2062 ton of methanol per day** with a methanol outlet mole fraction to be **0.1**.
- Using the kinetic model and equations that govern the reactor, the following results are obtained

Table 3: Comparisons between the results obtained from an actual Industrial reactor with a Pseudo-homogenous model [26,28].

Parameters	Industrial reactor	Pseudo-homogeneous model	Error
Temperature outlet (K)	530	530.16	0.03%
Pressure outlet (bar)	80.92	79.84	1.33%
Methanol production (ton/day)	2061	2067	0.29%
Methanol molar fraction	0.1	0.0992	0.8%

Results

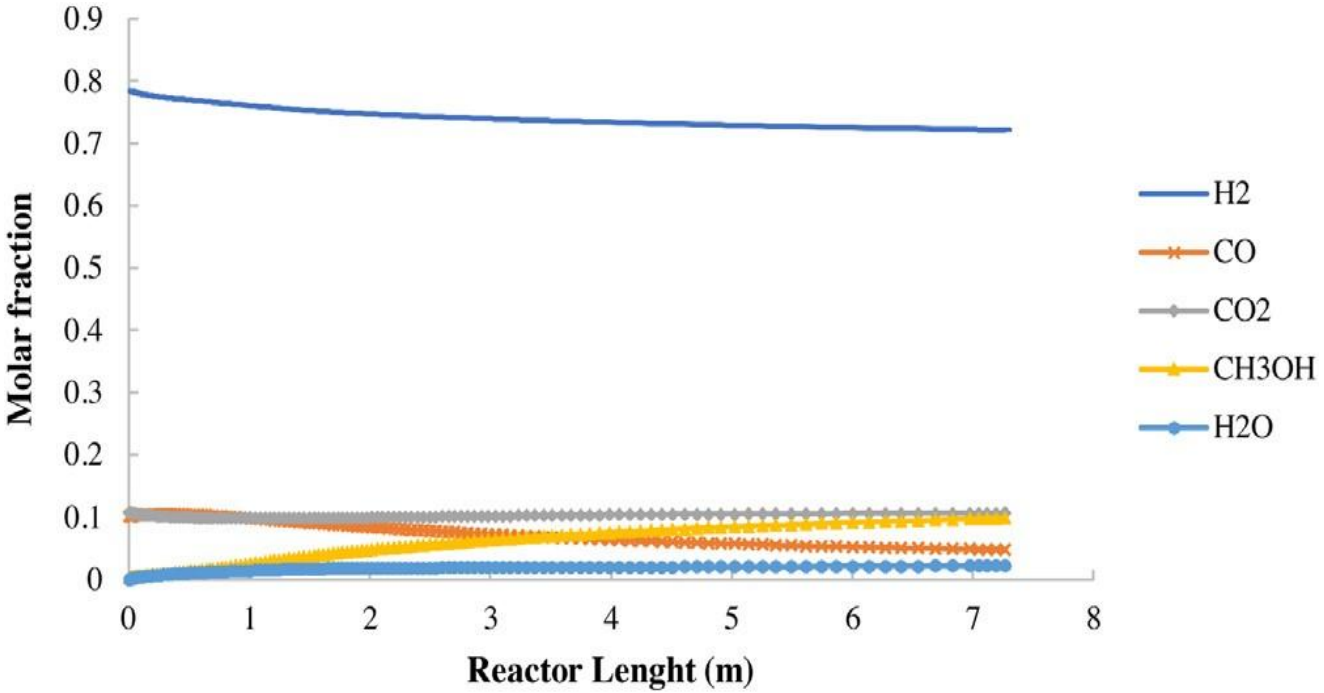


Figure 7: Mole fraction of each component along the length of the reactor

11,330 mol/s entering while 9511 mol/s leaving the reactor. This shows that there is a 20% carbon conversion to methanol. Moreover, in the figure it can be observed that concentrations of CO, CO_2 and H_2 decreases while concentrations of CH_3OH and H_2O increases along the length of the reactor.

Table 4: Outlet methanol composition

Total catalyst	35700	kg
Temperature outlet	530	K
Pressure outlet	79.84	bar
Flow rate CH_3OH | Composition CH_3OH	944 | 9.92	mol/s | mol %
H_2O	216 | 72.22	mol/s | mol %
H_2	6870 | 2.27	mol/s | mol %
CO_2	1024 | 10.76	mol/s | mol %
CO	460 | 4.83	mol/s | mol %
Total	9514 | 100	mol/s | mol %

Results

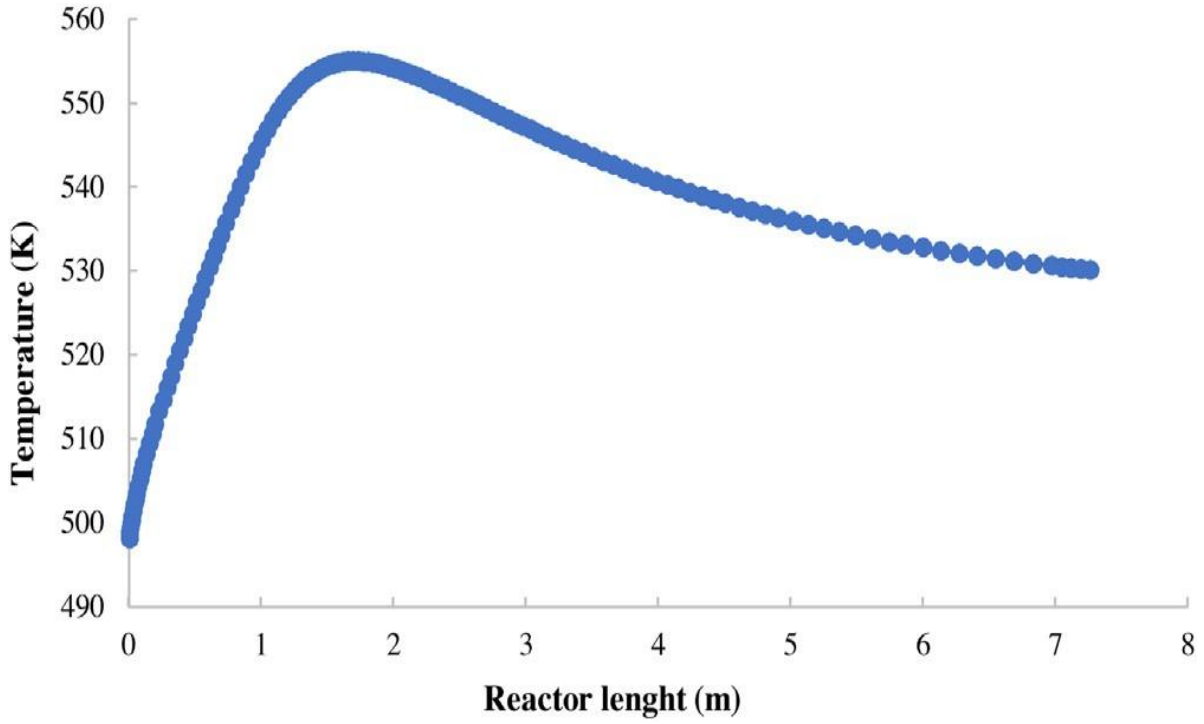


Figure 8: Temperature profile along the length of the reactor

- Inflation point which is the reverse water gas shift reaction that reaches its equilibrium.
- The reaction then changes direction and then all the reactions are in series.
- The hot spot point is noted to be **555 K**.
- The outlet temperature is **530 K** and the pressure drop along the length of the reactor is **1.08 bar**.

Comparative model

$$r_3 = \frac{k_1 \cdot K_{CO} \cdot \left(f_{CO} \cdot f_{H_2}^{\frac{3}{2}} - \frac{f_{CH_3OH}}{K_{eq,1} \cdot \sqrt{f_{H_2}}} \right)}{\left(1 + K_{CO} \cdot f_{CO} + K_{CO_2} \cdot f_{CO_2}\right) \cdot \left(f_{H_2}^{\frac{1}{2}} + \frac{K_{H_2O}}{K_{H_2}^{\frac{1}{2}}} \cdot f_{H_2O} \right)}$$

$$r_1 = \frac{k_3 \cdot K_{CO} \cdot \left(f_{CO} \cdot f_{H_2}^{3/2} - \frac{f_{CH_3OH} \cdot f_{H_2O}}{K_{eq,3} \cdot f_{H_2}^{3/2}} \right)}{\left(1 + K_{CO} \cdot f_{CO} + K_{CO_2} \cdot f_{CO_2}\right) \cdot \left(f_{H_2}^{\frac{1}{2}} + \frac{K_{H_2O}}{K_{H_2}^{\frac{1}{2}}} \cdot f_{H_2O} \right)}$$

$$r_2 = \frac{k_2 \cdot K_{CO_2} \cdot \left(f_{CO_2} \cdot f_{H_2} - \frac{f_{H_2O} \cdot f_{CO}}{K_{eq,2}} \right)}{\left(1 + K_{CO} \cdot f_{CO} + K_{CO_2} \cdot f_{CO_2}\right) \cdot \left(f_{H_2}^{\frac{1}{2}} + \frac{K_{H_2O}}{K_{H_2}^{\frac{1}{2}}} \cdot f_{H_2O} \right)}$$

$$k_1 = 4.89 \cdot 10^7 \cdot e\left(-\frac{113000}{RT}\right) \quad K_{CO} = 2.16 \cdot 10^{-5} \cdot e^{\left(\frac{98388}{RT}\right)}$$

$$k_2 = 9.64 \cdot 10^{11} \cdot e\left(-\frac{152900}{RT}\right) \quad K_{CO_2} = 7.05 \cdot 10^{-7} \cdot e^{\left(\frac{61200}{RT}\right)}$$

$$k_3 = 2.16 \cdot 10^{-5} \cdot e^{\left(\frac{46800}{RT}\right)}$$

$$\log_{10} K_{eq,i} = A + \frac{B}{R \cdot T} \qquad \frac{K_{H_2O}}{K_{H_2}^{\frac{1}{2}}} = 6.37 \cdot 10^{-9} \cdot e^{\left(\frac{84000}{RT}\right)}$$

Figure 9: Graaf et al., 1988[29] Kinetic Model

Comparative model

- By using Graaf et al. model, it was found that there is an intra-particle diffusion phenomenon when temperatures reach above 516 K in commercial catalysts.
- An experimental Graaf et al

effectiveness is also reported to be $\eta_{CO2} = 3.5 + 0.005\ P - 0.0056\ T - 0.038 d_p$ and $\eta_{CO} = 3.04 + 0.002\ P - 0.0043\ T - 0.054\ d_p$.

- A pseudo-zero order model has also

been proposed to be $r_{CH3OH} = 0.0546\ p_{CO2}^{-0.164}$ by the regression of the experimental data.

$$\theta_j = \frac{d_p}{6} \cdot \sqrt{\frac{k_j' \cdot \rho_{cat} \cdot \left(K_j'^{eq} + 1\right)}{K_j'^{eq} \cdot D_j^{eff}}}$$

$$\eta_j = \frac{1}{\theta_j} \cdot \left(\frac{1}{\tanh(3\theta_j)} - \frac{1}{3\theta_j}\right)$$

$$r'_{CH3OH} = k'_{CH3OH} \cdot \left(c_{H2} - \frac{c_{CH3OH}}{K'^{eq}_{CH3OH}}\right)$$

$$r'_{H2O} = k'_{H2O} \cdot \left(c_{H2} - \frac{c_{H2O}}{K'^{eq}_{H2O}}\right)$$

$$K'^{eq}_{CH3OH} = \frac{y^{eq}_{CH3OH}}{y^{eq}_{H2}}$$

$$K'^{eq}_{H2O} = \frac{y^{eq}_{H2O}}{y^{eq}_{H2}}$$

$$\frac{1}{D^{eff}_{CH3OH}} = \frac{\tau}{\varepsilon}\left(\frac{1}{D_{Knudsen,CH3OH}} + \sum_{i \neq CH3OH}^{N} \frac{y_i}{D_{CH3OH,i}}\right)$$

$$\frac{1}{D^{eff}_{H2O}} = \frac{\tau}{\varepsilon}\left(\frac{1}{D_{Knudsen,H2O}} + \sum_{i \neq H2O}^{N} \frac{y_i}{D_{H2O,i}}\right)$$

$$D_{Knudsen,i} = \frac{d_{pori}}{3} \cdot \sqrt{\frac{8 \cdot R_g \cdot T}{\pi \cdot M_i}}$$

$$D_{i,j} = \frac{3.1610^{-8} \cdot T^{1.75} \cdot \left(\frac{1}{M_i} - \frac{1}{M_j}\right)}{P \cdot \left[\left(\sum v_i\right)^{\frac{1}{3}} + \left(\sum v_i\right)^{\frac{1}{3}}\right]^2}$$

Figure 10: Equation that influence effectiveness factor

Results of the comparative study

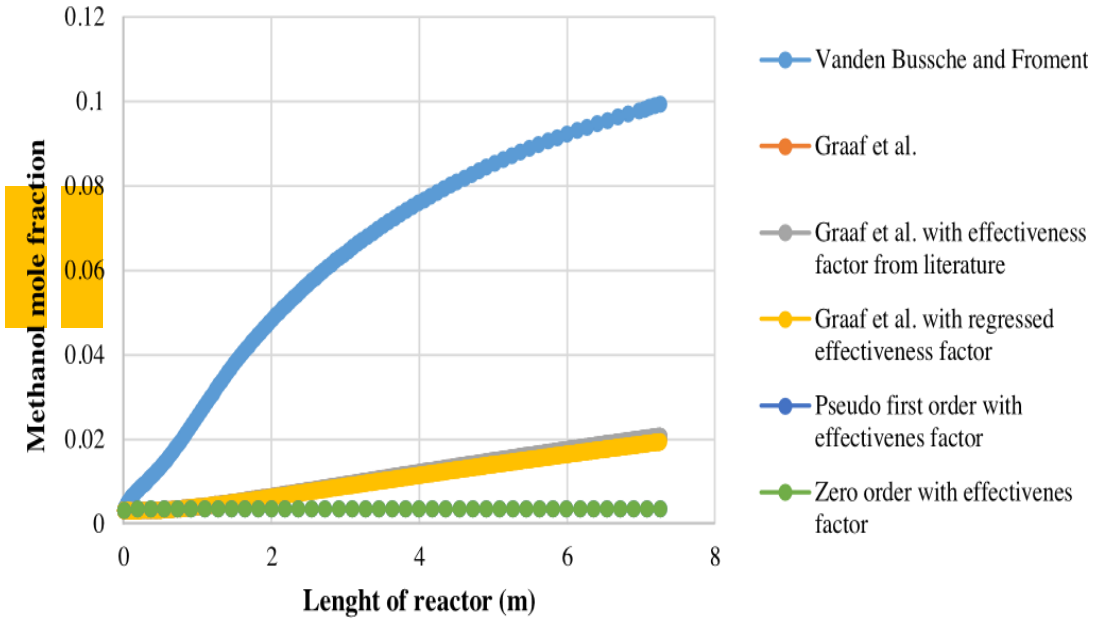


Figure 11: Graphic representation of the mole fraction vs reactor length using different kinetic models

Table 5: Comparative results of different models.

Kinetic model	Outlet temperature (K)	Outlet pressure (bar)	Outlet CH_3OH mole fraction	Outlet CH_3OH (mol/s)
Vanden Bussche and Froment	530.16	79.84	0.0992	944
Graaf et al.	527.43	79.68	0.0205	224
Pseudo first order with effectiveness factors	523.35	80.2	0.0034	39
Pseudo zero order with effectiveness factors	523.35	80.2	0.0034	39
Graaf et al. with regressed effectiveness factors	527.35	79.68	0.0194	212
Graaf et al. with effectiveness factors from literature	527.65	79.68	0.0207	226

Experimental results shows 0.1 to be outlet methanol mole fraction

Conclusion

- Copper phase is the active site
- Vanden Bussche and Froment, 1996 kinetic model is considered

RDS

- (1) The first rate determining step (rds) is the **dissociative adsorption of carbon dioxide as there a breakage of carbon oxygen bond**, and several studies[17,18,19] have proved it to be a rds.
- (2) The second rds if the formate hydrogenation as studies have shown[20,21,22] that it is the **longest living reactive intermediate on copper** in methanol synthesis, and also HCO_2.2s is **the most abundant reactive intermediate (mari)**[23].
- The reactor modeled is a catalytic multi-tubular reactor

APPENDIX A (MeOHheatCp.m)

```
function Cp = MeOHheatCp(T,P,F)
% by Richard K. Herz <rherz@ucsd.edu> 2011
% is called by function MeOHenergy
% returns Cp of mixture (J/K/mol)
% need mole fractions x below
Ftot = sum(F);
x = F/Ftot;
% coefficients for fit of Cp to 3rd order polynomial in T from
% Handbook of Chemistry and Physics at 1.0133 bar
% rows in order: H2, CO, CO2, MeOH, Water, N2, CH4
Cpcoef(1,1:4) = [-1.0653e-09 5.3794e-06 -0.004198 30.1063];
Cpcoef(2,1:4) = [-2.8314e-09 6.0321e-06 0.002423 27.5047];
Cpcoef(3,1:4) = [8.1713e-09 -3.5920e-05 0.059157 22.9484];
Cpcoef(4,1:4) = [9.8419e-09 -5.7293e-05 0.12811 8.9427];
Cpcoef(5,1:4) = [-3.6093e-09 1.0553e-05 0.002698 31.7360];
Cpcoef(6,1:4) = [-3.6077e-09 9.0963e-06 -0.001325 28.4826];
Cpcoef(7,1:4) = [-2.3256e-09 -1.2497e-05 .076466 12.0092];
% adjust each component Cp for pressure
% from Cp's from Aspen Plus, 500-501 K & values at
% 1.0133 and 70 bar except as noted
Pfac = [5.2762e-5 % H2
5.3402e-4 % CO
1.6103e-3 % CO2
6.9236e-4 % MeOH, 1.0133 & 10 bar
1.3890e-3 % H2O, 1.0133 & 20 bar
4.8512e-4 % N2
6.1509e-4]; % CH4
% adjust to get agreement with Cp in Aspen at 500 K, 70 bar
% of Chen et al. (2011) reactor outlet mixture
Pfac = Pfac * 0.9523;
Pcorrec = 1 + (P - 1.0133)*Pfac;
Cp = 0;
for i = 1:7
Cp = Cp + x(i) * Pcorrec(i) * polyval(Cpcoef(i,:),T);
end
```

Simpler model can be used

$$C_p^{ig}/R = A + BT + CT^2 + DT^{-2}$$

Where the temperature is in Kelvin and is valid from 298K to T_{max}

Specie	T_{max}	A	$10^3 B$	$10^6 C$	$10^{-5} D$
CO	2500	3.376	0.557	.....	-0.031
CO_2	2000	5.457	1.045	.....	-1.157
H_2	3000	3.249	0.422	.....	0.083
H_2O	2000	3.470	1.450	.....	0.121
CH_4	1500	1.702	9.081	-2.14	.....
CH_3OH	1500	2.211	12.216	-3.450	.....

APPENDIX A (MeOHheatrxn.m)

```
function Hrxn = MeOHheatrxn(T,P)
% by Richard K. Herz <rherz@ucsd.edu> 2011
% is called by function MeOHenergy
% returns delta-H reaction in (J/mol) for
% two Independent Stoichiometric Equations (ISE):
% ISE 1: CO2 + 3H2 = CH3OH + H2O
% ISE 2: CO2 + H2 = CO + H2O
% is called by function MeOHenergy
% get good agreement with Aspen Plus at all these conditions:
% 298 K and 1 bar
% 500 K and 1 bar
% 298 K and 60 bar
% 500 K and 70 bar
% need to correct del-Hf for both T and P
Hrxn298 = [-49.3160 ; 41.1540]; % kJ/mol, at 298.15 K, 1 atm
% correct Hrxn at 298.15 K and 1 atm for P
% from fit to Aspen results
% these pressure factors are for mixture of components
% specific to each stoich equation
Hrxn298(1) = Hrxn298(1) - 0.0686*(P - 1.0133); % P in bar
Hrxn298(2) = Hrxn298(2) - 0.0365*(P - 1.0133); % P in bar
% NOW NEED TO CORRECT FOR T NOT 298.15 K
% del-Hf(T) = del-Hf(Tr) + INTEG from Tr to T (del-Cp)
% delCpCoef = polynomial fit vs. T of
% Sum(stoich-coef-i * Cp-i) for each stoich equation
% for 3rd order fit, for Cp in J/mol/K
delCpCoef = [1.2571e-09 -2.6958e-05 0.084247 -72.5886
-1.3547e-08 4.7125e-05 -0.049837 6.1860];
% now get integral of delCp over Tr = 298.15 to T
Tr = 298.15;
Tfac = [(T^4-Tr^4)/4 ; (T^3-Tr^3)/3 ; (T^2-Tr^2)/2 ; (T-Tr)];
% THIS Tfac CORRECTS HRXN AT 1 ATM FOR T OK
% but Cp's increase with P
% here adjust Tfac for each reaction separately for agreement
% with Aspen heat of reaction at 500 K & 70 bar,
% where these pressure factors are for specific mixture of
% components in each stoich equation
Tfac1 = Tfac * (1 - 0.00466*(P-1.0133)); % P in bar
Tfac2 = Tfac * (1 - 0.01550*(P-1.0133)); % P in bar
% now compute full T correction adjusted for P
delCpInt(1,:) = delCpCoef(1,:) * Tfac1; % J/mol
delCpInt(2,:) = delCpCoef(2,:) * Tfac2; % J/mol
% finally compute Hrxn corrected for T and P Hrxn = Hrxn298 * 1e3 + delCpInt; % J/mol at T
```

$$H_i = H_i^o(T_{ref}) + \int_{T_{ref}}^{T} C_{p_i} dT$$

APPENDIX A (MeOHviscosity.m)

```
function visc = MeOHviscosity(T,P,F)
% by Richard K. Herz <rherz@ucsd.edu> 2011
% is called by function MeOHpress
% returns gas dynamic viscosity in units of (Pa s)
% viscosity is corrected for T but not for pressure
% NOTE: this doesn't change much with composition so if need to
% speed up the program you can set to a constant average value
% for example, using viscosity for air gave results not too different
% from mixture calculations below
% Air viscosity from Physical Chemistry by P.W. Atkins (1978), p. 810
% mu = 1.82e-5; % kg/m/s, for air at 293 K
% mu = mu*(T/293).^0.5; % correct for T
% From Properties of Liquids and Gases, 5th ed,
% by Poling, Prausnitz & O'Connell
% at low P, dynamic viscosity is independent of P
% and proportional to T^(1/2)
% see Wilke method on p. 9.21 for gas mixtures
% From data over 300-600 K in CRC Handbook of Chem and Phys
% coefficients for gas dynamic viscosity for 1st order polynomial in T^0.5
% Viscosity is given in units of (micro-Pa s)
% rows: % H2, CO, CO2, methanol, water, N2, CH4
Viscoef(1,:) = [0.7526 -4.0884];
Viscoef(2,:) = [1.5750 -9.4437];
Viscoef(3,:) = [1.8116 -16.4474];
Viscoef(4,:) = [1.4234 -15.2870];
Viscoef(5,:) = [1.5913 -17.9877];
Viscoef(6,:) = [1.6324 -10.4033];
Viscoef(7,:) = [1.1434 -8.5867];
Thalf = sqrt(T);
Vis(1) = polyval(Viscoef(1,:),Thalf);
Vis(2) = polyval(Viscoef(2,:),Thalf);
Vis(3) = polyval(Viscoef(3,:),Thalf);
Vis(4) = polyval(Viscoef(4,:),Thalf);
Vis(5) = polyval(Viscoef(5,:),Thalf);
Vis(6) = polyval(Viscoef(6,:),Thalf);
Vis(7) = polyval(Viscoef(7,:),Thalf); % (micro-Pa s)
Vis = Vis * 1e-6; % (Pa s) = (micro-Pa s) * 1 Pa / 1e6 micro-Pa
% now need to get mixture viscosity for this composition
% From Properties of Liquids and Gases, 5th ed,
% by Poling, Prausnitz & O'Connell
% see Wilke method on p. 9.21 for gas mixtures
% mole fractions in order: H2, CO, CO2, methanol, water, N2, CH4
Ftot = sum(F);
x = F/Ftot;
MW = [2 28 44 32 18 28 16]; % g/mol, only be used in ratio so grams OK
for i = 1:7
for j = 1:7
tNum = ( 1 + (Vis(i)/Vis(j))^0.5 * (MW(i)/MW(j))^0.25 )^2;
tDenom = ( 8*(1+MW(i)/MW(j)) )^0.5;
phi(i,j) = tNum/tDenom;
end
end
visc = 0;
for i = 1:7
tDenom(i) = 0;
for j = 1:7
tDenom(i) = tDenom(i) + x(j)*phi(i,j);
end
visc = visc + x(i) .* Vis(i) ./ tDenom(i);
end
% HOWEVER, gas viscosity increases with P at high P
% so later should include this
% for now just multiply by a factor to get agreement with
% Chen et al. (2011) plant data
% visc = visc*(1 + 0.01146*(P - 1.0133));
visc = visc*(1 + 0.013*(P - 1.0133));
```

Simpler model can be used

$$\mu_{mix} = \sum_{i=1}^{n} y_i \mu_i$$

APPENDIX A (MeOHrates.m)

```
function r = MeOHrates(T,P,F)
% by Richard K. Herz <rherz@ucsd.edu> 2011
% is called by function MeOHodes
% returns rates of the two reactions in mol/s/kg
% inputs: y(1) = T, y(2) = P, y(3) = e(1), y(4) = e(2)
% T in K, P in bar
% e = stoichimetric extents
% r(1,1) = de(1)/dW = rate of methanol formation (mol/kg/s)
% r(2,1) = de(2)/dW = rate of CO formation (mol/kg/s)
%
% SEE COMMENTS BELOW TO ADD OR DELETE REACTION PATHWAYS
R = 8.314472; % J/mol/K, for use in Arrhenius rate expressions below, ideal gas constant
% need mole fractions x below
Ftot = sum(F);
x = F/Ftot;
% partial pressures
ph2 = P*x(1); % bar
pco = P*x(2);
pco2 = P*x(3);
pm = P*x(4); % m = methanol
pw = P*x(5); % w = H2O
% equilibrium constants for the two
% Independent Stoichiometric Equations (ISE)
% K1 for ISE 1: CO2 + 3H2 = CH3OH + H2O
log10K1 = 3066/T - 10.592;
K1 = 10^log10K1;
% K2 for ISE 2: CO2 + H2 = CO + H2O
log10K2 = -2073/T + 2.029;
K2 = 10^log10K2;
% rates of reaction pathways from Vanden Bussche and Froment, 1996
% K. M. Vanden Bussche and G. F. Froment,
% "A Steady-State Kinetic Model for Methanol Synthesis
% and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al2O3 Catalyst,"
% J. Catalysis, vol. 161, pp. 1-10, 1996.
% rate coefficient parameters from Table 2
A(1) = 0.499; % pre-exp for sqrt(Kh2)
B(1) = 17197; % energy for sqrt(Kh2)
A(2) = 6.62e-11; % pre-exp for Kw
B(2) = 124119; % energy for Kw
A(3) = 3453.38; % pre-exp for Kw/K8/K9/Kh2
B(3) = 0; % energy for Kw/K8/K9/Kh2
A(4) = 1.07; % pre-exp for k'5aK'2K3K4Kh2
B(4) = 36696; % energy for k'5aK'2K3K4Kh2
A(5) = 1.22e10; % pre-exp for k'1
B(5) = -94765; % energy for k'1
% rate coefficients
k = A .* exp(B/R/T);
denom = (1+k(3))*pw/ph2 + k(1)*sqrt(ph2) + k(2)*pw;
% R1 is the rate of methanol formation only in the
% reaction pathway CO2 + 3H2 = CH3OH + H2O
R1 = k(4)*pco2*ph2*(1 - pw*pm/ph2^3/pco2/K1)/denom^3; % mol/s/kg
% R2 is the rate of CO formation only in the
% reaction pathway CO2 + H2 = CO + H2O
R2 = k(5)*pco2*(1 - pw*pco/pco2/ph2/K2)/denom; % mol/s/kg
% FOR ADDITIONAL REACTION PATHWAYS FORMING METHANOL AND CO,
% ADD THOSE REACTION PATHWAY RATE TERMS TO r(1,1) and r(2,1) BELOW
% r(1,1) = de(1)/dW = dFmeoh/dW = rate of methanol formation
r(1,1) = R1;
% r(2,1) = de(2)/dW = dFco/dW = rate of CO formation
r(2,1) = R2;
```

Rate Equations

$$r_1 = \frac{k_{MeOH} p_{CO2} p_{H2} . \left(1 - \frac{p_{CH3OH} p_{H2O}}{K_{eq1} p_{H2}^3 p_{CO2}}\right)}{\left(1 + k_c \frac{p_{H2O}}{p_{H2}} + k_a \sqrt{p_{H2}} + k_b p_{H2O}\right)^3}$$

$$r_2 = \frac{k_{RWGS} p_{CO2} . \left(1 - \frac{p_{CO} p_{H2O}}{K_{eq2} p_{H2} p_{CO2}}\right)}{\left(1 + k_c \frac{p_{H2O}}{p_{H2}} + k_a \sqrt{p_{H2}} + k_b p_{H2O}\right)}$$

APPENDIX A (MeOHenergy.m)

```
function dTdW = MeOHenergy(T,P,F,Bprop,r1,r2)
% by Richard K. Herz <rherz@ucsd.edu> 2011
% is called by function MeOHodes
% uses function MeOHheatrxn
% uses function MeOHheatCp
% returns dT/dW in K/kg
R = 8.314472e-05; % bar-m3/mol/K, for ideal gas law, ideal gas constant
% Bprop = [Bdiam,Btubes,Blen,Bdp,Bvoid,Bcatdens,Wcat,U,Tj];
Bdiam = Bprop(1);
Btubes = Bprop(2);
Blen = Bprop(3);
Wcat = Bprop(7);
U = Bprop(8); % J/s/m2/K, heat transfer coefficient
Tj = Bprop(9); % K, heat transfer jacket temperature
Aw = Btubes*pi*Bdiam*Blen/Wcat; % m2/kg, heat xfer area based on ID
% need total molar flow rate Ftot below
Ftot = sum(F); % mol/s
Cp = MeOHheatCp(T,P,F); % (J/K/mol), mixture heat capacity
% dH1 = delta-H of Independent Stoichiometric Eqn 1 per mol extent 1
% dH2 = delta-H of Independent Stoichiometric Eqn 2 per mol extent 2
dH = MeOHheatrxn(T,P); % J/mol
dH1 = dH(1); % J/mol
dH2 = dH(2); % J/mol
FA = U*Aw/Ftot/Cp*(Tj-T); % K/kg, heat transfer at wall term
FB = -dH1/Ftot/Cp*r1; % K/kg, ISE 1 heat of reaction term
FC = -dH2/Ftot/Cp*r2; % K/kg, ISE 2 heat of reaction term
dTdW = FA + FB + FC; % K/kg
```

Energy Balance

$$\frac{dT}{dw} = \frac{Ua(T_j - T)}{FC_{pm}} - \frac{\Delta H_j^{rxn} r_j \eta_j}{FC_{pm}}$$

APPENDIX A (MeOHpress.m)

```
function dPdW = MeOHpress(T,P,F,Bprop,Fin)
% by Richard K. Herz <rherz@ucsd.edu> 2011
% is called by function MeOHodes
% uses function MeOHviscosity
% returns dP/dW in bar/kg
R = 8.314472e-05; % bar-m3/mol/K
% Ergun from Fogler
% dP/dz = (-G/rho/gc/Dp)*((1-eps)/eps^3)*[150*(1-eps)*mu/Dp + 1.75*G]
% and finally
% dp/dW = dp/dz * Blen/Wcat
mu = MeOHviscosity(T,P,F); % (Pa s) = kg/m/s
% cross-sectional area of all tubes in bed
% Bprop = [Bdiam,Btubes,Blen,Bdp,Bvoid,Bcatdens,Wcat,U,Tj];
Bdiam = Bprop(1);
Btubes = Bprop(2);
Ax = Btubes*pi*Bdiam^2/4;
% gas volumetric flow rate assuming ideal gas law
Ftot = sum(F); % mol/s, total molar flow rate
flow = Ftot*R*T/P; % m3/s at this point in reactor
% molar flow rates in order: H2, CO, CO2, methanol, water, N2, CH4
MW = 1e-3*[2 28 44 32 18 28 16]; % kg/mol, molecular weights
massflow = Fin .* MW; % kg/s
massflow = sum(massflow); % kg/s
rho = massflow/flow; % kg/m3, gas density at this point in reactor
G = massflow/Ax; % kg/s/m2, superficial mass velocity
gc = 1; % kg-m/s^2/N, force unit conversion factor
% Bprop = [Bdiam,Btubes,Blen,Bdp,Bvoid,Bcatdens,Wcat];
Dp = Bprop(4);
vf = Bprop(5); % vf = void fraction, eps is std function name
dPdz = -G/rho/gc/Dp*(1-vf)/vf^3*(150*(1-vf)*mu/Dp + 1.75*G); % Pa/m
Blen = Bprop(3);
Wcat = Bprop(7);
dPdW = dPdz * Blen/Wcat; % Pa/kg = Pa/m * m/kg
dPdW = dPdW * 1e-5; % bar/kg = Pa/kg * 1 bar / 1e5 Pa
```

Pressure Drop (Ergun's Equation)

$$\frac{dP}{dw} = -\frac{G}{\rho g_c d_p}\left(\frac{1-\emptyset}{\emptyset^3}\right)\left[\frac{150(1-\emptyset)\mu}{d_p} + 1.75G\right]\frac{z}{w}$$

APPENDIX A (MeOHmolarflow.m)

```
function F = MeOHmolarflow(e,Fin)
% by Richard K. Herz <rherz@ucsd.edu> 2011
% is called by function MeOHodes
% returns current vector of molar flow rates (mol/s)
% INDEPENDENT STOICHIOMETRIC EQUATIONS (ISE) DEFINING EXTENTS e()
% ISE 1 for e(1): CO2 + 3H2 = CH3OH + H2O
% ISE 2 for e(2): CO2 + H2 = CO + H2O
% molar flow rates in order: H2, CO, CO2, methanol, water, inert,
total
F(1) = Fin(1) - 3*e(1) - e(2); % H2
F(2) = Fin(2) + e(2); % CO
F(3) = Fin(3) - e(1) - e(2); % CO2
F(4) = Fin(4) + e(1); % methanol
F(5) = Fin(5) + e(1) + e(2); % water
F(6) = Fin(6); % N2 (inert)
F(7) = Fin(7); % CH4 (inert)
```

Mass Balance

$$\frac{dF_{CO}}{dw} = r_{RWGS}$$

$$\frac{dF_{CO_2}}{dw} = -r_{MeOH} - r_{RWGS}$$

$$\frac{dF_{H_2}}{dw} = -3r_{MeOH} - r_{RWGS}$$

$$\frac{dF_{H_2O}}{dw} = r_{MeOH} + r_{RWGS}$$

$$\frac{dF_{MeOH}}{dw} = r_{MeOH}$$

$$\frac{dF_{CH_4}}{dw} = 0$$

$$\frac{dF_{N_2}}{dw} = 0$$

APPENDIX A (MeOHodes.m)[30,23]

```
function dydW = MeOHodes(W,y,flags,Bprop,Fin)
% by Richard K. Herz <rherz@ucsd.edu> 2011
% function MeOHodes is called by program MeOH
% uses function MeOHmolarflow
% uses function MeOHrates
% uses function MeOHenergy
% uses function MeOHpress
% inputs: y(1) = T, y(2) = P, y(3) = e(1), y(4) = e(2)
% outputs: dydW(1) = dT/dW, dydW(2) = dP/dW, dydW(3) = dFmeoh/dW, dydW(4) = dFco/dW
% T in K, P in bar
% r(1,1) = rate of methanol formation (mol/kg/s)
% r(2,1) = rate of CO formation (mol/kg/s)
T = y(1);
P = y(2);
e(1) = y(3);
e(2) = y(4);
% call 1st so can pass to other functions
F = MeOHmolarflow(e,Fin);
% call 1st so can pass rates to MeOHenergy function
r = MeOHrates(T,P,F); % mole/kg/s
r1 = r(1,1); % de(1)/dW = dFmeoh/dW
r2 = r(2,1); % de(2)/dW = dFco/dW
dydW(1,1) = MeOHenergy(T,P,F,Bprop,r1,r2); % dT/dW
dydW(2,1) = MeOHpress(T,P,F,Bprop,Fin); % dP/dW
dydW(3,1) = r1; % de(1)/dW = dFmeoh/dW
dydW(4,1) = r2; % de(2)/dW = dFco/dW
```

APPENDIX A (ODE45 solver)

```
% Methanol synthesis reactor simulation
% by Richard K. Herz <rherz@ucsd.edu> 2011
% main MATLAB file:
% MeOH.m
% other files required by the main file:
% MeOHodes.m - ode's to integrate for T, P, stoichiometric extents
% MeOHmolarflow.m - molar flow rates down bed
% MeOHheatCp.m - gas mixture heat capacity
% MeOHheatrxn.m - heats of reaction
% MeOHviscosity.m - gas mixture viscosity
% MeOHrates.m - reaction rates, currently from Vanden Bussche and Froment, 1996
% MeOHenergy.m - dT/dW, temperature down bed
% MeOHpress.m - dP/dW, pressure drop down bed
clear all
close all
fprintf('----------------------run separator---------------------------------\n')
% -------- SPECIFY INPUTS ---------------
% INPUT VALUES HERE ARE FROM Chen et al., 2011:
% L. Chen, Q. Jiang, Z. Song, and D. Posarac,
% "Optimization of Methanol Yield from a Lurgi Reactor,"
% Chemical Engineering & Technology, vol. 34, pp. 1-7, 2011.
% INPUT INLET TEMPERATURE AND PRESSURE OF REACTANT GAS
Tin = 225 + 273.15; % K
Pin = 69.7; % bar
% INPUT REACTOR CATALYST BED PROPERTIES
Bdiam = 0.04; % m, ID of one catalyst tube
Blen = 7; % m, length of tubes
Btubes = 1620; % number of tubes
% NOTE: Chen et al., 2011 had cylindrical pellets 5.4 mm in diam x 5.2 mm long
Bdp = 0.0054; % m, diam of catalyst pellets
Bvoid = 0.285; % bed void fraction, voids between pellets
Bcatdens = 1190; % kg/m3, catalyst pellet density, where bed dens = cat dens*(1-Bvoid)
% INPUT HEAT TRANSFER DATA
% for an adiabatic bed, set U = 0
% to approach a true isothermal bed, set Tj = Tin and U = large value, e.g., 1e4 or 1e5
% for a boiling water reactor (steam raising), enter appropriate Tj and U
Tj = 231.2 + 273.15; % K, heat transfer jacket temperature, Chen et al. steam temp 231.2 C
U = 118.44; % J/s/m2/K, heat transfer coefficient
% INDEPENDENT STOICHIOMETRIC EQUATIONS (ISE) DEFINING EXTENTS e()
% ISE 1 for extent 1: CO2 + 3H2 = CH3OH + H2O
% ISE 2 for extent 2: CO2 + H2 = CO + H2O
% initial values of extents
ein = [0, 0]; % mol/s
% INPUT INITIAL VALUES OF COMPONENT MOLAR FLOW RATES
% order of components in vectors: H2, CO, CO2, MeOH, water, N2, CH4
% ONE WAY is to specify total molar flow rate and components as relative molar flows
% and then compute vector of inlet molar flow rates, Fin
FtotIn = 1740.2; % mol/s, 1740.2 = 6264.8 kmol/h, 28.44 mol/s = 225.52 lbmol/h
% first list component flows as relative molar flow rates
% must have H2 and CO2 non-zero or will get div by zero in MeOHrates
% H2, CO, CO2, MeOH, water, N2 (inert), CH4 (inert)
xin = [9586.5/2 10727.9/28 23684.2/44 756.7/32 108.8/18 8072/28 4333.1/16];
% then compute mole fractions
xin = xin/sum(xin);
% then compute inlet molar flow rates
Fin = xin*FtotIn; % mol/s
% ALTERNATIVELY you can just specify vector of inlet molar flow rates, Fin
% must have H2 and CO2 non-zero or will get div by zero in MeOHrates
% -------- INTEGRATE DOWN REACTOR ------------
% calculate total mass of catalyst
Wcat = Btubes*Bcatdens*(1-Bvoid)*3.14*Blen*(Bdiam^2)/4; % kg, total mass catalyst
% Wspan = final catalyst weight (kg) for integration
Wspan = [0, Wcat];
% initial conditions for integration
yin = [Tin, Pin, ein];
% package bed and heat transfer conditions in an array
% to pass via ode45 to MeOHodes function
Bprop = [Bdiam,Btubes,Blen,Bdp,Bvoid,Bcatdens,Wcat,U,Tj];
% integrate using standard Matlab function ode45
[W,ya]=ode45('MeOHodes',Wspan,yin,[],Bprop,Fin);
%[W, ya] = ode15(@MeOHodes,Wspan,yin,[],Bprop,Fin);
```

APPENDIX A (ODE45 solver)

```
% ---------- POST PROCESSING ---------------
T = ya(:,1);
P = ya(:,2);
e1 = ya(:,3); % extent 1 for: CO2 + 3H2 = CH3OH + H2O
e2 = ya(:,4); % extent 2 for: CO2 + H2 = CO + H2O
% IDEAL GAS CONSTANT VALUES IF NEEDED FOR POST PROCESSING
R = 8.314472; % J/mol/K, for Arrhenius rate equations, ideal gas constant
Rg = 8.314472e-05; % bar-m3/mol/K, for ideal gas law, ideal gas constant
% can't use MeOHmolarflow here since e1 & e2 are column vectors
% molar flow rates in order: H2, CO, CO2, methanol, water, N2, CH4
% extent 1 for ISE 1: CO2 + 3H2 = CH3OH + H2O
% extent 2 for ISE 2: CO2 + H2 = CO + H2O
F(:,1) = Fin(1) - 3*e1 - e2; % H2
F(:,2) = Fin(2) + e2; % CO
F(:,3) = Fin(3) - e1 - e2; % CO2
F(:,4) = Fin(4) + e1; % methanol
F(:,5) = Fin(5) + e1 + e2; % water
F(:,6) = Fin(6); % N2 (inert)
F(:,7) = Fin(7); % CH4 (inert)
% get mole fractions
Ft = sum(F,2); % total
% F is a 2D array so can't divide by 1D Ft array
% need to contruct a 2D array Ftot to get 2D array of mole fractions
Ftot = [Ft Ft Ft Ft Ft Ft Ft];
% mole fraction
x = F./Ftot;
ph2 = P.*x(:,1); % bar
pco = P.*x(:,2);
pco2 = P.*x(:,3);
pm = P.*x(:,4); % m = methanol
pw = P.*x(:,5); % w = H2O
xm = x(:,4); % mole fraction methanol
[r c] = size(P);
Pout = P(r)
if Pout < 1
fprintf('WARNING: Pout < 1 bar. \n')
fprintf('Increase number of tubes (area for flow), or \n')
fprintf('decrease inlet flow rate. \n\n')
end
ToutK = T(r)
ToutC = T(r)-273.15
xMeOHout = x(r,4)
% mole fractions in order: H2, CO, CO2, methanol, water, N2, CH4
z = Blen*W/Wcat;
[AX,H1,H2] = plotyy([z z],[P/Pin T/Tin],z,100*xm); % ,'r--',z,T/Tin,'b--')
title('Methanol Reactor, left axis blue = P/Pin, green = T/Tin, right axis red = % methanol')
xlabel('distance down reactor (m)')
axis(AX(1),[0 8 0 1.4])
axis(AX(2),[0 8 0 14])
set(AX(1),'ytick',[0; 0.2; 0.4; 0.6; 0.8; 1.0; 1.2])
set(AX(2),'ytick',[0; 2; 4; 6; 8; 10])
set(get(AX(1),'ylabel'),'string','P / Pin or T / Tin')
set(get(AX(2),'ylabel'),'string','% methanol')
% from separate experiments to get equilibrium T & xMeOH at Pout = 66.7 bar
Teq = [569.9; 566.68; 563.63; 559.17; 556.2; 553.3; 545.21; 538.96; 533.11];
xmeq = [0.0330; 0.0355; 0.0380; 0.0419; 0.0445; 0.0472; 0.0558; 0.0613; 0.0672];
figure
plot(T,100*xm,'b',Teq,100*xmeq,'g')
title('Methanol Reactor, blue = with cooling, green = equilibrium at 66.7 bar')
ylabel('% methanol')
xlabel('T (K)')
```

References

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Thank You