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Original Research Article

Simulation Production of Dimethylether (DME) from Dehydration of Methanol Using Aspen Hysys

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Abstract

Dimethyl ether (DME) is used primarily as a propellant and a motor fuel alternative, (DME) is miscible with most organic solvents and has a high solubility in water. Recently, the use of (DME) as a fuel additive for diesel engines has been investigated due to its high volatility (desired for cold starting) and high cetane number of 55–60, with the advantage of high efficiency, and low exhaust emissions (no particulates, no Sulphur, and low NOx). Technical-quality (DME) is an alternative to liquefied petroleum gas (LPG). 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 (DME) synthesis is simulated in Aspen Hysys V3.1 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 was selected as the fluid package as it is able to handle selected pure components (methanol, water and dimethyl ether). The equilibrium reaction was selected to describe conversion of methanol to DME reaction and it is about 80%. A feasibility study and design of a plant producing 99.9 wt% Dimethyl ether (DME). The plant is designed which is capable of producing 50,000 metric tons of (DME) per year via the catalytic dehydration of methanol over an acid zeolite catalyst.

Keywords: dehydration, Aspen Hysys, simulation, Dimethyl ether, production.

INTRODUCTION

Simulation is a situation in which a particular set of conditions is created artificially in order to study or experience something that could really exist in reality. It is the act if pretending that something is real when it is not. A computer simulation is an attempt to model a real-life or hypothetical situation on a computer so that it can be studied to see how the system works.

Process simulator is defined also as an engineering tool which performs automated calculations, mass &energy balances, physical property estimations, design / rating calculations, costing, process optimization, accurate description of physical properties of pure components and complex mixture, models for a large variety of reactors and unit operations, numerical techniques for solving large systems of algebraic and differential equations [1].

In this work Aspen HysysV3.1 used to simulate production of DME. There are two modes of simulation- Steady state mode and Dynamic mode. Steady state models perform a mass and energy balance of a stationary process (a Process in an equilibrium state) but any changes over time had to be ignored. Dynamic simulations require increased calculation time and are mathematically more complex than a steady state simulation. It can be seen as a multiply repeated steady state simulation (based on a fixed time step) with constantly changing parameters.

Aspen HYSYS is a market leading process modeling tool for conceptual design, optimization, business planning, asset management and performance monitoring for oil in gas processing, petroleum refining, and air separation industries. Aspen HYSYS is a core element of Aspen Tech's aspen ONE Engineering applications. Aspen HYSYS has established itself as a very intuitive and easy to use process simulator in oil and gas refining industry. Users with little prior knowledge of Aspen HYSYS can pick up and train themselves in its modeling capabilities. Some of the very intuitive capabilities include a highly interactive process flow diagram for building and navigating through large simulations. The program also provides a very flexible and easy to use distillation column

modeling environment. Additionally the interactive nature of HYSYS enables users to build and use their models quickly and effectively. Aspen HYSYS offers a comprehensive thermodynamics foundation for accurate calculation of physical properties, transport properties, and phase behavior for the oil & gas and refining industries. Comprehensive library of unit operation models including distillation, reactors, heat transfer operation, rotating equipments, controllers and logical operations in both the steady state and dynamic environments [2, 3].

Dimethyl ether (DME), as a multi-source, multi-purpose product, has received growing attention due to the present global environmental pollution and energy supply problems. DME can be produced from syngas, which in turn is formed from natural gas, coal or biomass. DME has a wide range of applications such as LPG substitute,

Propellant, chemical feedstock and transportation fuel, and in fuel cells [4, 5]. Catalytic dehydration of methanol over an acidic catalyst offers a potential method for the production of DME, a new spray propellant. Being identified as a potential diesel and cooking fuel, DME has many excellent characteristics. It has the oxygen content of 34.78% and can be burned without soot emission, whereas for traditional diesel fuels, simultaneous NO*x* and soot emission control target cannot be expected. It has a boiling point of –25ºC, which is 20ºC higher than LPG and can be liquefied at 0.54 MPa (20ºC). Therefore, based on the matured technology of LPG application, as far as storage, transportation, and usage, no remarkable problem for the use of DME exists [5, 6].

DME also known as methoxy methane, wood ether, diethyl oxide or methyl ether, is the simplest ether. It is a colorless, slightly narcotic, nontoxic, highly flammable gas at ambient conditions, but can be handled as a liquid when lightly pressurized. The properties of DME are similar to those of Liquefied Petroleum Gas (LPG).

Low cost technologies for DME have been mainly carried out by JFE Group (Japan), Haldor Topsoe (Denmark) in Europe, Air Products and Chemicals in the United States, and others. The use of DME as an alternative fuel will be crucial in China, a country with so high pollution rates, in the near future.

Sweden is the leader in the development of bio-DME produced through the gasification and conversion of black liquor, a byproduct in Sweden's paper and pulp industry.

The production of DME in Spain is mainly carried out by aerosol and fuel industry. Due to its global increasing importance regarding energy and environmental advantages, as well as the proper personal interest in the topic, DME synthesis process was selected in this graduation project. Nowadays, the indirect synthesis of dimethyl ether is the conventional production method in the industry. Conditions may be correctly defined and controlled, but it takes two main synthesis steps in the process, whereas direct synthesis has been recently researched and is about to be implemented as a higher performance method that occurs in one synthesis step [7].

Currently, there are several licensors that offer technology for the production of DME based on a two-step process, including Haldor Topsøe, Lurgi, Mitsubishi Gas Chemical, Toyo Engineering Corporation and Uhde [8].

DME synthesis is a two-stage process. In the first step, methanol production is catalyzed over $CuO/ZnO/Al_2O_3$ at 50–100 bar and 270°C. In a second step, CH_3OH is dehydrated in the presence of an acid zeolite or Lewis acidic catalyst, such as Al_2O_3, ZSM-5

The reaction of DME synthesis is mainly dehydration of methanol that is exothermic and reversible. In the current work, the rate expression has been selected from [9, 10].
Methanol dehydration reaction:

$$2\,CH_3OH \leftrightarrows CH_3OCH_3 + H_2O \qquad (1)$$

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 Huaijun [11] and binary interaction parameters of DME-methanol, DME -water, methanol-water obtained from experiments were introduced in (Table 1).

Equations of multi-systems activity coefficient:

$$lng_i = \frac{\sum_j t_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{ki} x_k}\left[t_{ij} - \frac{\sum_k x_k t_{kj} G_{KJ}}{\sum_k G_{kj} x_k}\right] \qquad (2)$$

In equation (2),

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

$$G_{ij} = \exp(-a_{ji}t_{ji}), a_{ji} = a_{ji} + b_{ji}T$$

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 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 [12]:

$$P = \frac{RT}{(V-b)} - \frac{\theta_{PR}}{V^2+2bV-b^2} \quad (3)$$

In equation (3),

$$\theta_{PR} = a''[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2$$

$$a'' = \frac{0.45724R^2T_c^2}{P_c}$$

$$b = \frac{0.07780RT_c}{P_c}$$

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_3OH	1.1352	–785.15	182686	–0.0652	138.01	1.7135	0.3	0
DME	H_2O	13.402	–6561.2	974420	12.174	–6936.5	1108017	0.3	0
CH_3OH	H_2O	–1.8713	481.43	7592.5	3.3323	–689.48	39.157	0.3	0

REACTION KINETICS

The reaction equation of DME synthesis from dehydrogenation of methanol was listed in equation (1).

The intrinsic kinetics equation of methanol dehydration to DME reaction can be expressed as [10]:

$$r_M = -\frac{dN_M}{dW} = 1457.024e^{-\frac{78072.55}{RT}} f_M^{0.55}\left(1 - \frac{f_D f_W}{K_f f_M^2}\right) \quad (4)$$

$$r_D = -\frac{dN_D}{dW} = \frac{r_M}{2} \quad (5)$$

The reaction taking place is mildly exothermic with a standard heat of reaction of -21,225KJ/mol. The equilibrium constant for this reaction at three different temperatures is given below:

Table-2: Equilibrium constant

T	K_p
473 K (200°C)	92.6
573 K (300°C)	52.0
673 K (400°C)	34.7

The equilibrium conversions for pure methanol feed over the 200°C to 400°C range are all greater than 83%. By limiting conversions to 80%, the reaction will not be equilibrium limited.

PROCESS DESCRIPTION

DME is produced by dehydrogenation over an industrialized molecular sieve catalyst. The reaction temperature was set at between 200°C to 400°C and dehydration reaction is carried out in a multistage adiabatic reactor. Methanol is introduced to the system at 25°C, 262Kgmol.h^{-1} and 100KPa from methanol synthesis plant.

Then the pressure is increased to 1400KPa. The raw material is mixed with the recycle stream R 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. Then the pressure is increased to 1400KPa. The raw material is mixed with the recycle stream R 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, C_2H_5OH, *et al*. The reactor exit stream is

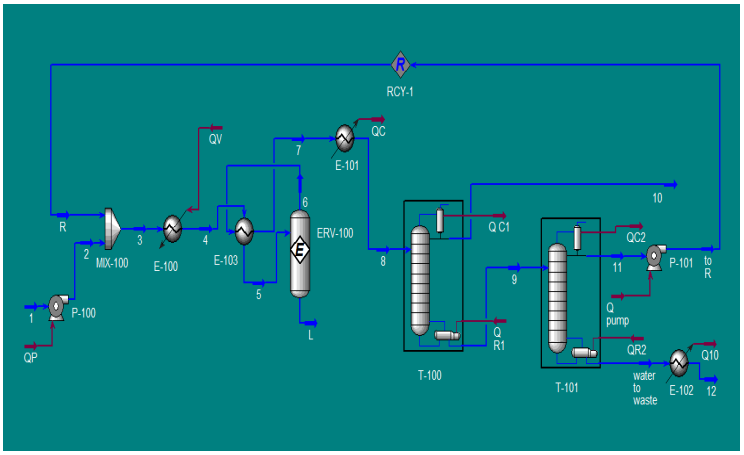

Fig-1: Process flow diagram of Production (DME) from Dehydration of Methanol

Cooled (Cooler), partially decompressed, and introduced in the separation train. DME is obtained in column T-100 with the purity higher than 99.9% (molar basis). The bottoms of column T-100 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, and the methanol recycled. The heat duty of the condenser in DME distillator is from engineering water, and any extra cryogen is undesired.

RESULTS AND DISCUSSION

The design capacity of the industrial DME production device from a factory is 50,000 metric tons of (DME) per year.

The data gathered from the manufacturing plant are introduced to perform the simulation results. In the reaction products, there is not only existed DME, CH_3OH and H_2O, but smaller amounts of CO, CO_2, CH_4, H2, C_2H_6O and CH_3CHO could be found.

Table 3 shows the main parameters of the simulation, and, DME distillation column (column T-100 in Fig. 1) consists of a 22 theoretical plates with a condenser and a reboiler. 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, and the twelfth tray is the optimum feed position.

Table 4 shows properties and components of the main stream in the simulation process (component mol%).

Table-3: The main parameters of the simulation

Feed stream	Reactor	DME column
Temperature: 25°C	Inlet temperature: 250°C	Column pressure: 1310 Kpa
Pressure: 100 Kpa	Outlet temperature: 361.4°C	Condenser: Total condensation
Flow rate: 262 Kgmol.h^{-1}	Pressure: 1480 Kpa	Feed stage: 12
Feed composition:	Reactor length: 10 m	Total number of theoretical stages: 22
Methanol: 99.01 mol%	Tube inside diameter: 0.720 m	Side product (liquid) stage: 2
DME: 0	Reactor volume: 4.072 m^3	Reflux ratio: 0.4590
Water: 0.99 mol%	Heat of reaction: -20.896 KJ.mol^{-1}	DME product purity: 99.9 mol%

Table-4: Properties and components of the main stream in the simulation process (component mol%)

Stream	DME	CH_3OH	H_2O	T/C°	P/Kpa	Flow/Kgmolh^{-1}
1	0.0000	0.9905	0.0095	25.000	100.00	262.20
2	0.0000	0.9905	0.0095	25.850	1550.0	262.20
3	0.0029	0.9887	0.0084	42.730	1550.0	314.90
4	0.0029	0.9887	0.0084	153.30	1500.0	314.90
5	0.0029	0.9887	0.0084	250.00	1480.0	314.90
6	0.4149	0.1649	0.4202	361.40	1400.0	314.90
7	0.4149	0.1649	0.4202	272.80	1350.0	314.90
8	0.4149	0.1649	0.4202	90.080	1310.0	314.90
9	0.0049	0.2798	0.7153	154.90	1050.0	185.10
10	0.9990	0.0010	0.0000	46.220	1030.0	129.80
11	0.0175	0.9800	0.0025	120.80	730.00	52.710
12	0.0000	0.0010	0.9990	50.080	160.00	132.30

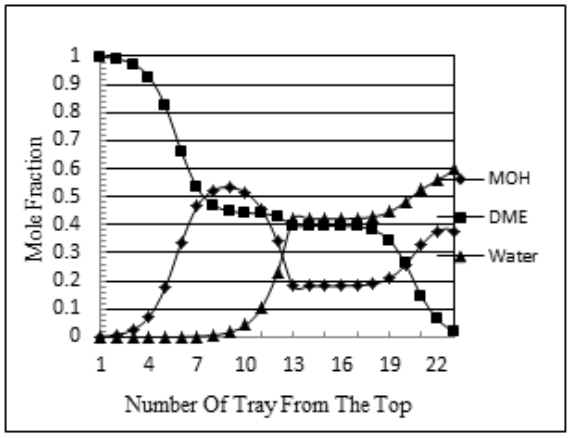

Fig-2: Composition versus tray position

Figure 2 shows change of composition versus tray position. The composition of DME decreases with increase of number of theoretical trays distillation column T-100.

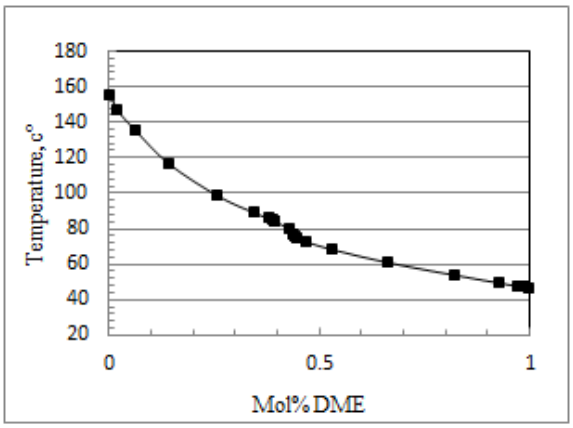

Fig-3: Change of temperature versus mol% DME

And Figure 3 shows change of temperature of the same column with change of composition of DME.

CONCLUSION

Simulation of a DME plant which is capable of producing DME with high purity (50,000 tons per year) from methanol is done using ASPEN HYSYS V3.1 process simulator. NRTL is chosen as the property method in the simulation. 80% of the methanol is converted into DME in the equilibrium reactor, the product stream from the reactor consists of 41.16 % DME, 42.16 % water and 16.68%unconverted methanol. After passing through Heat exchangers (to bring down the temperature to the desired range for separation), the output stream is feed into distillation columns.

Here, the separation into DME and water-methanol takes place.DME is separated from the first distillation column as top product and methanol, water as bottom product, which fed into second distillation column.

Design specifications are used to meet the required results. The reflux ratios and the distillate rates are manipulated as variable parameters and the high purity of DME is obtained by using two distillation columns with four Heat exchangers.

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NOMENCLATURE

MOH Methanol
DME Dimethyl ether
t model parameter
N mass flow rate, Kgmol.h^{-1}
W catalyst weight, Kg
g activity coefficients
V molar volume, m3.mol^{-1}
R universal gas constant, J.mol^{-1}.K^{-1}
G mixed Gibbs function, KJ.mol^{-1}
f fugacity, Kpa
K_p equilibrium constant
r reaction rate, mol.Kg^{-1}.h^{-1}

Subscripts

c critical state
D dimethyl ether
M methanol
r constant
W water

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