Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 79 (2015) 778 – 783

Energy Procedia

2015 International Conference on Alternative Energy in Developing Countries and Emerging Economies

The Effect of Feed Location of a Semi-Batch Reactive Distillation via Esterification Reaction of Acetic Acid and Methanol: Simulation Study

Suputtharagris Akkaravathasinp[a,b], Phavanee Narataruksa[a,b], Chaiwat Prapainainar[a*,b]

[a]*Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok*
[b]*Research and Development Center for Chemical Unit Operation and Catalyst Design, Science and Technology Research Institute, King Mongkut's University of Technology North Bangkok, 1518 Pracharat 1 Rd., Wongsawang, Bangsue, Bangkok 10800, Thailand*

Abstract

This paper studied the effect of feed location of semi-batch reactive distillation via esterification reaction of acetic acid and methanol producing methyl acetate using Aspen Batch Distillation model. The reactive distillation model used was developed following a design of an in-house made reactive distillation column, which comprised of seven stages: five possible feed stages, where solid catalyst for the reaction was contained, a reboiler and a condenser. The main objectives of this semi-batch reactive distillation operation were to obtain a high yield of methyl acetate product with 95wt% purity. In the operation, methanol was charged to the reboiler and acetic acid was fed to the column continuously at five different feed stages. From the simulation results, it showed that the feed location of acetic acid affecting on the yield and the purity of the main product at the top stage of the column. It was found that the optimum feed stage of acetic acid was at stage four giving the maximum yield and purity of methyl acetate at 74.74% by mole and 97.36wt%, respectively.

Peer-review under responsibility of the Organizing Committee of 2015 AEDCEE

Keywords: Reactive distillation; esterification; aspen batch distillation; simulation

* Corresponding author. Tel.: +66-2555-2000 ext. 8230; fax: +66-2587-0024.
E-mail address: chaiwat.r@eng.kmutnb.ac.th.

Peer-review under responsibility of the Organizing Committee of 2015 AEDCEE
doi:10.1016/j.egypro.2015.11.566

1. Introduction

A reactive distillation column (RD column) is a combination of reactor and distillation column in a single unit. This unit operation can be operated with two processes occurring at the same time, which are reaction and separation. A reactive distillation column comprises of reactive zone, normally at stripping and/or rectifying zone compared to a conventional distillation column. There are advantages of RD column compared to a conventional distillation column: increasing conversion, improving process efficiency and product selectivity, reducing the capital investment costs, saving energy costs by the reduction of reboiler duties for exothermic reaction, and avoidance of azeotropic mixture [1]. Furthermore, when reactive distillation is operated in batch or semi-batch operation, the advantages of the combination of semi-batch process and reactive distillation is a flexible operation compared to the continuous one [2, 3], leading to selectivity improvement [3].

Reactive distillation is suitable for equilibrium-limited reactions, such as esterification reaction (Eq.1), which is the reaction of methanol with acetic acid to produce methyl acetate that can be used in a wide range of coating and ink resins [4].

$$CH_3COOH + CH_3OH \xrightarrow{k} CH_3COOCH_3 + H_2O \tag{1}$$

From this reaction, acetic acid is reacted with methanol to produce methyl acetate and water and the reaction is reversible. Therefore, conversion of the reaction is limited by the concentration of products. In order to control the reaction in forward direction, removal of methyl acetate and water from the system is important. Accordingly, separation process will play important role. Reactive distillation can be used in this reaction and separation process. In this case, products and reactants can be separated by distillation process according to theirs boiling points. In order to obtain optimal operating strategy of the RD, operating parameter of RD is required. In this study, effect of feed stage of reactant, acetic acid, is studied in semi-batch reactive distillation using process simulation in order to find an optimal feed stage of the reactant, where the operation give a high yield of methyl acetate with a short operating time and the highest purity.

2. Methodology

Semi-batch reactive distillation simulation model is created on Aspen Batch Distillation V7.3 software following a specification of an in-house made column at King Mongkut's University of Technology North Bangkok. The column comprises of seven stages, including reboiler, condenser and reactive zone. The column made from stainless steel 316 with the inside diameter and the height of 11.43cm and 90cm, respectively. In a simulation model, methanol is charged at the stage seven, reboiler, while acetic acid is fed continuously to the column at stage two to stage six according to the case study. Methyl acetate product is withdrawn from the system at the condenser. Three specifications are assigned to the model consisting of reactive distillation column specifications, the esterification reaction data and catalyst, and operation steps. The column configuration shows in Figure.1 is created and used for a simulation. NRTL-HOC is used as the thermodynamics property method for esterification reaction in the model.

2.1 Reactive distillation column specifications

The in-house made column specification information used as input data to the simulation model is listed as follow:

- The reboiler is 13.14cm in diameter and 50cm in height giving a reboiler volume of 7.37×10^{-3} m^3. Jacket heater is enclosed to supply heat with the height of 40cm from the bottom.

- Column diameter is 11.43cm with the height equivalent to theoretical plate of 15cm giving the total height of 90cm. The column is filled with raschig rings packing type with the outside diameter, inside diameter, and length of 15mm, 7mm, and 15mm, respectively. The void fraction of packing and specific surface are 0.698 and 264 $m^2 \cdot m^{-3}$, respectively.
- The condenser dimension is 11.43cm in diameter and 25.40cm in height. The condenser is total condenser type with cooling water having the inlet temperature of 293K.
- Column is operated at the ambient pressure.

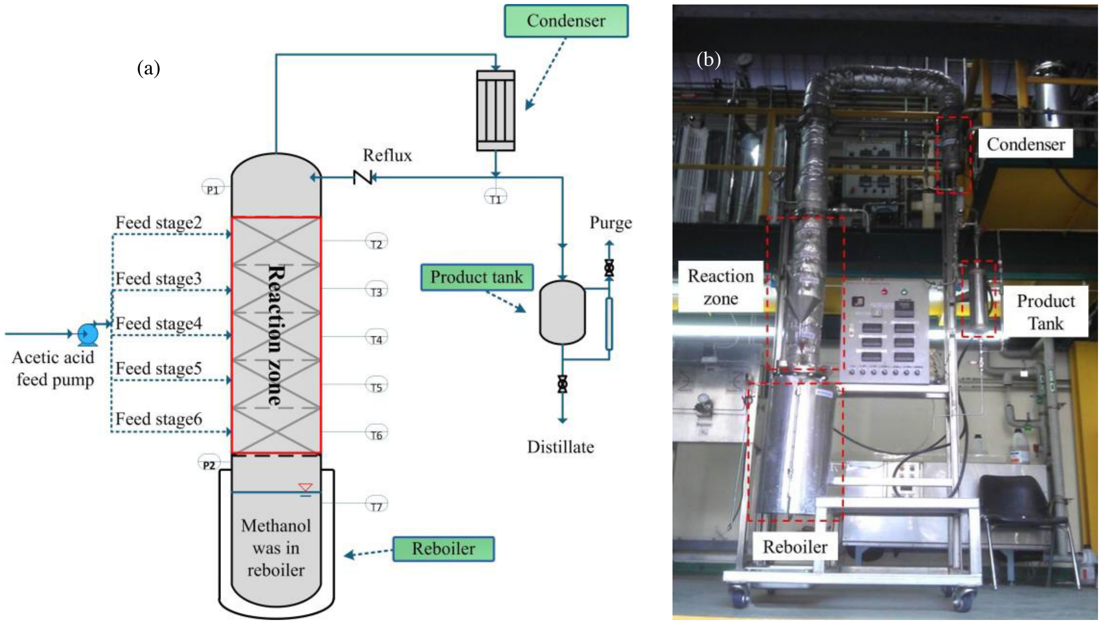

Fig.1. (a) The batch reactive distillation column model for esterification of acetic acid and methanol; (b) The in-house made reactive distillation column.

2.2 The esterification reaction data and catalyst

The catalyst used in the model column is Amberlyst36 and kinetics data of heterogeneous reaction of acetic acid with methanol used in the model is applied from Yu-Ting's report [5]. The assumption of the model is that the reverse reaction is neglected. The power law kinetics model is used to represent the reaction in Eq. (1) with *k* (kinetics factor) and *E* (activation energy) of 1.432×10^{11} $kmol \cdot m^{-3} \cdot s^{-1}$ and 5.188×10^4 $kJ \cdot kmol^{-1}$, respectively.

2.3 Operating steps

Acetic acid and methanol are fed with a 1:1 mole ratio according stoichiometry giving five litres of methanol charged at reboiler at the beginning of the operation and the total acetic acid approximately seven litres fed continuously at the rate of 115ml/min. The column is operated with the total reflux for 0.5hr, then distillate product is collected continuously from the top stage at product tank with a reflux rate of 200mole/hr. The semi-batch reactive distillation process simulation is terminated when the amount of methanol in the reboiler is lower than 1mol%.

In order to find the optimal feed stage with the given operating conditions, the output results with operating time from the model are collected and reported comprising of component mass fraction at all stages, yield in mole basis of methyl acetate, component mass fraction at the product tank.

3. Results and discussion

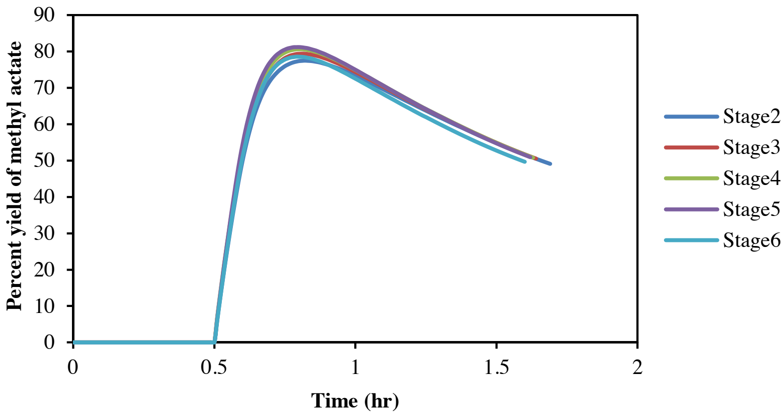

Fig. 2.The effect of feed location on percent yield of methyl acetate

Fig. 2 shows percentage yield of methyl acetate, defined as accumulative mole of methyl acetate at the product tank divided by accumulative total mole of acetic acid feed. It is found that the percent yield of methyl acetate is zero until 0.5 hour of operating time because it is operated in a total reflux mode. After that, the percent yield of methyl acetate is increased and reaches the maximum value at around 0.82 hour to 0.83 hour for every feed location. Then it is continuously decreased due to the decrease of methanol in system. It can be found that the feed location of acetic acid at stage four gives the maximum percent yield of 74.74% and at stage six, the yield is 71.43%. Table 1 shows operating time at the highest percent yield with component mass fraction at the product tank. It can be seen that at the feed location of stage four the highest purity of methyl acetate is achieved with 97.36wt%.

Table 1. The results of semi-batch reactive distillation at different acetic acid feed location.

Feed stage of acetic acid	Percent yield of methyl acetate	Operating time (hr)	Mass fraction at the product tank			
			Acetic acid	Methyl acetate	Methanol	Water
Stage2	72.39	0.83	0.0445	0.9369	0.0000	0.0186
Stage3	74.40	0.82	0.0091	0.9690	0.0000	0.0219
Stage4	74.74	0.82	0.0007	0.9736	0.0000	0.0257
Stage5	74.28	0.82	0.0000	0.9704	0.0001	0.0294
Stage6	71.43	0.82	0.0000	0.9531	0.0194	0.0276

Fig. 3 shows the effect of feed location of acetic acid on mass fraction profile through the column at the operating time when the highest percent yield is achieved. Fig.3 (a) shows the mass fraction profile of acetic acid and it can be seen that when the feed location of acetic acid in the column is changed from the top stage (stage2) to the bottom stage (stage6), the fraction of acetic acid above the feed location is lower due to the fact that it is a high density component compared to other components in the system and under the given operating condition, acetic acid is in the liquid phase and it flows downward along the column.

Fig.3 (b) and fig.3 (c) show the mass fraction profile of methanol and water. Feed location has insignificant effect on methanol and water fraction profile in the system. It can be seen that amount of methanol appears only at the bottom stage (reboiler) as there is some unreacted methanol remains in the system. As for water, from the graph, there is no noticeable change of mass fraction with the change of feed location. However, when the feed location is nearer to the bottom stage (stage6), mass fraction of water at above the feed stage significantly increases, which affect the purity of methyl acetate as can be seen from fig.3 (d). In fig. 3 (d), the change of feed location of acetic acid has significant effect on mass fraction profile in the column. It can be seen that the fraction of methyl acetate above the feed location is higher than that of below feed location.

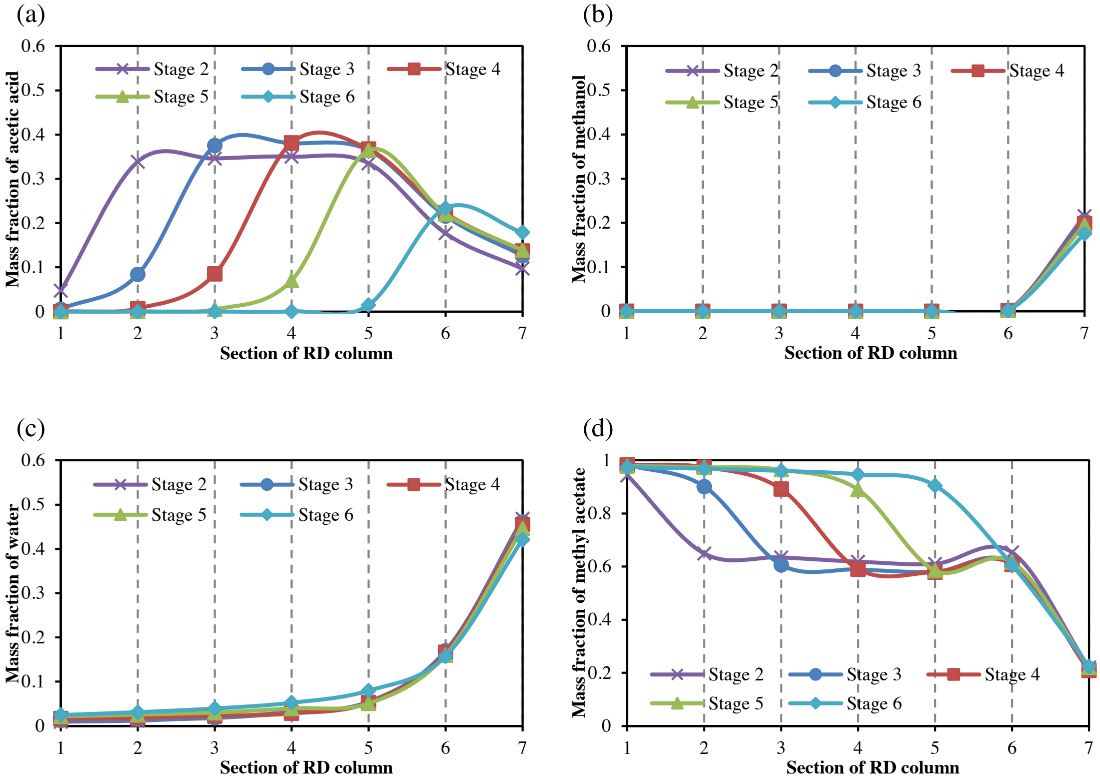

Fig.3.The liquid mass fraction profile when feed acetic acid at different locations
(a) acetic acid; (b) methanol; (c) water; (d) Methyl acetate

Additional results of material balance are presented in table 2, when the feed location is at stage4, at the operating time of 0.82hour, the operation gives the highest percent yield. It can be seen that total amount of acetic acid feed is 6.09 kg reacted with 3.96 kg of methanol. The total amount of liquid product at the product tank is 5.77 kg: 5.62 kg of methyl acetate and 0.15 kg of water.

From the simulation results, it can be concluded that the optimal feed location of methyl acetate with the given operating parameters is stage4 as feeding at this location gives the highest percent yield of 74.74% and the highest purity of 97.36 wt%.

Table 2. The material balance of component for reactive distillation simulation by using feed stage of acetic acid at stage four.

Component	Inlet		Outlet	
	Mole (mole)	Mass (kg)	Mole (mole)	Mass (kg)
Acetic acid	101.46	6.09	0.07	0.00
Methanol	123.73	3.96	0.00	0.00
Methyl acetate	0.00	0.00	75.84	5.62
Water	0.00	0.00	8.25	0.15

4. Conclusion

In this work, the effect of feed location of acetic acid for esterification reaction is studied in a semi-batch reactive distillation using process simulation model. Feed location has significant effect on the purity of methyl acetate. The optimal feed stage of RD column is stage4 under the operating condition of 393 K of reboiler medium temperature and reflux rate at 200mole/hr. At the optimal feed stage, the highest purity of methyl acetate is 97.04 wt%.

Acknowledgements

The author would like acknowledge the Graduate College, KMUTNB for the financial support.

References

[1] A.R.M.a.S.B. Muhamad Nazri Murat, Modeling of reactive distillation column:Methyl tertiary butyl ether(MTBE), IIUM Engineering Journal, 4 (2003) 17.
[2] G. Fernholz, W. Wei, S. Engell, K. Fougner, J.P. Bredehoft, Operation and control of a semibatch reactive distillation column, in: Control Applications, 1999. Proceedings of the 1999 IEEE International Conference on, 1999, pp. 397-402 vol. 391.
[3] W. Qi, M.F. Malone, Operating Parameters and Selectivity in Batch Reactive Distillation, Industrial & Engineering Chemistry Research, 49 (2010) 11547-11556.
[4] Eastman™ Methyl Acetate, in, Eastman Chemical Company.
[5] Y.-T. Tsai, H.-m. Lin, M.-J. Lee, Kinetics behavior of esterification of acetic acid with methanol over Amberlyst 36, Chemical Engineering Journal, 171 (2011) 1367-1372.