Modeling of Industrial Fixed Bed Reactor to Produce Dimethyl Ether from Methanol and Determination of Optimum Operating Conditions

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Abstract: Dehydration of methanol to dimethyl ether using γ-Al_2O_3 catalyst was modeled in an industrial adiabatic fixed-bed reactor by one-dimensional heterogeneous model. Longitudinal temperature and conversion profiles were predicted. By the model, the best temperature for pure methanol feed, through plotting temperature-conversion diagram at constant reaction rates and different inlet temperatures was determined. In addition, the optimum pressure was obtained and the effect of mass flow rate was discussed at this pressure and inlet temperature. Finally, it was found maximum obtainable conversion at optimum operating conditions was 81.36%.
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1. Introduction

Dimethyl ether (DME) is a new energy source, which is expected to be commercially viable as an environmentally friendly clean fuel [1]. The physical properties of dimethyl ether are similar to those of liquefied petroleum gases (i.e., propane and butane) [2]. In general, DME can be used in three primary applications: firstly, the immediate market allows the use of DME as a blend-stock with LPG for home heating and cooking; secondly, the developing market is exploring DME as a transportation fuel, and finally, it holds a promising future as fuel supply for electric power generation [3, 4].

There are two methods for manufacturing DME: direct synthesis [5, 6] and methanol dehydration [7-10] as an indirect one with both having corresponding advantages and disadvantages. In general, Methanol dehydration to dimethyl ether (indirect process) is a potential process and more favorable in views of thermodynamics and economy [9].

Solid acid catalysts such as γ-Al_2O_3, modified γ-Al_2O_3 with silica, phosphorus or boron oxide (B_2O_3) are excellent catalysts for dehydration of methanol to Dimethyl ether in bench and large scale [11]. For industrial production, γ-Al_2O_3 is usually preferred due to less production of by-products and high stability, however, the application is limited to pure methanol, since presence of water would result in deactivation of catalyst rapidly [12].

Fluidized-bed and fixed-bed DME synthesis reactors have been investigated through a number of research studies. Mahecha-Botero et al. [13] developed a generalized comprehensive model to simulate a wide variety of fluidized bed catalytic reactors. Kumar & Srivastava [14] modified the model proposed by Mahecha-Botero et al. and employed the modified model to simulate DME synthesis in a fluidized-bed reactor. Also, the modified model was used under various operating conditions to maximize DME productivity. Bercic & Levec [15] proposed a rate equation using experimental results from a differential fixed bed reactor. This equation is frequently used by researchers in the process modeling of dimethyl ether production from methanol [16-18]. Fazlollahnejad et al. [16] employed one dimensional plug flow model to simulate an adiabatic fixed bed reactor of methanol dehydration. Longitudinal temperature and conversion profiles predicted by this model were compared to those experimentally measured in a bench scale reactor. The reactor was packed with 1.5 mm γ-Al_2O_3 pellets as dehydration catalyst. Also, Farsi et al. [17] simulated the industrial reactor of DME synthesis accompanied by a feed pre-heater using Bercic & Levec equation. They investigated the controllability of the process through dynamic simulation of the process under a conventional feedback PID controller as well. At other work, Khademi et al. [18] performed a steady-state heterogeneous modeling in order to evaluate the optimal operating conditions and enhancement of dimethyl ether and benzene production in a thermally coupled reactor. Nasehi et al. [19] simulated an industrial adiabatic fixed bed reactor for DME production from methanol dehydration at steady state condition, and showed that the difference between one and two dimensional is negligible. Mollavali et al. [20] tested a series of commercial γ-Al_2O_3 samples for vapor-phase dehydration of methanol to dimethyl

ether and studied the influence of operating conditions on catalyst performance as well as the stability of catalysts towards water. Moreover, a new kinetic expression was developed for dehydration of methanol to DME by them.

2. Kinetics

The reaction equation of methanol dehydration to dimethyl ether is shown in the following:

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$

Table 1 shows the number of suggested rate equations by researchers. The parameters of Bercic & Levec equation are following as:

$$lnK_{eq} = \frac{4019}{T} + 3.707\,lnT - 2.783 \times 10^{-3}T + 3.8 \times 10^{-7}T^2 - 5.561 \times \frac{10^4}{T^3} - 26.64 \quad (1)$$

$$K_i = A_i \exp\left(-\frac{E_i}{RT}\right) \quad (2)$$

Parameters of A_i and E_i have been listed in Table 2.

3. Reactor model

In this study, one dimensional heterogeneous model has been considered for steady state simulation of the process using Bercic & Levec rate equation. Material balance equation is shown in the following:

$$\frac{dX}{dV} = \frac{\eta(-r_M)\rho_B}{F_{M,0}} \quad (3)$$

Also, the energy balance for an adiabatic reactor with pure methanol feed is following:

$$\frac{dT}{dV} = \frac{\eta(-r_M)\{-[\Delta H_r(T_{ref}) + \int_{T_{ref}}^{T} \Delta C_P dT]\}\rho_B}{F_{M,0}(C_{P_M} + X\Delta C_P)} \quad (4)$$

In the above equations, η is the effectiveness factor which is defined in Equation (5). Since the catalyst particles are so small that concentration and temperature variations in particles can be neglected, the effectiveness factor can be assumed 1. Thus, this factor does not have any significant effect on temperature of reactor and conversion of methanol.

$$\eta = \frac{\int r_M \, dV_P}{V_P \cdot r_M} \quad (5)$$

In the Equation (4), ΔC_P is calculated according to stoichiometric coefficients of species. The heat capacity data for methanol, water and dimethyl ether are given in Table 3. The coefficients found in this table should be set in the following equation:

$$C_P = a + bT + cT^2 + dT^3 \quad (6)$$

The following reasonable assumptions have been considered in this model:
- plug flow pattern along with negligible concentration and temperature variations in radial direction
- No heat loss to the surrounding from the reactor wall
- Tubular reactor with steady state operating conditions
- Pressure drop and diffusion in catalyst pores are negligible

In this case study, an industrial reactor with a length of 8 meters in height and 4 meters in diameter is available. The mass flow rate of pure methanol as feed of reactor is 51 kg/s. Also, the catalyst in use is gamma alumina from Suedchemie Company and catalyst bed density of 780 kg.m^{-3}.

4. Results and discussion
4.1. Temperature effect

One of the most important diagrams in the kinetics of a chemical reaction is the changes of conversion versus temperature. Figure 1(a) shows variations of methanol conversion versus temperature in different inlet temperatures and reaction rates. In this figure, adiabatic lines have been plotted at different inlet temperatures using Equation (7):

$$X_M = \frac{C_P \Delta T}{-\Delta H_r} \quad (7)$$

From Figure 1(b) it is obvious that in the exothermic reversible reactions like methanol dehydration, by increasing the temperature, the rate of reaction increased but the maximum obtainable conversion decreases. Therefore, when the system is far from equilibrium condition, temperature should be increased and by approaching to equilibrium, temperature must be decreased. Also, Figure 1(b) shows the best temperature progression by connecting the maximum of different reaction rates. According to this figure, a temperature ranging from 498 to 523 K is the best inlet temperature range, because of the highest mean value of rate of reaction and desirable conversion.

Figures 2(a) and 2(b) show profiles of methanol conversion and temperature along the reactor at different inlet temperatures, respectively. The optimum temperature between range of 498 to 523 K is found to be 498 K. From Figure 2(b), it is clear that the higher inlet temperature resulted the higher temperature distribution entire the reactor bed which is undesirable for exothermic reversible reactions. Moreover, increasing the temperature resulted to use more energy which is not appropriate from energy consumption point of view. On the other hand, from Figure 2(a) it is clear that the maximum conversion (81.36%) is reached at 498 K. Figure 3 shows maximum of reaction rate at different inlet temperatures. As expected when the temperature increased, the maximum of reaction rate increased, however, this was not a good reason for running of reaction in higher temperatures especially for an exothermic and reversible reaction.

(a)
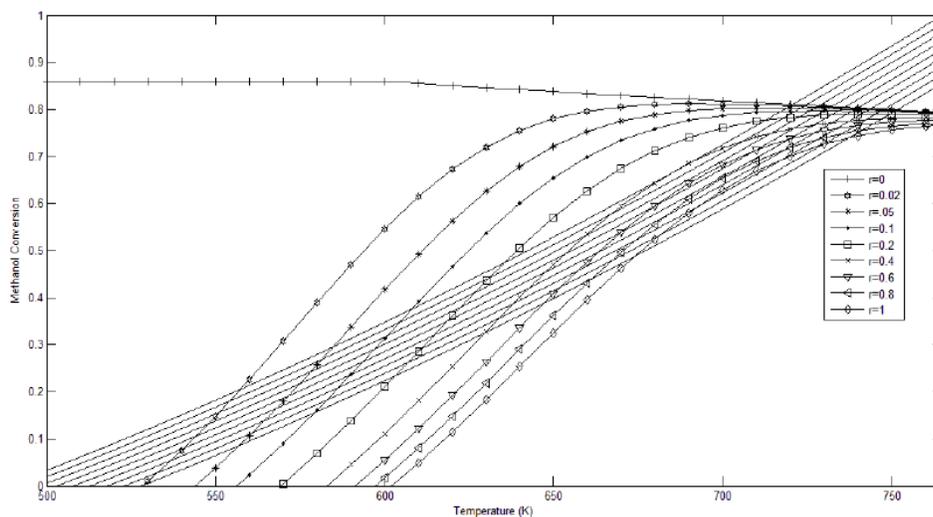
(b)
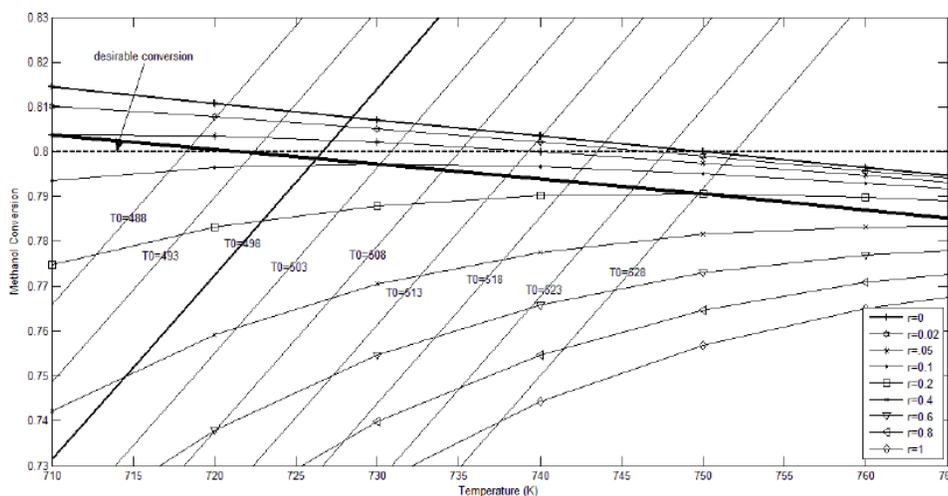
Figure 1. Conversion-temperature diagram at constant reaction rates and different adiabatic lines. Diagonal straight lines are adiabatic lines at different inlet temperatures. (a) In an overview. (b) With desirable conversion, and thick line shows the best temperature progression path

4.2. Pressure effect

Methanol dehydration is an equimolar reaction; therefore, pressure could not affect on equilibrium conversion and the only effect may be on the reaction rate. Profiles of methanol conversion and temperature along the reactor at different pressures have been shown for inlet temperature of 498 K and flow rate of 51 kg/s in Figures 4(a) and 4(b), respectively. These two diagrams show negligible effect of pressure on the final temperature of the reactor and maximum conversion of methanol. In order to clarify the effect of pressure on the rate of reaction, variation of reaction rate along the reactor has been plotted at different pressures in Figure 5. From this diagram it is obvious that maximum rate occurs at low pressures, but having the higher average reaction rate is the most important factor, which resulted to more production rate. The area under the curves of Figure 5 is a measure of production rate. For determination of optimum pressure, these areas versus different operating pressures were plotted in Figure 6. From this diagram, it is clear that the maximum production rate is obtained at 5 bar.

(a)

(b)
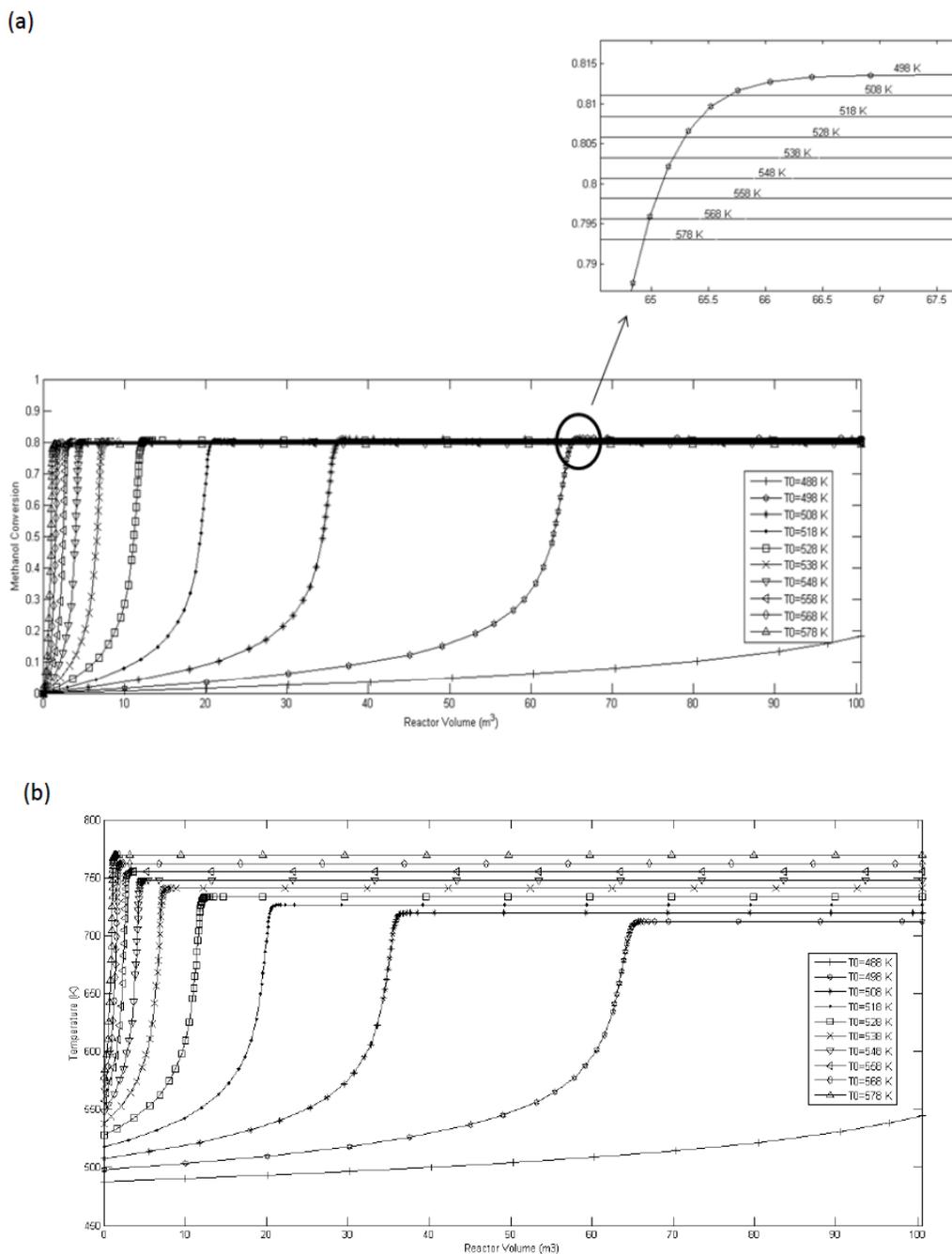
Figure 2. Effect of reactor inlet temperature under constant pressure of 5 bar and feed flow rate of 51 kg/s. (a) Methanol conversion profile. (b) Temperature profile

4.3. Flow rate effect

Figures 7(a) and 7(b) show profiles of methanol conversion and temperature at optimum inlet temperature and pressure along the reactor, respectively. The more flow rate leads to less residence time. Therefore, the time to reach equilibrium conversion is greater in higher flow rate. Accordingly, the maximum conversion occurs at the end of reactor for high flow rates. From Figure 7(a), it may be concluded that by using the total reactor volume for the reaction, maximum mass flow rate to reach equilibrium conversion is 104 kg/s, but it must be considered the hydrodynamic consideration and pressure drop across the reactor are the factors that would define the optimum mass flow rate.
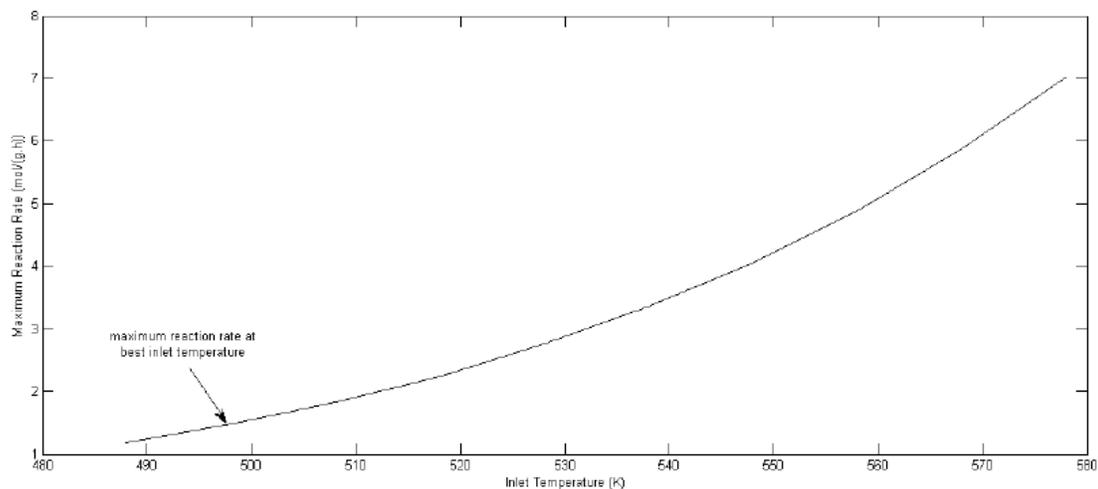
Figure 3. Effect of reactor inlet temperature on maximum reaction rate

(a)
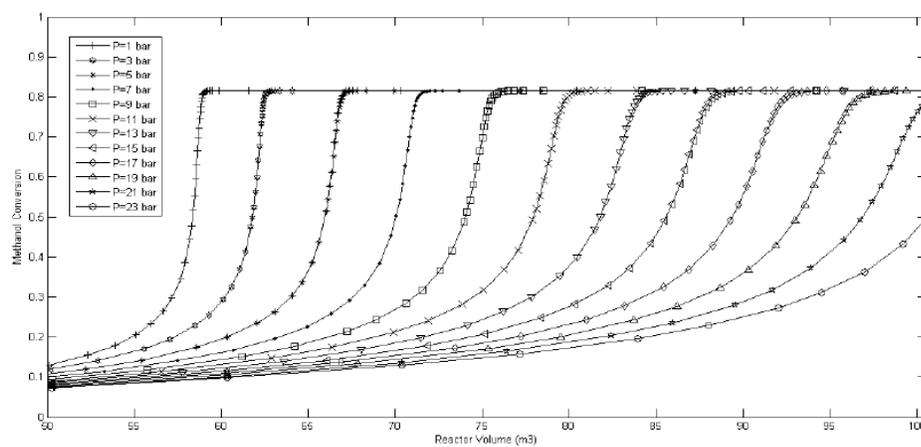
(b)
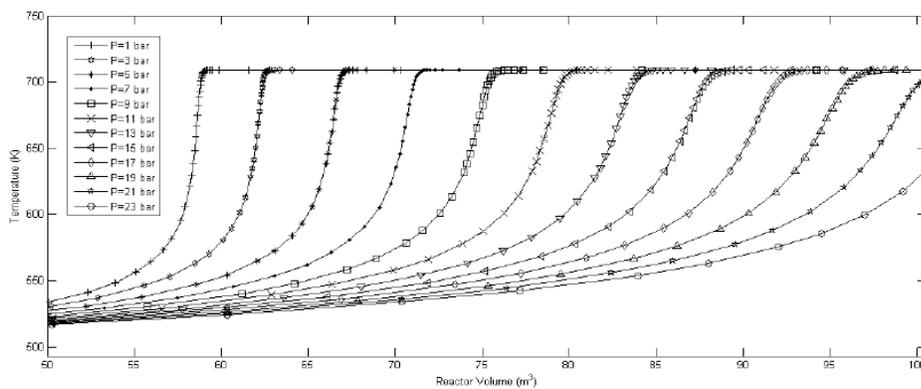
Figure 4. Effect of reactor total pressure under inlet temperature of 498 K and feed flow rate of 51 kg/s. (a) Methanol conversion profile. (b) Temperature profile
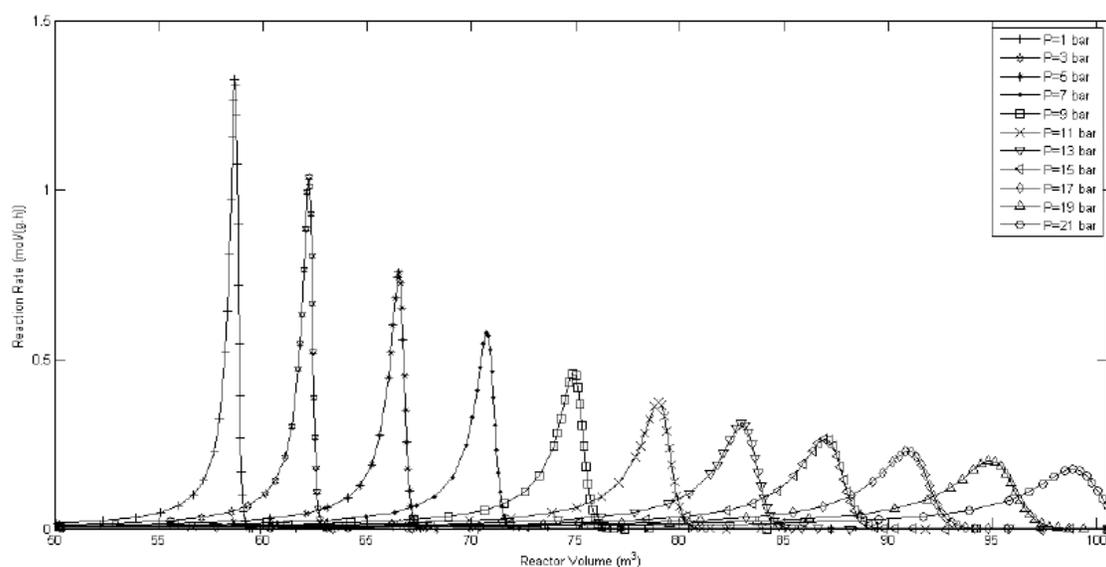
Figure 5. Effect of pressure on reaction rate along the reactor
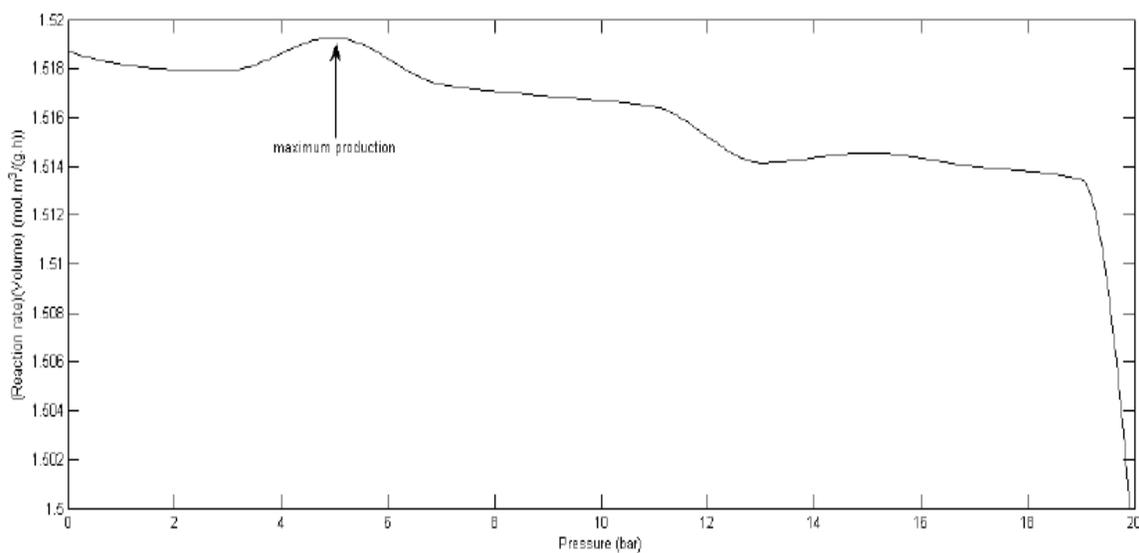
Figure 6. Effect of pressure on production rate

5. Conclusions

In this study, an industrial dimethyl ether synthesis reactor from dehydration of methanol with volume of 100 m^3 was simulated in steady state conditions on a one-dimensional heterogeneous model with γ-Al$_2$O$_3$ as catalyst. By plotting variations of methanol conversion versus temperature at different reaction rates, optimum inlet temperature for adiabatic operation was obtained. To determine optimum pressure, diagram of $(-r_M)$ (V) versus pressure was used. It was found that the maximum production rate was achievable at 5 bar. Moreover, the effect of flow rate on conversion and temperature was investigated. For the aforementioned reactor, it was shown at optimum operating conditions (pressure, inlet temperature and feed flow rate) maximum conversion was 81.36%.

(a)
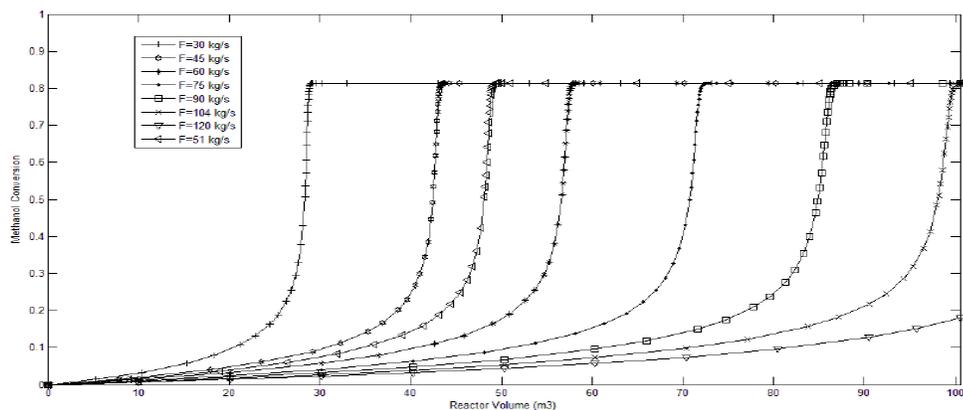
(b)
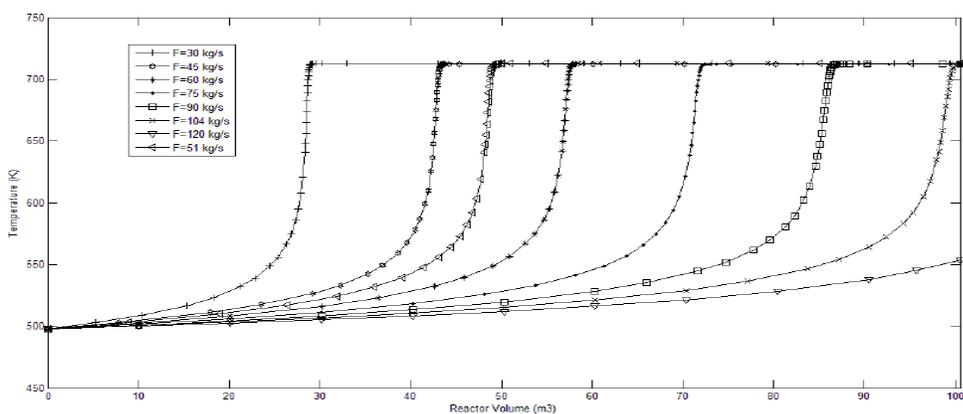
Figure 7. Effect of feed flow rate under inlet temperature of 498 K and total pressure of 5 bar. (a) Methanol conversion profile. (b) Temperature profile

Symbols used

A_i [-]   pre-exponential factor in Arrhenius' law
C_p [J/mol.K]   specific heat of the gas at constant pressure
E_i [J/mol]   activation energy
F   [kg/s]   mass flow rate
F_m [mol/s]   molar flow rate
k   [mol/g.h]   rate constant of reaction
K_i [m^3/kmol]   adsorption constant of component i
K_{eq} [-]   reaction equilibrium constant for methanol dehydration reaction
P   [bar]   total pressure
ρ_B [kg/m^3]   density of catalytic bed
r   [mol/g_{cat}.h]   rate of reaction for DME synthesis
ΔH_r [J/mol]   heat of reaction
T   [K]   temperature
η   [-]   effectiveness factor
V   [m^3]   volume

X   [-]   methanol conversion
Subscript
0   inlet conditions
i   chemical species
M   methanol
P   particle
w   water

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