

Design and Simulation of Reactive Dividing-Wall Distillation Column for Transesterification of Methyl Acetate with n-Propanol

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Abstract. A new process was designed for the transesterification of methyl acetate with n-propanol. That is, reactive dividing-wall distillation column technology is used instead of conventional reactive distillation column and methyl acetate - methanol separation column to product n-propyl acetate and methanol. The reaction distillation process was simulated by Aspen Plus simulation software. N-propyl acetate and methanol are produced from the bottom of the main column and the sub-column, respectively. The influence of feed position of n-propanol (PROH) and methyl acetate (MEAC), reflux ratio and liquid phase distribution ratio on the heat duty of reboiler was investigated on the premise of the purity of n-propyl acetate is ensured. The simulation result shows that the new process has great advantages on capital cost saving, because not only the equipment occupancy space but also the investment in condenser are reduced.

1. Introduction

Due to increasing awareness of limited energy resources in society, high energy-consuming industrial processes will face a great challenge. Many researches have shown that the energy consumed by the distillation process accounts for about one-third of that of whole chemical production process^[1]. Therefore, process intensification represents a dominating trend in the chemical process engineering, such as, the heat integrated distillation technology and the integration of the distillation process with other chemical process units. Besides, the last achievements in the process modelling, growing computational power as well as advanced numerical methods make process intensification possible. Reactive distillation is a special distillation method that combines separation and reaction in one piece of equipment, and therein reaction process and separation process could promote each other. Dividing-wall distillation column was utilized, that is, two columns are integrated into one shell^[2], which can cut down the equipment cost. For the separation of multicomponent mixtures, a sequence of distillation columns is applied most often^[3]. In case of

three components, at least two distillation columns are necessary. If a dividing-wall distillation column was used, three components could be separated simultaneously. Thus, the dividing-wall distillation column (DWC) offered an alternative to conventional column, with the possibility of savings in both energy and capital costs^[4,5]. The reactive dividing-wall distillation column was a process which could couple the process of reactive distillation with the dividing-wall distillation column, then reaction and separation processes could be carried out simultaneously. Many reports on the reactive dividing-wall distillation column were available in the open literature^[6-10]. Those researches showed that, reactive dividing-wall distillation could overcome the equilibrium limitations of reversible reactions, increase the selectivities and conversion rates of reactions, and then improve production capacity. The process could reduce energy consumption and equipment investment.

N-propyl acetate is an extremely important organic solvent that was widely used in the food spices, printing, dyeing and other industrial products, and has broad market prospects^[11]. It was often synthesized through the esterification of acetic acid (AC) and n-propanol (PROH) with strong sulfuric acid as catalyst. The traditional production takes reaction and distillation separation method^[12-13], that is, the reaction process and the separation process were separately carried out in a pre-reaction tank and a distillation column. Firstly, n-propyl acetate was generated by transesterification reaction or esterification reaction in the reaction tank. Specifically, methyl acetate and n-propanol are transesterified to give n-propyl acetate and methanol, or acetic acid and propanol are esterified to form n-propyl acetate and water. Then reaction products entered the distillation column for separation. Lastly, high purity products would be obtained at the bottom of the distillation column. It is worth noting that the conversion of the reactants is no longer increased after the equilibrium has been reached. There are two reasons to explain this phenomenon: on one hand, the transesterification and esterification reactions are reversible, and the reaction process is in equilibrium; On the other hand, reaction and separation are carried out in different equipments, which limits the conversion rate to some extent. In this case, the conversion of the reactants was not high and the reaction time was long.

In recent years, the development of reactive distillation technology had replaced the traditional process gradually. On the reaction distillation technology for the production of n-propyl acetate, many scholars had done the relevant researches. Brehelin, M^[12] et al. systematically studied the catalytic reaction distillation process of production of n-propyl acetate. Not only the experiment of the production process of n-propyl acetate but also the simulation process were studied. Meanwhile, the kinetics for homogeneously reaction with sulphuric acid as catalyst and heterogeneously reaction with strong acid cation (Amberlyst 15) as catalyst were investigated and the constants for a pseudo-homogeneous model are presented. The simulation results were in agreement with the experimental data, acetic acid conversion and n-propyl acetate purity may be dramatically increased just by adding to the pilot plant a stripping section in an additional column. Six different configurations were put forward to achieve such a production. Lan^[11] and et al. studied the experimental process of production n-propyl acetate which took acetic acid and propanol as raw materials and strong acid cation exchange resin as catalyst. In this process, the effects of the molar ratio of acid and alcohol, the reaction time and the amount of catalyst on the reaction were investigated. The research results presented that the conversion of the reaction achieved 68.79%. Using cation exchange resin as catalyst in the reaction had overcome a series of shortcomings of taking strong sulfuric acid as catalyst, such as corrosion equipments, reacting with the reactants and further unsatisfied conversion rate. Wang^[14] and et al. focused on the traditional production process of n-propyl acetate. There, reducing energy consumption and cost were chosen as the objective function. There were three kinds of improvement processes which were simulated by Aspen Plus software. The results displayed that for a reaction distillation process where mass fraction is 98.5%, energy

consumption and equipment investment is least if the organic phase in the phase separator would be all recycled to the reaction distillation column and the product of n-propyl acetate would be extracted in the middle side of the rectification section of the distillation column. Although the purity of n-propyl acetate had greatly improved, two or three distillation columns are used in those processes. The first process used a reactive distillation column and a recovery column; The second and the third processes both had a reactive distillation column, a recovery column and a secondary column. Those three industrial processes had increased equipment investment and equipment occupancy area. Man^[15] and et al. proposed a new process where the production process of synthesis n-propyl acetate in two columns was replaced by reactive dividing-wall distillation column. The two kinds of production process were simulated under the same conditions, which revealed the reactive dividing-wall distillation column could reduce power consumption by 15% and conserve equipment investment. It's obvious that using reactive dividing-wall distillation column was an effective way to cut down on equipment investment and energy consumption. Man^[15] and et al. expressed the process of esterification of acetic acid with n-propanol. The transesterification of methyl acetate and n-propanol was carried out by Shen^[16] and et al. Heterogeneous reaction kinetics of transesterification was studied. And the activation energies of the positive and negative reactions and the adsorption constants of methyl acetate were determined. But, for the transesterification of methyl acetate and n-propanol, the design and simulation of reactive dividing-wall distillation column has not been reported.

However, this paper proposed a new process of the reactive dividing-wall distillation column which was based on the conventional two-column simulation process. A model of three columns was put forward which was equivalent to reactive dividing-wall distillation column in the thermodynamics. The model was simulated by Aspen Plus software, the effects of feed ratio, reflux ratio and liquid phase distribution ratio on the reboiler heat duty of reactive distillation dividing wall column were investigated.

2. Experiment and Simulation

The original process is shown in Figure 1. Methyl acetate and n-propanol flow into the theoretical plates of 34th and 74th of the reactive distillation column, respectively, at a speed of 50 Kmol/hr. The reaction product n-propyl acetate was extracted from the bottom of the C1 column and a mixture of methyl acetate and methanol was obtained at the top of the C1 column. Then the mixture entered to the C2 column for separation. Methyl acetate and methanol would form azeotrope which can be refluxed to C1 and continue to react. Purity of methanol obtained from C2's bottom is up to 99.5%. In this process, two distillation columns, two reboilers and two condensers are used, investment in equipment and energy is very large.

2.1 The Process of Reaction Distillation Dividing-Wall Column Modeling

Compared with conventional transesterification process of methyl acetate and n-propanol, using of reactive dividing-wall distillation column could theoretically reduce equipment investment. Figure 2 shows the process of reactive dividing-wall distillation column for transesterification of methyl acetate with n-propanol. In the new process, C1 column and C2 column are integrated into a reactive distillation column. It could be seen that a wall is added to the reaction rectification column, and the lower right side of the partition is closed. The process could achieve the reaction and separation in a column shell simultaneously.

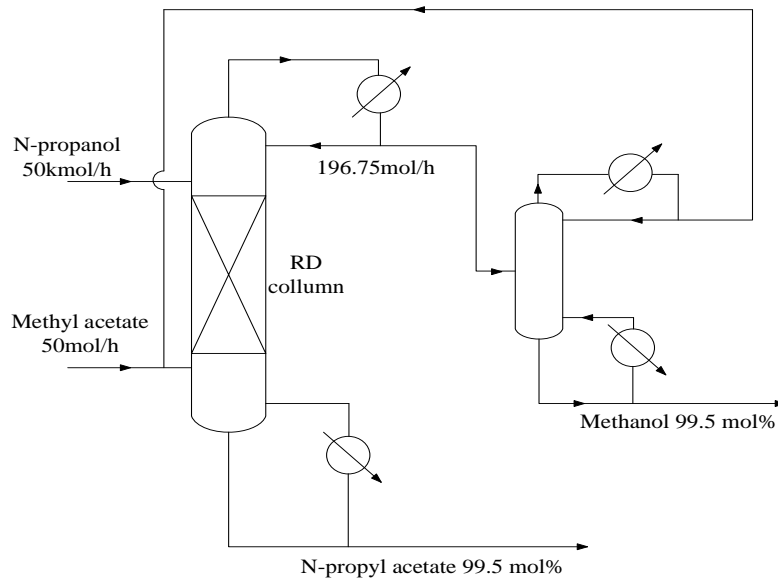


Figure 1: RD process of methyl acetate conventional transesterification system.

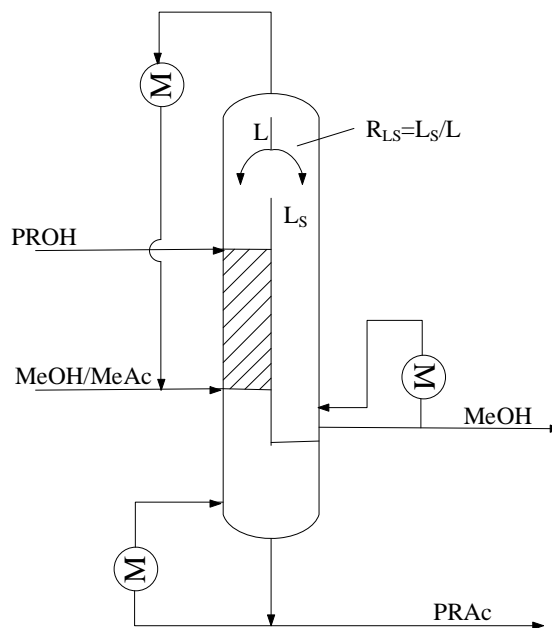


Figure 2: The diagram of reactive dividing-wall column.

Figure 3 shows the three-column model of the reactive dividing-wall distillation column. The model is thermally equivalent to the reactive dividing-wall distillation column. The gas phase extracted from top of C2 column was designed to provide a heat duty for the C1 column, a liquid phase was withdrawn in the the bottom of the public distillation column (C1 column) where methanol had a higher purity. Through the splitter, the liquid phase would be divided into two parts, one part of the liquid phase flows into the reaction distillation column (C2 column), and the other part of the liquid phase flows into the C3 column for purification. The steam from the top of the C3 column would enter to the C1 column, then methyl acetate and methanol in the C1 column would form azeotrope. The azeotrope extracted from the top of the C1 column would be reintroduced into the reaction zone to participate in the reaction. The liquid phase which flows into the C3 column

would provide condensation effect for the C3 column. Comparing with the original process, the new process saves equipment investment on a condenser.

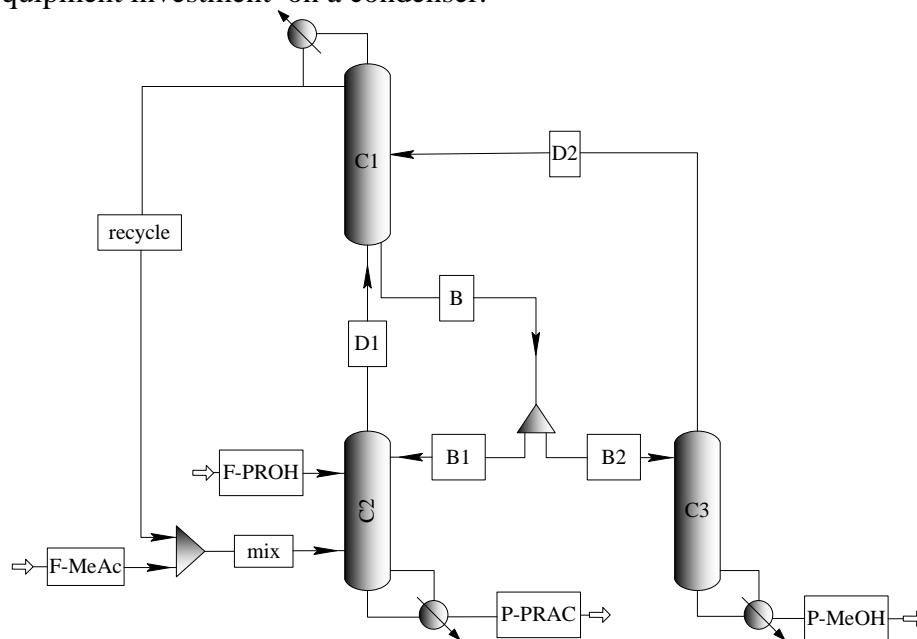


Figure 3: The three-column model of the reactive dividing-wall distillation column in Aspen Plus.

2.2 Reaction Kinetic Equation and Gas-Liquid Equilibrium

The esterification reaction of methyl acetate (MEAC) and n-propanol (PROH) is expressed in the general form :



The reaction rate is as followed:

$$r = k_+ \alpha_{\text{C}_3\text{H}_6\text{O}_2} \alpha_{\text{C}_3\text{H}_7\text{OH}} - k_- \alpha_{\text{C}_5\text{H}_{10}\text{O}_2} \alpha_{\text{CH}_3\text{OH}} \quad (1.2)$$

Where, k_+ , k_- are the reaction rate constants of positive and negative reactions, respectively. Pre-exponential factors of positive reaction of forward reaction k_+^0 , k_-^0 are $461.66 \pm 9.23 \text{ kmol} \cdot \text{s}^{-1} \cdot \text{kg}_{\text{cat}}^{-1}$, $74.97 \pm 1.5 \text{ kmol} \cdot \text{s}^{-1} \cdot \text{kg}_{\text{cat}}^{-1}$, respectively. Activation energy $E_{A,1}$, $E_{A,2}$ are $49.05 \pm 0.93 \text{ kJ} \cdot \text{mol}^{-1}$ and $42.66 \pm 0.81 \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

There are a variety of azeotropes in the reaction distillation system of producing n-propyl acetate at atmospheric pressure, such as methyl acetate-methanol azeotrope and propanol-n-propyl acetate azeotrope. When Aspen Plus was used to simulate the reaction distillation column, UNIQUAC, NRTL, and UNIFAC models and so on could be used to calculate the activity coefficient. The following table 1,2 show the content and temperature of methyl acetate-methanol azeotrope and propanol-n-propyl acetate in NRTL model and UNIQUAC model. As shown in figure 4a,4b the difference between the azeotrope content and temperature is very small in NRTL model and UNIQUAC model (error within 3%). Therefore, NRTL model and UNIQUAC model both could be used to calculate the activity coefficient. Because the NRTL model is more likely to converge in Aspen Plus simulations, NRTL model was used to calculate the activity coefficient in this paper. There are many azeotropes in the system, so it is a typical non-ideal system. In this system, the liquid phase concentration could be replaced by activity.

Table 1: The boiling point and composition of each component and azeotrope of reaction system (UNIQUAC).

component	boiling point (K)	content
MEAC	330.20	1.00
MEOH	337.68	1.00
PROH	370.35	1.00
PRAC	374.59	1.00
MEAC-MEOH	326.52	0.6644-0.3356
PROH-PRAC	367.9	0.6333-0.3667

Table 2: The boiling point and composition of each component and azeotrope of the reaction system (NRTL).

component	boiling point (K)	content
MEAC	330.15	1.00
MEOH	337.71	1.00
PROH	370.32	1.00
PRAC	374.62	1.00
MEAC-MEOH	326.55	0.6644-0.3356
PROH-PRAC	367.93	0.6333-0.3667

3 Simulation Results and Analysis

There are many variables in the reactive dividing-wall distillation column, and the variables are interrelated and interacted with each other. In order to simplify the simulation process and facilitate comparison, the structural parameters of the reactive dividing-wall distillation column are basically the same as those of the conventional reactive distillation column. By adjusting the operating parameters, such as heat duty of reboiler of the C2 column and C3 column, the feed position of PROH and MEAC, reflux ratio and the liquid distribution ratio, the requirements of the quality of products could be met, then further achieve the reduction of equipment investment and energy consumption.

3.1 The Effect of Feed Position of PROH and MEAC on Purity of PRAC

According to the original document of the feed position, the values of the feed position for PROH and MEAC are set at the 34th plate and the 74th plate in the C2 column, respectively. Those two values were used to act the initial values to find the optimum feed position. In the case of ensuring other conditions unchanged, the purity of PRAC at the bottom of the column was difficult to achieve the desired value. When the number of reaction plates were too small, the reaction can not be sufficiently performed. By increasing the number of theoretical plates of the reaction section, the high purity of the product can be achieved. However, the total heat duty of reboiler would also increase. The effect of the feed position of MEAC and PROH on the purity of the PRAC at the

bottle of column was showed in the figure4,5. Therefore, it is preferable to design the reaction section as at the 28th to 77th theoretical plates.

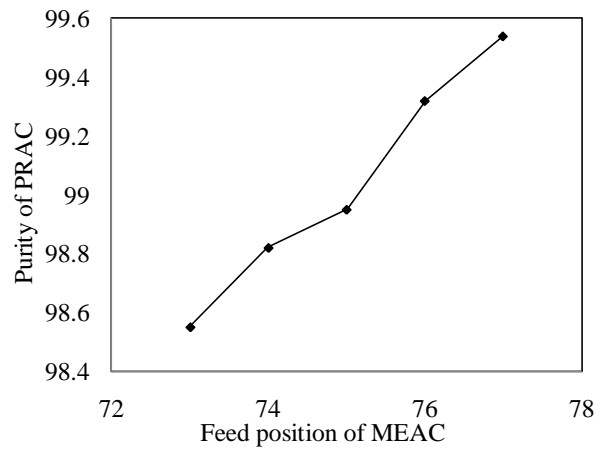


Figure 4: The feed position of MEAC and the purity of PRAC.

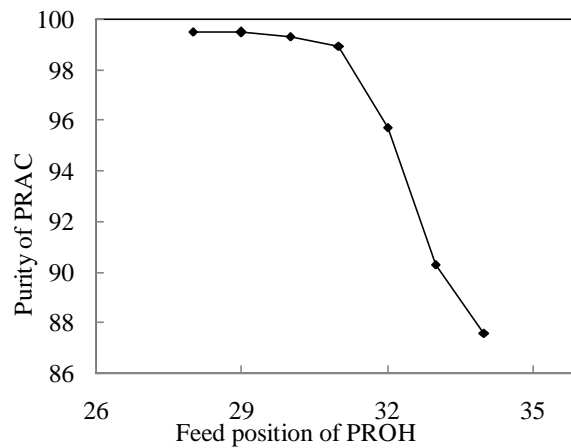


Figure 5: The feed position of PROH and the purity of PRAC.

3.2 The Effect of Reflux Ratio on the Heat Duty of Reboiler

The effect of reflux ratio on the heat duty of reboiler is shown in Fig.6. The temperature of the bottom of the column increased as the reflux ratio increasing, thereby the purity of n-propyl acetate would also increasing. But, when the reflux ratio increases to a certain value, the purity of the product of n-propyl acetate would not change significantly. So the optimum reflux ratio is 6.5.

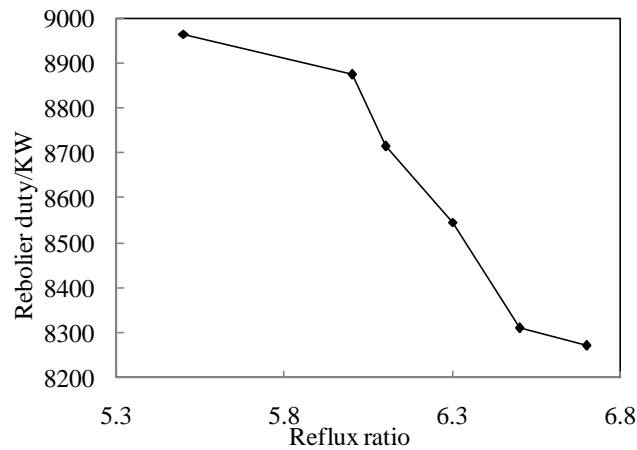


Figure 6: Reflux ratio and reboiler heat duty.

3.3 The Effect of Liquid Phase Distribution Ratio on the Heat Duty of Reboiler

Define the liquid phase distribution ratio: the ratio of the liquid phase molar flow to the C2 column and the total liquid phase flow at the bottom of the C1 column. On the basis of ensuring product purity, change the liquid phase distribution ratio of the reactive distillation dividing wall column, and observe the response of the heat duty of the reboiler. The results are shown in Fig.7. It can be seen that with the increase of liquid phase distribution ratio, the heat duty of the reboiler increased significantly. After increasing the liquid phase distribution ratio, the liquid flowing into the C2 column is increased. In order to ensure the purity of the n-propyl acetate at the bottom of the column satisfies the industrial requirement, the heat duty of the reboiler below C2 column and the heat duty of reboiler below C3 column both need to be increased. Therefore, it is important to choose a suitable liquid phase distribution ratio. Considering the requirements of product purity and energy consumption, the reasonable liquid distribution ratio is 0.545.

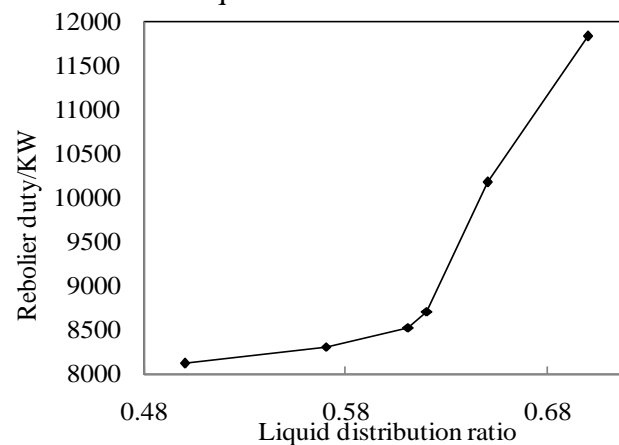


Figure 7: Liquid phase distribution ratio and reboiler heat duty.

4 Conclusions

In this paper, Aspen Plus software is used to simulate the process of producing n-propyl acetate and methanol. The new process uses a reactive dividing-wall distillation technology. When the purity of product of n-propyl acetate at the bottom of the C2 column meet the product requirements, the plate number of C1 column, C2 column and C3 column are 6, 88, 25, respectively. The feed position of PROH and MEAC are the 28th to 77th theoretical plates of the C2 column. Reflux ratio

and liquid phase distribution ratio are investigated to set as 6.5 and 0.545. Comparing to the conventional reactive distillation column, the reactive dividing-wall distillation column can not only reduce the equipment occupancy space but also save a condenser's equipment investment in the structure of the column.

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