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Research Article

Dynamic Simulation of a Reactive Distillation Column for Ethyl Acetate Production: Optimization of Operating Conditions Using Response Surface Methodology

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Abstract: In this study, we aimed to determine the optimum operating conditions for the production of ethyl acetate (EtAc) through the esterification of ethanol (EtOH) with acetic acid (HAc) in a reactive distillation (RD) column. For this, the designed column was simulated for the production of EtAc. HAc flow rate, EtOH flow rate, HAc feed stage, EtOH feed stage, reflux ratio, and reactive feed temperatures were changed and the effects of these parameters on EtAc production were observed. Central Composite Design was employed to define the optimum operating conditions for the RD column. The determination coefficient R^2 was equal to 0.9197 suggesting a good relationship between the predicted and simulated responses. Adjusted R^2 and predicted R^2 values obtained from the program were 0.8823 and 0.7956, respectively. The optimal conditions for the EtAc production response were HAc flow rate of 120.00 kmol/h, EtOH flow rate of 150.00 kmol/h, HAc feed stage 6, EtOH feed stage 14, reflux ratio 2.2, and feed temperature 70.28 °C, which were designated by the maximum desirability function.

Etil Asetat Üretimi için Bir Reaktif Distilasyon Kolonunun Dinamik Simülasyonu: Cevap Yüzey Yöntemi ile İşletme Koşullarının Optimizasyonu

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Anahtar Kelimeler
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Yanıt yüzey yöntemi

Öz: Bu çalışmada, etanolün (EtOH) asetik asit (HAc) ile reaktif distilasyon (RD) kolonunda, esterleştirilmesi yoluyla etil asetat (EtAc) üretimi için optimum çalışma koşullarının belirlenmesi amaçlanmıştır. Bunun için tasarlanan kolonun EtAc üretimi için simüle edilmiştir. HAc akış hızı, EtOH akış hızı, HAc besleme aşaması, EtOH besleme aşaması, geri akış oranı ve reaktif besleme sıcaklıkları değiştirilmiş ve bu parametrelerin EtAc üretimi üzerindeki etkileri gözlemlenmiştir. RD kolonu için optimum çalışma koşullarını tanımlamak için Merkezi Kompozit Tasarım kullanılmıştır. Regresyon katsayısı R^2, 0.9197'ye eşittir ve bu, tahmin edilen ve simüle edilen yanıtlar arasında iyi bir ilişki olduğunu göstermiştir. Programdan elde edilen düzeltilmiş ve tahmin edilen R^2 değerleri sırasıyla 0.8823 ve 0.7956'dır. EtAc üretim yanıtı için optimal koşullar, 120.00 kmol/saat HAc akış hızı, 150.00 kmol/saat EtOH akış hızı, HAc besleme aşaması 6, EtOH besleme aşaması 14, geri akış oranı 2.2 ve reaktif besleme sıcaklığı 70.28 °C olarak maksimum istenilirlik fonksiyonu ile belirlenmiştir.

1. Introduction

Distillation is a widely used method for chemical separation processes and distillation columns consume about 3% of the entire energy around the world and up to 80% of the energy in chemical processes (Bumbac et al., 2009; Diggelen et al., 2010; Nguyen & Demirel, 2011). One of the foci in the separation of distillation columns is to decrease energy consumption in chemical plants. An efficient method for the reduction of energy consumption in distillation consists of process intensification (PI), combining other operations in one piece of equipment (Li et al., 2019; Masuku & Biegler, 2019). Reactive distillation (RD) units combine the reactor and distillation column in a single unit, where separation and reactions occur at the same time. RDs are common examples in the PI field (Ciric & Gu, 1994; Cardoso et al., 2000; Cheng et al., 2009; Huang et al., 2017). In all cases, once RD is employed, a reduction of 20% or more is obtained in the various process requirements including cost, capital expenditure, and energy in comparison to the plant set-up of a reactor followed by distillation. Therefore, many academic and commercial studies have been performed to utilize the benefits of RD (Segovia-Hernandez et al., 2015; Carrera-Rodriguez et al., 2014; Georgiadis et al., 2002; Petchsoongsakul et al., 2017). RD applications are used in many different chemical processes such as esterification which is an exothermic and equilibrium-limited reaction, regulated by chemical equilibrium in the presence of water as a by-product (Aqar et al., 2017; Zhang et al., 2019). In a RD process, the reactor is also a separator. The combination of these two important units to enhance process performance is considered to be an important subject in chemical plants. No separate distillation step is required for separating the product from the reaction mixture; thus, resulting in energy (for heating) and material savings (Taylor & Krishna, 2000; Luyben & Yu, 2009). This separation process provides unique advantages, especially for equilibrium-limited reactions. In this context, RD has arisen as a robust candidate for disproportionate reactions due to the elimination of the conversion and phase limitations (Jie et al., 2016). Since the products are continually removed from the medium, the conversion can exceed the regular one that is governed by equilibrium (Sundmacher & Kienle, 2002; Harvianto et al., 2017).

Research is in progress about various aspects of the RD design, a relatively new field, such as modeling, simulation, column construction, dynamics, and control applications (Zhang et al., 2017). The design and evaluation of the RD column aim especially on the identification and optimization parameters of the separation system to increase its efficiency. It is possible to use optimization strategies reliably for overcoming this related design problem in engineering. Optimization is important particularly for modeling, design, operation of chemical processes (Rangaiah & Bonilla-Petriciolet., 2013). Response Surface Methodology (RSM) is a widely-used statistical approach for the reduction of the research workload and provides a model more appropriate for optimizing the preparation technology than the conventional variable control approaches (Candioti et al., 2014). Accordingly, the RSM method has been widely utilized in various chemical engineering procedures such as separation processes. However, there have been a few studies concerning the optimization of the operation parameters of the RD column (Komesu et al., 2015; Feyzi & Behesti, 2017; Kaewwisetkul et al., 2017).

Ethyl acetate (EtAc) is a valuable industrial product mainly employed as a solvent and there are several methods for its production. EtAc is mainly produced through some methods such as acetylation of ethylene, esterification of acetic acid and ethanol, and dehydrogenation of ethanol (Santaella et al., 2015). In this study, we determined the optimum operating conditions for the reaction of ethanol (EtOH) and acetic acid (HAc) for the production EtAc and water (H_2O) as a by-product in a RD column. For this, the CHEMCAD program was used to simulate the RD column designed for producing EtAc. HAc flow rate, EtOH flow rate, HAc feed stage, EtOH feed stage, reflux ratio, and reactive feed temperatures were changed and then the effects of these parameters on the EtAc production were observed. The simulation design run by the CHEMCAD program was used in RSM created with the Design-Expert program. In this study, Central Composite Design (CCD) one of the best techniques for RSM, was chosen to determine the optimum operating conditions of the RD column. Analysis of variance (ANOVA) was used to examine the interaction between the response and independent variables and resultant production data. In this optimization framework, the goal was to maximize the production rate as the objective function.

2. Process Description and Methodology

2.1. Design and operation of a RD column

A single RD column was selected in the CHEMCAD program and connected to two feed streams for ethyl acetate production. In the RD column, acetic acid (CAS number: 64-19-7) and ethanol (CAS number: 64-17-5) were selected as reactives and acetic acid was fed from the upper part of the column and ethanol from the bottom of the column. Ethyl acetate (CAS number: 141-78-6) was obtained as the top product and water (CAS number: 7732-18-5) as the bottom product, as a result of reactions in the RD column. The kinetic model expressions with different catalysts and configurations of different RD designs were summarized in previous studies for increased production (Santaella et al., 2017). In our study, this reversible reaction was completed without a catalyst and the kinetic model for this chemical reaction system is adopted from (Lee et al., 2007). The designed RD process was simulated using the CHEMCAD program (trial version). HAc flow rate, EtOH flow rate, HAc feed stage, EtOH feed stage, reflux ratio, and feed temperatures of reactives were selected as important parameters and then the effects of these parameters on EtAc production were observed. The number of stages is an important parameter in the column design since the increase in the number of stages leads to an increase in column dimensions and thus increases the cost (Santaella et al., 2017). In a RD column, the reflux ratio both increases separation and conversion due to the recycles unreacted reactants to the reaction zone (Norkobilov et al., 2017). In the column design, the reflux ratio was varied to achieve high purity EtAc at the top of the column. But the reboiler duty was fixed to ensure the water purity at the bottom stage of the column due to energy savings. The equilibrium stage model, which assumes that the vapor and liquid phase are in thermodynamic equilibrium, was used for modeling and simulation of the RD column (Feyzi & Behesti, 2017). Negligible side reactions and by-product formation, vapor hold-up, adiabatic and perfect mixing on plates, constant pressure, and ideal vapor phase assumptions were used for simulation of the designed RD column. In general, azeotrope formation in the column is accomplished as a result of the increase in the conversion level due to the removal of the products continually (Aqar et al., 2017). The components are complemented by a minimum boil-up ratio for the prevention of azeotrope between reactive and products. For simplicity, all the equilibrium constants were independent of temperature in the simulations (Perez-Cisneros et al., 2016).

In our research, we have used the EtAc production rate as an objective function for the designed RD column, which operated at atmospheric pressure. Reactive flow rates, reactive feed stages, reflux ratio, and feed temperatures were selected as the optimization variables for the RD column to maximize the EtAc production rate. Figure 1 and Table 1 present the RD column representation and flow summaries of reactive and products, respectively. The esterification reaction of EtOH and HAc is a reversible exothermic reaction. Eq. (1) summarizes the equation for this reaction and kinetic model equations for this reaction are given in Eqs. (2) - (4);

$$EtOH + HAc \underset{k_2}{\overset{k_1}{\rightleftarrows}} EtAc + H_2O \tag{1}$$

$$r_1 = k_1 C_{HAc} C_{EtOH} - k_2 C_{EtAc} C_{H_2O} \tag{2}$$

$$k_1 = 4.76x10^{-4} \exp\left(-\frac{59.774}{R*T}\right) \tag{3}$$

$$k_2 = 1.63x10^{-4} \exp\left(-\frac{59.774}{R*T}\right) \tag{4}$$

where k_1 is the forward reaction rate constant (m^3/mol s), k_2 is the backward reaction rate constant (m^3/mol s), T is the temperature (K), and R is the gas constant (J/mol K).

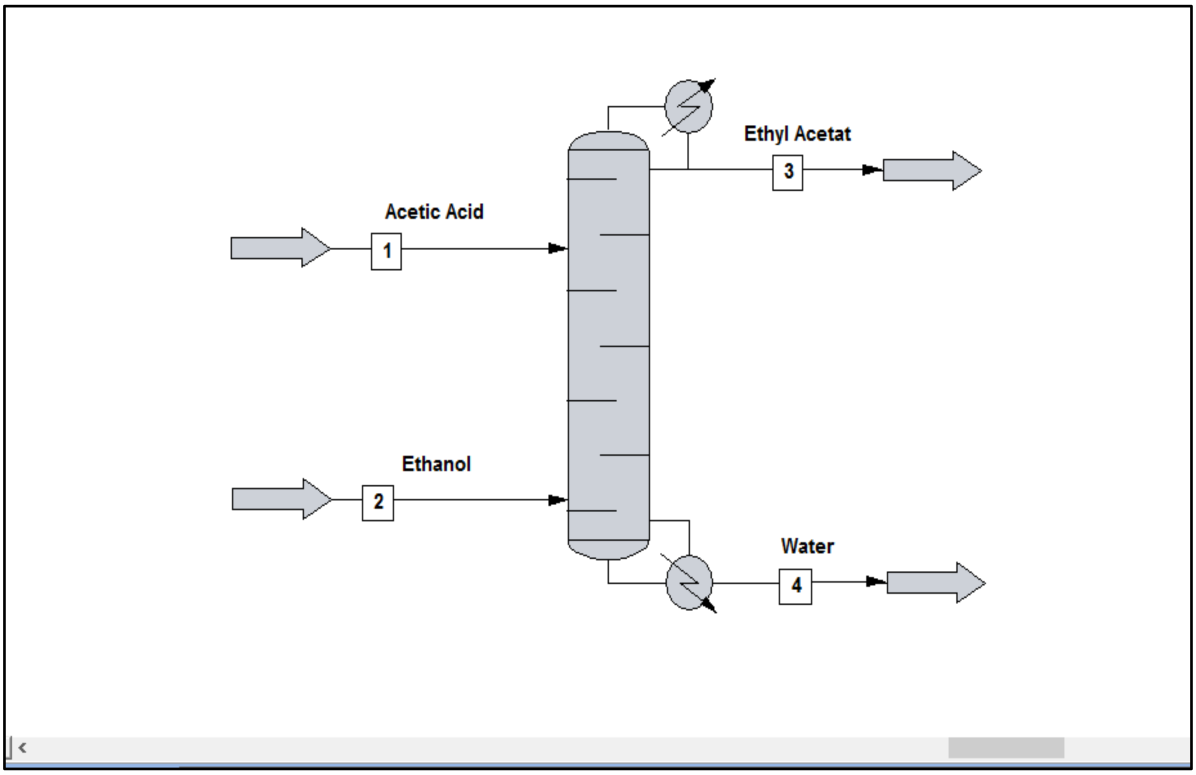


Figure 1. Presentation of reactive distillation column with reactive and product flows.

2.2. Design of simulation set and optimization criteria

HAc flow rate, EtOH flow rate, HAc feed stage, EtOH feed stage, reflux ratio, and reactive feed temperatures were selected as independent parameters and the effects of these parameters on the EtAc production rate were observed. Preliminary simulations performed for all mentioned design variables showed that a rapid convergence of the simulations was obtained EtAc production rate as the response. CCD is widely used for studying the effect of variables and exploring the optimum conditions for a multivariable process. CCD was applied by using the Design-Expert 7.0.0 program, which is experimental design software that can perform numerical optimization. The total number of experiments with six variables being the most influential parameters was 86 (=2k + 2k + 10), where k is the number of independent variables. To evaluate pure error, seventy-six experiments were increased by ten replications at the center values (zero level). Table 2 presents the range and levels of the variables under investigation in this study. Simulation data were processed by the Design-Expert 7.0.0 program, including ANOVA to obtain the interaction between the response and process variables. The quality of the fit of the polynomial model was expressed by the regression coefficient (R^2) and statistical significance was checked by the F-test in the same program. In the next step, the model that best represents the designed RD column was determined with ANOVA. For the model representing the process, the following conditions must be met;

- Model; ‘Significant’
- Lack of fit; ‘Insignificant’
- All model terms; ‘95% confidence interval’
- Coefficient of regression (R^2); highest value (~1),

After determining the model, 3D figures were created by the program, and the optimization results recommended by the program for different conditions were used in this study. Selected optimization criteria;

- Selected dependent parameters (HAc flow rate (X_1), EtOH flow rate (X_2), HAc feed stage (X_3), EtOH feed stage (X_4), reactive feed temperatures (X_5), and reflux ratio (X_6)): ‘in range’
- Response (ethyl acetate production rate (R)): ‘maximize’
- The optimum operating conditions of the RD column that provide the highest ethyl acetate production rate and desirability value close to 1.0 were chosen as the solution. It is assumed that the relationship between the selected operation variables and the response can be represented by a mathematical model given by Eq. (5);

$$y=\beta_0+\sum_{i=1}^{3}\beta_i X_i+\sum_{i=1}^{3}\beta_{ii} X_j^2+\sum_{i\leq 1}^{3}\sum_{j=1}^{3}\beta_{ij} X_i X_j+err \qquad (5)$$

where y is the response, β_0 is the constant coefficient, X_i (i=1–3) are non-coded variables, β_{is} are the linear, β_{iis} are the quadratic and β_{ijs} (I and j=1–3) are second-order interaction coefficients.

Table 1. A sample of flow summaries of reactive and products in the simulated RD column

Simulation Name:	Reactive Distillation			
Stream Number	1	2	3	4
Stream Name	Acetic Acid	Ethanol	Ethyl Acetate	Water
Temp (°C)	70.0000	70.0000	71.4387	75.0296
Pressure (bar)	1.2000	1.2000	1.0130	1.0130
Enthalpy (kcal/h)	$-2.689e^{+6}$	$-3.265e^{+6}$	$-4.319e^{+6}$	$-1.762e^{+6}$
Vapor mole frac.	0.0000	0.0000	0.11129	0.00048441
Total (kmol/h)	25.0000	50.0000	48.6626	26.3374
Total (kg/h)	1501.325	2106.623	3117.918	490.004
Total std L (m^3/h)	1.4241	2.6132	3.5497	0.4965
Total std V (m^3/h)	560.34	1120.68	1090.71	590.32
Flow rates (kg/h)				
Ethanol	0.0000	1980.2299	822.7657	25.4986
Acetic Acid	1501.3251	0.0000	25.7469	0.0127
Ethyl Acetate	0.0000	0.0000	2164.8577	0.0002
Water	0.0000	126.3932	104.5480	464.4926

Table 2. Simulation range and levels of the parameters for EtAc production rate

		Range	and	Level
Variables	Index	-1	0	+1
HAc flow rate (kmol/h)	X_1	30.0	75.0	120.0
EtOH flow rate (kmol/h)	X_2	40.0	85.0	150.0
HAc feed stage	X_3	4.0	7.0	10.0
EtOH feed stage	X_4	10.0	14.0	18.0
Feed temperature (°C)	X_5	30.0	50.0	70.0
Reflux ratio	X_6	2.2	3.2	4.2

3. Results and Discussion

3.1. CCD simulation results

EtAc was produced from aqueous solutions using six parameters with the CCD. By modifying the HAc flow rate, EtOH flow rate, HAc feed stage, EtOH feed stage, reflux ratio, and reactive feed temperatures, the effects of these parameters on EtAc production were observed. The goal was to maximize the EtAc production rate in the designed RD column. For the evaluation of the pure error, seventy-six simulations in total were performed for optimization purposes, together with ten same replications conducted at the center values. Table 3 presents the order of the simulations and levels of variables in coded (-1, 0, +1) and uncoded forms and responses.

In Table 2, the data obtained as a result of the study about the effect of six independent variables, namely, the HAc flow rate (X_1), EtOH flow rate (X_2), HAc feed stage (X_3), EtOH feed stage (X_4), reactive feed temperatures (X_5), and reflux ratio (X_6), on the response EtAc production rate (R) are presented. The data presented in Table 2 were run through RSM to construct empirical models to represent R values regarding the six independent parameters (selected operation parameters). The p-values and lack of fit error of the parameter estimations were significant based on the regression analysis at a confidence interval of 95%. This indicates that a non-linear model would better fit the data. The quadratic model was utilized to fit the observed data with the least-squares analysis and the empirical model was obtained for the response to the actual and coded factors of Eq. (6) and Eq. (7), respectively.

$$\begin{aligned}
&\text{Ethyl Acetate Production Rate } (kmol/h) \\
&= +12.62812 + 0.38753[\text{HAc flow rate}] + 0.52069[\text{EtOH flow rate}] + 2.44562[\text{HAc feed stage} \\
&- 0.36267[\text{EtOH feed stage}] - 0.020118[\text{Temperature}] - 13.68964[\text{Reflux ratio}] \\
&+ 1.51254e^{-3}[\text{HAc flow rate}][\text{EtOH flow rate}] - 0.01062[\text{HAc flow rate}][\text{HAc feed stage}] \\
&+ 4.21810e^{-3}[\text{HAc flow rate}][\text{EtOH feed stage}] - 1.25224e^{-4}[\text{HAc flow rate}][\text{Temperature}] \\
&- 0.065426[\text{HAc flow rate}][\text{Reflux ratio}] - 2.06354e^{-4}[\text{EtOH flow rate}][\text{HAc feed stage}] \\
&+ 1.54293e^{-3}[\text{EtOH flow rate}][\text{Temperature}] - 0.054235[\text{EtOH flow rate}][\text{Reflux ratio}] \\
&+ 0.078265[\text{HAc feed stage}][\text{EtOH feed stage}] + 5.63107e^{-3}[\text{HAc feed stage}][\text{Temperature}] \\
&- 107.80[\text{HAc feed stage}][\text{Reflux ratio}] - 2.28529e^{-3}[\text{EtOH feed stage}][\text{Temperature}] \\
&- 0.067594[\text{EtOH feed stage}][\text{Reflux ratio}] + 8.32852e^{-3}[\text{Temperature}][\text{Reflux ratio}] \\
&- 1.01863e^{-3}[\text{HAc flow rate}]^2 - 1.01863e^{-3}[\text{EtOH flow rate}]^2 - 0.25441[\text{HAc feed stage}]^2 \\
&+ 1.29233e^{-3}[\text{EtOH feed stage}]^2 - 1.30568e^{-5}[\text{Temperature}]^2 + 3.33993[\text{Reflux ratio}]^2
\end{aligned} \tag{6}$$

$$\begin{aligned}
&\text{Ethyl Acetate Production Rate } (kmol/h) \\
&= +39.33 + 6.47[X_1] + 5.44[X_2] - 2.19[X_3] + 1.14[X_4] + 0.013[X_5] - 3.41[X_6] + 3.74[X_1][X_2] \\
&- 1.43[X_1][X_3] + 0.76[X_1][X_4] - 0.056[X_1][X_5] - 2.94[X_1][X_6] - 0.034[X_1][X_6] \\
&- 0.034[X_2][X_3] + 0.34[X_2][X_4] - 7.001e^{-3}[X_2][X_5] - 2.98[X_2][X_6] + 0.94[X_3][X_4] \\
&+ 0.17[X_3][X_5] - 0.32[X_3][X_6] - 0.091[X_4][X_5] - 0.27[X_4][X_6] + 0.083[X_5][X_6] - 2.06[X_1]^2 \\
&- 6.06[X_2]^2 - 2.29[X_3]^2 + 0.021[X_4]^2 - 1.306e^{-3}[X_5]^2 + 3.34[X_6]^2
\end{aligned} \tag{7}$$

3.2. Analysis of variance (ANOVA) results for response

For the quadratic model utilized to explain the experimental data at a confidence level of 95% to be statistically significant, the model was tested by using ANOVA. For the EtAc production values, Table 3 lists the ANOVA data of the RSM quadratic model for the RD column operating parameters. Statistical test of the simulation values was performed by using the Fisher's test for ANOVA. The regression was observed to be statistically significant in Table 4 at an F-value of 24.60 for the EtAc production rates with very low probability (P model < 0.0001). The statistical importance of the second-order equation reveals that the regression, but not the lack of fit, is significant at a confidence level of 99%. The "Prob > F" values less than 0.0500 indicate that the model terms are significant. In this case, the terms X_1, X_2, X_6, X_1X_2, X_1X_6, and X_2X_6, are significant model terms. The response equation was proven suitable for the CCD experiments as indicated by the results. The determination coefficient R^2 controls the fit of the model. The ANOVA results show that HAc flow rate, EtOH flow rate, and reflux ratio are the most effective parameters since they have the lowest p-values. The single and binary interactions of these parameters have a large F-value and p-value <0.0001. Thus, the effect of EtAc production rate in the RD is most strongly modeled with the quadratic term. The model reports a higher R^2 value of 91.97% than found for the response, based on the ANOVA results. In addition, an acceptable agreement with the adjusted determination coefficient is also a requisite. The adjusted R^2 and predicted R^2 values were found to be 88.23% and 79.56%, respectively. The values of R^2 show an acceptable correlation between the observed and predicted indicating that the model provides a good explanation of the correlation between the response and six variables. Figure 2 presents the percentage of probability and residuals plot. As the points on the plot follow a straight line, it is possible to conclude that the residuals were normally distributed. Therefore, the prediction of the simulated data using the quadratic model developed for the response is quite satisfactory and it is possible to use the regression model for predicting the EtAc production rate values from the simulated conditions. The ANOVA results of a previous optimization study showed that the most effective variables were feed stream temperature, boil-up ratio, and reflux ratio for minimization of exergy losses (response) in the RD column (Feyzi & Behesti, 2017).

The 3D surface plots of the response are shown in Figure 3 for the production rate of EtAc by varying independent variables. In these plots, the y-axis indicates the EtAc production rate (kmol/h), and the other axis titles were changed HAc flow rate (X_1), EtOH flow rate (X_2), HAc feed stage (X_3), EtOH feed stage (X_4), reactive feed temperatures (X_5) and reflux ratio (X_6), respectively. The effect of feed temperatures on the EtAc production rate is constant. The flow rates of HAc and EtOH have linear and positive effects on the response. Binary effects of the HAc flow rate with EtOH feed stage and HAc flow rate with feed temperatures have similar, linear and positive effects on the EtAc production rate. Also, binary interactions of the EtOH flow rate with EtOH feed stage and EtOH flow rate with feed temperatures have similar and positive effects on the response. As the number of HAc feed stages increased in the designed column, the EtAc production rate was negatively affected.

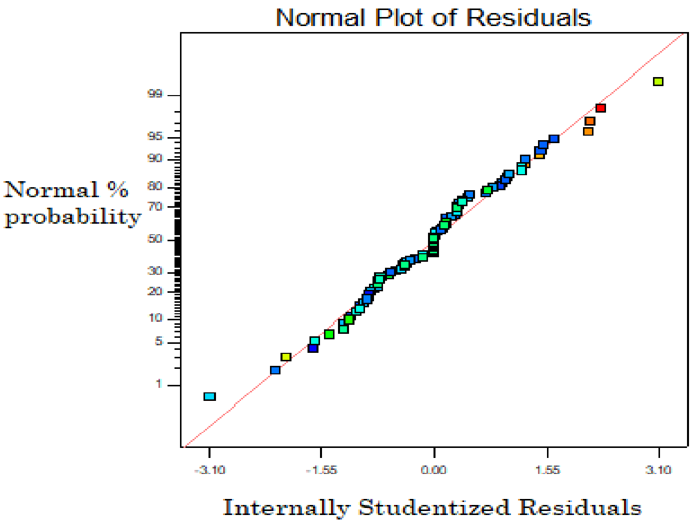


Figure 2. Normal probability plot of the residuals for the response.

Table 3. ANOVA results of the CCD for EtAc production rate

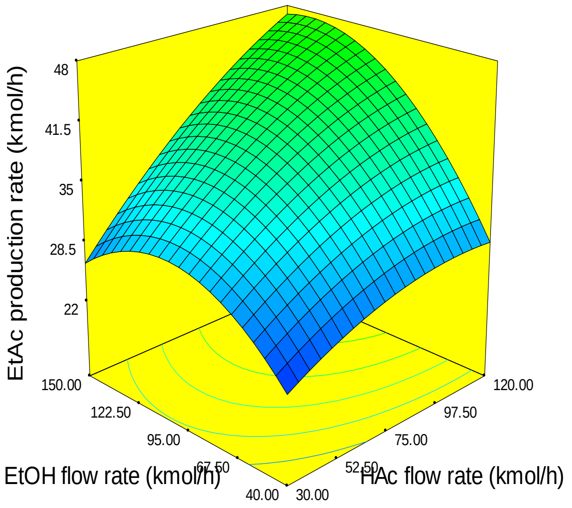
Resource	SS value	df	F-value	p-value	
Model	9429.90	27	24.60	<0.0001	Significant
X_1	831.20	1	58.54	<0.0001	
X_2	588.68	1	41.46	<0.0001	
X_3	95.75	1	6.74	0.0119	
X_4	25.87	1	1.82	0.1823	
X_5	1.695E-4	1	1.194E-5	0.9973	
X_6	230.87	1	16.26	<0.0001	
X_1X_2	896.90	1	63.17	<0.0001	
X_1X_3	131.76	1	9.28	0.0035	
X_1X_4	36.89	1	2.60	0.1124	
X_1X_5	0.81	1	0.057	0.8117	
X_1X_6	554.76	1	39.07	<0.0001	
X_2X_3	0.074	1	5.226E-3	0.9426	
X_2X_4	7.37	1	0.52	0.4740	
X_2X_5	0.013	1	8.837E-4	0.9764	
X_2X_6	569.46	1	40.11	<0.0001	
X_3X_4	56.45	1	3.98	0.0509	
X_3X_5	7.31	1	0.51	0.4761	
X_3X_6	6.69	1	0.47	0.4950	
X_4X_5	2.14	1	0.15	0.6993	
X_4X_6	4.68	1	0.33	0.5682	
X_5X_6	1.78	1	0.13	0.7249	
X_1^2	10.16	1	0.72	0.4010	
X_2^2	87.77	1	6.18	0.0158	
X_3^2	12.52	1	0.88	0.3516	
X_4^2	1.021E-3	1	7.192E-5	0.9933	
X_5^2	6.515E-5	1	4.588E-6	0.9983	
X_6^2	26.64	1	1.88	0.1760	
Residual	823.49	58			
Lack of fit	823.49	49	8.681E+6	<0.0001	
Pure error	1.742E-5	9			
Cor total	10253.39	85			

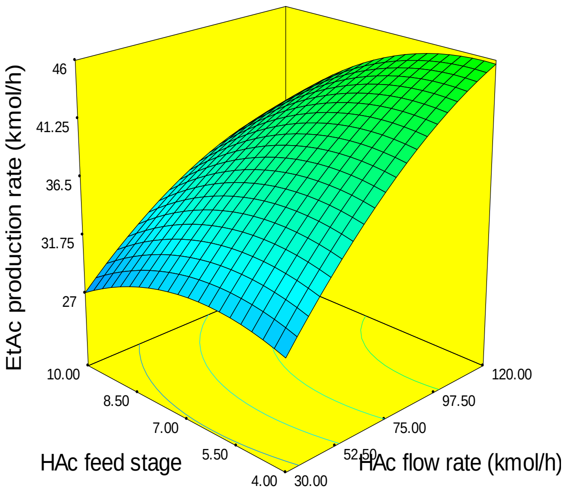
Table 4. CCD simulation results for EtAc production rate according to design parameters

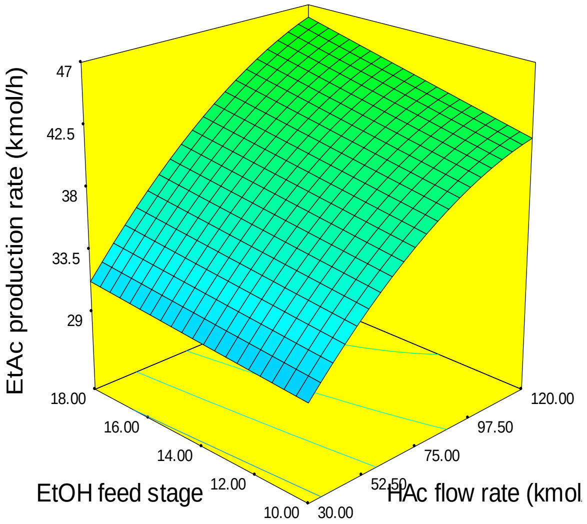
Simulation No	HAc flow rate (kmol/h)	EtOH flow rate (kmol/h)	HAc feed stage	EtOH feed stage	Temperature (ºC)	Reflux ratio	EtAc production rate (kmol/h)
1	120(+1)	150(+1)	10(+1)	10(-1)	70(+1)	4.20(+1)	30.0309
2	30(-1)	150(+1)	4(-1)	18(+1)	30(-1)	4.20(+1)	27.7271
3	120(+1)	40(-1)	4(-1)	10(-1)	70(+1)	2.20(-1)	33.9147
4	120(+1)	150(+1)	4(-1)	10(-1)	70(+1)	2.20(-1)	65.8321
5	120(+1)	150(+1)	10(+1)	18(+1)	70(+1)	2.20(-1)	63.9097
6	30(-1)	95(0)	7(0)	14(0)	50(0)	3.20(0)	29.4944
7	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2727
8	30(-1)	150(+1)	10(+1)	18(+1)	70(+1)	4.20(+1)	25.6424
9	30(-1)	40(-1)	10(+1)	10(-1)	70(+1)	2.20(-1)	22.4866
10	30(-1)	150(+1)	4(-1)	10(+1)	30(-1)	2.20(-1)	29.1249
11	120(+1)	40(-1)	4(-1)	18(+1)	70(+1)	4.20(+1)	31.6377
12	120(+1)	150(+1)	10(+1)	18(+1)	30(-1)	2.20(-1)	51.7768
13	120(+1)	40(-1)	4(-1)	18(+1)	30(-1)	4.20(+1)	31.5682
14	120(+1)	150(+1)	10(+1)	10(+1)	30(-1)	4.20(+1)	29.0854
15	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2727
16	30(-1)	150(+1)	4(-1)	10(-1)	30(-1)	4.20(+1)	26.3671
17	30(-1)	150(+1)	10(-1)	10(+1)	70(+1)	2.20(-1)	28.8583
18	30(-1)	40(-1)	4(-1)	10(-1)	70(+1)	2.20(-1)	23.6629
19	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2727
20	30(-1)	150(+1)	10(-1)	18(+1)	70(+1)	2.20(-1)	29.4488
21	120(+1)	150(+1)	4(-1)	18(+1)	30(-1)	4.20(+1)	42.8061
22	30(-1)	150(+1)	4(-1)	10(-1)	70(+1)	2.20(-1)	29.1213
23	120(+1)	150(+1)	4(-1)	18(+1)	70(+1)	4.20(+1)	44.3588
24	30(-1)	150(+1)	4(-1)	10(-1)	70(+1)	4.20(+1)	26.6121
25	30(-1)	40(-1)	4(-1)	10(-1)	30(-1)	4.20(+1)	26.0657
26	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2727
27	30(-1)	40(-1)	10(+1)	10(-1)	30(-1)	2.20(-1)	21.7368
28	120(+1)	40(-1)	10(+1)	18(+1)	30(-1)	4.20(+1)	24.3984
29	120(+1)	40(-1)	10(+1)	10(-1)	30(-1)	4.20(+1)	23.5351
30	120(+1)	40(-1)	4(-1)	10(-1)	70(+1)	4.20(+1)	33.4785
31	120(+1)	150(+1)	4(-1)	18(+1)	70(+1)	2.20(-1)	56.2931
32	120(+1)	150(+1)	10(+1)	18(+1)	30(-1)	4.20(+1)	33.8189
33	120(+1)	40(-1)	10(+1)	10(-1)	70(+1)	4.20(+1)	24.3474
34	30(-1)	150(+1)	10(+1)	10(-1)	30(-1)	4.20(+1)	24.0057
35	75(0)	95(0)	7(0)	14(0)	30(-1)	3.20(0)	38.8091
36	120(+1)	150(+1)	10(+1)	10(-1)	70(+1)	2.20(-1)	46.8278
37	120(+1)	40(-1)	4(-1)	10(-1)	30(-1)	4.20(+1)	33.6163
38	120(+1)	40(-1)	10(+1)	10(-1)	30(-1)	2.20(-1)	23.0528
39	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2727
40	30(-1)	150(+1)	10(+1)	10(-1)	70(+1)	4.20(+1)	24.2141
41	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2727
42	30(-1)	40(-1)	4(-1)	18(+1)	30(-1)	2.20(-1)	25.5772
43	75(0)	95(0)	4(-1)	14(0)	50(0)	3.20(0)	38.6152
44	30(-1)	40(-1)	10(+1)	18(+1)	70(+1)	2.20(-1)	22.5311
45	120(+1)	150(+1)	10(+1)	18(+1)	70(+1)	4.20(+1)	35.1806
46	30(-1)	150(+1)	10(+1)	10(-1)	30(-1)	2.20(-1)	28.8071
47	30(-1)	40(-1)	10(+1)	18(+1)	70(+1)	4.20(+1)	24.2502
48	75(0)	95(0)	7(0)	14(0)	70(+1)	3.20(0)	39.7471
49	120(+1)	40(-1)	10(+1)	10(-1)	70(+1)	2.20(-1)	23.3009
50	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2771
51	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2727
52	120(+1)	150(+1)	4(-1)	10(-1)	30(-1)	4.20(+1)	37.9799
53	75(0)	95(0)	10(+1)	14(0)	50(0)	3.20(0)	35.3721
54	75(0)	95(0)	7(0)	18(+1)	50(0)	3.20(0)	42.7487
55	30(-1)	150(+1)	4(-1)	18(+1)	70(+1)	2.20(-1)	29.1125

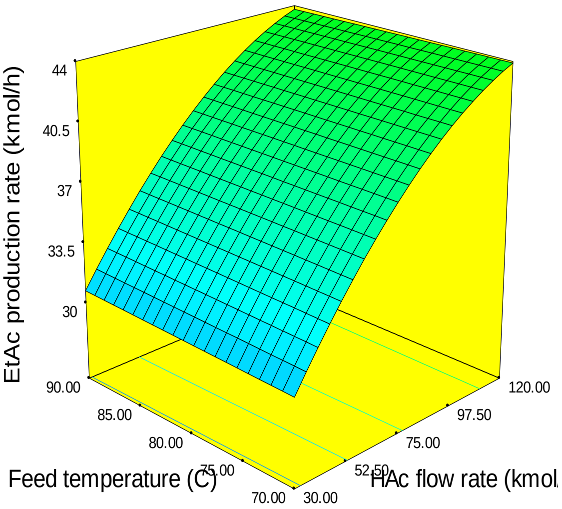
Table 4. CCD simulation results for EtAc production rate according to design parameters (continued)

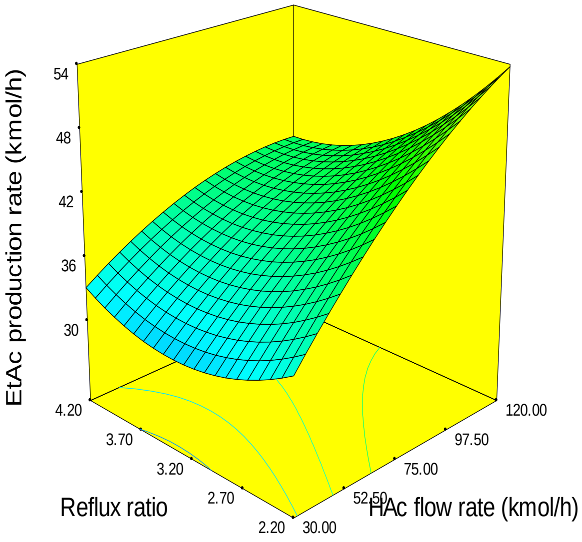
Simulation No	HAc flow rate (kmol/h)	EtOH flow rate (kmol/h)	HAc feed stage	EtOH feed stage	Temperature (ºC)	Reflux ratio	EtAc production rate (kmol/h)
56	120(+1)	150(+1)	4(-1)	10(-1)	30(-1)	2.20(-1)	63.8984
57	120(+1)	40(-1)	4(-1)	10(-1)	30(-1)	2.20(-1)	33.8099
58	75(0)	95(0)	7(0)	14(0)	50(0)	4.20(+1)	30.4552
59	75(0)	40(-1)	7(0)	14(0)	50(0)	3.20(0)	26.8664
60	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2727
61	30(-1)	150(+1)	4(-1)	18(+1)	30(-1)	2.20(-1)	29.1145
62	120(+1)	150(+1)	4(-1)	18(+1)	30(-1)	2.20(-1)	64.1871
63	120(+1)	40(-1)	10(+1)	18(+1)	30(-1)	2.20(-1)	32.1951
64	30(-1)	150(+1)	10(+1)	18(+1)	30(-1)	4.20(+1)	25.3977
65	120(+1)	150(+1)	10(+1)	10(-1)	30(-1)	2.20(-1)	45.3955
66	120(+1)	95(0)	7(0)	14(0)	50(0)	3.20(0)	44.9468
67	30(-1)	40(-1)	4(-1)	18(+1)	70(+1)	4.20(+1)	27.3786
68	30(-1)	40(-1)	10(+1)	10(-1)	30(-1)	4.20(+1)	20.0371
69	30(-1)	40(-1)	4(-1)	18(+1)	70(+1)	2.20(-1)	25.5028
70	30(-1)	40(-1)	10(+1)	18(+1)	30(-1)	4.20(+1)	24.3252
71	120(+1)	150(+1)	4(-1)	10(-1)	70(+1)	4.20(+1)	39.2469
72	30(-1)	40(-1)	4(-1)	18(+1)	30(-1)	4.20(+1)	27.3892
73	30(-1)	40(-1)	10(+1)	10(-1)	70(+1)	4.20(+1)	19.3629
74	75(0)	95(0)	7(0)	14(0)	50(0)	3.20(0)	39.2727
75	120(+1)	40(-1)	10(+1)	18(+1)	70(+1)	4.20(+1)	24.6579
76	120(+1)	40(-1)	4(-1)	18(+1)	30(-1)	2.20(-1)	34.0072
77	30(-1)	40(-1)	4(-1)	10(-1)	70(+1)	4.20(+1)	25.9465
78	75(0)	95(0)	7(0)	14(0)	50(0)	2.20(0)	54.7913
79	120(+1)	40(-1)	4(-1)	18(+1)	70(+1)	2.20(-1)	34.2129
80	75(0)	150(+1)	7(0)	14(0)	50(0)	3.20(0)	39.5758
81	30(-1)	40(-1)	10(+1)	18(+1)	30(-1)	2.20(-1)	22.5674
82	30(-1)	150(+1)	10(+1)	18(+1)	30(-1)	2.20(-1)	25.3977
83	120(+1)	40(-1)	10(+1)	18(+1)	70(+1)	2.20(-1)	32.5359
84	75(0)	95(0)	7(0)	10(-1)	50(0)	3.20(0)	35.8593
85	30(-1)	150(+1)	4(-1)	18(+1)	70(+1)	4.20(+1)	27.9916
86	30(-1)	40(-1)	4(-1)	10(-1)	30(-1)	2.20(-1)	23.9921

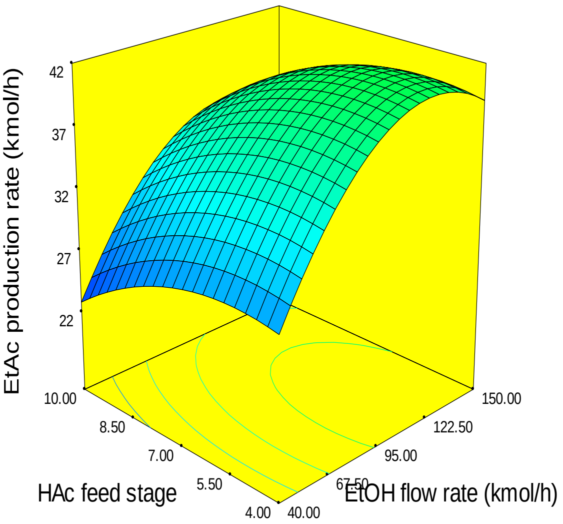


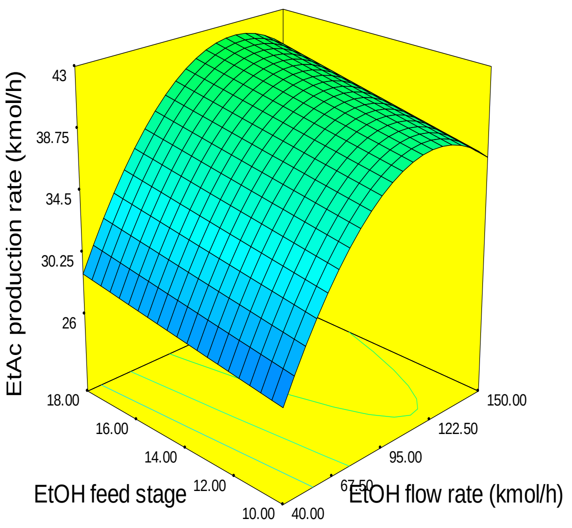


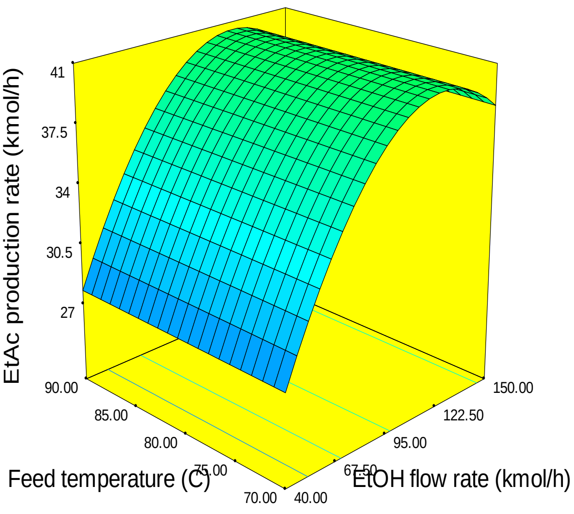

EtAc production rate (kmol/h)
47
42.5
38
33.5
29
18.00
16.00
14.00
12.00
10.00
EtOH feed stage
30.00
52.50
75.00
97.50
120.00
HAc flow rate (kmol

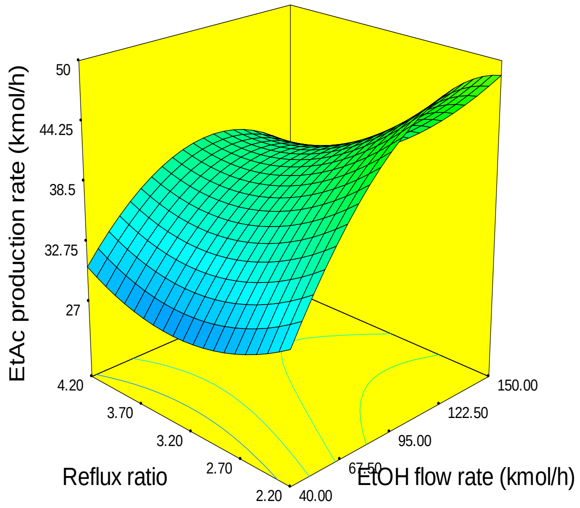

EtAc production rate (kmol/h)
44
40.5
37
33.5
30
90.00
85.00
80.00
75.00
70.00
Feed temperature (C)
30.00
52.50
75.00
97.50
120.00
HAc flow rate (kmol

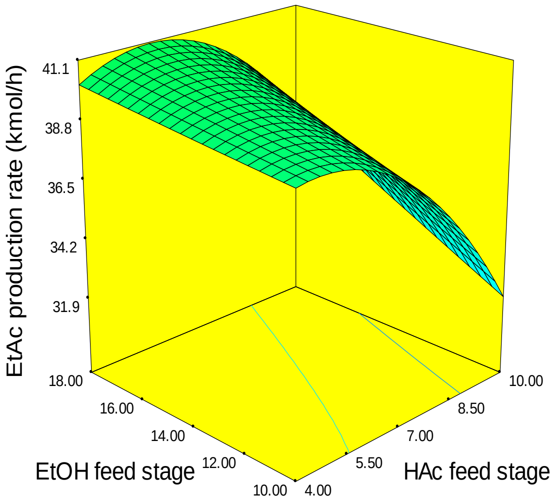

EtAc production rate (kmol/h)
54
48
42
36
30
4.20
3.70
3.20
2.70
2.20
Reflux ratio
30.00
52.50
75.00
97.50
120.00
HAc flow rate (kmol/h)

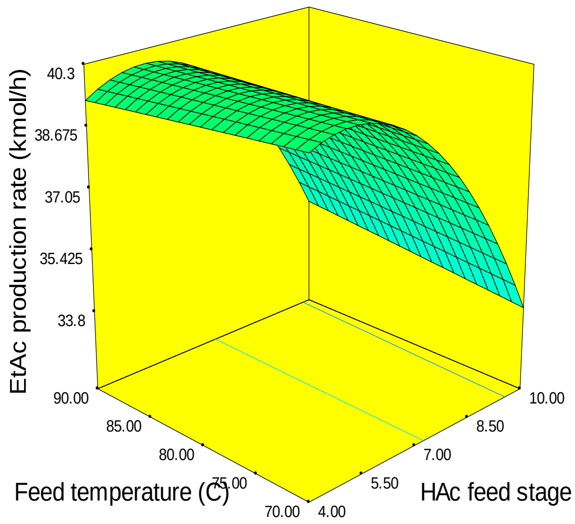

EtAc production rate (kmol/h)
42
37
32
27
22
10.00
8.50
7.00
5.50
4.00
HAc feed stage
40.00
67.50
95.00
122.50
150.00
EtOH flow rate (kmol/h)

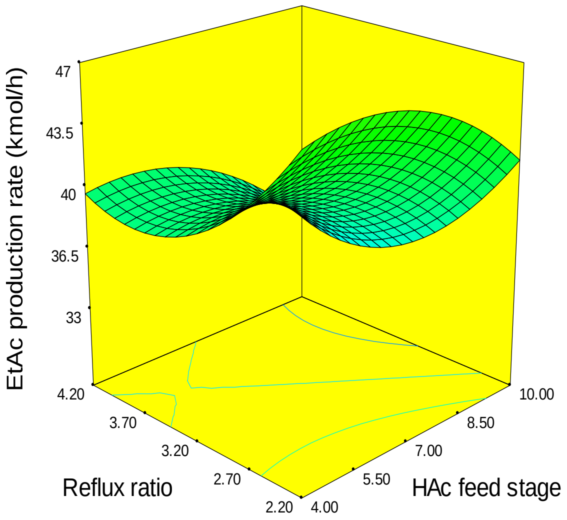

EtAc production rate (kmol/h)
43
38.75
34.5
30.25
26
18.00
16.00
14.00
12.00
10.00
EtOH feed stage
40.00
67.50
95.00
122.50
150.00
EtOH flow rate (kmol/h)

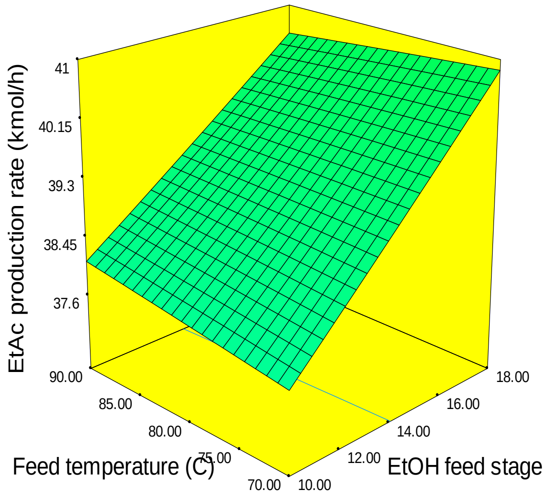

EtAc production rate (kmol/h)
41
37.5
34
30.5
27
90.00
85.00
80.00
75.00
70.00
Feed temperature (C)
40.00
67.50
95.00
122.50
150.00
EtOH flow rate (kmol/h)

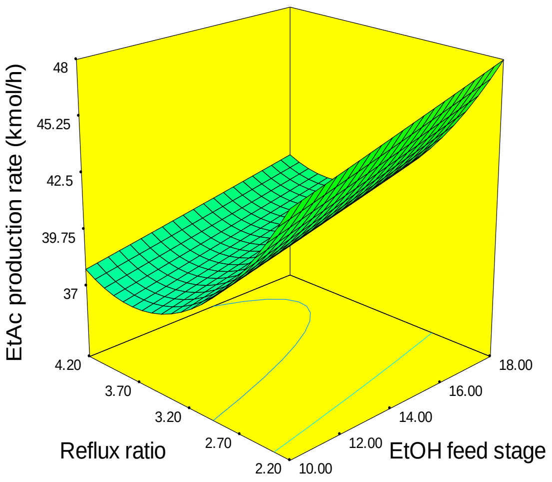

EtAc production rate (kmol/h)
50
44.25
38.5
32.75
27
4.20
3.70
3.20
2.70
2.20
Reflux ratio
40.00
67.50
95.00
122.50
150.00
EtOH flow rate (kmol/h)


EtAc production rate (kmol/h)
41.1
38.8
36.5
34.2
31.9
18.00
16.00
14.00
12.00
10.00
EtOH feed stage
4.00
5.50
7.00
8.50
10.00
HAc feed stage


EtAc production rate (kmol/h)
40.3
38.675
37.05
35.425
33.8
90.00
85.00
80.00
75.00
70.00
Feed temperature (C)
4.00
5.50
7.00
8.50
10.00
HAc feed stage


EtAc production rate (kmol/h)
47
43.5
40
36.5
33
4.20
3.70
3.20
2.70
2.20
Reflux ratio
4.00
5.50
7.00
8.50
10.00
HAc feed stage


EtAc production rate (kmol/h)
41
40.15
39.3
38.45
37.6
90.00
85.00
80.00
75.00
70.00
Feed temperature (C)
10.00
12.00
14.00
16.00
18.00
EtOH feed stage


EtAc production rate (kmol/h)
48
45.25
42.5
39.75
37
4.20
3.70
3.20
2.70
2.20
Reflux ratio
10.00
12.00
14.00
16.00
18.00
EtOH feed stage

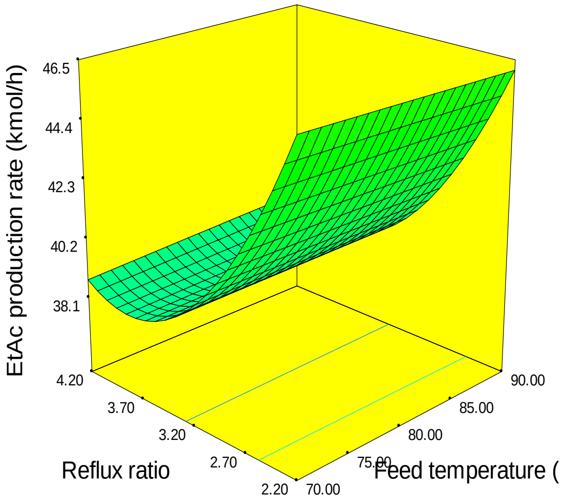


Figure 3. 3D figures for the simultaneous effects on the EtAc production rate.

3.3. Optimization results

In this part, the results of the optimization analyses were explained and discussed in detail. The model was subjected to a validation test and the EtAc production rate was optimized to test the validity of the model. Based on the Design-Expert program, a set of simulations was generated, ten sets of replicate simulations were performed, and the EtAc production rates were compared with the predicted and simulated values. As depicted in Table 6, the optimization was performed by employing the targeted criteria. In the validation test, the response, namely the EtAc production rate, is fixed as maximum whereas the other factors are studied in range. The optimal conditions for the EtAc production rate were determined as HAc flow rate of 120.00 kmol/h, EtOH flow rate of 150.00 kmol/h, HAc feed stage 6, EtOH feed stage 14, reflux ratio of 2.20, and reactive feed temperatures of 70.28 °C, which were chosen using a maximum desirability function (D = 0.901). Table 6 presents the values desired for all independent parameters and optimization responses by utilizing the desirability function. According to the optimum conditions given in Table 5, HAc and EtOH flow rates had no limitations on the EtAc production rate. The optimum reflux ratio was determined by the program as the minimum value of 2.2 due to the increase in the production rate and to prevent accumulation in the column. The optimum feed temperature was obtained as 70 ºC because of providing a higher ethyl acetate production rate to avoid ethanol condensation through the column. The 6th stage for HAc feed and the 14th stage for EtOH feed was selected as the optimum feed stages by the program because of supplying more interactions of these reactants in the column.

Table 5. Optimization criteria applied to EtAc production rate

Parameters	Index	Goal	Lower limit	Upper limit
HAc flow rate (kmol/h)	X_1	in range	30	120
EtOH flow rate (kmol/h)	X_2	in range	40	150
HAc feed stage	X_3	in range	4	10
EtOH feed stage	X_4	in range	10	18
Feed temperature (ºC)	X_5	in range	30	70
Reflux ratio	X_6	in range	2.2	4.2
EtAc production rate	R	maximum	19.3629	65.8321

Table 6. Optimization results for maximum response according to the operating parameters

Parameters	X_1	X_2	X_3	X_4	X_5	X_6	R	Desirability
Values	120.00	150.00	6.0	14.0	70.28	2.20	67.2745	0.901

4. Conclusion

In this study, optimization of important variables for an esterification reaction in a RD column was explored. The performance of the designed RD column was simulated according to the EtAc production rate. The HAc and EtOH flow rates, HAc and EtOH feed stage, reflux ratio, and reactive feed temperatures were selected as independent parameters and the effects of these parameters on the production rate were observed. CCD, one of the best techniques for RSM, was applied to optimize the operating parameters. The EtAc production rate in the designed RD column was modeled by using an empirical correlation as an objective function of the selected operating parameters. The optimal response conditions were determined as HAc flow rate of 120.00 kmol/h, EtOH flow rate of 150.00 kmol/h, HAc feed stage 6, EtOH feed stage 14, reflux ratio 2.20, and reactive feed temperatures of 70.28 °C, which were designed using a maximum desirability function (D = 0.901). The results of ANOVA demonstrate that the most effective operating parameters are the HAc flow rate, EtOH flow rate, and reflux ratio. Also, the interactions of these three parameters are very significant for the response. In summary, the RD process appears to be the best option to achieve production and separation together in one column compared to conventional processes and it is also an attractive option to revamp existing processes.

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