Methanol Synthesis Reactor Simulator

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Nomenclature

ΔH^o_{Rxj} Standard enthalpy of reaction at 298 K of reaction j.

$\dot{m}_c$ Coolant mass flow (kg/s).

$\hat{C_{p_c}}$ Coolant mass defined heat capacity (J/(kg·K).

μ Mixture viscosity (Pa·s)

ϕ Void fraction of catalyst.

ρ_b Bulk density (kg/m^3), $definedas \rho_b = \rho_c(1-\phi)$.

ρ_c Catalyst density (kg/m^3)

A_c Cross section (m^2).

C_{p_i} Heat capacity of i.

D_p Catalyst diameter.

F_{T_o} Initial mole flow (mol/s).

F_T Actual mole flow (mol/s).

P_o Initial pressure (Pa)

r'_i Rate law of reaction i.

a Section over reactor volume, defined as $a = 4/D[m^{-1}]$.

G Mass velocity (kg/(s·m^2).

Mw Molecular weight (g/mol).

P Actual pressure (Pa).

R Constant of ideal gases.

T Reactor temperature.

U Global heat transfer coeficient (W/(m$^2 K$).

W Mass of catalyst (kg).

1 Introduction

The emission counter of CO_2 does not stop, a solution must be found. The chemist George A. Olah, winner of the Nobel Prize in chemistry in the 1990s, proposed the economy of methanol. For this reason, the design of a reactor capable of producing methanol from synthesis gas is presented. This document is intended to support the content found in *File Exchange*[1]. The application presented is a simulator of a methanol synthesis reactor. It has been developed only for educational purposes. The reactor that has been designed is a multitubular packed bed reactor, non-isothermal with pressure drop. Reactions take place in gas phase. The catalyst used by the Vanden Bussche & Froment kinetic model[3] is $Cu/ZnO/Al_2O_3$. Helpful comments and suggestions from the paper's reviewers are gratefully acknowledged.

2 Reactor Design

This section presents a technical diagram of the reactor and the design equations. Firstly, the kinetic model used to model the reactions will be presented, followed by the individual molar balances, and lastly, the energy balance and pressure drop.

2.1 Technical diagram of the reactor

As mentioned above the reactor that has been designed is a multitubular packed bed reactor (PBR). The raw material is the synthesis gas, it is formed mainly by hydrogen, carbon dioxide, carbon monoxide and species that act as inerts. As can be seen in the image, the reactor has a cooling jacket.

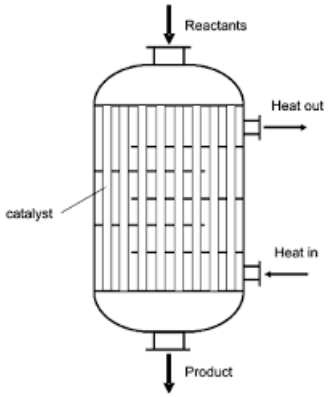

Figure 1: Technical diagram of PBR

[1] https://es.mathworks.com/matlabcentral/fileexchange/76856-methanolsynthesisreactor

The reactions that are of interest for the modeling of the reactor are as follows.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O, \quad \Delta H^o_{Rx1}(298K) = -49.58\ kJ/mol \tag{1}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O, \quad \Delta H^o_{Rx2}(298K) = +41.19\ kJ/mol \tag{2}$$

2.2 Kinetic model

The kinetic model that has been used is the Vanden Bussche & Froment kinetic model[3]. The authors of this article have developed a model to simulate the synthesis of methanol from synthesis gas. The kinetic laws and the parameters used are shown below.

$$r'_{MeOH}\left[\frac{mol}{kg\cdot s}\right] = \frac{k'_{5a}K'_2K_3K_4K_{H_2}p_{CO_2}p_{H_2}\left[1-\frac{1}{K^*}\left(\frac{p_{H_2O}p_{MeOH}}{p^3_{H_2}p_{CO_2}}\right)\right]}{\left(1+\frac{K_{H_2O}}{K_8K_9K_{H_2}}\frac{p_{H_2O}}{p_{H_2}}+\sqrt{K_{H_2}p_{H_2}}+K_{H_2O}p_{H_2O}\right)^3} \tag{3}$$

$$r'_{RWGS}\left[\frac{mol}{kg\cdot s}\right] = \frac{k'_1p_{CO_2}\left[1-K_3\left(\frac{p_{H_2O}p_{CO}}{p_{CO_2}p_{H_2}}\right)\right]}{\left(1+\frac{K_{H_2O}}{K_8K_9K_{H_2}}\frac{p_{H_2O}}{p_{H_2}}+\sqrt{K_{H_2}p_{H_2}}+K_{H_2O}p_{H_2O}\right)} \tag{4}$$

The dependence of the constants with the temperature follows the equation of *Arrhenius*: $k_i = A_i \exp\left(\frac{B_i}{RT}\right)$. The values of A and B are shown in the following table [3].

Constant	A_i	B_i
$\sqrt{K_{H_2}}$	0.499	17197
K_{H_2O}	6.62×10^{-11}	124119
$\frac{K_{H_2O}}{K_8K_9K_{H_2}}$	3453.38	0
$k'_{5a}K'_2K_3K_4K_{H_2}$	1.07	36696
k'_1	1.22×10^{10}	-94765

Table 1: Kinetic parameters constants.

The calculation of the equilibrium constants K^* and K_3 has been carried out using the following equations [3] .

$$\log_{10} K^* = \frac{3066}{T} - 10.592 \tag{5}$$

$$\log_{10}\left(\frac{1}{K_3}\right) = -\frac{2073}{T} + 2.029 \tag{6}$$

2.3 Design Equations

First, the individual molar balances are shown.

$$\frac{dF_{CO}}{dW} = r'_{RWGS} \tag{7}$$

$$\frac{dF_{CO_2}}{dW} = -r'_{MeOH} - r'_{RWGS} \tag{8}$$

$$\frac{dF_{H_2}}{dW} = -3 \cdot r'_{MeOH} - r'_{RWGS} \tag{9}$$

$$\frac{dF_{H_2O}}{dW} = r'_{MeOH} + r'_{H_2O} \tag{10}$$

$$\frac{dF_{MeOH}}{dW} = r'_{MeOH} \tag{11}$$

$$\frac{dF_{CH_4}}{dW} = 0 \tag{12}$$

By performing an energy balance inside a tube, the temperature profile of the inside of a tube is obtained.

$$\frac{dT}{dW} = \frac{Ua(T_a - T)/\rho_b - r'_{MeOH}\Delta H_{Rx1} - r_{RWGS}\Delta H_{Rx2}}{\sum_{i=1}^{n} F_i C_{p_i}} \tag{13}$$

Kirchoff's law has been used to calculate the enthalpy as a function of temperature [2].
The variation of the temperature of the refrigerant fluid with respect to the catalyst mass is as follows.

$$\frac{dT_a}{dW} = \frac{n_{tubes}Ua(T - T_a)/\rho_b}{\dot{m}_c \hat{C_{p_c}}} \tag{14}$$

The Ergun equation has been used to determine the pressure drop [1].

$$\frac{dP}{dW} = -\frac{G}{\rho_o D_p \phi^3 A_c \rho_c}\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right]\frac{P_o}{P}\frac{F_T}{F_{T_o}}\frac{T}{T_o} \tag{15}$$

3 Reactor Simulation

The numerical method to solve the ODEs system is the *odesuit45*. The initial condition of ODEs and its parameters that can be modified are mentioned below. The input variables are classified into three blocks: reactor geometry, input flow, and energy transfer.

Regarding the geometry of the reactor, the variables to be defined are:

- Catalyst mass per tube in kg.
- Tube diameter in cm.
- Catalytic particle diameter in mm.
- Void fraction of catalyst.
- Number of tubes.

Regarding the inflow, the following parameters must be set.

- Molar flow rates to the reactor in mol / s.
- Inlet temperature to the reactor in ^{o}C.
- Inlet pressure to the reactor in bars.

Finally, the last initial conditions and parameters that must be entered regarding the reactor cooling jacket are the following.

- Refrigerant fluid inlet temperature. In this case a thermal oil named $MARLOTHERM^{TM}$.
- Global heat transfer coefficient.
- Coolant flow.

References

[1] H. Scott Fogler. “Elements of chemical reaction engineering”. 2008. Perason. Penitence Hall. 4th Edition.

[2] Smith & Van Ness. “Introduction Chemical Engineering Thermodynamics”. 2005. Mc Graw Hill. 7th Edition.

[3] Vanden Bussche & Froment. “A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al2O3 Catalyst”. 1995. Journal of Catalysis.

[4] F. D. Incroperas. ”Fundamentals of Heat and Mass Transfer”. 1999. Pearson. Penitence Hall. 4th Edition.

Appendices

A Thermodynamics data

Kirchoff's law has been used to obtain more precise calculations [2] of the enthalpies as a function of temperature. Kirchoff's law is defined in the equation (16).

$$H_i = H_i^o(T_{ref}) + \int_{T_{ref}}^{T} C_{p_i} dT \tag{16}$$

The heat capacities that have been used in the simulator are those described in table 2. The Cp polynomial has the following structure, shown in equation (17)[2].

$$C_p^{ig}/R = A + BT + CT^2 + DT^{-2} \tag{17}$$

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	.....

Table 2: Constant heat capacities [2].

The heat capacity of the refrigerant has been obtained from the *MARLOTHERM* oil technical data sheet, which has an average value of $\hat{c}_{p_c} = 2.20 \frac{kJ}{kg \cdot K}$.

B Physical roperties of reagents and products

Because the purpose of this application is educational, rigorous calculations have not been carried out on the physical properties of the mixture. The viscosity of the mixture has been estimated with the expression (18).

$$\mu_{mix} = \sum_{i=1}^{n} y_i \mu_i \tag{18}$$

The viscosity values used are at atmospheric pressure and a temperature of 550K [4].

The density of the mixture has been estimated with the ideal gases equation despite the fact that the reactor is not in a range of conditions that ensure the validity of this approach.

$$\rho_{mix} = \frac{P}{R \cdot T} \sum_{i=1}^{n} y_i M w_i \tag{19}$$

The mass speed, which appears in the Ergun equation, is calculated using equation (20).

$$G \left[\frac{kg}{s \cdot m^2} \right] = \rho_o \cdot v / A_c \tag{20}$$

Where the volumetric flow (v) has been estimated with the ideal gases equation.