

MODELING AND SIMULATION OF METHANATION CATALYTIC REACTOR IN AMMONIA UNIT

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Abstract

In ammonia synthesis units the amount of CO and CO₂ shall be minimized as they are considered as poisons for the related catalysts. To achieve this, methanation catalytic reactor is incorporated after the high and low temperature shift reactor to decrease the concentration of carbon monoxide and carbon dioxide to an allowable limit.

The nature of the reactions taken place in methanation catalytic reactor is similar to that of steam reforming one. So the reaction kinetic is somehow known but the important point is the approach incorporated to measure the effectiveness factor of catalytic reactions. In this paper the influence coefficient has been measured using Orthogonal Collocation approach. The system equation set has been solved using the general available approaches.

The results taken from simulation show a good compatibility with the available industrial data in Khorasan petrochemical complex.

Keywords: *Methanation, Modeling, Simulation, Catalytic Reactor, Effectiveness factor*

1. Introduction

Carbon monoxide and carbon dioxide are considered as catalyst poisons in lots of hydrogenation processes such as ammonia production. So in ammonia production units as well as other hydrogen production units, after adsorption of carbon dioxide, the amount of the residual carbon oxides shall be decreased as much as possible. In an ammonia unit, methanation is the last step of purgation. In this section the concentration of carbon monoxide and carbon dioxide is 0.1 to 0.5 percent, which will be purged using catalytic reaction with hydrogen. The concentration of residual carbon oxides in outgoing gas of the methanation reactor will be less than 5 ppm.

Methanation is a catalytic reaction from kinetic point of view and adiabatic considering its thermal characteristics. So in simulation of this reactor, the mathematical model includes the kinetics of the reactions carried out on the catalyst. Also considering penetration of reactor gases to internal surface of the catalyst, the mass transfer issues will be very important. In this paper, kinetic and mass transfer relations have been incorporated in simulation to yield proper results.

2. Modeling of Methanation Reactor

2.1 Reaction Kinetics ^[1,2,3,4]

The following assumptions have been considered in modeling of the reactor:

1. Gas mixture is considered ideal
2. System is in steady state condition

3. Relations of mass transfer, temperature, and momentum are assumed to be one-dimensional. Also distribution of concentration, heat and pressure is uniform in each cross section of the reactor.

4. Axial mass and heat transfer are assumed to be negligible.

Researches show that among the 11 equations outlined in table 1, the following three primary equations play substantial role:



In fact the above equations are the reverse of steam reforming reactions.

Table-1: Probable reactions in methanation reactor [5]

No	Reactions	$\Delta H_{298}, \text{kg/mol}$
1	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-206.1
2	$CO + H_2O \leftrightarrow CO_2 + H_2$	41.15
3	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-165
4	$CH_4 + CO_2 \leftrightarrow +2CO + 2H_2$	-247.3
5	$CH_4 + 3CO_2 \leftrightarrow +4CO + 2H_2O$	-330
6	$CH_4 \leftrightarrow C + 2H_2$	-74.82
7	$2CO \leftrightarrow C + CO_2$	-173.3
8	$CO + H_2 \leftrightarrow C + H_2O$	131.3
9	$CO_2 + H_2 \leftrightarrow C + 2H_2O$	90.13
10	$CH_4 + 2CO \leftrightarrow 3C + 2H_2O$	187.6
11	$CH_4 + CO_2 \leftrightarrow 2C + 2H_2O$	15.3

Considering the Xu & Froment kinetic [5], reaction rate equations 1 to 3 are as follow:

$$\text{For reaction 1: } r_1 = \frac{k_1}{P_{H_2}^{2.5}} \left(P_{H_2O} P_{CH_4} - \frac{P_{H_2}^3 P_{CO}}{K_1} \right) / (DEN)^2$$

$$\text{For reaction 2: } r_2 = \frac{k_2}{P_{H_2}} \left(P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_2} \right) / (DEN)^2$$

$$\text{For reaction 3: } r_3 = \frac{k_3}{P_{H_2}^{3.5} (DEN)^2} \left[P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_1 K_2} \right]$$

In which

$$DEN = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + K_{H_2O} P_{H_2O} / PH_2$$

$$\text{For steam reforming: } \begin{cases} r_{CO} = r_1 - r_2 \\ r_{CO_2} = r_2 + r_3 \\ r_{CH_4} = r_1 + r_3 \end{cases} \tag{4}$$

$$\text{For methanation: } \begin{cases} r'_{CO} = r_2 - r_1 \\ r'_{CO_2} = -(r_2 + r_3) \\ r'_{CH_4} = -(r_1 + r_3) \end{cases} \tag{5}$$

Rate constants of the above equations are defined as functions of temperature [5,6]:

$$\begin{aligned}
 k_1 &= 9.490 \times 10^{16} \exp\left(-\frac{28879.0}{T}\right) \frac{\text{kmol.kPa}^{0.5}}{\text{kg.h}} \\
 k_2 &= 4.390 \times 10^4 \exp\left(-\frac{8074.3}{T}\right) \frac{\text{kmol.kPa}^{-1}}{\text{kg.h}} \\
 k_3 &= 2.290 \times 10^{16} \exp\left(-\frac{29336.0}{T}\right) \frac{\text{kmol.kPa}^{0.5}}{\text{kg.h}}
 \end{aligned} \tag{6}$$

K_{CO} , K_{CH_4} , K_{H_2} And K_{H_2O} are the constants which related to surface adsorption in equilibrium that are functions of temperature. The functions types are given in the references^[6].

The equilibrium constants of reactions 1-3 are defined as below:

$$\begin{aligned}
 K_1 &= 10266.76 \times \exp\left(-\frac{26830.0}{T} + 30.11\right) ; \text{kPa}^2 \\
 K_2 &= \exp\left(\frac{4400.0}{T} - 4.063\right) \\
 K_3 &= K_1 K_2 ; \text{kPa}^2
 \end{aligned} \tag{7}$$

2. 2 Mass, Energy and Momentum Balance Equations ^[5,6,7]

Before modeling of the reactor, equilibrium constraints on considered system have to be considered. For instance the process is exothermal and increase of temperature will reduce the conversion rate.

Considering that two of the three main reactions are independent from each other, by definition of two corresponding variables, by means of the conversion rate, it is possible to determine all the concentration variables.

$$X_{CH_4} = \frac{F_{CH_{4,0}} - F_{CH_4}}{F_{CH_{4,0}}} \tag{8}$$

$$X_{CO_2} = \frac{F_{CO_2} - F_{CO_{2,0}}}{F_{CH_{4,0}}} \tag{9}$$

With the above definitions, it will be possible to drive all the model's flow rates in terms of X_{CO_2} and X_{CH_4} . For example the molar flow rate of methane F_{CH_4} will be as follows:

$$F_{CH_4} = F_{CH_{4,0}} (1 - X_{CH_4}) \tag{10}$$

Hence, partial pressures are defined based on the components molar flow rates:

$$P_{H_2O} = P_t \left[\frac{F_{H_2O,0} - F_{CH_{4,0}} (X_{CH_4} + X_{CO_2})}{F_{total,0} + 2F_{CH_{4,0}} X_{CH_4}} \right] \tag{11}$$

$$P_{CH_4} = P_t \left[\frac{F_{CH_{4,0}} (1 - X_{CH_4})}{F_{total,0} + 2F_{CH_{4,0}} X_{CH_4}} \right] \tag{12}$$

$$P_{H_2} = P_t \left[\frac{F_{H_2,0} + F_{CH_{4,0}} (3X_{CH_4} + X_{CO_2})}{F_{total,0} + 2F_{CH_{4,0}} X_{CH_4}} \right] \tag{13}$$

$$P_{CO} = P_t \left[\frac{F_{CH_4,0} (3X_{CH_4} + X_{CO_2})}{F_{total,0} + 2F_{CH_4,0} X_{CH_4}} \right] \quad (14)$$

Substituting of the above partial pressure equations of feed and product in reaction rate equations will cause the rate equations to be in terms of conversion rate variables. Now it will be possible to derive the balance equations.

Mass balance equations for CH_4 and CO_2 are as follow:

$$\frac{dF_{CH_4}}{dz} = \pi \rho_B (+\eta_1 r_1 + \eta_3 r_3) \quad (15)$$

$$\frac{dF_{CO_2}}{dz} = -\pi \rho_B (+\eta_2 r_2 + \eta_3 r_3) \quad (16)$$

In which z is the length of the reactor (m), π is the cross section of the reactor (m^2), ρ_B is the catalyst mass density ($\frac{kg}{m^3}$) and η_1, η_2, η_3 are Effectiveness Factors of the reaction.

r_1, r_2, r_3 are reaction rates ($\frac{kgmol}{kg \text{ catalyst.hr}}$) in absence of penetration constraints.

Substitution of molar flow with conversion variables yields:

$$\frac{dX_{CH_4}}{dz} = \frac{-\pi \rho_B (\eta_1 r_1 + \eta_3 r_3)}{F_{CH_4,0}} \quad (17)$$

$$\frac{dX_{CO_2}}{dz} = \frac{-\pi \rho_B (\eta_2 r_2 + \eta_3 r_3)}{F_{CH_4,0}} \quad (18)$$

Energy balance equation, with considering that the reactor is adiabatic, simultaneously solved with equations 17 and 18:

$$\frac{dT}{dz} = \frac{1}{\rho_g C_{\rho_g} u_s} [\rho_B ((-\Delta H_1) \eta_1 r_1 + (-\Delta H_2) \eta_2 r_2 + (-\Delta H_3) r_3 \eta_3)] \quad (19)$$

In which ρ_g is the density of gas mixture and u_s is its artificial speed inside reactor.

Momentum balance equation, which yields pressure drop along the reactor, is as follows:

$$\frac{dP_t}{dz} = -f \frac{\rho_g u_s^2}{dp} \quad (20)$$

In which dp is the equivalent diameter of the catalyst particle. To determine friction coefficient f , experimental and semi-experimental relations are used.

The artificial speed can be determined by means of continuity equation:

$$u_s = u_{so} \left(\frac{P_{t,0}}{P_t} \right) \left(\frac{T}{T_0} \right) \left(\frac{F_{total,0} + 2F_{CH_4,0} X_{CH_4}}{F_{total,0}} \right) \quad (21)$$

Inlet flow speed u_{so} can be calculated using molar flow rate and input temperature and pressure conditions:

$$u_{s,0} = \frac{F_{total,0}}{\pi} \left(\frac{RT_0}{P_{t,0}} \right) \quad (22)$$

Boundary conditions for balance equations (17-20) are as below:

$$X_{CH_4} = 0, \quad X_{CO_2} = 0, \quad T = T_0, \quad P_t = P_{t,0} \quad \text{at} \quad z = 0 \quad (23)$$

The set of equations with the mentioned boundary conditions are solved using Matlab software.

3. Calculation of Reaction Effectiveness Factor ^[5,8]

Mass transfer or penetration resistances against the reaction materials, play important roles in the results obtained from modeling of catalytic reactions. So to modify the kinetic behavior of reaction rate equations, Effectiveness Factor is defined.

In achieved modeling, the effectiveness factors can be calculated by definition of penetration equations in radial direction of the catalyst.

Continuity equations for CH_4 and CO_2 in a spherical element is as follows:

$$D_{e,CH_4} \times \frac{1}{r^2} \cdot \frac{d}{dr} \left(r^2 \frac{dP_{CH_4}}{dr} \right) + \rho_g RT(r_1 + r_3) = 0 \quad (24)$$

$$D_{e,CO_2} \times \frac{1}{r^2} \cdot \frac{d}{dr} \left(r^2 \frac{dP_{CO_2}}{dr} \right) - \rho_g RT(r_2 + r_3) = 0 \quad (25)$$

In which D_{e,CH_4} is the effective penetration coefficient in component i. Catalyst particle has been considered to be isothermal and it is assumed that there isn't any heat transfer from the catalyst particle to the outside. The obtained equations shall be solved in every radial position of the reactor with the assigned boundary conditions. Having partial pressures of CH_4 and CO_2 , concentrations of other components could be obtained by means of stoichiometry. Xu & Froment has used a similar model for determination of effective penetration factor. The boundary conditions for dimensionless catalytic particle equations are as below:

$$\frac{dP_{CH_4}}{d\zeta} = \frac{dP_{CO_2}}{d\zeta} = 0 \quad \text{at} \quad \zeta = 0 \quad (26)$$

$$P_{CH_4} = P_{CH_4,B} = P_{CO_2} = P_{CO_2,B} \quad \text{at} \quad \zeta = 1 \quad (27)$$

In which ζ is the dimensionless radius of the catalyst particle, P_{CH_4} , P_{CO_2} are local partial pressures in catalyst and $P_{CH_4,B}$, $P_{CO_2,B}$ show the partial pressures in the fluid outside the particle. As the catalyst is assumed to be isothermal, there will be no energy balance equation satisfied for that and the reaction rate will be determined in fluid temperature. Also partial differential equations 26 and 27 have been derived by differential approximation. These equations are converted to a set of algebraic equations, which have been solved by Newton method. Because of the complexity of reaction rate equations, jacobian numerical method has been incorporated instead of analytical method. When effectiveness factor equations are solved, then the balance equations of the reactor will be also solvable.

3. 1 Simulation Results

Reactor dimensions, catalyst specifications, operating conditions and concentration of the reactor input components adopted from available documents of methanation reactor of Khorasan Petrochemical Complex Ammonia Unit. It has been given in table (2) ^[9]. Simulation results and input/output data of the industrial reactor has been compared in table (3).

Table-2: Methanation reactor design and operation specifications ^[9].

Dimensions	
length of methanator	4.8 m
inside diameter of the methanator	2.686 m
The Catalyst pellet	
Shape	spherical particles
Diameter	0.00494-0.00476 m
Porosity	0.625
Tortuosity factor	2.74
Bulk density	1014 kg/m ³
Catalyst length	0.0010583 m
Mean pore radius	8000 Å
Inlet conditions	
	design actual

Feed flow rate, kmol/hr	3392.288	3298.251
Methane flow rate, kmol/hr	16.557	13523
Temperature, K	586.30	577.78
Pressure, kPa	2074.75	1823.82
Composition, Mol%		
	Design	Actual
CO	0.4280	0.1600
CO ₂	0.0500	0
H ₂	74.052	73.410
CH ₄	0.488	0.41
H ₂ O	0.483	0.120
Inerts	24.499	25.9

In figures 1 and 2, distribution of methane and carbon dioxide concentration along the reactor has been illustrated. As expected, it shows decrease of the carbon dioxide while increase of methane along the reactor. Molar flow rates of the outlet components show a good compatibility with the output data of the available industrial reactor. This matter is also satisfied for the temperature and pressure conditions. Figures 3 and 4 illustrate temperature and pressure distribution along the reactor catalytic bed. Because of absence of industrial data along the bed, there is only the output data, which could be comparable. These figures show good compatibility with the industrial data.

Table-3: Simulation Results and Industrial Methanation Reactor Data ^[9].

	Input		Output	
	Industrial	Simulation	Industrial	Simulation
CO, kmol/hr	20.5	0	0.0	0
CO ₂ , kmol/hr	3.4	0	0.0	0
H ₂ , kmol/hr	4186.7	4407.53	4111.5	4407.53
CH ₄ , kmol/hr	26.1	55.61	50.1	55.61
H ₂ O, kmol/hr	58.0	92.12	85.3	92.12
Inerts, kmol/hr	16.6	16.6	16.6	16.6

In table 4 the error percentage of the simulation have been given.

Table-4: Comparison of simulation data with those of the industrial data

	Actual	Simulation	Error%
CO ₂ mol%	0	0	0
CH ₄ mol%	0.012	0.0132	10%
T _{out} , K	589	598	1.5%
P _{out} , bar	29.2	29.381	0.6%

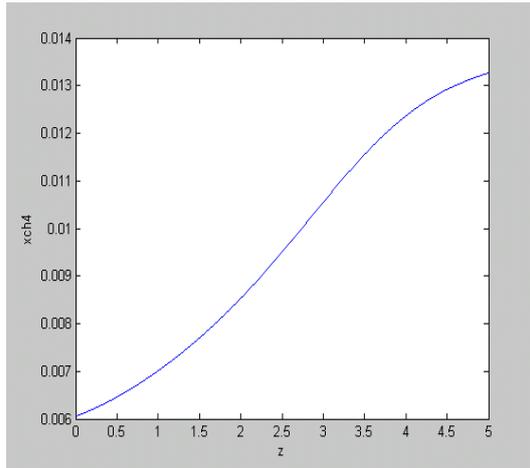


Fig-1: Methane concentration along the bed

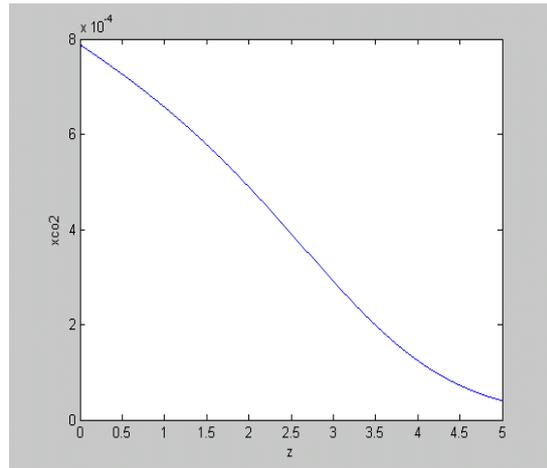


Fig-2: Carbon Dioxide concentration along the reactor

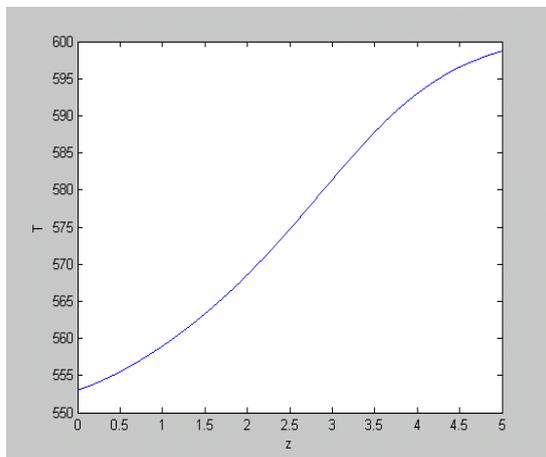


Fig-3: Temperature variation along the reactor

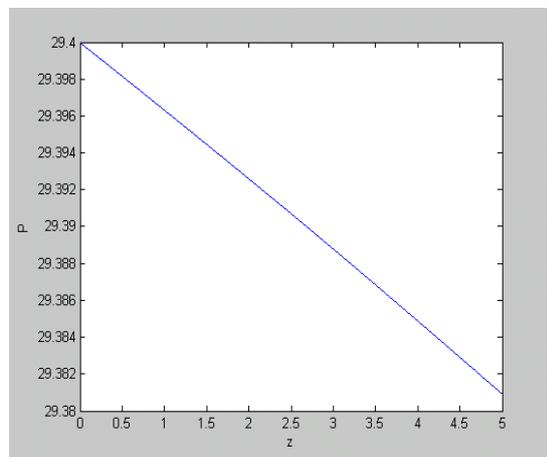


Fig-4: Pressure variation along the reactor

4. Conclusions

The achieved simulation shows that penetration constraints of the feed gases play an important role in control of the reaction rate. Considering the effects of the mass transfer resistances in reaction kinetics, called effectiveness factor, considerable results have been obtained which show quite a good compatibility with the industrial data. This in turn satisfies the simulation which has been done for the methanation reactor.

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Nomenclature

C_p : Heat capacity

D_e : Effective penetration

dp : Equivalent particle diameter

F : Molar flow

f : Fraction coefficient

K : Equilibrium constant

k : Reaction constant

P : Pressure

R : Gas constant

T : Temperature

u_s : Artificial speed

X : Conversion

z : Reactor length

π : Reactor cross-section area

ρ : Density

η : Effectiveness factor

ξ : Dimensionless radius of particle

Greek letters

5. References

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