Research Article

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Optimization of Semi-batch Reactive Distillation Using Response Surface Method: Case Study of Esterification of Acetic Acid with Methanol in a Process Simulation

Suputtharagris Akkaravathasinp, Phavanee Narataruksa and Chaiwat Prapainainar*
Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand
Research and Development Center for Chemical Unit Operation and Catalyst Design, Science and Technology Research Institute, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand

* Corresponding author. E-mail: chaiwat.r@eng.kmutnb.ac.th DOI: 10.14416/j.ijast.2018.11.001
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Abstract
An optimization method was applied to determine optimal operating parameters on Reactive Distillation column (RD column) via esterification of acetic acid with methanol to produce methyl acetate using Aspen Batch Distillation. The set-up reactive distillation model was adopted from an in-house made RD column, which comprised of seven stages including reboiler and condenser, five possible feed stages, where solid catalyst for the reaction was contained. In this work, effect of temperature of heater at reboiler, feed stage and reflux rate on yield of methyl acetate and purity of total distillated product were studied. Case studies were designed by design of experiment and consequently simulation results were optimized by using Response Surface Methodology (RSM) to determine optimal condition. The results indicated that the optimum temperature of heater at reboiler, feed stage and reflux rate were 141.87°C, Stage4 and 332.48 mol·h^{-1}, respectively, giving maximum yield and purity of methyl acetate at 57.50 mol% and 80.46 wt%, respectively.

Keywords: Reactive distillation, Esterification, Aspen batch distillation, Response surface method

1 Introduction

RD column is a combination of reactor and distillation column in one unit, where phase separation and chemical reaction occur at the same time. There are advantages of RD column compared to conventional processes, for example, capital investment and operating costs can be reduced [1], [2], improvement of process efficiency and selectivity, avoidance of azeotropic mixture [3]. RD is, especially, suitable for reversible reaction, in which chemical equilibrium constraint limits conversion [4]. Conversion can be increased by removing product from the system by separation at the same time. In this work, esterification reaction of acetic acid with methanol are of interest for an operation in an RD column. This reaction is equilibrium-limited reaction, which is reaction of acetic acid with methanol to produce main product of methyl acetate that can be used in a wide range of coating and ink resins [5]. The esterification reaction used in this study can be shown in Equation (1).

$$CH_3COOH+CH_3OH \xleftrightarrow{k} CH_3COOCH_3+H_2O \qquad (1)$$

Operating parameters plays an important role in the performance of RD column as shown by Sert and Atalay [6] works in their case study of determining operating conditions of esterification of acetic acid with butanol in a packed bed reactive distillation column. The operating conditions, such as total feed flow rate,

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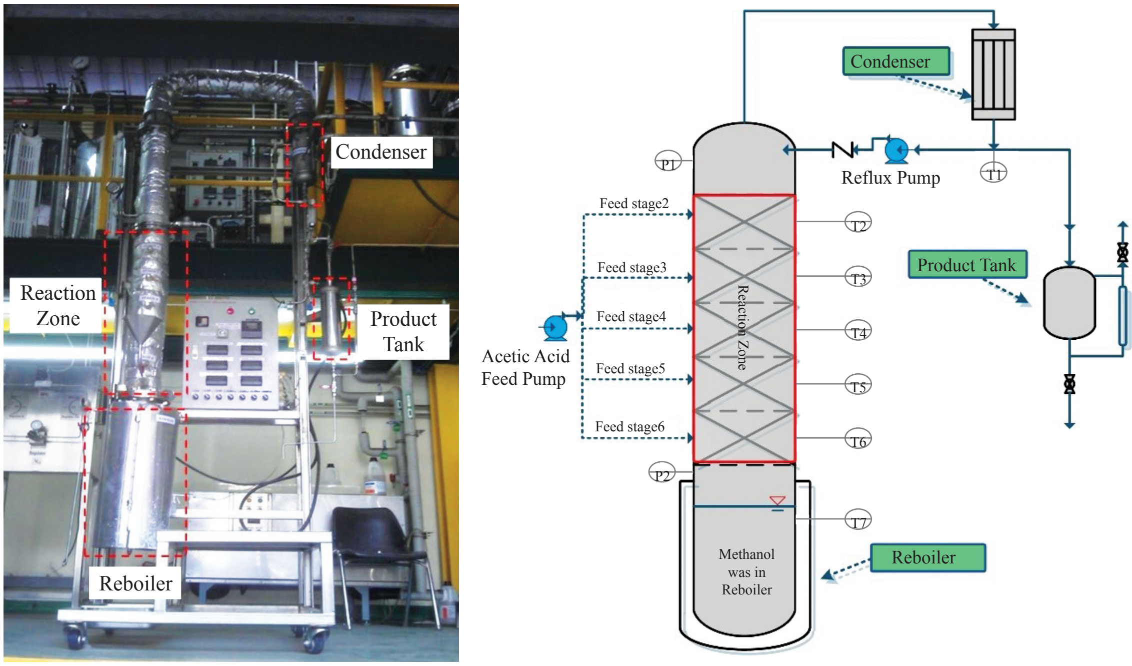

Figure 1: (a) The in-house made reactive distillation column, (b) Batch reactive distillation column model for esterification of acetic acid and methanol.

molar ratio of reactant, amount of catalyst and reboiler temperature were realized experimentally to provide high purity butyl acetate. The optimum values of these parameters obtained were 1.6 mol·h^{-1}, 1, 25 g and 383 K, respectively. The maximum purity of butyl acetate and conversion of acetic acid at 82 and 80.5% at the optimum operating conditions. For the system of removing acetic acid from water by esterification with methanol in the RD column [7], effects of reflux ratio, feed stage location, column pressure, catalyst loading and distillate rate were studied on a process simulation to provide the maximum acetic acid conversion. They obtained optimized operating conditions as follows: reflux ratio of 14, feed location at stage7, and distillate rate of 240 kg·s^{-1}, the reasonable column pressure of 0.935×10^5 Pa, and catalyst loading of 0.27 kg, giving maximum conversion of acetic acid of 64.9%.

In this study, effect of operating parameters: temperature of heater at reboiler, feed stage and reflux rate were studied in a semi-batch reactive distillation using process simulation to find optimal operating parameters, where the operation gave the highest yield and purity of methyl acetate and no water and acetic acid in distillated product. The optimization was using RSM as a tool to determine optimal operating parameters.

2 Methodology

The semi-batch reactive distillation model was 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 made from stainless steel 316, comprises of seven stages: reboiler, condenser and five stages of reactive zone. The column configuration can be shown in Figure 1(a) and the details of specifications can be shown in the previous work [8].

2.1 *Modelling*

In a simulation model, methanol was charged at stage-seven, reboiler, while acetic acid was fed continuously to the column at a designed feed stage. Esterification reaction occurred in the reaction zone between stage2 to stage6.

Methyl acetate product was withdrawn from the system at the condenser. The model configuration can be shown in Figure 1(b). The NRTL-HOC is used as thermodynamics property method because of dimerization of acetic acid.

Esterification reaction data used in the model column was applied from Yu-Ting's report [9]. Assumption of the model was that reverse reaction was neglected. The power law kinetics model was used to represent reaction in Equation (1) with k (kinetics factor) and E (activation energy) of 2.2912×10^8 $kmol\cdot m^{-3}\cdot s^{-1}$ and 5.188×10^4 $kJ\cdot kmol^{-1}$, respectively.

2.2 *Simulation procedure*

Acetic acid and methanol were fed with 1:1 mole ratio according stoichiometry giving four liters of methanol charged at reboiler and it was heated up by the heater at the reboiler, which was controlled between 135°C and 155°C. The column was operated with total reflux until the system approached steady state. Then total acetic acid approximately 5.6 liters was fed continuously to the column at stage2 to stage6 at a rate of 139 mL/min, while distillate was collected continuously from the top stage at the product tank and the reflux rate was kept at a rate between 300 and 500 mol/h.

The full factorial design was applied for studying effect of operating parameters consisting of temperature of heater at reboiler, feed stage of acetic acid and reflux rate by varying in five level for each parameter as shown in Table 1. Consequently, there were 125 simulation cases. In the process simulation, a semi-batch reactive distillation was terminated when amount of distillated product in the product tank was steady. Simulation results, yield of methyl acetate and purity of distillated product in product tank were collected. Subsequently, they were used as input data for optimization using statistical software, Design Expert version 7.0.

Table 1: The full factorial design table for effect of the operating parameters study

Parameters	Level				
	–2	–1	0	1	2
A: Reflux rate ($moles\cdot hour^{-1}$)	300	350	400	450	500
B: Feed stage of acetic acid	Stage2	Stage3	Stage4	Stage5	Stage6
C: Temperature of heater at reboiler (°C)	135	140	145	150	155

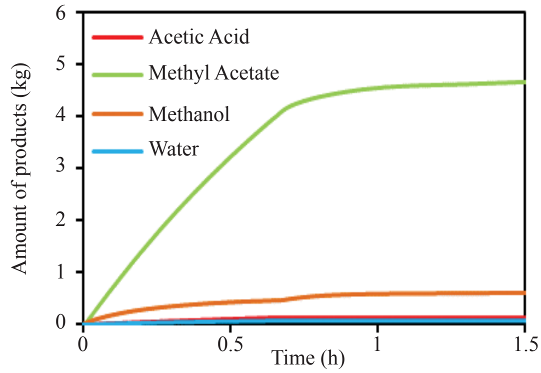

Figure 2: Amount of each component in product tank.

2.3 *Optimization*

RSM was used to demonstrate the effect and interaction of the variables and determine the optimal operating parameters [10] by optimizing five responses; yield in mole basis of methyl acetate and four components mass fraction at the product tank. The objectives were to get the highest yield and purity of methyl acetate but no water or acetic acid in the distillated product.

3 Results and Discussion

Results from the simulation models in all cases have similar trend. An example of the results with the column operated with the temperature of heater at reboiler of 135°C, feed stage of acetic acid at stage2 and reflux rate of 300 mol/h can be shown in Figures 2 and 3.

From Figure 2, it can be seen that the amount of methyl acetate in product tank was rapidly increased and approached steady state at around one hour of operation due to the decrease of reactant in the system.

Figure 3, showing mass fraction in product tank, can confirm that the operation gave high purity of methyl acetate at the operating time of one hour. Accordingly, the operating time of one hour was used for comparing the result for every case study in this work. The results of 125 simulation cases by using one hour of operating time were collected and statistical software, Design Expert version 7.0, was used as a tool for RSM method for optimizing the responses to determine optimal operating parameters.

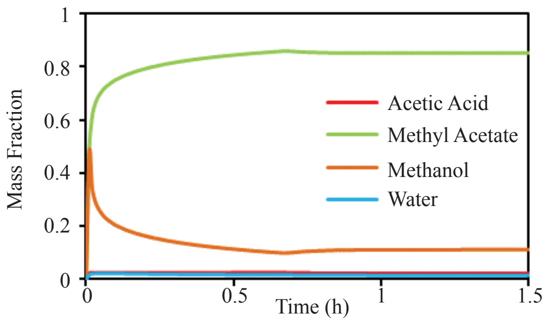

Figure 3: Mass fraction of products in product tank.

3.1 *The RSM results*

The effect of three independent variables; reflux rate (A), feed stage of acetic acid (B), and Temperature of heater at reboiler (C) on five dependent variables; mass fraction of acetic acid (R1), mass fraction of methyl acetate (R2), mass fraction of methanol (R3), mass fraction of water (R4) and yield of methyl acetate (R5) were studied. The analysis of variance (ANOVA) was used to evaluate empirical relationship between the independent variables and responses and it was expressed in form of a polynomial equations.

An example of the summary of ANOVA of R1 can be shown Table 2. The associated probability value (*p*-value) from the model was lower than 0.05 (α = 0.05 or 95% confidence) exhibiting the significance of model. In this case, A, B, C, interaction effect of AB, AC, A^2 (quadratic effect) and cubic effect of A^2B, A^2C are significant terms on response of mass fraction of acetic acid.

Table 3 shows a summary of all models including type of polynomial equation for each response, the value of regression coefficient (R^2), predicted R^2, and adjusted R^2. The high value of R^2 indicates a good fit of the model, high value of predicted R^2 is an indication of precision of fitted model, high value of adjusted R^2 indicates the high significance of the model [11]. The 3D response surfaces were plotted from these equations for optimizing the responses.

3.2 *The optimization results*

Optimization of responses were performed together to achieve the desired response and the 3D response surfaces of the optimal operating parameters can be shown in Figure 4. The optimum temperature of heater at reboiler, feed stage and reflux rate are 141.87°C, Stage4 and 332.48 mol·h^{-1}, respectively, giving the maximum yield and purity of methyl acetate at 57.50 mol% and 80.46 wt%, respectively.

Table 2: Summary of ANOVA for response R1: cubic model

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	P value prob > F
Model	2.20×10^{-1}	17	1.3×10^{-2}	2116.78	< 0.0001
A-Reflux rate	3.64×10^{-3}	1	3.64×10^{-3}	582.72	< 0.0001
B-Feed stage of acetic acid	2.10×10^{-1}	4	5.4×10^{-2}	8587.44	< 0.0001
C-Temperature of heater at reboiler	1.04×10^{-4}	1	1.04×10^{-4}	16.61	< 0.0001
AB	6.00×10^{-3}	4	1.50×10^{-3}	240.18	< 0.0001
AC	1.30×10^{-4}	1	1.30×10^{-4}	20.83	< 0.0001
A^2	2.21×10^{-4}	1	2.21×10^{-4}	35.42	< 0.0001
A^2B	9.35×10^{-5}	4	2.34×10^{-5}	3.74	0.0069
A^2C	2.66×10^{-5}	1	2.66×10^{-5}	4.26	0.0414
Residual	6.69×10^{-4}	107	6.25×10^{-6}		

Table 3: Summary of the models

Responses	Model	Std. Dev.	R-Squared	Predicted R-Squared	Adjusted R-Squared
R1	Cubic	0.0025	0.9975	0.9930	0.9965
R2	Cubic	0.0060	0.9935	0.9805	0.9912
R3	Cubic	0.0044	0.9969	0.9909	0.9958
R4	2FI	0.1113	0.9269	0.8850	0.9168
R5	Cubic	0.0107	0.9950	0.9891	0.9932

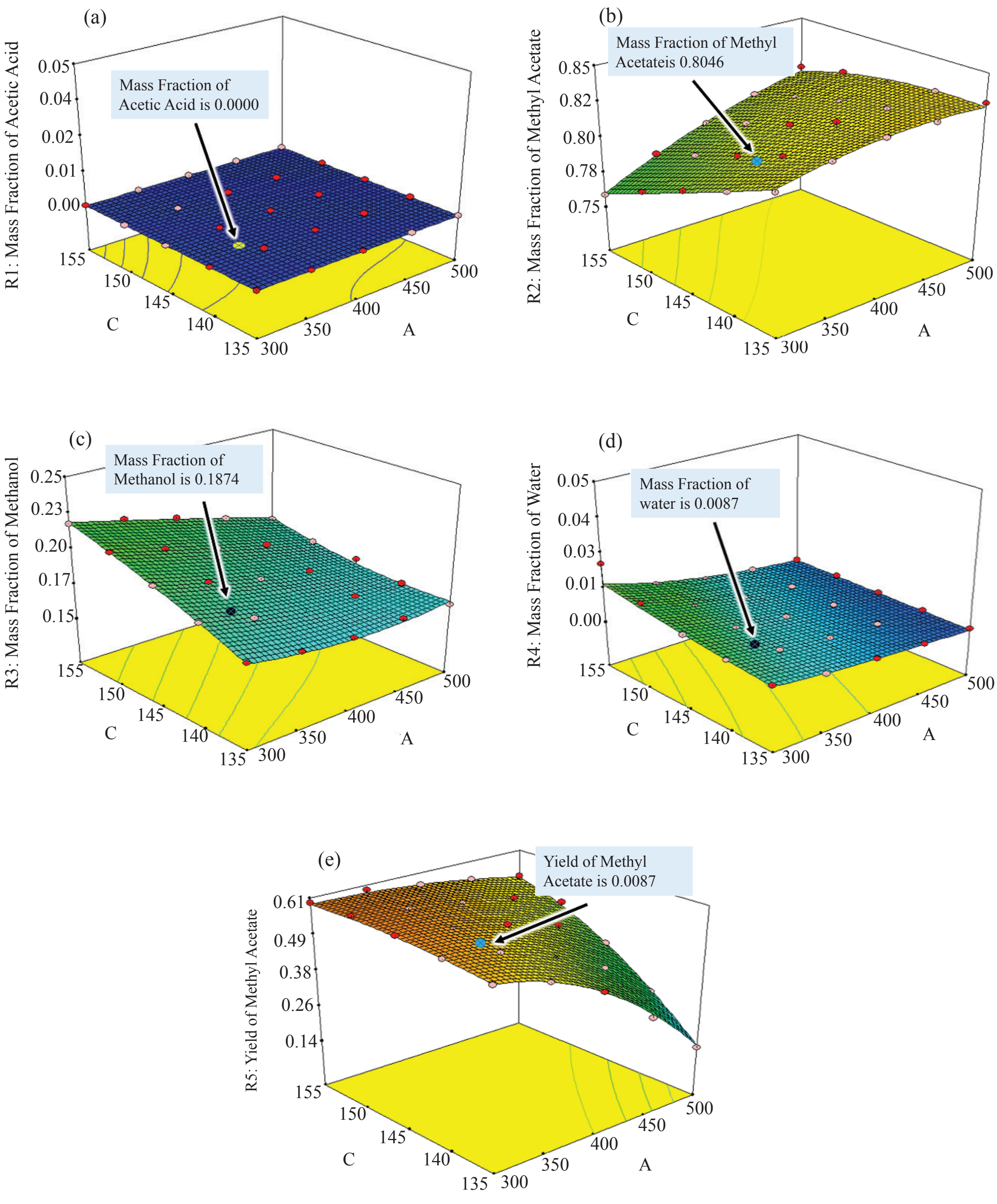

Figure 4: Response surface plot represent effect of temperature of heater at reboiler and reflux rate on the responses: (a) Mass fraction of acetic acid, (b) Mass fraction of methyl acetate, (c) Mass fraction of methanol, (d) mass fraction of water, (e) yield of methyl acetate, respectively by using feed stage of acetic acid at Stage4.

The 3D response surface plots can be used to explain the effect of the independent variables on the responses. Figure 4(a) shows the effect of temperature of heater at reboiler and reflux rate on mass fraction of acetic acid at product tank by using feed stage of acetic acid at stage4, indicating that temperature of heater at reboiler and reflux rate has no effect on mass fraction of acetic acid at the product tank.

Feed stage of acetic acid has important effect on mass fraction of acetic acid and water. When feed stage was changed from the top stage (stage2) to the bottom stage (stage6), mass fraction of acetic acid was dropped to near zero. On the contrary, when feed stage was changed from the bottom stage (stage6) to the top stage (stage2), mass fraction of water was decreased, these results can be confirmed with the previous work [8].

Reflux rate has significant effect on mass fraction of methyl acetate and yield of methyl acetate. Figure 4(b) indicates that reflux rate has positive effect on methyl acetate, as purity of methyl acetate increases when reflux rate increases, but it has negative effect on yield of methyl acetate as shown in Figure 4(e). This is because when the reflux rate increase, the product obtained at product tank is decreased. Moreover, when the reflux rate increases, methyl acetate as main product in system is also increased, resulting in compositions in the column and reboiler limiting forward reaction.

Temperature of heater at reboiler has significant effect on purity of methyl acetate as shown in Figure 4(b) and (c) revealing that temperature of the heater at reboiler has negative effect on mass fraction of methyl acetate, as purity of methyl acetate decrease when temperature of the heater increases due to increasing of methanol in the product tank.

4 Conclusions

The operating parameters of semi-batch reactive distillation via esterification of acetic acid and methanol: temperature of heater at reboiler, feed stage and reflux rate, were studied by using process simulation model. There is more complex interaction between parameters, whereby RSM was utilized to analyze the responses of interaction, and thus obtain the optimal operating parameters. The results showed that the optimal conditions were obtained at 141.87°C, Stage4 and 332.48 ($mol{\cdot}h^{-1}$), respectively.

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