



Effect of In-situ Membrane Removal of H₂O on Methanol Conversion during Dimethyl Ether Synthesis Reaction

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Abstract

An adiabatic tubular fixed bed reactor with and without a membrane was modeled and simulated to study the effect of in-situ H₂O membrane removal on methanol conversion during dimethyl ether (DME) synthesis. An optimization approach was implemented to determine the best feed conditions for maximum conversion. A steady state one dimensional reactor model was used to process 100,000 tons per year of methanol over γ -Al₂O₃ pellets as reaction catalyst using a novel kinetic model. Pressure, temperature, conversion, and components molar flow rates profiles along the reactor were predicted. Results showed that methanol conversion exceeded the thermodynamic equilibrium limits when a membrane fixed bed reactor is used instead of a traditional fixed bed reactor. Methanol conversion reached 96% at optimum feed conditions in the fixed bed reactor with a membrane.

Keywords: Dimethyl Ether; Methanol; Simulation; Fixed bed reactor; Membrane.

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1. Introduction

Recently Dimethyl Ether (DME) attracted considerable attention due to its excellent properties as an environment friendly fuel beside its wide applications as a solvent, propellant and chemical products feedstock. For diesel engines as a substitute for conventional diesel fuel, DME emits less pollutants than diesel such as CO, NO_x and particulates, also it has good ignition quality, with a high cetane number (60 compared to 50 for diesel) [1]. Furthermore DME can be used as a blend with LPG and it has a promising future as an electric power generation fuel [2]. One of the most important applications of DME today is as an aerosol propellant. Over 50% of the demand for DME is for this application [3]. DME could be produced directly from synthesis gas (direct method) or by methanol dehydration (indirect method) [4]. The indirect method is preferred in industry. Methanol dehydration reaction is a reversible reaction so that methanol conversion is limited by the thermodynamic equilibrium.



DME is commercially produced from methanol in an adiabatic fixed-bed reactor [5]. Adiabatic and isothermal fixed, fluidized and slurry bed reactor were simulated, optimized and studied to enhance methanol conversion. Bai and Hongfang [4] simulated DME production process in an adiabatic fixed-bed reactor with inlet conditions of temperature 533.15 °K, pressure 12 bar and flow 3540 kmol/h, the reactor outlet conversion reached 80%. Faris [6] simulated adiabatic and isothermal fixed-bed reactor for methanol dehydration with optimum feed inlet temperature and pressure 533.15°K and 18.2 bar methanol conversion of the isothermal and adiabatic fixed-bed reactor were 85.75 % and 81.9 % , respectively. Alavi and Jazayeri [7] optimized the feed conditions in a DME production process to maximize the methanol conversion. They found that 84% methanol conversion could be achieved with a feed temperature of 496.15 °K and feed flow rate of 1.1 dm³/h. Mahecha [8] developed a generalized comprehensive model to simulate a wide variety of fluidized bed catalytic reactors. Kumar and Srivastava [9] modified the model proposed by Mahecha 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. Moradi studied DME synthesis in a slurry reactor [10]. A few articles in the literature discussed modeling and simulation of membrane reactors for DME production from methanol. Rahimpour [11] modeled a membrane fixed bed reactor for methanol production from syngas; he investigated enhancement of methanol production in a membrane reactor and showed that the methanol production increased using membrane. Farsi and Jahanmiri [12] simulated membrane fixed bed reactor for DME synthesis from methanol, and compared the performance of the proposed reactor with conventional reactor which increases the DME mole flow rate at the reactor outlet by about 5.2 % compared with adiabatic reactor. Iliuta [13] simulated membrane reactor for DME production from syngas and showed that the fixed-bed membrane reactor technology with in situ H₂O removal is more efficient for DME synthesis than a fixed-bed reactor without H₂O removal. In this work a conventional fixed bed reactor without a membrane (FBR) and a fixed bed reactor with a membrane (M-FBR) will be modeled and simulated to study the effect of water vapour removal through a hydrophilic membrane from dimethyl ether synthesis reaction zone on methanol conversion and compare it with the conversion at equilibrium, without membrane usage.

2. Reaction kinetics

Many publications were made on methanol dehydration to DME reaction kinetics. Ereña and Sierra [14] studied thirteen different kinetic models to describe the effect of H₂O partial pressure on reaction rate accurately and proposed a new rate equation with an exponential expression for the adsorption of methanol, H₂O and DME on the catalyst surface. In this study Irene Sierra model will be chosen as an intrinsic description of water vapour effect on the reaction rate. Irene Sierra & Javier Ereña kinetic model is as follows:

$$r_D' = k \left(P_M^2 - \frac{P_W P_D}{K_{eq}} \right) \Theta_M \cdot \Theta_W \cdot \Theta_D \quad (1)$$

$$\Theta_M = e^{-K_M P_M^m} \quad (2)$$

$$\Theta_W = e^{-K_W P_W^n} \quad (3)$$

$$\Theta_D = e^{-K_D P_D^q} \quad (4)$$

$$k = k^\circ e^{\left(\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{T^\circ}\right)\right)} \quad (5)$$

$$K_i = K_i^\circ e^{\left(\frac{\Delta H_i}{R} \left(\frac{1}{T} - \frac{1}{T^\circ}\right)\right)} \quad (6)$$

$$K_{eq} = \exp\left(-9.76 + \frac{3200}{T} + 1.07 \log T - 0.000675T + 4.9 \times 10^{-8} T^2 + 6050/T^2\right) \quad (7)$$

All reaction rate parameters constants are presented in Table 1.

Table1: Reaction rate parameters constants

Parameter	Value
k [°]	7.33*10 ⁻¹¹ kmol/kg cat.Pa.s
K _M [°]	1.6*10 ⁻⁹ Pa ^{-1.86}
K _W [°]	0.171 Pa ^{-0.36}
K _D [°]	3.47*10 ⁻⁴ Pa ^{-0.86}
E _a	263.6 *10 ⁶ J/kmol
ΔH _M	2.01*10 ⁶ J/kmol
ΔH _W	3.60*10 ⁶ J/kmol
ΔH _D	7.20*10 ⁶ J/kmol
T [°]	573.15 K
m	1.86
n	0.36
q	0.86

Where P_i is the partial pressure of component i , k is reaction rate constant, K_{eq} is the equilibrium constant and K_i is component i adsorption constant.

3. Reactor modeling and simulation

In this study, a steady state simulation of an adiabatic single tube FBR and M-FBR of 1.9 meter (internal diameter) was made using γ - Al_2O_3 pellets as catalyst with the following specifications:

Void fraction $\phi = 0.45$

Bulk density $\rho_b = 972 \frac{kg}{m^3}$

Pellet diameter $D_p = 170 \mu m$

To achieve the goal of using a suitable membrane reactor in this study carefully membrane selection to be simulated was made according to the process conditions and demands. A new hydrophilic ceramic supported polymer membrane (CSP2) developed by Energy research Center of the Netherlands (ECN) will be chosen because of its high water vapor permeability, perm selectivity and high thermal stability (<600 °K) with the following Specifications [15]:

CSP2 membrane consists of four layers on a commercially available macro porous tube coated with two layers of macro porous α - Al_2O_3 (40 μm thick) and a thin layer of γ - Al_2O_3 (2 μm thick) and the functional polymeric layer **P84**® (1 μm thick)

MeOl permepility = $0.028 \times 10^{-10} \frac{kmol}{Pa \cdot s \cdot m^2}$

H₂O permepility = $0.588 \times 10^{-10} \frac{kmol}{Pa \cdot s \cdot m^2}$

3.1. Material balances

$$\frac{dX}{dW} = \frac{-r'_M}{F_{M^o}} \quad (8)$$

$$\frac{dP_D}{dW} = (0.5 r'_M) \frac{R T}{v} \quad (9)$$

$$\frac{dP_M}{dW} = (-r'_M - R_M) \frac{R T}{v} \quad (10)$$

$$\frac{dP_W}{dW} = (0.5 r'_M - R_W) \frac{R T}{v} \quad (11)$$

3.2. Energy balance

The energy balance for the adiabatic reactor for impure methanol feed enters the reactor is as follows:

$$\frac{dT}{dW} = \frac{(-r'_M)(-\Delta HR_{x(T)})}{F_M \circ (\sum \theta_i C_{p_i} + X \Delta C_p)} \quad (12)$$

3.3. Pressure drop

Pressure deference with catalyst weight neglecting diffusion resistance in catalyst pores is given by Ergun equation:

$$\frac{dP}{dW} = \frac{U(1 - \phi)}{Ac \cdot Dp \cdot \rho_b \cdot \phi^3} \left(\frac{\beta_1}{Dp} + \frac{\beta_2}{T \cdot P_{in}} \right) \quad (13)$$

$$\beta_1 = 150(1 - \phi)\mu \quad (14)$$

$$\beta_2 = 1.75U \cdot P \cdot T_{in} \cdot \rho_{feed} \quad (15)$$

3.4. Solution of the model equations

Reactors model consists of three non-linear deferential equations for FBR and five for M-FBR relating components partial pressure, pressure, temperature and conversion to the catalyst. These equations are amenable to numerical solution; and the MATLAB ODE45 program based on Runge-Kutta 4th degree method was used for this purpose as an initial value ODEs solver. Plots of the simulation and optimization were presented using model solution results.

4. Results and discussions

Reactors models were used firstly to optimize feed temperature and pressure to maximize methanol conversion for each reactor separately. Then methanol conversion was compared between FBR and M-FBR. Methanol conversion at equilibrium profile along the reactor was predicted and compared to the M-FBR. Finally a simulation of M-FBR was made and profiles of conversion, temperature, pressure and components molar flows were plotted.

4.1. Feed temperature optimization

Methanol conversion is very sensitive to inlet temperature conditions as studied in the inlet temperature range of (365.15~413.15 °K) for FBR and (368.15~488.15°K) for M-FBR. Figures 1 and 2 show that the optimum temperatures for maximum methanol conversion are 383 °K and 398 °K for FBR and M-FBR respectively.

4.2 Feed pressure optimization

Methanol dehydration reaction is an equimolar reaction so that its conversion is independent on feed pressure at constant temperature when carried out in FBR as confirmed by Figure 3. Even when this reaction is carried out in a M-FBR it its conversion still independent on feed pressure for single fed inlet temperature, as shown in Figure 4, but inlet pressure has upper limits which when exceeded forces methanol through the membrane and thus results in a sharp drop in methanol conversion.

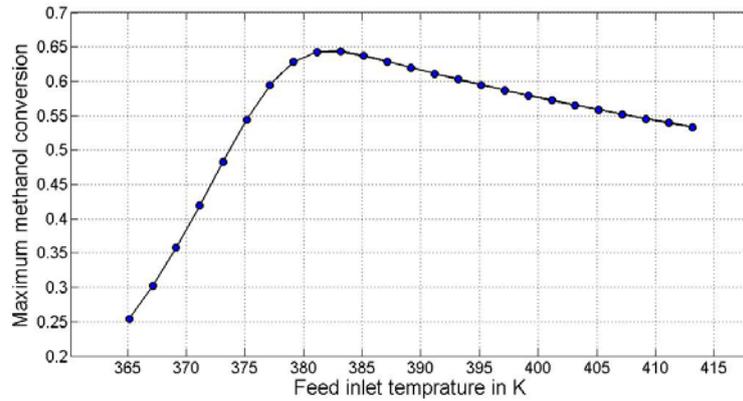


Figure 1: Feed inlet temperature effect on maximum methanol conversion in FBR.

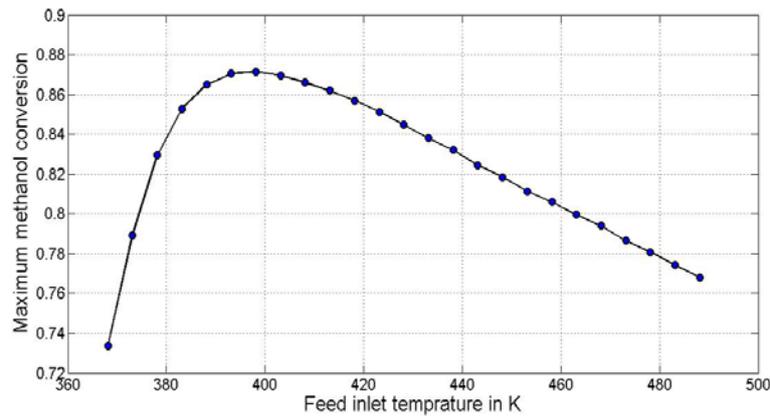


Figure 2: Feed inlet temperature effect on maximum methanol conversion in M-FBR.

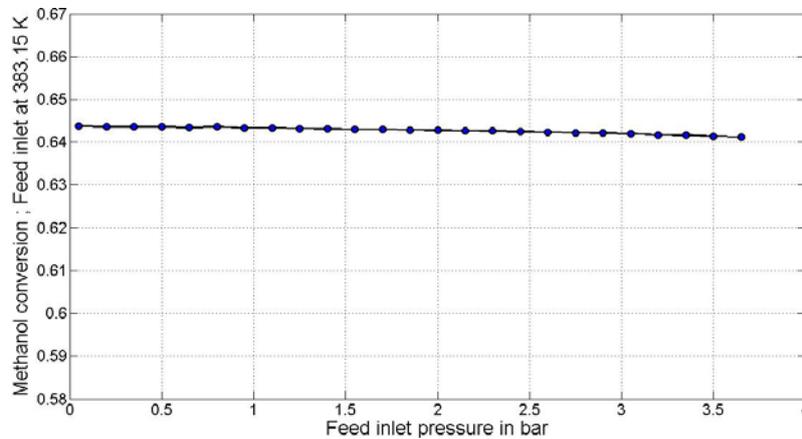


Figure 3: Feed inlet pressure effect on maximum methanol conversion in FBR.

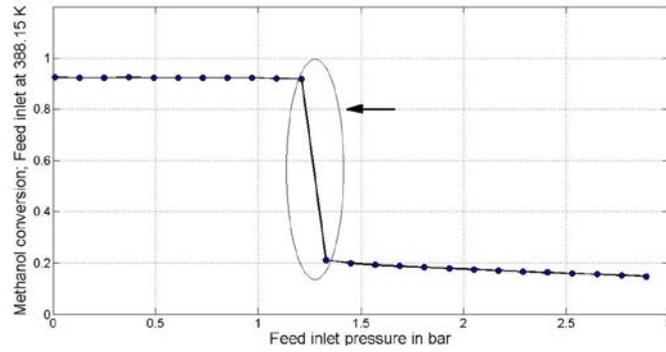


Figure 4: Feed inlet pressure effect on maximum methanol conversion in M-FBR and the upper limit of inlet pressure.

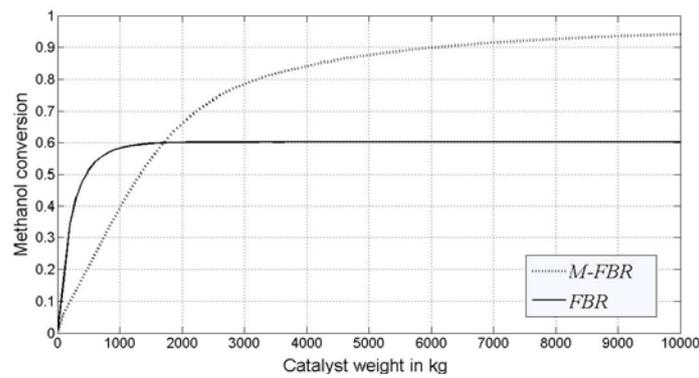


Figure 5: Methanol conversion profile along FBR and M-FBR.

4.3 Methanol conversions investigation

Results showed a great enhancement for methanol conversion for M-FBR over FBR. Figure 5 presents conversion of methanol in the FBR and M-FBR simultaneously. Methanol conversion increased by 32% at the reactor outlet at optimum reactor conditions.

Methanol conversion at equilibrium along the reactor against M-FBR methanol conversion presented in figure 6 which confirmed that using M-FBR takes the reaction beyond the equilibrium limits. Conversion crossed the equilibrium conversion at 3000kg of catalyst and kept rising.

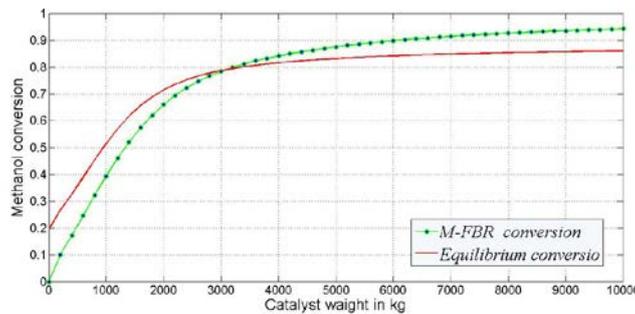


Figure 6: Methanol conversion profile for M-FBR comparing to the conversion at equilibrium.

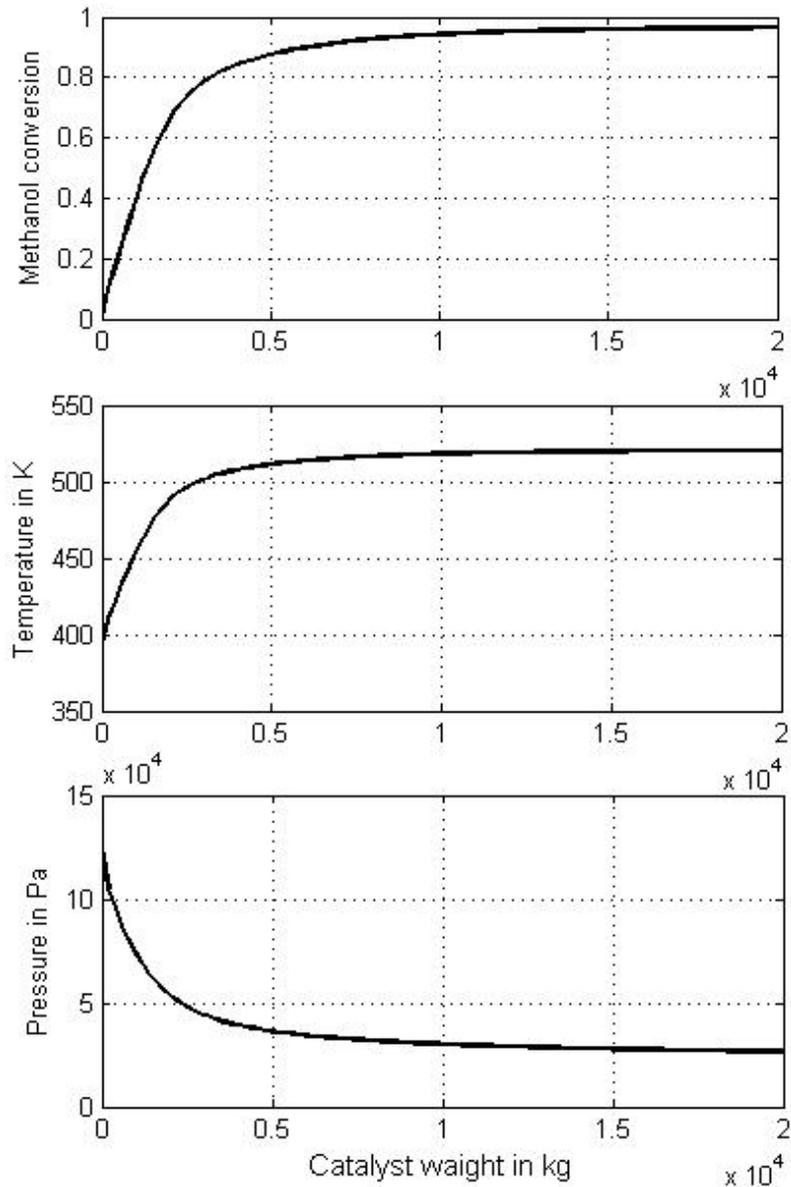


Figure 7: Methanol conversion, temperature and pressure profiles.

4.4 M-FBR running simulation

At optimum feed conditions M-FBR simulation was carried out to determine reactor effluent composition temperature and pressure and also to observe temperature distribution along the reactor. Figure 7 shows conversion propagation temperature profile and pressure drop along the reactor. Methanol conversion increases rapidly for the first 5000kg of catalyst, then gradually until it reaches 94.25% at 10000kg of catalyst. From that point to 20000kg conversion gains only 2.32 %, so that from an order of magnitude economic estimate it is sufficient to use only 1000kg of catalyst as total weight. Temperature rises and pressure drops as methanol conversion increases. Reactor outlet temperature and pressure are 520 °K and 0.265 bar.

Figure 8 illustrates molar flow rate profiles of reactants and products. DME production was determined as 0.04744 kmol/sec from figure 8. This is equivalent to an annual production of 66546 DME ton/year.

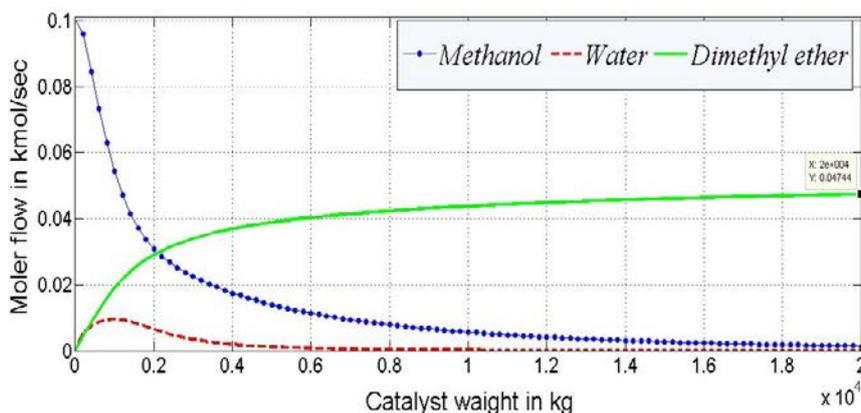


Figure 8: Molar flow profiles of methanol, H₂O and DME

5. Conclusions

The in-situ H₂O removal approach during dimethyl ether syntheses reaction in a fixed bed reactor using membrane greatly enhanced methanol conversion. Moreover, this approach took the methanol conversion beyond the equilibrium limits until it reached 96% at the reactor exit.

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Appendix A: Nomenclatures

$-r'_M \equiv$ reaction rate; kmol/kgcat.sec

$A_c \equiv$ Reactor cross section area; m²

$C_p \equiv$ Specific heat; J/kmol.K

$E_i \equiv$ Activation energy; J/kmol

$F_i^o \equiv$ Component i molar flow rate; kmol/s

$k \equiv$ reaction rate constant ; kmol/kg.s

$K_i \equiv$ Adsorption constant of component i

$K_{eq} \equiv$ equilibrium constant

$P \equiv$ pressure; bar

$P_i \equiv$ component i partial pressure; bar

$\Delta H_i \equiv$ component i heat absorption ; J/kmol

$T \equiv$ Temperature; K

$\rho \equiv$ density; kg/m³

$\mu \equiv$ viscosity; cp

$\theta_i \equiv$ component i feed ratio

$\Delta H_{R_x(T)} \equiv$ reaction Heat at T; J/kmol

$W \equiv$ Catalyst weight; kg

U ; Velocity; m/s

$R_M \equiv$ Permeation rate; kmol/kgcat.sec

$R \equiv$ Gas constant ; kj/kmol.K

$v \equiv$ Volumetric flow rate; m³/s