

Process simulation of dimethyl ether synthesis via methanol vapor phase dehydration

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The production processes included catalytic dehydration of methanol in an adiabatic fixed-bed reactor and two columns product separations. In this study, the technological process for dimethyl ether (DME) synthesis is built on PRO/II platform based on the combined parameters of the reaction dynamic model for methanol dehydration reaction, the improved NRTL model of the liquid phase, the PR model of vapor phase. In order to validate the proposed model, the simulation results have been compared with the available data from a set of industrial production equipment with a production capacity of 200 000 tonnes per annum. A comparison between the calculated and measured results has proved that these results are satisfactory. The bed height and the volume of the catalytic bed are calculated aim at one million t/a DME yields and while taking account of high-purity DME production. After discussing the influence of feed stage location and reflux ratio for DME product purity, the suitable unit operation conditions are chosen. Accordingly, accurate process simulation results provide the basis and guidance for an improvement and development of the similar industrial device.

Keywords: dimethyl ether, methanol dehydration to DME, process simulation.

INTRODUCTION

Over the past few years, dimethyl ether has been given the widespread attention as an environmentally friendly chemical product. DME is used as an aerosol propellant and solvent¹ because of its chemically inactive, low-toxic, higher solubility of non-polar and polar substances. High levels of DME can be used as an anesthetic. Due to its easy compression, condensation, vaporization, Freon is traded for DME as the refrigerant. As an important chemical raw material, DME can go straight to develop downstream products and cultivate new consumption market. At present, most attention has been focused on syngas via dimethyl ether to light olefins. Furthermore, DME has been suggested recently as an alternative fuel for diesel engines. The experimental study of the diesel engine fueled with high proportion DME exhaust contains no smoke, the noise also decreases, and NO_x exhausts obviously decreases²⁻³. It also means that DME has excellent combustion characteristics. In addition, since the physical properties of DME are similar to liquefied petroleum gas⁴ and given its low saturation steam pressure, high heating value. It has been speculated that DME could be used as domestic fuel⁵.

DME can be produced by direct synthesis of DME from syngas or dehydration of methanol⁶⁻⁸. The direct synthesis refers to a single step via the circulating fluidized bed⁹ or a slurry bubble column reactor using a bifunctional catalyst. The compositions of reaction products are complex compared with the methanol dehydration process. However, it is still in the stage of being developed and practiced continuously at the present time. Methanol dehydration using solid acid catalyst in an adiabatic fixed-bed reactor¹⁰⁻¹² has proven to be more commercial. Practical application also indicates that this method has various advantages including fewer byproducts, high selectivity and high purity, et al.

The modeling and simulation of DME production have been studied for many pilot scales and industrial units. For instance, Hu et al. modeled and analyzed DME

production from syngas in a pipe-shell reactor under the steady-state condition¹³. Farsi et al. simulated the industrial reactor of DME synthesis and proposed a model consisting of a set of algebraic and partial differential equations¹⁴. The good agreement between the simulating results and available data from an industrial reactor shows that the model is rational. Karl et al. modeled a catalytic distillation process based on RadFRac block using the kinetic parameter¹⁵ determined by the experiment. The results showed that synthesis of high-purity DME can be achieved using a single catalytic distillation column.

Although many research studies have been carried out on the reactor simulation or distillation process modeling of DME production, the process simulation of DME synthesis from methanol dehydration seems rare. Han Yuanyuan et al. presented a production process for DME synthesis with syngas in a slurry bed reactor¹⁶. Experimental research and process analysis were just sufficient to determine the unit modules and thermodynamic calculation methods for the simulation process. Then the whole production process was simulated, and the simulation results were identical with the experimental data.

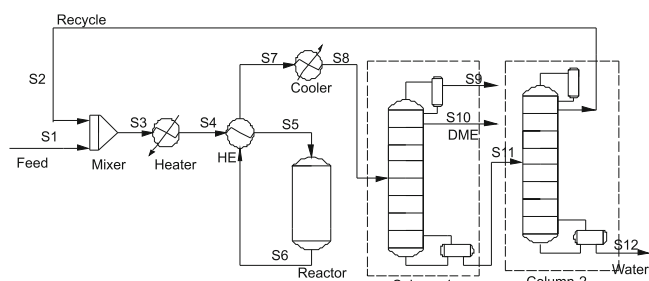
In our previous work, the macroscopic reaction kinetics of reaction on the dehydration of methanol to DME was calculated as the pressure of 0.1–1.0 MPa and temperature of 240–340°C over the industrial solid acidic catalysts in an integral isothermal reactor¹⁷. A new multi-stage quench type adiabatic fixed bed reactor was proposed based on the analysis of the characteristics of existing reactor in actual production. One-dimensional mathematical model of the reactor with inter-stage quenching has been established, according to the features of methanol dehydration to DME reaction. A set of techniques for one million t/a DME production processes to gain high-purity DME product was present. The production method has been applied for an invention patent, and it granted by the Chinese Patent Office in October 2011¹⁸. The system of methanol dehydration to DME was simulated and

analyzed. The unit operation parameters and material streams' data were also calculated.

PROCESS DESCRIPTION

DME is produced by dehydrogenation over an industrialized molecular sieve catalyst. The commercial domestic γ - Al_2O_3 catalyst provided by a DME production factory is used in methanol dehydration due to its good catalytic activity.

The reaction temperature was set at between 240 to 400°C and dehydration reaction is carried out in a multistage adiabatic reactor. Methanol is introduced to the system at 4°C from methanol synthesis plant. Then the pressure is increased to 4.3 MPa. The raw material is mixed with the recycle stream 2 (S2) coming from the separation. This mixture is vaporized in the heater (see Fig. 1) and preheated in the heat exchanger (HE) before entering the reactor. After dehydration, the components in the stream consist of DME, CH_3OH , H_2O and a smaller amount of CO , CO_2 , CH_4 , H_2 , $\text{C}_2\text{H}_5\text{OH}$, et al. The reactor exit stream is cooled (Cooler), partially decompressed, and introduced in the separation train. DME is obtained in column 1 with the purity higher than 99.9% (molar basis). The bottoms of column-1 are decompressed again and introduced into a second distillation column that separates water from methanol. Water is sent to a treatment section to remove traces of organic compounds (not represented in Fig. 1), and the methanol recycled. The heat duty of the condenser in DME distillator is from engineering water, and any extra cryogen is undesired.



(Column-1) DME rectifying column; (Column-2) Methanol rectifying column

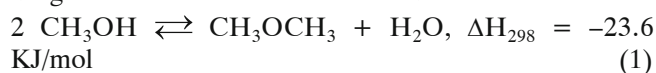
Figure 1. Process flow diagram of DME production

SIMULATION MODELING

In this study, simulations were performed using the commercial simulation package PRO/II (version 8.2). The production process will be built according to the Figure 1 structure. The Plug flow reactor module was used to model the reactions in the fixed-bed reactor. Making use of the secondary development function of PRO/II, the reaction kinetics model was simulated as a sub-program input. The distillation module was used to simulate the distillation process. The rigorous equilibrium stage model, also called MESH model, consists of a set of nonlinear equations to represent material balance, vapor-liquid equilibrium, mole fraction summation and heat balance. In distillation modules the algorithms is inside-out. Flash, simple HX, mixer, splitter, and pump module were used to set up the process.

Reaction kinetics

The reaction equation of DME synthesis from dehydrogenation of methanol was listed as below.



A detailed study of this reaction was taken up in our previous work and this kinetics equation was verified by experiments¹⁹.

The intrinsic kinetics equation of methanol dehydration to DME reaction can be expressed as:

$$r_M = -\frac{dN_M}{dW} = 1457.024e^{-\frac{78072.55}{RT}} f_M^{0.55} \left(1 - \frac{f_D f_W}{K_f f_M^2}\right) \quad (2)$$

$$r_D = \frac{dN_D}{dW} = \frac{r_M}{2} \quad (3)$$

After data processing, the experimentally determined reaction kinetic data can be included in the plug flow reactor model as submodels which are defined by writing subroutines. In addition, the result of the reaction can be exported only if the modules importing the reaction kinetics subroutine are compiled using a compiler built-in function from the PRO/II. Then choose the subroutine name in the process flow window, the reaction unit model was embed in the programs (See Fig. 1 reactor module). The NRTL model is chosen to describe and calculate the properties of the reaction system.

Thermodynamic model selection

An important consideration in distillation simulation is the choice of physical equilibrium model and the ability to reliably predict the multi-component vapor-liquid equilibrium (VLE). Reliable VLE are needed to establish distillation boundaries and to determine if and where azeotrope and phase separation occurs. Several equations can be used to model DME-methanol-water system such as Van Laar, Margules, Wilson, NRTL, UNIQUAC.

The NRTL equation was developed by Renon and Prausnitz to make use of the local composition concept while avoiding the Wilson equation's inability to predict liquid-liquid phase separation. The resulting equation correlates the liquid activity coefficient for each binary in terms of three parameters. This method has been used extensively to fit a wide variety of VLE and LLE systems. NRTL model was recommended by Song Huaijun²⁰ and binary interaction parameters of DME-methanol, DME-water, methanol-water obtained from experiments were introduced to PRO/II data banks (see Table 1).

Equations of multi-systems activity coefficient:

$$\ln g_i = \frac{\sum_j t_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{ki} x_k} \left[t_{ij} - \frac{\sum_k x_k t_{kj} G_{kj}}{\sum_k G_{kj} x_k} \right] \quad (4)$$

In equation (4),

$$t_{ij} = a_{ij} + \frac{b_{ij}}{T} + \frac{c_{ij}}{T^2} \quad (\text{unit is K})$$

$$G_{ij} = \exp(-a_{ji} t_{ji}), \quad a_{ji} = a'_{ji} + b'_{ji} T$$

And vapor phase properties are calculated from the Peng-Robinson equation of state. The Peng-Robinson equation of state (PR) is a modification of the Redlich-Kwong equation of state and was published by Peng and Robinson in 1976. Only the critical data of pure

Table 1. Eight constants of NRTL binary interaction parameters

| Component i | Component j | a _{ij} | b _{ij} | c _{ij} | a _{ji} | b _{ji} | c _{ji} | α _{ij} | β _{ij} |
|--------------------|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| DME | CH ₃ OH | 1.1352 | -785.15 | 182686 | -0.0652 | 138.01 | 1.7135 | 0.3 | 0 |
| DME | H ₂ O | 13.402 | -6561.2 | 974420 | 12.174 | -6936.5 | 1108017 | 0.3 | 0 |
| CH ₃ OH | H ₂ O | -1.8713 | 481.43 | 7592.5 | 3.3323 | -689.48 | 39.157 | 0.3 | 0 |

substance are a prerequisite for application due to the plain pattern and the generalized parameters for PR equation. Moreover, analytical solutions could be observed mathematically, which makes PR equation widely applied in engineering. The expression is as follows:

$$p = \frac{RT}{(V-b)V(V+b)+b(V-b)} a(T) \quad (5)$$

In equation (5),

$$a(T) = a_c \alpha(T_r, \omega)$$

$$a_c = 0.457235R^2 T_c^2 / P_c$$

$$a(T_r, \omega) = [1 + m(1 - T_r^{0.5})]^2$$

$$m = 0.37646 + 1.54226 - \omega - 0.26992 \omega^2$$

$$b = 0.077780 R T_c / P_c$$

Iteration of the process

A sequential modular approach was adopted to develop the simulation system. The basic idea is that the output variable of the modular units was calculated in order and the output streams were drawn out by giving some parameters of the initial stream. As we can see from the process flow diagram of DME production, S2 is the recycle stream. In this way S2 becomes the input stream of the previous module, but the rear of the module is still to come according to the sequential modular approach. To deal with recycle streams, Upadhye-Grens proposed the principle of tearing stream. The idea is to specify S2 with an initial value x^k , by solving a serious unit module calculated value x^{k+1} and S3-S12 could be obtained. Then x^k and x^{k+1} are compared, if there's a mismatch, x^k must be adjusted for them to be in tolerant errors extent. Now the data of S2-S12 is the end results and indicating that the simulation ended.

The discriminant of iteration convergence shows as formula 6.

$$\left| \frac{x^k - x^{k+1}}{x^k} \right| \leq e \quad (6)$$

RESULTS AND DISCUSSION

After the physical equilibrium and reaction kinetics have been confirmed, the reaction and separation process can be simulated. To make the simulation closer to reality, which means the parameters model should be related directly to the actual, the actual production process is brought to validate this model. The design capacity of the industrial DME production device from a factory is 200000 t/a. The domestic γ -Al₂O₃ catalyst is used in the technological method because of the special specific surface area and pore volume. It has longer catalyst life circle and high activity.

The data gathered from the manufacturing plant are introduced to perform the simulation results. In the reaction products, there is not only existed DME, CH₃OH and H₂O, but smaller amounts of CO, CO₂, CH₄, H₂, C₂H₆O and CH₃CHO could be found. These smaller amounts of gas outgrowth like CO, CO₂, CH₄, H₂ can be represented by non-condensable gas (NCG).

Table 2 shows the main parameters of the practical data from the plant. Secondly, to prove the accuracy of the simulation, the practical data are used to optimize and prove the submodels after the establishment of the DME production simulation process. The comparison between the predicted and the actual values of chief operating points (outlet streams of reactor and column) listed in Table 3 and Table 4. Fig. 2 gives simulated temperature distribution, and the values are compared with the original measurement data.

The simulation results are compared with the actual production data to verify the reliability of the simulation. As the comparison results show, the selection of reactor model, system parameter and simulation module could predict the behavior of the main unit process. In

Table 2. The main parameters used in the simulation of the manufacturing plant

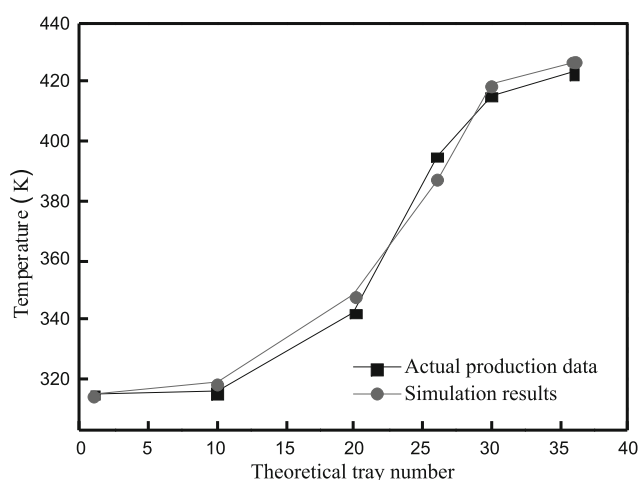
| Feed stream | Reactor | DME column |
|--|--|---------------------------------|
| Temperature: 40°C | Inlet temperature: 260°C | Column pressure: 1.0 MPa |
| Pressure: 0.1 MPa | Outlet temperature: 325°C | Actual column plate: 36 |
| Flow rate: 1521 kmol · h ⁻¹ | Pressure: 1.2 MPa | Condenser: partial condensation |
| Feed composition: | Reactor length: 6.1 m | feed stage: 24 |
| Methanol: 100 mol% | Tube inside diameter: 2800 mm | Side product (liquid) stage: 2 |
| DME: 0 | Heat of reaction: -20.896 kJ · mol ⁻¹ | DME product purity ≥ 99.9 mol% |
| Water: 0 | | Reflux ratio: 1.60 |

Table 3. Comparison between the predicted and actual values of the chief operating points

| Component (mol%) | Bottoms of reactor (S6) | | Side liquid of column 1 (S10) | | Bottoms of column 1 (S11) | | Recycle stream of column 2 (S2) | |
|---------------------------------|-------------------------|--------|-------------------------------|---------|---------------------------|---------|---------------------------------|---------|
| | Pred. | Act. | Pred. | Act. | Pred. | Act. | Pred. | Act. |
| Flow/kmol · h ⁻¹ | 1521 | 1521 | 605 | 600 | 906 | 910 | 302 | 320 |
| DME | 0.4021 | 0.3761 | 99.9000 | 99.8600 | 0.0001 | 0.0014 | 0.0002 | 0.0003 |
| CH ₃ OH | 0.1994 | 0.2474 | 0.0153 | 0.0270 | 33.3906 | 35.2363 | 99.5808 | 99.5000 |
| H ₂ O | 0.3961 | 0.3737 | 0.0065 | 0.0146 | 66.3458 | 64.4518 | 0.0379 | 0.05000 |
| NCG | 0.0007 | 0.0010 | 0.0756 | 0.0932 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| C ₂ H ₆ O | 0.0016 | 0.0017 | 0.0000 | 0.0000 | 0.2634 | 0.3102 | 0.3808 | 0.4492 |
| CH ₃ CHO | 0.0001 | 0.0001 | 0.0026 | 0.0052 | 0.0002 | 0.0003 | 0.0003 | 0.0005 |

Table 4. Comparison between the predicted and actual values of the chief operating index

| Operating parameters | Outlet temperature of reactor/ $^{\circ}\text{C}$ | Tower top temperature of column $1/^{\circ}\text{C}$ | Bottoms temperature of column $1/^{\circ}\text{C}$ | Sensitive stage temperature of column $1/^{\circ}\text{C}$ | Reflux ratio of column 1 | Annual output of DME/ ton |
|----------------------|---|--|--|--|--------------------------|---------------------------|
| Pred. | 325.15 | 41.75 | 150.50 | 43.20 | 1.57 | 211892 |
| Act. | 325.00 | 42.00 | 150.00 | 42.00 | 1.66 | 210000 |

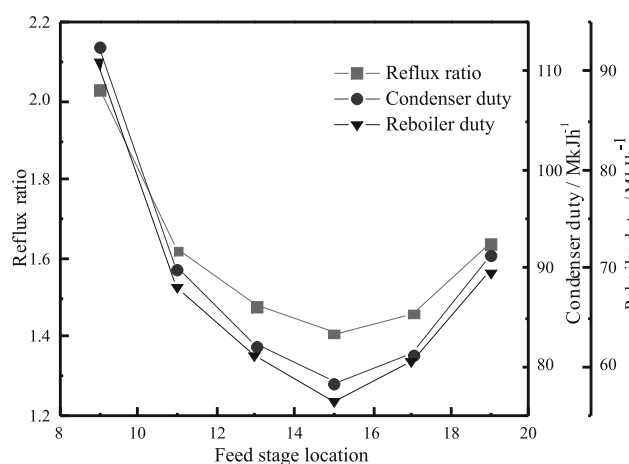
**Figure 2.** Temperature distribution of DME rectification column

this way, the whole process of DME production from methanol dehydration in an adiabatic fixed-bed reactor for high purity DME can be simulated in actual process conditions.

The main parameters for the base case simulation are given in Table 5. Then we present a set of techniques for one million t/a DME production processes to gain high purity DME product. The use of the scale of industrial fixed-bed reactor as reference to choose the internal diameter of the reactor is 5m. To ensure the DME productions, the material quantity demands no less than 7640 kmol/h. The operating pressure of the catalyst bed is 1.2 MPa.

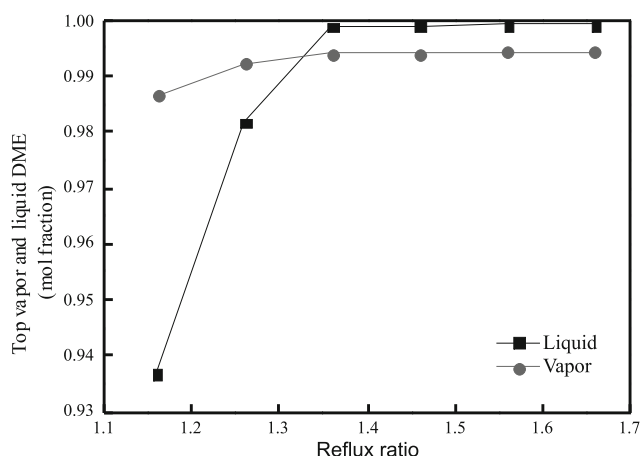
DME distillation column (column-1 in Fig. 1) consists of a 22 theoretical plates with a condenser and a reboiler. The compared results of the simulation with the actual data in the next part, 22 theoretical stages are suitable. The optimum location for the DME distillation feed was determined by varying the feeding location. In case of meeting the DME purity requirement, making the reflux ratio, condenser duty and reboiler duty minimum, Figure 3 illustrates that the fifteenth tray is the optimum feed position.

The reflux ratio influences both the separation performance and the economical efficiency in distillation columns. In Figure 4, the feed stock, column pressure and DME production is kept uniform while the reflux ratio is changed gradually. The essence of the changes of the reflux ratio is the reflux rate changed, and the variance of the reflux rate is dependent on condenser and reboiler load. It was found that high purity of DME

**Figure 3.** The influence of the feed stage location (Number of theoretical plate = 22; DME purity = 0.999 mol%)

(99.9% as the top liquid) can be achieved at a reflux ratio of 1.46. Figure 6 shows no significant effect of the continuing increase of the reflux ratio on DME purity. Instead, the cold and hot energy cost will be higher. Consequently, the selection of reflux ratio, to be used in practical applications of the distillation operation for methanol dehydration to DME will be dictated by the compromise between the required purity of the product and economic considerations.

The whole process simulation is carried out on the methods mentioned above, and the final DME product with the content no less than 99.9%. In the case of production time of 8000 hours per year, the annual DME production 10 million tonnes, the detailed data of the

**Figure 4.** Dependence of DME product purity on the reflux ratio**Table 5.** The main parameters used in the simulation of one million t/a DME production

| Feed stream | Reactor | DME column |
|--|--|--|
| Temperature: 40°C | Inlet temperature: 260°C | Column pressure: 1.0 MPa |
| Pressure: 0.1 MPa | Outlet temperature: 330°C | Total number of theoretical stages: 22 |
| Flow rate: $6445 \text{ kmol} \cdot \text{h}^{-1}$ | Pressure: 1.2 MPa | Condenser: partial condensation |
| Feed composition: | Reactor length: 9.6 m | Feed stage: 15 |
| Methanol: 100 mol% | Tube inside diameter: 5 m | Side product (liquid) stage: 2 |
| DME: 0 | Heat of reaction: $-20.896 \text{ kJ} \cdot \text{mol}^{-1}$ | DME product purity $\geq 99.9 \text{ mol}\%$ |
| Water: 0 | | Reflux ratio: 1.46 |

Table 6. Properties and components of the main stream in the simulation process (component mol%)

| Stream | DME | CH ₃ OH | H ₂ O | NCG | C ₂ H ₆ O | CH ₃ CHO | Flow/kmol·h ⁻¹ | T/°C | P/MPa |
|--------|---------|--------------------|------------------|--------|---------------------------------|---------------------|---------------------------|--------|-------|
| S1 | 0.0000 | 99.2000 | 0.8000 | 0.0000 | 0.0000 | 0.0000 | 5620.77 | 40.32 | 0.10 |
| S2 | 0.0002 | 99.2000 | 0.0328 | 0.0000 | 0.7665 | 0.0004 | 1407.86 | 78.36 | 0.17 |
| S3 | 0.6065 | 99.2332 | 0.0064 | 0.0000 | 0.1537 | 0.0001 | 7028.63 | 50.65 | 1.56 |
| S4 | 0.6065 | 99.2332 | 0.0064 | 0.0000 | 0.1537 | 0.0001 | 3539.63 | 148.02 | 1.33 |
| S5 | 0.6065 | 99.2332 | 0.0064 | 0.0000 | 0.1537 | 0.0001 | 3539.63 | 260.00 | 1.23 |
| S6 | 40.2126 | 19.9413 | 39.6132 | 0.0746 | 0.1572 | 0.0011 | 7028.63 | 326.86 | 1.06 |
| S7 | 40.2126 | 19.9413 | 39.6132 | 0.0746 | 0.1572 | 0.0011 | 7028.63 | 72.00 | 0.96 |
| S8 | 40.2126 | 19.9413 | 39.6132 | 0.0746 | 0.1572 | 0.0011 | 7028.63 | 69.70 | 0.96 |
| S9 | 93.6300 | 0.0002 | 0.0004 | 6.3700 | 0.0000 | 0.0003 | 49.32 | 38.86 | 0.94 |
| S10 | 99.9000 | 0.0153 | 0.0065 | 0.0756 | 0.0000 | 0.0026 | 2783.00 | 41.75 | 0.94 |
| S11 | 0.0001 | 33.3906 | 66.3458 | 0.0000 | 0.2625 | 0.0002 | 4196.31 | 152.84 | 0.96 |
| S12 | 0.0000 | 0.0100 | 99.9900 | 0.0000 | 0.0000 | 0.0000 | 2783.86 | 118.64 | 0.29 |

main streams including components, flow, temperature, and pressure are obtained and given in Table 6.

As showed in Table 6, the average DME yield is 2783 kmol · h⁻¹, which converts to yearly production is 1.0257 million t/a. The result indicates that the purity and yield of DME can reach above 99.9% and 98% respectively. The purity of DME in the final product reaches the requirement of aerosol level DME quality standards.

CONCLUSIONS

This paper proposed a DME production process system, which includes: methanol dehydration reaction system, heat transfer system and separation system after the reaction. An invention patent application for the process was filed and the scheme has approved in China. Accordingly, the whole process for high purity DME synthesis via methanol vapor phase dehydration in a multistage adiabatic fixed-bed reactor was developed. And then the technological process was built on PRO/II platform combined the parameters of reaction dynamic model for methanol dehydration reaction, regression constants of parameters in NRTL model for binary component in DME separation system. Next, one set of real survey data from a factory concerning a DME productive capacity of 200 thousand tonnes per year was used to contrast between the predicted and the actual results. It showed that the simulation results are in good agreement with the actual value.

The target for one million t/a DME yields, the bed height and the volume of the catalytic bed was calculated. On the inlet operating conditions of temperature 260°C, pressure 1.2 MPa and flow 3540 kmol · h⁻¹, the reactor outlet conversion reached 80%, and the DME yield was 1026 kt/a. The distillation parameters of the product were also determined: column bottom temperature 150–155°C, overhead temperature 42°C and reflux ratio 1.46. The purity of DME can reach above 99.9%. The entire process simulation results provided the outputs of the key units, the properties data for the main streams between equipments or in columns, and offered useful reference for the actual process design and operation optimization.

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NOMENCLATURE

| | |
|----------------------|---|
| <i>f</i> | fugacity, MPa |
| <i>G</i> | mixed Gibbs function, kJ · mol ⁻¹ |
| <i>K_f</i> | equilibrium constant |
| <i>N</i> | mass flow rate, kmol · h ⁻¹ |
| <i>p</i> | pressure, MPa |
| <i>R</i> | universal gas constant, J · mol ⁻¹ · K ⁻¹ |
| <i>r</i> | reaction rate, mol · g ⁻¹ · h ⁻¹ |
| <i>V</i> | molar volume, ml · mol ⁻¹ |
| <i>W</i> | catalyst weight, kg |
| <i>g</i> | activity coefficients |
| <i>t</i> | model parameter |
| <i>w</i> | acentric factor |

Subscripts

| | |
|----------|----------------|
| <i>c</i> | critical state |
| <i>D</i> | dimethyl ether |
| <i>M</i> | methanol |
| <i>r</i> | contrast |
| <i>W</i> | water |

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