

A SIMULATION STUDY OF AN INDUSTRIAL METHANOL REACTOR BASED ON SIMPLIFIED STEADY-STATE MODEL

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ABSTRACT

Methanol is recognized as a potential renewable energy source for its uses in gasoline blending and direct methanol fuel cells. This work aims to develop a simulation model that can adequately represent an industrial real-life methanol reactor from a petrochemical plant at steady-state conditions. The main purpose is to provide a tool for investigating the effects of inlet temperatures, coolant inlet temperatures and velocity on the reactor's performance under steady-state conditions. From the results obtained, it is revealed that the simplified model is able to approximate the plant's operating conditions with sufficient accuracy of less than 5% error. The validated model allows a better temperatures, feed superficial velocities and coolant inlet temperatures. This model can serve as a base for future improvement studies on the said reactor.

Keywords: *Methanol reactor, simulation, steady-state modeling.*

1. INTRODUCTION

METHANOL is multipurpose based chemical. It is a volatile, poisonous, colorless liquid that is used as antifreeze, solvent, fuel, denaturant for ethyl alcohol and feedstock to produce formaldehyde, methyl tertiary butyl ether (MTBE) and acetic acid. The recent trend has shown that the demand of methanol is increasing as it is considered as one of the best potential renewable sources to replace gasoline with no environmental effect. [1] noted that the fastest growing demand on methanol and its derivatives is notable especially in Asia. Methanol can be blended with gasoline to run combustion engine without significant modification on the engine configurations [2]. Methanol is also used in direct methanol fuel cell in consumer electronics.

Methanol is generally produced from syn-gas (a mixture of CO, CO₂ and H₂) by two processes ICI and Lurgi. ICI process was first commercialized in 1970 and currently accounts for more than 70% of undergoing projects [1]. Lurgi process, on the other hand, is popular with the shell and tube heat exchanger configuration reactor in which catalyst is packed in tubes and cooling steam is circulated in the shell side.

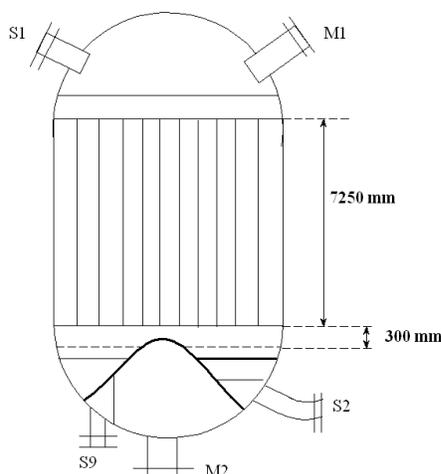


Fig. 1 Methanol reactor – Lurgi type

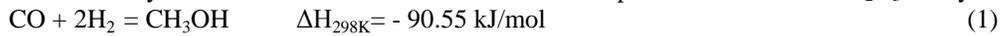
This work aims to develop a simulation model that can adequately represent an industrial real-life methanol reactor from a petrochemical plant at steady-state conditions. The main purpose is to provide a tool for investigating the effects of inlet temperatures, coolant inlet temperatures and velocity on the reactor's performance under steady-state

conditions. The industrial methanol reactor is a Lurgi type methanol synthesis reactor as shown in Fig 1. This reactor has shell-and-tube configuration with catalyst packed in tubes and cooling steam is circulated in the shell side. The shell side is compartmentalized and contains 4801 tubes per reactor and flow will go through all tubes at once. This is to ensure the flow is evenly distributed and the desired heat flux can be achieved. In this paper, a simplified steady-state model based on [3] is presented and its performance is validated against the industrial real-life methanol reactor data.

2. LITERATURE REVIEW

2.1 Reaction Kinetics

Many studies have been done on the methanol synthesis process. Most of them focus on methanol reaction kinetics. The most accepted reaction kinetics are those of [4] and [5]; both are based on Langmuir-Hinshelwood mechanism. Few reactions that may occur under methanol reactor condition in presence of Cu/ZnO/Al₂O₃ catalyst are as follows:



The synthesis reactions occur due to dual-site Langmuir-Hinshelwood mechanism where CO and CO₂ absorbed on site s1 and H₂ and H₂O absorb on site s2. In reaction 1, CO and H₂ are first absorbed on two active sites of the catalyst surface. The adsorption rate depends on partial pressures of CO and H₂ in the stream. CO and H₂ then react to form CH₃OH on the catalyst surface and CH₃OH molecule later desorbs to the fluid stream. The overall reaction rate is a combination of adsorption, surface reaction and desorption rates in which the slowest step is the rate controlling step. In [3], the model was derived by comparing 48 combinations of elementary steps from each of the above three reactions to the experimental data.

2.2 Reactor Modeling and Simulation

[6] studied internal mass transport limitations in methanol synthesis. Different internal mass transport model results were compared to conclude that all models including dusty gas model and Thiele-Modulus model were sufficient to account for pore diffusion in catalyst particles. Hence, Thiele Modulus concept could be applied to simulate complex reaction system.

Using the kinetic model presented by [5], [7] developed a pseudo-steady state homogeneous and heterogeneous dynamic model, which verified the result against design flow sheet and process data and concluded that heterogeneous model gave better results for optimization purpose. The deactivation model was estimated from historic process data from a methanol plant. However, the model parameters were not good for total catalyst lifetime because the deactivation process was fast in the beginning and slower in the end.

[8] simulated a heterogeneous one-dimensional methanol reactor model under steady state and dynamic conditions. Reactor yield was optimized using trained feedforward neural network. [9], on the other hand, considered dynamic behavior of three methanol reactors in sequence. They investigated the effect of feed position on the production. They have shown that the control of the ring reactor network can be optimized by switching the feed at a fixed time interval to allow safe start-up.

[3] studied dynamic simulation of a Lurgi type industrial methanol reactor in the presence of long term catalyst deactivation using kinetic model from [4]. Homogeneous and heterogeneous dynamic model were investigated and compared. [3] concluded that homogeneous model was good enough to reduce level of computation. The models were simpler than [7] as it did not include axial diffusion as well as pressure drop over catalyst pellet. In this paper, the models developed by [3] are chosen as the base for the steady-state model development.

3. REACTOR MODELING

Methanol synthesis reaction is heterogeneous catalytic reaction which is highly exothermic. The kinetics of the reaction is therefore taken following the kinetics developed by [4] which is the most suitable kinetics for this kind of reaction. The reaction is surface-reaction-limiting. The kinetics and its parameters are presented below:

$$r_1 = \frac{k_1 K_{\text{CO}} [f_{\text{CO}} f_{\text{H}_2}^{3/2} - f_{\text{CH}_3\text{OH}} / (f_{\text{H}_2}^{1/2} / K_{\text{P1}})]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) [f_{\text{H}_2}^{1/2} + (K_{\text{H}_2\text{O}} / K_{\text{H}_2}^{1/2}) f_{\text{H}_2\text{O}}]}$$

$$r_2 = \frac{k_2 K_{\text{CO}_2} [f_{\text{CO}_2} f_{\text{H}_2}^{3/2} - f_{\text{CH}_3\text{OH}} f_{\text{H}_2\text{O}} / (f_{\text{H}_2}^{3/2} / K_{\text{P2}})]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) [f_{\text{H}_2}^{1/2} + (K_{\text{H}_2\text{O}} / K_{\text{H}_2}^{1/2}) f_{\text{H}_2\text{O}}]} \quad (4)$$

$$r_3 = \frac{k_3 K_{\text{CO}_2} (f_{\text{CO}_2} f_{\text{H}_2} - f_{\text{H}_2\text{O}} f_{\text{CO}} / K_{\text{P3}})}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) [f_{\text{H}_2}^{1/2} + (K_{\text{H}_2\text{O}} / K_{\text{H}_2}^{1/2}) f_{\text{H}_2\text{O}}]}$$

Note that f_i is fugacity of gas component. In this work, to simplify the level of computation, gas is assumed to be ideal and f_i is equal to partial pressure P_i . The following model has been developed by [3]. This reactor model is based on shell balance technique, in which the material and/or energy balances are considered in a finite section of the reactor tube with same cross-sectional area and width of Δz .

Solid phase:

Mole balance:

No. of mole accumulate on solid surface = No. of mole diffuse onto solid surface + No. of mole change due to surface reaction

$$\varepsilon_B c_t \frac{\partial y_{is}}{\partial t} = k_{gi}(y_s - y_{is}) + \eta r_i \rho_B a \quad (5)$$

Energy balance:

Heat accumulated on solid surface = Heat convection on solid surface + Heat generated by reaction

$$\rho_B c_{ps} \frac{\partial T_s}{\partial t} = a_v h_f (T - T_s) + \rho_B a \sum_{i=1}^n \eta r_i (-\Delta H_{f,i}) \quad (6)$$

Fluid phase:

Mole balance:

Total number of mole = Difference between inlet and outlet mole + No. of mole diffuse from solid phase

$$\varepsilon_B c_t \frac{\partial y_i}{\partial t} = -\frac{F_t}{A_c} \frac{\partial y_i}{\partial z} + a_v c_i k_{gi}(y_{is} - y_i) \quad (7)$$

Energy balance:

Heat in fluid phase = Difference between heat inlet and outlet + Heat convection from solid to liquid + Heat transfer from coolant fluid

$$\varepsilon_B c_t c_{pg} \frac{\partial T}{\partial t} = -\frac{F_t}{A_c} c_{pg} \frac{\partial T}{\partial z} + a_v h_f (T_s - T) + \frac{\pi D_i}{A_c} U_{shell} (T_{shell} - T) \quad (8)$$

Boundary conditions:

$$z = 0, y_i = y_{i0}, T = T_0$$

$$t = 0, y_i = y_i^{ss}, T = T^{ss}, T_s = T_s^{ss}, a = 1$$

As the gas flow through pores in packed bed, its pressure drops due to the effect of drag force in the flow. Pressure drop in the flow increases with the height of the reactor. The pressure drop is calculated using Ergun's equation with correction factor for a packed bed [7].

$$\frac{dP}{dz} = -L_r \cdot 10^{-6} \cdot (1.75 + 150 \frac{1-\varepsilon}{Re}) \cdot \frac{1-\varepsilon}{\varepsilon^3} \frac{u_g^2 \rho_g}{D_p} \quad (9)$$

3.1 Steady-state Model

For our analysis, the steady state model is derived based on the [3] dynamic model as presented in the previous section. The dynamic model is simplified by adopting an additional steady-state assumption, i.e. removing the accumulation term in the equations (5) to (9). These equations are solved using MATLAB. Equations (10) to (11) are the resulting equations for the steady state model for both solid and fluid phases. Additional assumptions include surface reactant limiting, adiabatic reactor and the T_{shell} is assumed constant along the reactor length.

Solid phase:

$$0 = -\frac{F_t}{A_c} \frac{dy_i}{dz} + a_v c_i k_{gi}(y_{is} - y_i) \quad (10)$$

$$0 = -\frac{F_t}{A_c} c_{pg} \frac{dT}{dz} + \frac{\pi D_i}{A_c} U_{shell} (T_{shell} - T) + a_v h_f (T_s - T)$$

Fluid phase:

$$0 = k_{gi}(y_s - y_{is}) + \eta r_i \rho_B a$$

$$0 = a_v h_f (T - T_s) + \rho_B a \sum_{i=1}^n \eta r_i (-\Delta H_{f,i}) \quad (11)$$

These ODEs in the model can be solved using analytical or numerical method. To avoid rigorous implementation of analytical method, numerical method is employ to solve this problem. The reactor is divided into small segments; properties of each segment are calculated from previous segment (shell balance technique). MATLAB offers built-in function ode45 and ode23 for general ODEs. However, for stiff problem like this model, the change of solution is very short compared to the scale of interval integration that is designed for a non-stiff problem. Stiff problem is best solved using backward differentiation formula (also known as Gear's method). In MATLAB, this method is built as function ode15s. Tables 1 to 3 state the kinetic constants used for the simulation. The reactor parameters taken from a Methanol Plant are listed in Table 4.

Table 1: Reaction rate Constants $k = A \exp^{(B/RT)}$

	A	B
k_1	2.69e-7	-109900
k_2	4.36e-2	-65200
k_3	7.31e-8	-123400

Table 2: Adsorption Equilibrium Constant $k = A \exp^{(B/RT)}$

	A	B
K_{CO}	7.99e-7	58100
K_{CO_2}	1.02e-7	67400
$(K_{H_2O}/K_{H_2})^{1/2}$	4.13e-11	104500

Table 3: Reaction Equilibrium Constant $K_p = 10^{((A/T)-B)}$

	A	B
K_{p1}	5139	12.621
K_{p2}	3066	10.592
K_{p3}	-2073	-2.029

Table 4: Reactor Parameters

Tube inner diameter (mm), D_i	44.5
Tube outer diameter (mm), D_o	48.5
Number of tubes	4801
Tube length (m), z	7260
Tube inlet temperature ($^{\circ}C$), T_o	225
Shell steam temperature ($^{\circ}C$), T_s	250
Catalyst diameter (mm), D_p	6
Bed porosity (Φ), ϵ_B	0.4
Specific surface area (m^2/g), a_v	80
Catalyst density (kg/m^3), ρ_B	1100
Feed flowrate (kmol/h), F_i	40789
Inlet Pressure (bar)	82
Feed compositions:	
% CO ₂	8.42
% CO	7.95
% H ₂	60.87
% CH ₄	21.83
% N ₂	0.63
% H ₂ O	0.06
% CH ₃ OH	0.24

Fig. 2 shows The MATLAB algorithm for solving the steady state model.

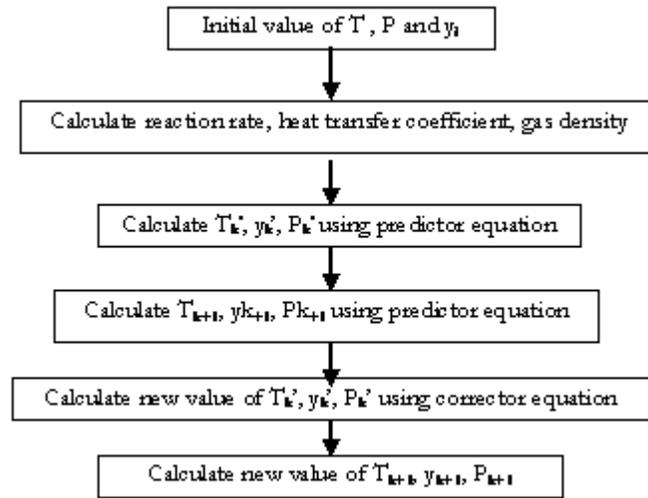
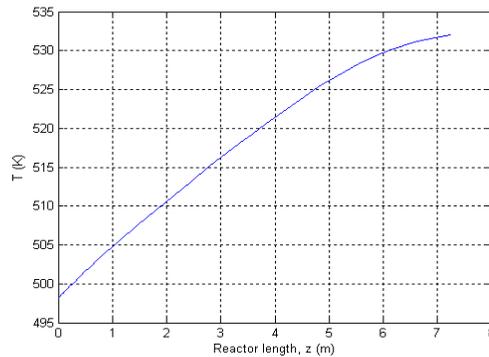


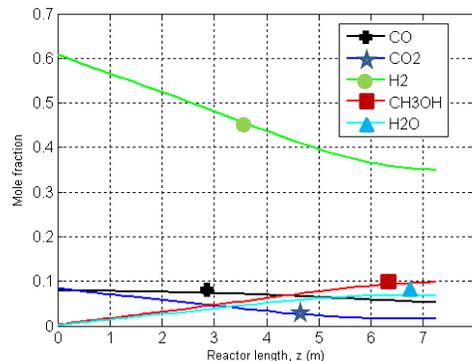
Fig. 2 MATLAB Algorithm

4. RESULTS AND DISCUSSIONS

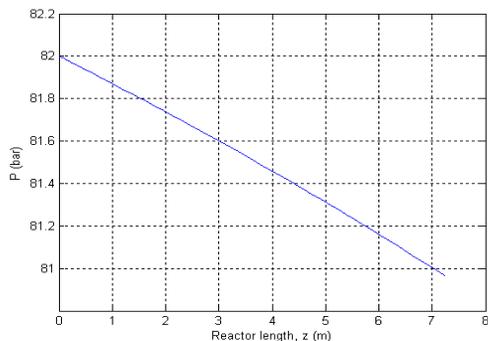
Fig. 3 shows the resulting profiles for the temperature, concentrations and pressure drop in the reactor. As the reaction progresses along the reactor length, a gradual increase in the reactor temperature can be observed due to the exothermic nature of the reaction – see Fig. 3(a). Cooling steam in the reactor’s shell side is important to reduce the temperature and maintain the reaction rate. Although temperature increases along the reactor length, it shows no sign of hot spot formation. This could possibly be due to the low rate of reaction that does not significantly affect the reactor. In Fig. 3(b), the concentrations of the components inside the reactor change accordingly as the reactions progress along the reactor length. A steady decrease in the concentrations of the reactants (H₂, CO₂, CO) can be seen along the reactor length as they are being consumed by the reactions to produce CH₃OH and H₂O.



(a) Temperature profile



(b) Concentration profile



(c) Pressure drop in the reactor

Fig. 3 The temperature, concentrations, and pressure drop profiles in the reactor

The next step in the analysis is to validate the model’s performance against real-life data taken from an industrial petrochemical plant. The operating data was taken during the first few months of the catalyst life time (September 2007 to November 2007). Table 5 shows that the two data are in good agreement with percentage error smaller than 5%. This indicates that the simplified model is able to approximate the real-plant behavior accurately, and can be reliably used for further analysis of the industrial methanol reactor performance.

Table 5: Comparison of Simulation Data to Operating Data

Parameter	Simulation result	Plant data	% error
CH3OH production (ton/day)	2153	2062	4.41
Reactor outlet temperature (K)	532	530	0.38
Reactor pressure drop (bar)	1.078	1.08	-0.19
Carbon efficiency (%)	99.09	99	0.09

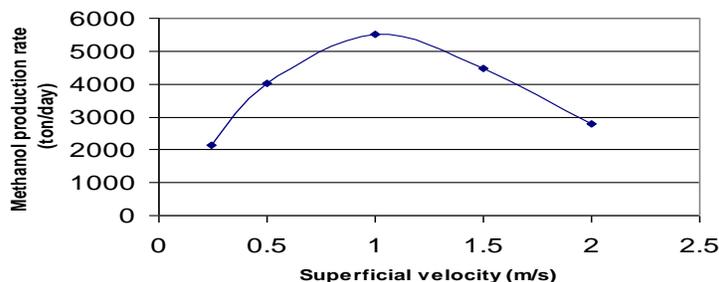


Fig. 4 Effect of superficial velocity on methanol production

Fig. 4 shows the effect of feed velocity on methanol production. There is an initial upward trend that can be observed from the graph whereby an increase in velocity causes a corresponding increase in the methanol production. This is to be expected since higher velocity increases the amount of reactants to the reactor and promotes mixing. However, when the velocity is higher than 1 m/s, methanol production rate significantly deteriorates. The main reason for this is because reactants do not have enough time to diffuse into the catalyst pores and react. It is important to understand that methanol production does not increase linearly with superficial velocity. Too high superficial velocity produces lesser methanol at higher cost of gas compression. Also, high superficial velocity produces higher pressure drop as in Fig. 5, since pressure drop is a function of u^2 , increase in u results in significant increase in pressure drop. Hence, the operating cost increases with higher pressure drop.

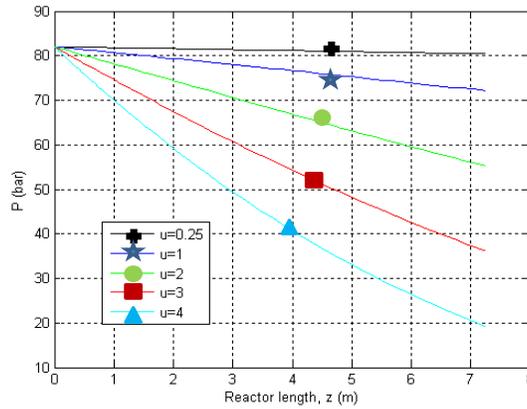


Fig. 5 Effect of superficial velocity on pressure drop

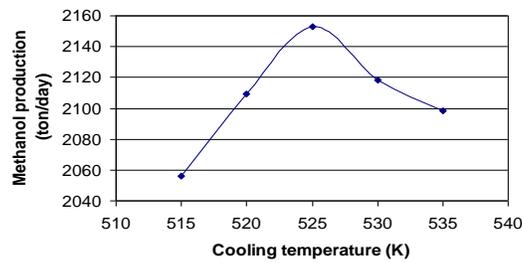


Fig. 6 Effect of coolant inlet temperature on methanol production

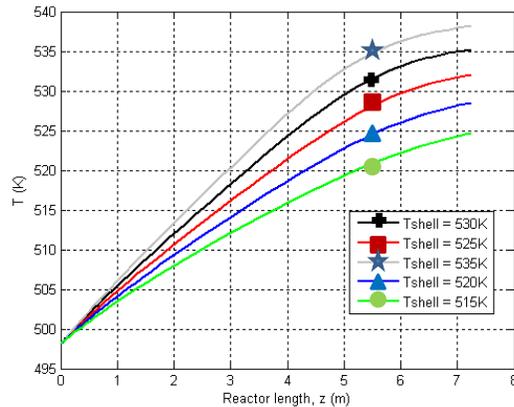


Fig. 7 Effect of coolant inlet temperature on reactor temperature profile

Fig. 6 and 7 demonstrate the effect of the cooling steam inlet temperature to the overall methanol yield as well as the reactor temperature, respectively. The coolant inlet temperature in this case study is a load to the process and is governed by other processes. It is not expected to vary substantially during normal operation; however, these figures show the effects in the worst case scenario. It may not be beneficial for the current case studies, but probably useful for future yield improvement projects for the plant. Fig. 6 reveals that there is an optimal coolant inlet temperature that will yield the optimum methanol amount. As the coolant inlet temperature increases, the reaction inside the tubes will reach a point where heat balance is established and reversed reactions occur, hence the reduction in the production rate. On the other hand, when coolant inlet temperature is too low, reaction rates also decreases. Fig. 7 presents tube temperature profile with different coolant inlet temperatures. For this case study, coolant inlet temperature should be maintained around 525K for best yield of methanol.

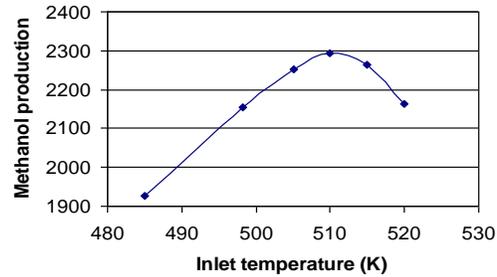


Fig. 8 Effect of inlet feed temperature on methanol production

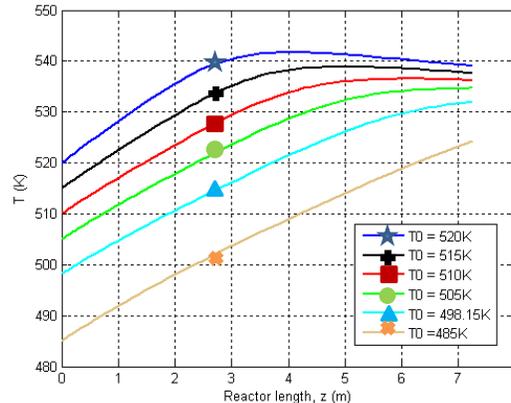


Fig. 9 Effect of inlet feed temperature on reactor temperature profile

From Fig. 8 and 9, it is discernable that the inlet feed temperature has the same effect as coolant inlet temperature on methanol production. This is due to the forward reaction rate that tends to be highest only within a certain range of temperatures. From Fig. 8, this range is around 510K. Further increase in feed temperature results in lesser methanol produced. Fig. 10 shows that when inlet temperature is lower than 510K or 237°C, reactor temperature profiles increase gradually along reactor length and do not exceed 540K (267°C). It is noted that reaction progresses at a much slower rate and lower methanol production is obtained.

5. CONCLUSIONS

In this paper, a simulation study of an industrial methanol reactor based on a simplified steady-state model has been carried out. The main objective of the current work is to develop a tool that can be used to provide steady-state evaluation study and analysis. From the results obtained, it is revealed that the simplified model is able to approximate the plant's operating conditions with sufficient accuracy of less than 5% error. The validated model allows a better understanding of the reactor behavior under varying inlet feed temperatures, feed superficial velocities and coolant inlet temperatures. This model can serve as a base for future improvement studies on the said reactor

6. APPENDIX

a	activity of catalyst
av	specific surface area of catalyst pellet ($m^2 m^{-3}$)
$A0$	outside are of each tube (m^2)
Ac	cross section area of each tube (m^2)
Ai	inner area of each tube (m^2)
c_{pg}	specific heat of the gas at constant pressure ($J mol^{-1}$)
c_{ps}	specific heat of the solid at constant pressure ($J mol^{-1}$)
c_t	total concentration ($mol m^{-3}$)
D_p	particle diameter (m)

D_o	tube outside diameter (m)
D_t	tube inside diameter (m)
E_d	activation energy used in the deactivation model (J mol ⁻¹)
f_i	partial fugacity of component i (bar)
F_t	total molar flow per tube (mole s ⁻¹)
h_o	heat transfer coefficient between coolant stream and reactor wall (W m ⁻² K ⁻¹)
h_f	gas–solid heat transfer coefficient (W m ⁻² K ⁻¹)
h_i	heat transfer coefficient between fluid phase and re-actor wall (W m ⁻² K ⁻¹)
k_1	reaction rate constant for the 1st rate equation (mol kg ⁻¹ s ⁻¹ bar ^{-1/2})
k_2	reaction rate constant for the 2nd rate equation (mol kg ⁻¹ s ⁻¹ bar ^{-1/2})
k_3	reaction rate constant for the 3rd rate equation (mol kg ⁻¹ s ⁻¹ bar ^{-1/2})
k_{gi}	mass transfer coefficient for component i (m s ⁻¹)
K	conductivity of fluid phase (W m ⁻¹ K ⁻¹)
K_d	deactivation model parameter constant (s ⁻¹)
K_i	adsorption equilibrium constant for component i (bar ⁻¹)
K_{pi}	equilibrium constant based on partial pressure for component i thermal conductivity of reactor wall (W m ⁻¹ K ⁻¹)
K_w	
L	length of reactor (m)
M_i	molecular weight of component i (g mol ⁻¹)
P	total pressure (bar)
P_a	atmospheric pressure (bar)
r	radial coordinate (m)
r_1	rate of reaction for hydrogenation of CO (mol kg ⁻¹ s ⁻¹)
r_2	rate of reaction for hydrogenation of CO ₂ (mol kg ⁻¹ s ⁻¹)
r_3	reversed water–gas shift reaction (mol kg ⁻¹ s ⁻¹)
r_i	reaction rate of component i (mol kg ⁻¹ s ⁻¹)
R	universal gas constant (J mol ⁻¹ K ⁻¹)
R_p	particle diameter (m)
Re	Reynolds number
Sc_i	Schmidt number of component i
t	time (s)
T	bulk gas phase temperature (K)
T_R	reference temperature used in the deactivation model (K)
T_s	temperature of solid phase (K)
T_{sat}	saturated temperature of boiling water at operating pressure (K)
T_{shell}	temperature of coolant stream (K)
u_g	linear velocity of fluid phase (m s ⁻¹)
	superficial velocity of fluid phase (m s ⁻¹)

U_{shell}	overall heat transfer coefficient between coolant and process streams ($\text{W m}^{-2} \text{K}^{-1}$)
w	auxiliary variable
y_i	mole fraction of component i in the fluid phase (mol mol^{-1})
y_{is}	mole fraction of component i in the solid phase (mol mol^{-1})
z	axial reactor coordinate (m)

Greek letters

ε_B	void fraction of catalytic bed
ε_s	void fraction of catalyst
η	catalyst effectiveness factor
λ_c	thermal conductivity of catalyst ($\text{W m}^{-1} \text{K}^{-1}$)
μ	viscosity of fluid phase ($\text{kg m}^{-1} \text{s}^{-1}$)
ν	stoichiometric coefficient
ρ	density of fluid phase (kg m^{-3})
ρ_B	density of catalytic bed (kg m^{-3})
ρ_s	density of catalyst (kg m^{-3})
τ	tortuosity of catalyst

Superscripts and subscripts

0	inlet conditions
k	reaction number index (1, 2 or 3)
s	at catalyst surface
ss	initial conditions (i.e., steady-state condition)

7. ACKNOWLEDGMENT

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