Journal of the Taiwan Institute of Chemical Engineers 59 (2016) 86–90

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Short communication

Dehydration of methanol to dimethyl ether in a dual-catalyst system catalytic distillation tower

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ARTICLE INFO

Article history:
Received 28 January 2015
Revised 27 July 2015
Accepted 28 July 2015
Available online 17 August 2015

Keywords:
Dimethyl ether
Catalytic distillation
Dehydration
Tower design

ABSTRACT

A novel design of a dimethyl ether (DME) catalytic distillation (CD) tower is explored. Due to the wide boiling range among the reaction mixture components: water, methanol and DME, a dual-catalyst system CD tower is designed to minimize the tower temperature and catalyst deactivation rate. A DME CD tower model was developed and validated with both VLE data and pilot test data, and the model so obtained agrees with the results published by An et al. The dual-catalyst system CD tower, wherein the upper section of bed is loaded with low temperature catalysts and the lower section of bed is loaded with high temperature catalysts, are arranged such that both catalysts are used at optimum dehydration temperatures and the product DME can still be condensed with normally available cooling water.

1. Introduction

Methanol dehydration to DME as shown in Eq. (1) is a reversible reaction [1]. The coproduct water is strongly adsorbed on the catalyst surface and thus inhibits the dehydration rate [2]. The process is exothermic and the heat of reaction should be removed from the reactor. The CD tower [3–5] can replace one dehydration reactor and two distillation towers used in the conventional DME process [6]. Application of CD technology in DME synthesis offers many advantages, such as higher conversion, energy saving and capital cost reduction. However, only a few reports were published for this process [3–5].

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{1}$$

The concept to design a CD tower for undergoing methanol dehydration seems clear. The reactant methanol has an intermediate boiling point among three species in the reaction mixture so that methanol can be concentrated in the middle of the CD tower, where catalyst is located. DME and water can be withdrawn respectively from the top and bottom of the CD tower. Due to a large difference in the boiling point between DME and water, the design pressure of the tower shall enable the use of the available low cost heat sink and heat source. For example, the dew point of DME is 40.3 °C when the CD tower pressure is 9 bar and therefore using 30 °C cooling water as heat sink to condense DME is impractical. Another consideration for a CD tower is that higher tower pressure results in higher temperature in the reaction zone, thus the catalyst may be deactivated. The CD tower pressure selection has been included in this study because it was never been explored [3–5].

Starting with the vapor–liquid equilibrium data for H_2O–MeOH–DME system [7–10], the binary parameters for VLE methods were regressed and validated. Combining available kinetic data [3] and the VLE method, a pilot CD model was formulated and validated with pilot test data. The activity and aging tests were performed in a bench-scale fixed bed to evaluate the commercial catalysts life. Instead of a single-catalyst system, a dual-catalyst system CD tower is designed and a model is setup to explore the relationship between operating pressure and catalyst bed locations.

2. Experimental

2.1. Pilot tower and test procedure

The pilot system consists of a fully instrumented CD column. The inside diameter of the column was 76.2 mm and the height was 5.79 m. The reaction section was loaded with 949 g of dry Amberlyst 35 (A35) (Rohm and Haas). The distillation sections were packed with 20 mm Raschig rings. The column configuration is shown in Fig. 1. Real-time temperature was monitored via on-line instrumentation. Test data was collected under steady-state conditions.

Before start-up, the system was blanketed with nitrogen at 1.36 bar. After the column reached the steady state at total reflux for one hour, a 99.5% methanol was continuously fed to the reaction zone. The control for reflux ratio and liquid level across reboiler was turned on. After the column was operated for six hours, six samples were taken. The sampling points were S-1, S-2, S-3 and S-4, which corresponded to 5.182, 3.962, 1.524 and 0.305 m height above the

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http://dx.doi.org/10.1016/j.jtice.2015.07.037
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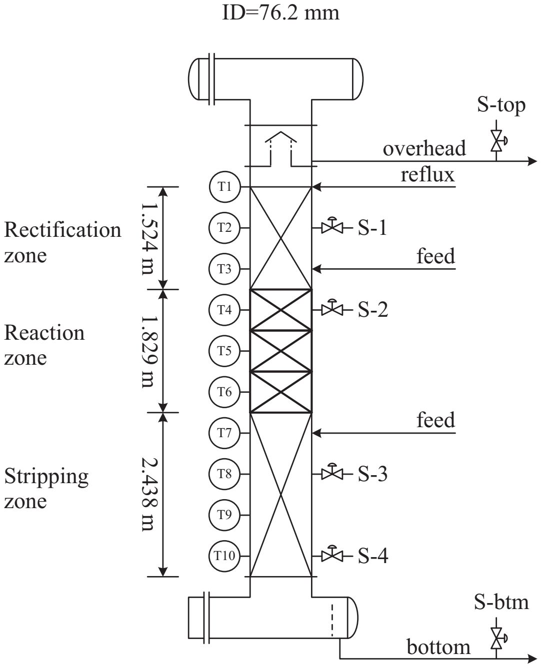

Fig. 1. The pilot CD tower configuration.

reboiler shown in Fig. 1. Other two samples, S-top and S-btm, were taken at the outlet of the condenser and reboiler.

2.2. Aging and residual activity test

The catalyst aging test was performed with a feed of 50/50% by weight methanol/soften water in a continuousdownflow fixed-bed reactor. The experiments with 99.5% methanol feed were performed to observe the residual catalysts activity after a period of operation. A gradient packing method was used so that the catalyst bed would have a nearly uniform temperature and minimum wall effects. Mass balance was 99% and the loss material can be attributed to the fugitive dimethyl ether in the overhead sample.

3. VLE method and parameters

Generally, a cubic equation of state (EOS) coupling with an activity model for liquid phase e.g., NRTL–RK method can predict reliable phase behavior. The Wong–Sandler (W–S) mixing rule was developed to implement the EOS, allowing VLE data obtained at low pressures to make good VLE predictions for non-ideal mixtures at high pressures [11]. To simplify VLE method, programming parameter regression was performed on a commercial simulator, Aspen V8. The VLE data include three sets of *T-x-y* data at 5, 8, and 11.2 atm for H_2O-MeOH [7] and fourteen sets of *P-x-y* data for MeOH–DME [8] and H_2O–DME [9], measured at temperatures up to 160 °C. These pressures and temperatures are within the range of operating conditions of the CD tower, as shown later in this paper. The ternary data for VLE method evaluation are four sets of *P-x-y* data at 60, 80, 100 and 120 °C [10].

The recommended PRWS–UNIFAC [10], Peng–Robinson (PR) EOS [8], RKSWS–UNIQUAC [12], and NRTL–RK [13] methods were evaluated. To understand the differences among various property methods, RKSWS–UNIFAC and UNIFAC method were included in the evaluation. The average absolute, maximum and minimum relative error between the calculated and experimental VLE data for the ternary system showed that the PRWS–UNIFAC and RKSWS–UNIFAC methods were comparable and superior to others. The VLE prediction by UNIFAC method was reasonable but its deviation interval was quite different. According to Pozo and Streeett [9], there existed VLL equilibria for H_2O–DME system. Carefully checked with the VLLE data, the theoretical UNIFAC method can't give a good prediction. This is shown in Fig. 2. The regressed interaction parameters k_{ij} for PRWS–UNIFAC method are 0.1113, 0.3654, and 0.0992 for H_2O–MeOH, H_2O–DME and MeOH–DME system, respectively. These results were used in the CD tower simulation.

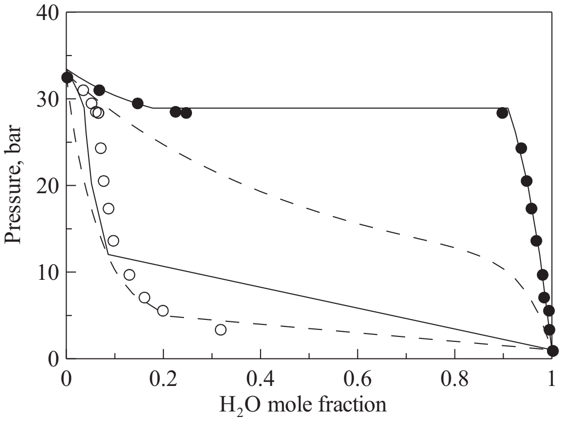

Fig. 2. The vapor–liquid–liquid data of DME-H_2O at 100.11 °C. • x_{H2O}, o y_{H2O}, ——— PRWS-UNIFAC, – – UNIFAC.

It should be noted that the VLE predictions derived from various property methods via different commercial software, such as Aspen Plus, Hysys or ChemCAD, aren't always consistent. Even with the same software, different VLE predictions may result from different versions. The parameters for PRWS–UNIFAC method are only suitable for use in Aspen V8. It is important that parameters for the VLE method should be regressed with VLE data, so that the selected method can give a good VLE prediction.

4. Kinetic model

The past studies for DME synthesis showed that suitable catalysts are acidic ion exchange resins, e.g. A35 [3–5]. The reaction mechanism was reported to fit with either Langmuir–Hinshelwood (LH) or Eley–Rideal (ER) kinetic model, and the LH model was found to be superior [2]. The coproduct water competes with methanol for adsorption and inhibits the methanol dehydration rate [2,3,5]. So the water concentration plays a key role in rate of reaction. The published kinetic data were conducted at temperatures in the range of 110–135 [2], 70–130 [3] °C. Because the data from the above references cover the reaction temperature in our column, the kinetic data reported in [3] were used in this study.

5. Results and discussion

5.1. Pilot CD model validation

The pilot CD tower shown in Fig. 1 comprised ten stainless steel sections, three for rectification zone, three for reaction zone, and four for stripping zone. The length per section was 0.61 m. A thermocouple was positioned at the middle of each section. So there are twelve measurement points, including the condenser and reboiler. The simulated vapor compositions were compared with the four sampling points located at the middle of each section. Including the condenser and the reboiler, the total stage number was 18. The reactive stages were number 7, 8 and 9. Table 1 summarizes the operating conditions and outlet streams analysis of the pilot tests.

From tower configuration (Fig. 1), operating conditions (Table 1), VLE method and kinetic data, the pilot CD model can be formulated as a RadFrac block in Aspen V8. In the model, a parameter – overall