

## Modeling and Simulation of Production Process on Dimethyl Ether Synthesized from Coal-based Syngas by One-step Method\*

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**Abstract** As a result of shortage supply of oil resources, the process for the alternative coal-based fuel, dimethyl ether (DME), has emerged as an important process in chemical engineering field. With the laboratory experiment data about DME synthesis and separation, the production process for DME with high purity is proposed when one-step synthesis of DME in slurry bed reactor from syngas is adopted. On the basis of experimental research and process analysis, the proper unit modules and thermophysical calculation methods for the simulation process are selected. Incorporated the experimentally determined parameters of reaction dynamic model for DME synthesis, regression constants of parameters in non-random two-liquid equation (NRTL) model for binary component in DME separation system with built-in properties model, the process flowsheet is developed and simulated on the Aspen Plus platform. The simulation results coincide well with data obtained in laboratory experiment. Accordingly, the accurate simulation results offer useful references to similar equipment design and process operation optimization.

**Keywords** dimethyl ether, process simulation, Aspen Plus

### 1 INTRODUCTION

It is important for china to develop process technology for coal-based chemical products since China is a country with abundant coal, whereas lack in oil and natural gas. Syngas is first obtained from coal, and then alcohol, ether, and other chemical products are synthesized, which is the deep processing for coal in chemical engineering [1]. Among the ether products, great interest is focused on dimethyl ether (DME) because of the advantages the fuel offered and many researches are being carried out on this clean-burning fuel [2]. New processes for DME product is in a single step via autothermal reactors or slurry phase reactors from syngas. Compared with the methanol dehydration process for DME, the separation process for high purity DME are relatively more complex because unreacted syngas and produced CO<sub>2</sub> are in the one-step synthesis process for DME. Unit operations of chemical engineering are commonly used to separate DME from the one-step reaction resultants in the synthesis process. Through absorption, flash, and distillation unit process [3–6], H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> are removed; methanol is recovered and the final DME product is obtained.

Process simulation technology in chemical engineering is one of the effective tools to analyze performance of the flow. The resultful adjustment and control on the process can be obtained using simulation and analysis on chemical engineering process. The operative effect in some fields of chemical engineering is significant [7–9]. DME is synthesized in

slurry bed reactor by one-step method from syngas, and then certain separation process is adopted to gain high purity DME product. Presently, the relative flowsheet research is in exploiting stage in China [1]. Simulation technique is not sufficiently applied and demonstrated. Combined with the process simulation technology, experimental research results about DME synthesis and separation, the purpose of this article is to simulate and analyze the production process for pure DME using the software Aspen Plus.

### 2 A PROCESS FOR DME WITH HIGH PURITY

DME is synthesized in slurry bed reactor from coal-based syngas. After one-step reaction, the main components in the system are H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, DME, and H<sub>2</sub>O. The aim of the separation is to make the final DME product with mole concentration of greater than or equal to 99%.

Compared with other components in condensed gas phase stream of one-step reaction resultants, DME has the highest solubility in methanol or water [10], so the unreacted gas and other inert gases is removed when the solvent absorption method is carried out. The difficulty in the separation system is to detach CO<sub>2</sub> from DME. Generally, DME has low boiling point at ambient temperature and normal pressure, so it can be easily liquefied. DME and CO<sub>2</sub> can be separated by means of pressurized distillation.

According to the synthesis principle about reaction separation [11], ordinary phase separation will be first carried out by partial condensation or vaporization,

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and then next separation step proceeds if volatility of the components in reaction resultants stream is in wide bound. Chen [12] found that in the research system with DME,  $\text{CO}_2$ , and water, at 323K, when  $\text{CO}_2$  partial pressure is 0.25 MPa, the separation coefficient for DME and  $\text{CO}_2$  is 35; whereas in the DME,  $\text{CO}_2$ , and methanol system, at 310 K, the value becomes much smaller and comes to 1.5, although at the same  $\text{CO}_2$  partial pressure. The results indicate that there is more difficulty in separation of DME and  $\text{CO}_2$  when methanol is in system. So methanol and water in one-step reaction resultants are first removed by condensation, then gas stream of condensed reaction resultants is absorbed by water; liquid stream containing DME is distilled for final DME product. This separation process for DME with high purity is feasible.

Condensed gases of one-step reaction resultants were absorbed by water in the packed absorber with CY 700 corrugated packing [13]. The influence on DME absorption, caused by operating pressure, temperature, the ratio of volume loading between gas and liquid, gas velocity, and  $\text{CO}_2$  concentration, were researched. With the absorption experimental results, appropriate range of operating pressure, temperature, and absorbent flow can be determined. Liquid feed containing DME,  $\text{CO}_2$ , methanol, and water was introduced to the distillator for DME product with high purity [14]. The experimental results indicate the proper separation sequence as following:  $\text{CO}_2$  is discharged as uncondensed gas from the top; final DME product is drawn from the side; bottom stream containing methanol and water is processed.

Grounded on the experimental research mentioned above, the DME production process is schematically illustrated in Fig. 1. First, disposed coal-based fresh syngas stream mixes with the recovered gas stream from off-gas in the absorber, and then sent into the slurry bed reactor to synthesize DME with an effective bifunctional catalyst. The reaction resultants leave the reactor and enter the condenser to gain gas and liquid phase resultants. Gas phase resultants are introduced

into the absorber after reducing pressure, and deionized water is used as absorbent. The gas from the top of the absorber is transported to the recovery equipment. Liquid products from bottom of the absorber mix with the liquid resultants from the condenser and enter into the DME distillator. DME product is as side run-off and drawn out at the proper stage. Uncondensed gas from the DME distillator is conveyed to fuel gas pipe and the liquid stream from the bottom is fed to the methanol distillator. Methanol product is obtained on the top of the distillator and water from the bottom is used as absorbent after heat exchange.

### 3 MODELING AND SIMULATION OF THE WHOLE PROCESS

In this work, the production process of DME is simulated using Aspen Plus software. Dynamics of the reaction system and gas-liquid equilibrium of the separation system are in close relation with the process simulation calculation. At certain process conditions, the nonideal nature of gas/liquid phase should be taken into account. Polar compound water and methanol are in the process; the in and out stream in each module are in closeness conjoint. After the whole process is established, the selection of proper representation components, unit module, and thermophysical properties and application of effective simulation strategy is important for carrying out the accurate process simulation.

#### 3.1 Component selection

$\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$ , DME, and  $\text{H}_2\text{O}$  are the main components in the whole process. With the recovery gas stream from off-gas in the absorber, coal-based syngas is desulfated and proportioned, then sent into the slurry bed reactor to synthesize DME.  $\text{H}_2/\text{CO}$  ratio in the reactant steam should be proportioned to comply with the requirement of the catalyst.

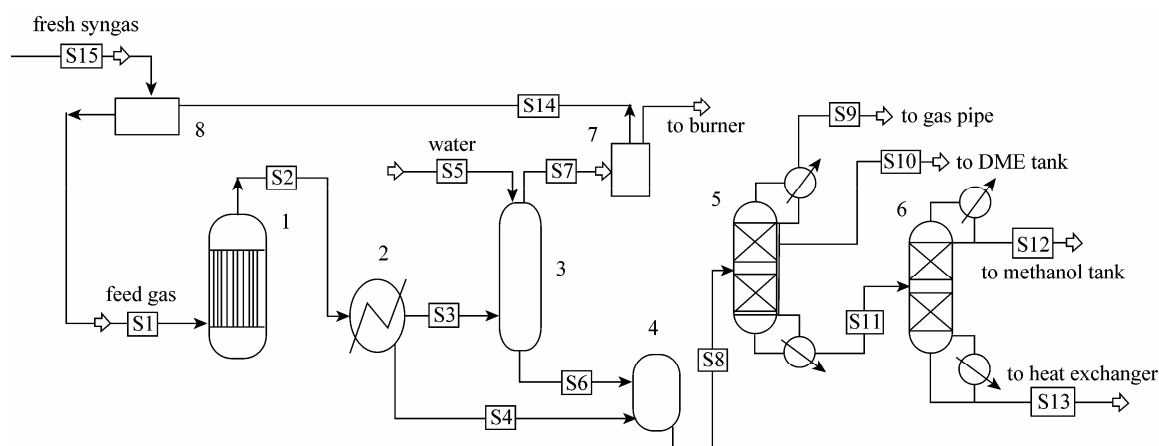


**Figure 1** Process flow diagram of synthesis and separation of high purity DME

1—reactor; 2—condenser; 3—absorber; 4—mixer; 5—DME distillatory; 6—methanol distillatory; 7—recovery equipment; 8—compressor

In the simulation process,  $H_2/CO$  ratio in reactant stream is adjusted to 1.5 or so.

### 3.2 Unit module selection

Continuous stirred tank reactor (CSTR) module is used to simulate the reaction synthesis process for DME and the reaction kinetics model provided by user through the built-in reactor model. Absorption and distillation processes are simulated using the rigorous fractionation (RADFRAC) module, which is a rigorous model for simulating multistage vapor-liquid fractionation operation, and the nonideal deviation is modified by Murphree plate efficiency. Flash2, Heater, and Tank module represents condenser, heater or cooler, holder and mixer, respectively.

### 3.3 Properties selection and modification

The flowsheet for the whole process is built. In the whole simulation process, it is important to choose an appropriate thermodynamic model. Meanwhile, the change in the setup of unit modules or operating conditions will lead the simulation calculation divergence. It is imperative to estimate and adjust the parameters of the relative models so that simulation calculations can converge quickly and the final simulation results can describe the actual data.

The critical modules in the simulation process are reactor, absorber, and distillator. In the modeling process, the experimentally determined reaction kinetics model [15] is applied in the reaction module. BWR-LS model equation is chosen to describe and calculate the properties of reaction system. Except for water and methanol, other components in the separation process are nonpolar. Non-random two-liquid equation (NRTL) is used to calculate liquid phase properties, and vapor phase properties are calculated

from the Redlich-Kwong equation of state. Gas-liquid equilibrium of the research system can be accurately predicted when the state equation combines with activity coefficient model. As for absorption module, NRTL-RK properties model is desired, in which binary interaction parameters [16, 17] in NRTL model for binary component in DME separation system are introduced to the properties setup. NRTL-RK properties model is also applied in the distillator module through UNIFAC model and the properties estimation tools in the software to gain the wanting binary interaction parameters between components. Convergence method in absorption and distillation modules is Wegstein and Newton, respectively.

## 4 SIMULATION RESULTS AND DISCUSSION

As can be seen, reactor, absorber, and distillator are major process units. Experimental data in the literature are introduced to perform the reactor simulation, and the comparison between simulation and the experimental results are listed in Table 1. Except for DME and  $CO_2$ , other components in gas phase stream of condensed reaction resultants hardly dissolves in water; and the influence on DME absorption caused by these inert gases can be represented by  $N_2$ . Results of absorption experiment and simulation on gas phase components are given in Table 2, and data in table 3 detail the results between distillation experiment and simulation for high purity DME as well.

The simulation results are compared with the experimental data to verify the reliability of the simulation. As the comparison results show, the simulation module selection and calculation strategy presented in Section 3 could predict the behavior of the main unit process. In this way, the whole process, one-step reaction in a slurry bed reactor from syngas for high purity DME product, can be simulated at actual process conditions. The whole process simulation is carried out on

Table 1 Simulation results of reactor module versus experiment data

| Components       | $H_2$  | CO     | $CO_2$ | DME    | $CH_3OH$ | $H_2O$ | Flow/mol·h <sup>-1</sup> | T/°C | p/MPa |
|------------------|--------|--------|--------|--------|----------|--------|--------------------------|------|-------|
| feed gas         | 0.7732 | 0.1750 | 0.0518 |        |          |        | 0.93                     | 40   | 5.1   |
| experiment value | 0.6297 | 0.0558 | 0.039  | 0.0956 | 0.0653   | 0.1046 | 0.57                     | 270  | 5     |
| simulation value | 0.6489 | 0.0481 | 0.0404 | 0.1029 | 0.0724   | 0.0873 | 0.61                     | 270  | 5     |

Table 2 Simulation results of absorber module versus experiment data

|                            | $CO_2$  | DME     | $N_2$   | $H_2O$  | Flow/mol·h <sup>-1</sup> | T/°C | p/MPa |
|----------------------------|---------|---------|---------|---------|--------------------------|------|-------|
| feed stream                | 0.1966  | 0.1046  | 0.6988  | —       | 7.3                      | 40   | 2     |
| off gas (exp.)             | 0.22174 | 0.00382 | 0.76962 | 0.00481 | 7.22                     | 39.5 | 1.95  |
| bottom liquid (exp.)       | 0.00181 | 0.01949 | 0.00028 | 0.97842 | 24.01                    | 40.5 | 2     |
| off gas (simulation)       | 0.21073 | 0.00368 | 0.78062 | 0.00497 | 7.13                     | 40   | 1.95  |
| bottom liquid (simulation) | 0.00177 | 0.02146 | 0.00032 | 0.97645 | 23.93                    | 40   | 2     |

**Table 3** Simulation results of distillator module versus experiment data

|                            | CO <sub>2</sub>        | CH <sub>3</sub> OH | H <sub>2</sub> O      | DME      | Flow/mol·h <sup>-1</sup> | T/°C  | p/MPa |
|----------------------------|------------------------|--------------------|-----------------------|----------|--------------------------|-------|-------|
| feed stream                | 0.00043                | 0.006687           | 0.961075              | 0.031808 | 15.4                     | 40    | 1.1   |
| side liquid (exp.)         | 0.000866               | 0.000146           | —                     | 0.998988 | 0.38                     | 43.9  | —     |
| bottom liquid (exp.)       | —                      | 0.006902           | 0.992538              | 0.00056  | 15.1                     | 179.4 | 1.03  |
| side liquid (simulation)   | 0.000756               | 0.000127           | 7.96×10 <sup>-9</sup> | 0.999112 | 0.403                    | 44.8  | 1.01  |
| bottom liquid (simulation) | 4.485×10 <sup>-7</sup> | 0.006865           | 0.996801              | 0.000456 | 14.9                     | 179.9 | 1.03  |

**Table 4** Properties and components of the main stream in the simulation process

| No. stream | H <sub>2</sub>         | N <sub>2</sub>         | CO                     | CO <sub>2</sub>        | CH <sub>4</sub>        | H <sub>2</sub> O      | CH <sub>3</sub> OH     | DME                    | Flow /kmol·s <sup>-1</sup> | T/K    | p/MPa |
|------------|------------------------|------------------------|------------------------|------------------------|------------------------|-----------------------|------------------------|------------------------|----------------------------|--------|-------|
| S1         | 0.455881               | 0.048277               | 0.293113               | 0.079225               | 0.120838               | 0.001302              | 5.12×10 <sup>-10</sup> | 0.000136               | 0.83                       | 313.15 | 5.17  |
| S2         | 0.189788               | 0.073641               | 0.163805               | 0.161403               | 0.184562               | 0.077882              | 0.028485               | 0.119524               | 0.55                       | 523.15 | 5.07  |
| S3         | 0.215866               | 0.083746               | 0.186274               | 0.181946               | 0.209826               | 0.002819              | 0.004140               | 0.115384               | 0.48                       | 313.15 | 3.04  |
| S4         | 0.001185               | 0.000562               | 0.001309               | 0.012926               | 0.001857               | 0.625465              | 0.206103               | 0.150592               | 0.066                      | 313.15 | 3.04  |
| S6         | 0.000270               | 0.000079               | 0.000192               | 0.002613               | 0.000185               | 0.963482              | 0.001276               | 0.031902               | 1.56                       | 319.33 | 3.04  |
| S8         | 0.000307               | 0.000099               | 0.000237               | 0.003032               | 0.000253               | 0.949763              | 0.009589               | 0.036719               | 1.62                       | 321.28 | 3.04  |
| S10        | 2.35×10 <sup>-6</sup>  | 1.21×10 <sup>-6</sup>  | 3.54×10 <sup>-6</sup>  | 0.00089                | 4.53×10 <sup>-6</sup>  | 1.10×10 <sup>-6</sup> | 1.76×10 <sup>-6</sup>  | 0.999095               | 0.05                       | 318.15 | 1.02  |
| S11        | 1.75×10 <sup>-24</sup> | 3.49×10 <sup>-24</sup> | 1.36×10 <sup>-23</sup> | 1.23×10 <sup>-15</sup> | 1.30×10 <sup>-23</sup> | 0.989719              | 0.009993               | 0.000288               | 1.56                       | 452.09 | 1.03  |
| S13        | 0                      | 0                      | 0                      | 1.07×10 <sup>-25</sup> | 0                      | 0.999993              | 7.14×10 <sup>-6</sup>  | 2.92×10 <sup>-11</sup> | 1.54                       | 378.36 | 0.12  |

the methods mentioned above, and final DME product with content no less than 99.9%. In the case of production time of 300 days per year, namely 7200 hours, the output of product DME of about 60 thousands tons, detailed data of the main streams including components, flow, temperature, and pressure are obtained and given in Table 4.

The whole process simulation results provide the outputs of the key units, properties data about the main streams between equipments or in columns, and offer reference for actual process design and operation. As shown in Table 4, DME mole fraction in the absorption liquid stream reaches 0.0319; after distillation, the purity of DME is no less than 99.9%. The content of DME in condensed reaction gas phase is 0.1154 or so; after absorbed by water, the DME mole fraction in off-gas from top of the absorber is 0.0086 and the absorptivity is greater than 93%. The heat duty of the condenser in DME distillator is from engineering water, and any extra cryogen is undesired. DME product with purity no less than 99.9% is as object, the DME yield by the separation process is 83.9%; water from the methanol distillator has no impurity and reused as absorbent after heat exchange, avoiding wastewater pollution and reducing charge of public project.

One-step reaction from syngas is exothermic [18], and the reaction heat is moved away in time for assuring operating reaction temperature at certain range. After heat change, water from the methanol distillator is reused as absorbent in the absorption column. So the main two distillator in the process is the heat providing objects. Without consideration to the heat integration, for final 99.91% DME product with flow 0.05

kmol·s<sup>-1</sup>, the thermal load in the top and bottom of the DME distillator is 30.5 and 36.8 GJ·h<sup>-1</sup>; the number for methanol distillator is 24.7 and 20.9 GJ·h<sup>-1</sup>. In terms of the reduced coefficient of 1 kW steam corresponding to 0.18 kg standard coal per hour [19], the separation expenditure of energy for 1 kg DME is 0.71 kg standard coal.

Sensitivity analysis is carried out on absorber and DME distillator modules, results are shown in Figs. 2 and 3.

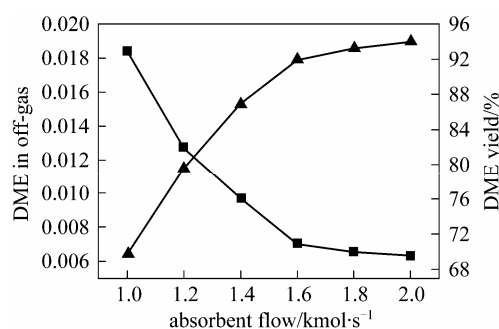
**Figure 2** Influence of absorbent flow on DME absorption  
■ DME concentration; ▲ DME yield

Figure 2 indicates that the DME concentration in bottom liquid stream of the absorber and DME yield decrease with the increasing absorbent flow at given gas flow. Fig. 3 demonstrates that side run-off position has obvious impact on content and yield of product DME. As shown in Fig. 2, flow of absorbent water should be controlled in a proper range so that the low

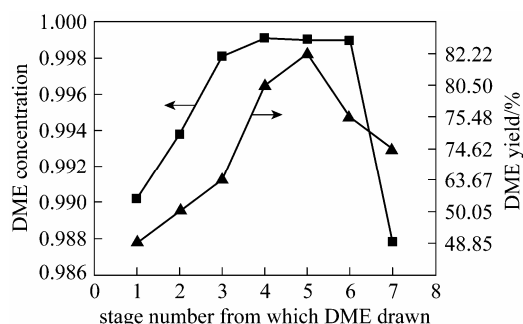


**Figure 3** Influence of produced position on the distillation  
 ■ DME concentration; ▲ DME yield

content of DME in off-gas of the absorber is guarantee, and the flow of bottom liquid stream is not increased in large scale to add load on the follow process unit. As the simulation and experiment results for reference, DME content in input gas is at 0.08–0.15, the mole flow ratio between absorbent water and absorption gas is better at 3–4. The heat duty of the condenser in DME distillator is from engineering water, and plate numbers, feed flow, and thermal load of the distillator are definite, the proper side position is at 3–5 theory tray. Exploiting the process simulation results and using the analysis tools in the software, the improvement on the whole process and optimization operation on the key units are on reliable platform. The analysis and corresponding strategy for modification of the sticking point in the process can be offered.

## 5 CONCLUSIONS

(1) On the experiment research about one-step reaction, gas mixture with DME absorption, and liquid stream containing DME distillation, the whole process for high purity DME synthesized in a slurry bed reactor from coal-based syngas is developed.

(2) Combined the parameters of reaction dynamic model for DME synthesis reaction, regression constants of parameters in NRTL model for binary component in DME separation system with properties model in the simulation software, the flowsheet for accurate describing the whole process is built on Aspen Plus platform.

(3) To different modules in the process, with experimental results for reference, corresponding thermophysical models and calculation strategy are applied in the simulation process. In such way, simulation calculation quickly converges, and the simulation results are in good agreement with that in previous work. The module selection and calculation strategy for the process simulation are suitable. On the foundation of successful simulation for the process, some suitable strategy can be expediently and quickly executed for better control on the fluctuant process parameters using sensitivity analysis tool. Simulator is proved helpful for operational modifications as well as design considerations.

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