

The Study of Process Design for Production of the Clean Fuel – Dimethyl Ether (DME)

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Abstract

It is known that dimethyl ether (DME) has wide application, such as solvent, propellant, chemical intermediate, refrigerant replacement, LPG substitute and transportation fuel. Furthermore, DME has currently attracted considerable attention as an alternative clean fuel for diesel engines because it can emit much less pollutants such as CO, NO_x and particulates. Traditionally, in industrial processes, DME is produced by dehydration of methanol using acidic porous catalyst. Methanol is commercially synthesized from CO/CO₂ hydrogenation over Cu-based catalyst. Thus one can prepare DME from synthesis gas (syngas) in a two-step process of syngas to methanol and further to DME, or in a single-step process of synthesis gas direct to DME.

Due to attracting attention of the DME synthesis research, this work first uses commercial process simulators to analyze different DME synthesized methods presented in the literature. The optimal operating conditions for DME direct synthesis are then clearly evaluated. Finally, a feasible process flow diagram for the direct DME process is developed to meet the desired production specifications. These steady-state simulation results are demonstrated to fit with those shown in the literature.

Introduction

Dimethyl ether (DME) has wide application, such as solvent, propellant, chemical intermediate, refrigerant replacement, LPG substitute and transportation fuel. Recently, dimethyl ether has attracted attention as an alternative fuel for diesel engines and LPG substitute. Moreover, because it can emit much less pollutants such as CO, NO_x and particulates, dimethyl ether really meets the standards for clean fuel (Ng et al., 1999). In the future, DME will be much used in fuel industries.

It is known DME is commercially prepared by dehydration of methanol using acidic porous catalyst. Some of the proposed reaction rates for this traditional DME synthesis are presented in Table 1 (Chen, 2008). In industrial process, methanol is synthesized from CO/CO₂ hydrogenation over Cu-based catalyst. Therefore, one can prepare DME from synthesis gas (syngas) in a two-step (or indirect) process of syngas to methanol and further to DME. Recently, it has been reported that DME can be synthesized from syngas in a single-step (or direct) process, which is more thermodynamically and economically favorable than the indirect process (Lu et al., 2004). Recently, Lee et al. (2006) have developed a simulator of a shell and tube type fixed bed reactor for DME direct synthesis. Ohno et al. (2007) have demonstrated their slurry phase DME direct synthesis technology by long term operation of 100 tons/day plant.

Due to powerful development of the commercial process simulators and attracting attention of the DME synthesis research, this work tries to apply the most widely used commercial process design simulation software to constructing process flowsheets for the direct DME process. First, commercial

process simulators such as AspenPlus and AspenDynamics are used to analyze different DME synthesized methods presented in the literature. The optimal operating conditions for DME direct synthesis are then clearly evaluated. Finally, a feasible process flow diagram for the direct DME process is developed to meet the desired production specifications. These steady-state simulation results are demonstrated to fit with those shown in the literature.

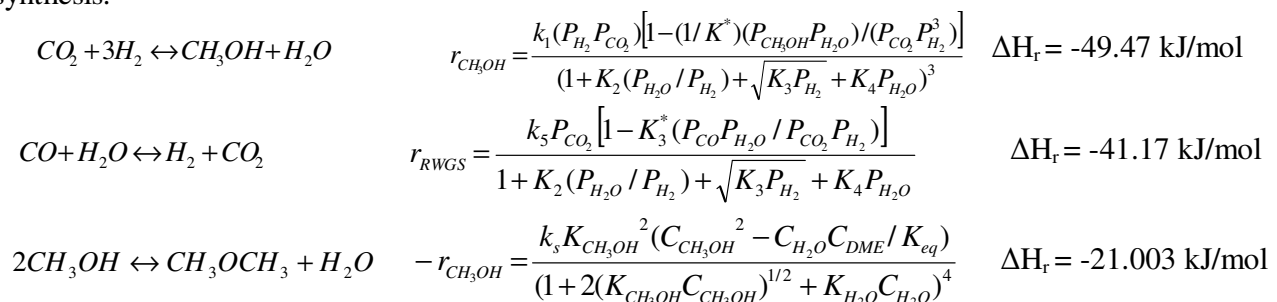
Steady-state Simulation for DME Synthesis

In industrial processes, DME is traditionally produced by dehydration of methanol using acidic porous catalyst. Bondiera and Naccache (1991) have provided a simple kinetic expression in power law for this reaction. Later, Bercic and Levec (1992) propose the following rate equation

$$-r_{CH_3OH} = \frac{k_s K_{CH_3OH}^2 (C_{CH_3OH}^2 - C_{H_2O} C_{DME} / K_{eq})}{(1 + 2(K_{CH_3OH} C_{CH_3OH})^{1/2} + K_{H_2O} C_{H_2O})^4} \quad \Delta H_r = -21.003 \text{ kJ/mol.}$$

By using this more complicated expression of reaction rate, Figure 1 shows the temperature distribution of the adiabatic fixed bed reactor for traditional DME synthesis. Simulation results for traditional DME synthesis in adiabatic fixed bed reactor are shown as Table 2. In this case, methanol conversion is about 9% higher.

It is known methanol is commercially synthesized from CO/CO₂ hydrogenation over Cu-based catalyst. Thus one can prepare DME from synthesis gas (syngas) in a single-step (or direct) process. In this study, the following reaction rate equations given by Bussche and Froment (1996) and Bercic and Levec (1992) are utilized to find the optimal operating conditions of the fixed bed reactor for DME direct synthesis.



By using this more complicated expression of rate, Figure 2 shows the temperature distribution of the adiabatic fixed bed reactor for DME direct synthesis. Simulation results for DME direct synthesis in adiabatic fixed bed reactor shown as Table 3 are consistent with those provided by Lee et al. (2006).

Optimal Operating Conditions for DME Direct Synthesis

Due to facts of the going up prices of feedstock and thermodynamic and economical advantages of DME direct synthesis from syngas, this study tries to determine the optimal operating conditions for DME direct synthesis. The effects of important process variables on DME reactor have been clearly tested by use of the reaction rates presented in previous section (Chen, 2008). Then, it is found the following suitable ranges of variables: inlet temperature 450~470 K, inlet pressure 70~80 atm, H₂/(CO₂+CO) flow ratio 3.5~4.5, CO₂/(CO+CO₂) flow ratio 0~0.1, and exit temperature 470~478 K.

Table 4 shows the determined optimal operating conditions of the fixed bed reactor for DME direct synthesis. Figure 3 presents the temperature distribution of the optimal fixed bed reactor for DME

direct synthesis. It is clear that within the middle-section reactor temperature range of 500~520 K, the better DME productivity could be obtained (Lee et al., 2006). The CO conversion is about 99% in this case.

Design Flowsheet for Direct DME Process

According to the obtained optimal operating conditions of the fixed bed reactor for DME direct synthesis shown in Table 4, a feasible process flow diagram for the direct DME process is then developed to meet the desired production specifications. The designed steady-state process flowsheet is shown as Figure 4. This direct DME process flowsheet involves following major unit operations: a fixed bed chemical reactor, a vapor-liquid separator, a product stripper, and two distillation towers.

Table 5 shows the simulated operating conditions of the fixed bed reactor for overall direct DME process. The obtained reactor conditions are consistent with those shown in Table 4. Table 6 illustrates all information of the recycle and purge streams for this proposed direct DME process. It is easy to find the DME production rate of 54.5 tons/day under the proposed design flowsheet for direct DME process.

Conclusions

Due to powerful development of the commercial process simulators and attracting attention of the DME synthesis research, this work tries to apply the most widely used commercial process design simulation software to constructing process flowsheets for the direct DME process. First, commercial process simulators such as AspenPlus and AspenDynamics are used to analyze different DME synthesized methods presented in the literature. The optimal operating conditions for DME direct synthesis are then clearly evaluated. Finally, a feasible process flow diagram for the direct DME process is developed to meet the desired production specifications. These steady-state simulation results are demonstrated to fit with those shown in the literature.

Acknowledgements

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Table 1. Some published rate equations for traditional DME synthesis (Chen, 2008).

Author (Year)	Rate equation
Kallo and Knözinger (1967)	$-r_{CH_3OH} = k \frac{C_{CH_3OH}^{1/2}}{C_{CH_3OH}^{1/2} + k_2 C_{H_2O}}$
Figueras et al. (1971)	$-r_{CH_3OH} = \frac{kK_{CH_3OH}C_{CH_3OH}^{1/2}}{1 + K_{CH_3OH}C_{CH_3OH}^{1/2} + K_{H_2O}C_{H_2O}}$
Than et al. (1972)	$-r_{CH_3OH} = \frac{kK_{CH_3OH}C_{CH_3OH}}{(1 + K_{CH_3OH}C_{CH_3OH})^2}$
Schmitz (1978)	$-r_{CH_3OH} = k_1 + k_2 C_{CH_3OH}$
Klusaček and Schneider (1982)	$-r_{CH_3OH} = \frac{kK_{CH_3OH}C_{CH_3OH}}{[1 + 2(K_{CH_3OH}C_{CH_3OH})^{1/2} + K_{H_2O}C_{H_2O}]^2}$ $-r_{CH_3OH} = \frac{kK_{CH_3OH}C_{CH_3OH}}{[1 + 2(K_{CH_3OH}C_{CH_3OH})^{1/2} + K_{H_2O}C_{H_2O}]^3}$ $-r_{CH_3OH} = \frac{kK_{CH_3OH}C_{CH_3OH}}{[1 + 2(K_{CH_3OH}C_{CH_3OH})^{1/2} + K_{H_2O}C_{H_2O}]^4}$
Berčič and Levec (1992)	$-r_{CH_3OH} = \frac{k_s K_{CH_3OH}^2 (C_{CH_3OH}^2 - C_{H_2O} C_{DME} / K_{eq})}{[1 + 2(K_{CH_3OH}C_{CH_3OH})^{1/2} + K_{H_2O}C_{H_2O}]^4}$

Table 2. Simulation results for traditional DME synthesis in adiabatic fixed bed reactor.

	Reactor inlet	Reactor outlet
DME (kmol/hr)	0	113.86
Methanol (kmol/hr)	262	34028
Water (kmol/hr)	0	113.86
Total flow (kmol/hr)	262	262
Temperature (K)	551.45	681.71
Pressure (atm)	14.9	14.4

Table 3. Simulation results for DME direct synthesis in adiabatic fixed bed reactor.

	Reactor inlet	Reactor outlet
DME (kmol/hr)	0	4.39
CO (kmol/hr)	110.55	94.64
CO ₂ (kmol/hr)	0	6.35
H ₂ (kmol/hr)	221.1	208.35
Methanol (kmol/hr)	0	0.78
Water (kmol/hr)	3.35	1.38
Total flow (kmol/hr)	335	315.9
Temperture (K)	555	683.5
Pressure (atm)	49.35	48.26

Table 4. Optimal operating conditions of the fixed bed reactor for DME direct synthesis.

	Reactor inlet	Reactor outlet
Total flow (kmol/hr)	335	238.84
DME	0	23.64
CO	54.27	0.52
CO ₂	6.03	11.7
H ₂	271.35	180.86
Menthanol	0	0.81
Water	3.35	21.31
Temperaure (K)	468	480
Pressure (atm)	78.95	77.97

Table 5. Simulated operating conditions of the fixed bed reactor for direct DME process.

	Reactor inlet	Reactor outlet
DME (kmol/hr)	0.59	50.36
CO (kmol/hr)	100.4	0.47
CO ₂ (kmol/hr)	21.58	2.68
H ₂ (kmol/hr)	452.23	252.59
Methanol (kmol/hr)	0	0.33
Water (kmol/hr)	10	59.67
Total flow (kmol/hr)	584.83	385.1
Temperture (K)	468	480
Pressure (atm)	78.95	77.97

Table 6. Information of recycle and purge streams for direct DME process.

	Recycle	Purge
DME (kmol/hr)	0.59	0.50
CO (kmol/hr)	0.44	0.03
CO ₂ (kmol/hr)	21.58	20.39
H ₂ (kmol/hr)	252.22	0.36
Methanol (kmol/hr)	0	0
Water (kmol/hr)	0	0
Total flow (kmol/hr)	274.83	21.29
Temperture (K)	450	295.28
Pressure (atm)	79.15	37.5

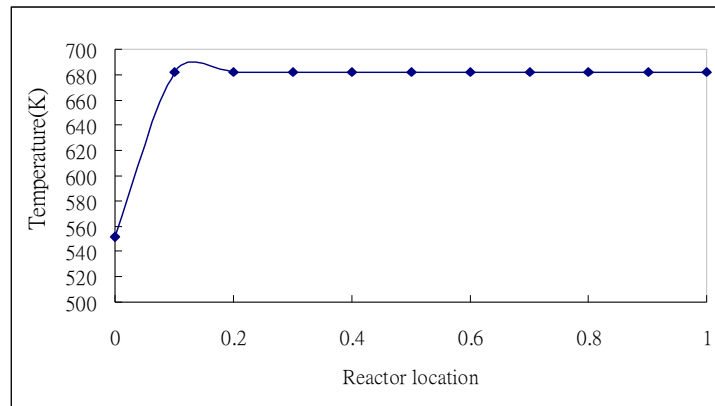


Figure 1. Temperature distribution of the adiabatic fixed bed reactor for traditional DME synthesis.

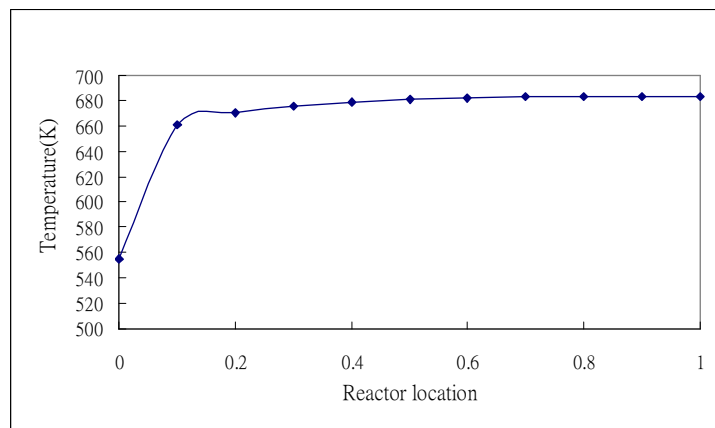


Figure 2. Temperature distribution of the adiabatic fixed bed reactor for DME direct synthesis.

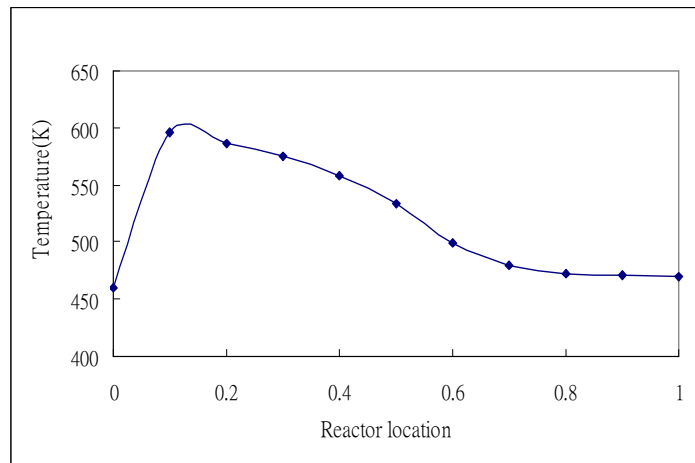


Figure 3. Temperature distribution of the optimal fixed bed reactor for DME direct synthesis.

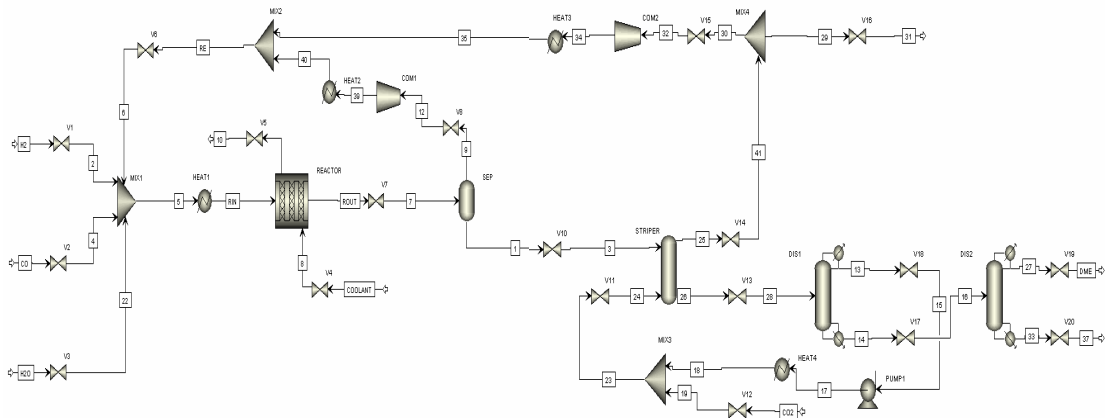


Figure 4. Overall flowsheet of the direct DME process.