

# Modeling of a Reaction-Distillation-Recycle System to Produce Dimethyl Ether through Methanol Dehydration

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**Abstract.** The increase in the dimethyl ether yield through methanol dehydration due to a recycle integration to a reaction-distillation system was studied in this research. A one-dimensional phenomenological model of a methanol dehydration reactor and a shortcut model of distillation columns were used to achieve the aim. Simulation results show that 10.7 moles/s of dimethyl ether is produced in a reaction-distillation system with the reactor length being 4 m, the reactor inlet pressure being 18 atm, the reactor inlet temperature being 533 K, the reactor inlet velocity being 0.408 m/s, and the distillation pressure being 8 atm. The methanol conversion is 90% and the dimethyl ether yield is 48%. The integration of the recycle stream to the system increases the dimethyl ether yield by 8%.

## 1. Introduction

Dimethyl ether (DME), previously known as a building block in the production of valuable chemicals such as methyl acetate and dimethyl sulfate, is finding its way to become a potential eco-friendly substitute for petroleum-derived diesel fuel and residential liquefied petroleum gas (LPG) replacing fuel [1, 2]. With its similar physical properties to LPG, it is possible to decrease the investment cost of its application as the material supply can be accomplished using existing LPG infrastructure.

Dimethyl ether is traditionally produced in a two-step process involving syngas conversion to methanol and subsequently methanol dehydration to DME on solid acid catalysts. When adequate supply of methanol is available, only a single step of methanol dehydration is necessary to produce dimethyl ether using solid acid catalysts, such as  $\gamma$ -alumina, zeolites, and ion-exchange resins in a fixed-bed reactor in the temperature range of 523 K – 673 K and at the pressure up to 10 bar [3]. The main reaction is considered as follows:



In the normal temperature range, no significant side reaction exists. The equilibrium conversion for pure methanol feed can also exceed 92%.

Modeling of packed-bed reactors for methanol dehydration to DME was usually accomplished for many industrial- and pilot-scale reactors. Bercic and Levec investigated the reaction kinetics of catalytic dehydration of methanol to DME [4], and then Shahrokhi & Baghmisheh developed a control system for methanol dehydration in a fixed-bed reactor [5]. In 2014, Ghavipour & Behbahani

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developed a practical kinetic model that would be valid at 593 K [6]. Finally, Dadgar, et al. analyzed the influence of methanol dehydration on methanol synthesis in two-step DME synthesis [7].

Extensive researches on modeling of DME production reactors have been performed to obtain the maximum production rate of DME. None of them considers the integration of reaction, distillation and recycle stream. Through the use of a computer simulation, it is possible to determine the effects of the integration to the DME yield. In this study a model of reaction-distillation-recycle system was developed to predict the increase in the DME yield through methanol dehydration.

## 2. Methodology

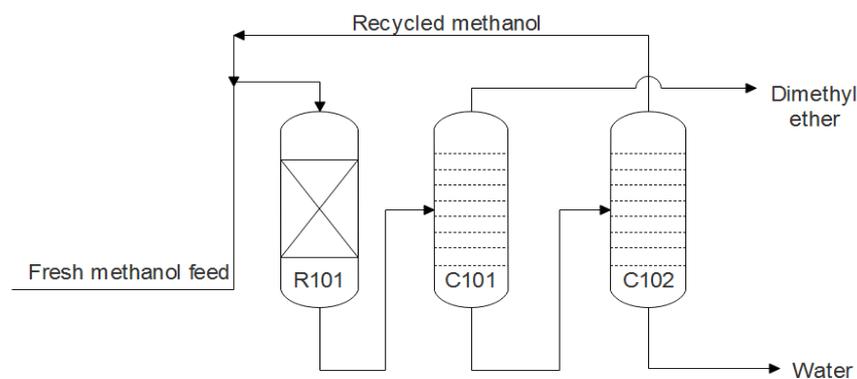
The reaction-distillation-recycle system is shown in figure 1. A one-dimensional phenomenological model of a steady state, isothermal and heterogeneous reactor was developed. The mass transfer in the bed is assumed in axial direction and expressed by

$$v_z \frac{dC_i}{dz} - D_i \left( \frac{d^2 C_i}{dz^2} \right) + ka(C_i - C_{i,s}) = 0 \quad (2)$$

The mass transfer in the catalyst particles is assumed in radial direction and described by

$$\frac{1}{r^2} D_{\text{eff}} \left[ \frac{d}{dr} \left( r^2 \frac{d(C_{i,s})}{dr} \right) \right] + R_i = 0 \quad (3)$$

where  $C_i$  and  $C_{i,s}$  are the concentrations of species  $i$  in the bed and the catalyst particles, respectively,  $D_i$  is the bulk diffusion of species  $i$  in the bed,  $D_{\text{eff}}$  is the effective diffusion of species  $i$  in the catalyst pore,  $k$  is the gas-solid interphase mass transfer coefficient,  $a$  is the specific area of gas-solid interphase, and  $R_i$  is the generation or consumption rate of species  $i$ .



**Figure 1.** Process flow diagram.

The boundary conditions of those equations are as follows:

$$\text{At } z = 0, C_i = C_{i,\text{inlet}}$$

$$\text{At } z = L \text{ (the reactor length), } dC_i/dz = 0$$

$$\text{At } r = 0, dC_{i,s}/dr = 0$$

$$\text{At } r = R_p \text{ (the catalyst particle radius), } D_{\text{eff}} (dC_{i,s}/dr) = k(C_i - C_{i,s})$$

There have been extensive researches on the appropriate and accurate kinetic models of methanol dehydration. However, as several models sustain major deviation on operating temperature of below 593 K, Ghavipour and Behbahani proposed a new empirical kinetic model [6]. This model considers an equilibrium constant expressed by

$$K_{eq} = 863.2 \exp\left[\frac{1}{8314} \left\{ 74,870 \ln \frac{T}{298} - 761.555(T - 298) + 1.127955(T^2 - 298^2) - 0.00117633(T^3 - 298^3) + 4.68550 \times 10^{-7}(T^4 - 298^4) + 4478947026 \left( \frac{1}{T} - \frac{1}{298} \right) \right\}\right] \quad (4)$$

The methanol dehydration rate used in this study is

$$-r_M = k_0 \exp\left(-\frac{E_a}{RT}\right) \left( C_{MeOH} - \frac{C_W}{K_{eq}} \right) \quad (5)$$

where  $k_0$  is the pre-exponential factor,  $E_a$  is the activation energy,  $C_{MeOH}$  denotes the methanol concentration, and  $C_W$  denotes the water concentration.

Since the reactor outlet goes to distillation columns to separate the mixture, it is necessary to incorporate a mathematical model for the distillation columns. In this instance, the multicomponent distillation was calculated using a shortcut method. A widely-used approximate method, the Fenske-Underwood-Gilliland Method, is used to estimate the minimum number of trays, the minimum reflux ratio, and the number of stages at a finite reflux.

The derivation of the Fenske's Equation is based on the assumption that the stages are at equilibrium and that no overhead product distillate is withdrawn from the column, resulting in equation (6):

$$N_{min} = \frac{\log \left[ \left( \frac{LK_d}{HK_d} \right) \left( \frac{HK_b}{LK_b} \right) \right]}{\log \alpha_{average}} \quad (6)$$

The minimum reflux ratio for a multicomponent distillation means that at a specified reflux ratio, an infinite number of plates is required to achieve the desired separation. The Underwood's Equation works under this assumption so that there are constant molal overflows and constant relative volatilities at an average temperature of the column. This is followed by solving the Underwood's Equation for the variable  $\varphi$ :

$$q(1 - F) = \sum_i \frac{\alpha_i n_{i,F}}{\alpha_i - \varphi} \quad (7)$$

When an appropriate value of variable  $\varphi$  is found, it is possible to calculate the minimum reflux ratio, as shown by equation (9):

$$R_m + 1 = \sum_i \frac{\alpha_i x_{i,D}}{\alpha_i - \varphi} \quad (8)$$

Gilliland uses an empirical correlation to calculate a final number of stage  $N$  from the values calculated through the Fenske's Equation and the Underwood's Equation. The procedure is quite simple as one simply enters a diagram with a known abscissa value and read the co-ordinate of the corresponding point on the Gilliland curve.

In order to determine the effect of a recycle stream, it is necessary to calculate two recovery fractions between two flowrates. The first fraction,  $X_1$  is between the flowrate exiting the reactor and the that exiting the bottom product of the first distillation column. The second fraction,  $X_2$  is between the flowrate exiting the bottom product of the first distillation column and the that exiting the distillate product of the second distillation column.

The iteration to calculate the recycle stream is as follows:

$$\begin{aligned}
 R_1 &= (Feed)(X_1)(X_2) \\
 R_2 &= (Feed + R_1)(X_1)(X_2) \\
 &\vdots \quad \quad \quad \vdots \quad \quad \quad \vdots \quad \quad \quad \vdots \\
 R_k &= (Feed + R_{k-1})(X_1)(X_2) \\
 &\vdots \quad \quad \quad \vdots \quad \quad \quad \vdots \quad \quad \quad \vdots \\
 R_n &= (Feed + R_{n-1})(X_1)(X_2)
 \end{aligned} \tag{9}$$

The iteration lasts until there is no significant difference between the recycle stream calculated in the  $k$  iteration to that in the  $k-1$  iteration.

### 3. Results and discussion

The simulation was carried out for the reactor length of 4 m, the inlet velocity of 0.408 m/s, the inlet temperature of 533 K and the inlet pressure of 18 atm.

Figure 2 shows the concentration profiles of methanol and dimethyl ether along the reactor without recycle. As exhibited in the figure, the methanol concentration decreases as it is dehydrated into dimethyl ether. The concentration curves that never reach the flat shape indicates that the reactor length is effective under these parameters. The methanol conversion reaches 93% as shown in figure 3. The conversion correlates to the Damkohler number of 11.18. As a rule of thumb, if the Damkohler number is higher than 10, a conversion of more than 90% may be expected. This makes the recycle stream of this process to have low flowrate, since more than 90% of methanol is converted into dimethyl ether. Nonetheless, the reaction occurs at optimum condition and thus can be tweaked for efficiency and sustainability in the future. As depicted in figure 4, the dimethyl ether yield increases along the reactor. At the position of 2 m from the reactor inlet, the dimethyl ether yield is 42% and continues to increase up to 48% at the reactor outlet.

In this study, the Fenske's Equation, the Underwood's Equation, and the Gilliland's Correlation were used to calculate the minimum number of theoretical stages at the reflux ratio of 1.5. Table 1 shows operating parameters of dimethyl ether–methanol separation. It can be observed from the table that the minimum number of the theoretical stage of dimethyl ether–methanol separation is relatively small, i.e. 4. This is due to the fact that dimethyl ether, which is the light-key component, has very high relative volatility to methanol, which is the heavy-key component, and water. The calculated relative volatility of dimethyl ether to methanol at average column temperature of 376 K is 9.1. Therefore, it is very easy for dimethyl ether to separate from methanol and water.

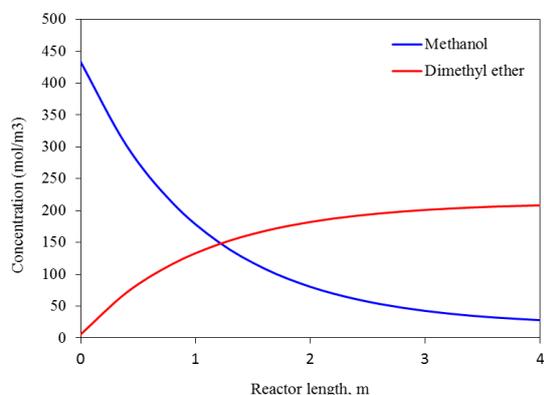
The minimum number of theoretical stages in the second column to separate methanol from water is more than three times larger than that in the first column. This is due to the fact that the boiling point of methanol and water is not that far apart from each other, and thus their relative volatility is not as high as dimethyl ether. The average relative volatility of methanol to water is 2.8, which is lower than that of dimethyl ether to methanol in the first column.

As water was stripped from the mixture in the second distillation column, the top product of the second column was recycled and fed into the reactor as additional feed. Although the addition of this recycle stream to the reactor brought water to the reaction, it should be noted that its fraction was much lower than that of methanol.

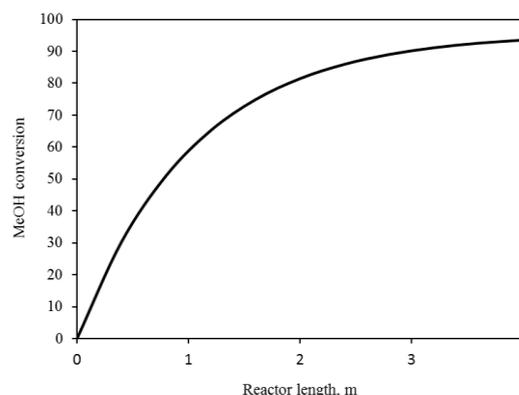
The recycle stream was calculated under the assumption that there was no major pressure or temperature losses during the whole process that would affect the conversion. It is possible to calculate the recycle stream in this method since the distillation calculation used is shortcut method, with the assumption that the compositions in the top and bottom products were constant. Therefore, the overall conversion of methanol in the process was also constant. The iterative calculation of the recycle stream could then be calculated and the results are tabulated in table 2.

From table 2 it is clear that the flowrates of all components out of reaction-distillation-recycle system decrease during the iteration course. However, if we observe the mole fractions in the final iteration, we can see that the mole fraction of dimethyl ether increases. This can be attributed to the

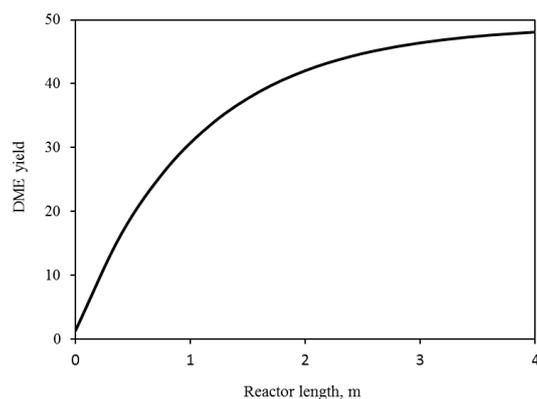
overall increase of dimethyl ether yield due to methanol recycled to the reactor. This is also supported by the fact that there is an increase in smaller number of water fraction.



**Figure 2.** The methanol and dimethyl ether concentrations along the reactor without recycle.



**Figure 3.** The methanol conversion along the reactor without recycle.



**Figure 4.** The dimethyl ether yield along the reactor without recycle.

**Table 1.** Operating parameters for dimethyl ether–methanol separation.

Operating parameters	Dimethyl ether–methanol	Methanol–water
Pressure	8 atm	8 atm
Inlet temperature	533 K	428 K
Top temperature	324 K	403 K
Bottom temperature	428 K	444 K
Reflux ratio	1.7 moles/s	10.5 moles/s
Minimum number of theoretical stages	4	15

The addition of recycle stream into the reactor has several effects on the whole process. At the first calculation, only fresh methanol was fed into the reactor. As the reactor outlet was processed further in the series of distillation columns, the recycle stream obtained as the top product of the second distillation column was then mixed with the fresh methanol. Therefore, the different composition of the feed to the reactor occurred during the process, as shown in Table 3. Although the feed of the reactor becomes less pure, thus decreasing the methanol conversion, it increases the overall yield of

dimethyl ether. This is because moles of methanol recycled is higher than that unconverted. Therefore, the addition of small fraction of water in the feed does not affect the production rate to a large extent. Table 4 shows the change in the flowrates exiting the reactor after the iterative calculation.

As shown in Table 4, the integration of the recycle stream increases dimethyl ether yield from 192.58 moles/s to 208.26 moles/s or increases by 8%. This may be a small number but it should be noted that this study operates under the best condition for the reaction. If the operating condition of the reactor can be set such that less energy consumed and the same yield of dimethyl ether produced, then the capital investment of the recycle system would be feasible.

**Table 2.** Component flowrates and mole fractions in dimethyl ether–methanol separation.

Component	First iteration		Final iteration	
	Flowrate (moles/s)	Fraction	Flowrate (moles/s)	Fraction
Methanol	1.6390	0.7801	1.6170	0.7791
Dimethyl ether	0.3221	0.1534	0.3198	0.1541
Water	0.1397	0.0665	0.1387	0.0668

**Table 3.** The different composition of the feed to the reactor.

Component	Before recycle	After recycle
Methanol	1	0.9809
Dimethyl ether	0	0.0126
Water	0	0.0066

**Table 4.** Reactor outlet flowrates.

Component	Before recycle (moles/s)	After recycle (moles/s)
Dimethyl ether	192.58	208.26
Methanol	24.400	28.090
Water	192.58	205.61

#### 4. Conclusion

Modelling of the reaction-distillation-recycle system for methanol dehydration to dimethyl ether has been performed successfully in this research. The addition of recycle stream from the second distillation column to the reactor increases the dimethyl ether yield by 8%.

#### 5. Acknowledgement

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