

**RESPONSE SURFACE METHODOLOGY
TO EVALUATE ENERGY IN EXTRACTIVE DISTILLATION
PROCESS FOR THE MIXTURE OF METHYLAL AND METHANOL
WITH GLYCEROL AS ENTRAINER**

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Abstract

Glycerol could be possible to be an entrainer to separate the mixture of methylal and methanol (minimum-boiling azeotropic mixture) for the extractive distillation process. The effect of the structure parameters (total stages of column, feed locations) and operation parameters (entrainer to feed mass ratio, temperature of entrainer feeding, and mass reflux ratio) in the extractive distillation column on product purity and reboiler heat duty was investigated based on response surface methodology (RSM). Results demonstrated that the operational variables had more significant effect on reboiler heat duty than the structural variables for the ED column. Moreover, the influence of the interaction between temperature of entrainer feeding and entrainer to feed ratio influenced on the reboiler heat duty for ED column. The predicted results with the RSM provided good agreement with the simulated results to optimize the process parameters of ED column to achieve the target values, and energy consumption in reboiler heat duty was 73,293.4 kJ/h.

Keywords: Azeotropic mixture, Extractive distillation, Glycerol, Optimization, Response surface methodology.

1. Introduction

The pollutant emissions and energy crisis have increased the awareness to select cleaner alternative fuel. One of alternative fuels for the future is biodiesel. Biodiesel is attracting more attention of clean energy due to its properties similar to conventional diesel. Therefore, biodiesel has been studied by several academic research and industrial applications to develop properties for commercial fuel [1-3]. The chemical addition into biodiesel can improve the performance and/or corrosion protection of engines and reduce the pollutant emission problems. It is oxygenated fuel additives such as oxy-methylene dimethyl ethers (OMEs). Dimethoxymethane, DMM or methylal is the simplest compound in the OMEs class.

Methylal is important solvent that can apply in cosmetics, medicines, household goods, polymer materials, etc. It comprises 42 wt % oxygen; besides, methylal is a colourless liquid, lower boiling point, non-toxic and miscible in diesel, as a result, methylal as well oxygenated additive to blend into diesel fuel (DMM-blend) [4]. Methylal can be synthesized by the reversible reaction between methanol and formaldehyde with a heterogeneous acidic catalyst. Since the yield of methylal is limited chemical equilibrium, adding overload of reactant (methanol) will shift the equilibrium towards the side of the products [5]. Therefore, the final product consists of an excess methanol and methylal that will be separated. However, the separation of methylal from this mixture given high purity cannot apply in the conventional distillation column because of the mixture form to be a minimum boiling azeotrope at atmospheric pressure. For the azeotrope separation, there are many techniques to propose such as membrane pervaporation, pressure swing distillation, and extractive distillation. Using a pervaporation membrane can obtain the purification of methylal 99.5 wt %. However, due to the degradation of organic membranes, it is impossible in the long run pervaporation [6]. Although the purity of methylal can be achieved to 99.9 wt % by pressure swing distillation process, the operating at different pressure increases the investment cost [7]. The extractive distillation is most frequently applied for separation due to a greater variety of entrainer and a wider range of operation conditions.

In extractive distillation process, entrainer is added into an azeotropic mixture to improve the relative volatility of methylal to methanol. The most important step is the selection of the appropriated and effective entrainer that must have low toxicity, easy recovery, thermal stability, high boiling point, high relative volatility between key components and high solvent capacity. In recent years, entrainers have classified into four types (liquid solvents, solid salts, polymers, and ionic liquid) [8]. A common organic entrainer to eliminate the azeotrope of the methylal-methanol mixture is the dimethylformamide (DMF) because of its high capacity and high selectivity of methylal. Moreover, reboiler heat duty in the extractive distillation (ED) column for using DMF as entrainer is higher than that for using the organic entrainers. It is well known, DMF is not an environment friendly entrainer. [7-9]. To improve the separation of methylal and methanol, several organic entrainers have been proposed such as ethylene glycol, cyclohexanol, and propylene glycol [10-12].

According to selection the entrainer, natural agent (glycerol) is considered as the entrainer to separate the mixture of methylal and methanol in this work. The feasibility study of applying glycerol to eliminate the azeotrope needs to understand the behaviour of the mixture through the thermodynamic analysis of phase diagrams as presented in the residue curve maps (RCMs). Furthermore, the energy consumption in the extractive distillation process needs to evaluate for the design of the ED column.

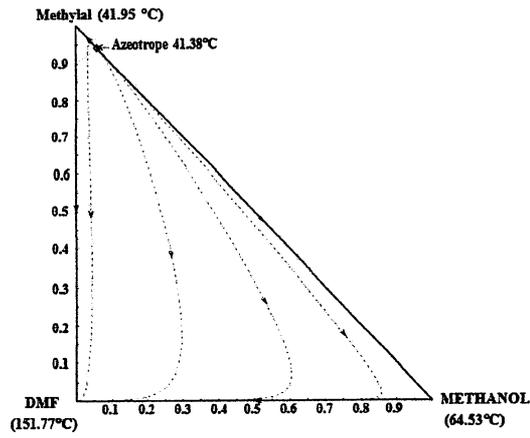
Design an extractive distillation process, many process simulators used to aid process creation. The relationship between input process parameters and output responses (distillate product purity and energy consumption in the reboiler) in the extractive column was analysed by using response surface methodology (RSM) that applied for the design of experiments and process simulation [12-16]. RSM could predict the relative significance of several effect parameters and their interactions on the process and optimize the process parameters to design the distillation column [16].

In this work, glycerol as an entrainer is introduced to the upper feed of the mixture (methylal and methanol) in the extractive column. Relative analysis of process parameters (total stages of column, feed locations, entrainer to feed mass ratio, temperature of entrainer feeding, and mass reflux ratio) has been investigated by using response surface methodology (RSM) based on central composite design (CCD). The RSM can determine the tendency of each parameters and apply to find the optimal parameters in terms of product purity and energy consumption in the extractive distillation column to reduce the simulation run scenario in Aspen Plus simulation.

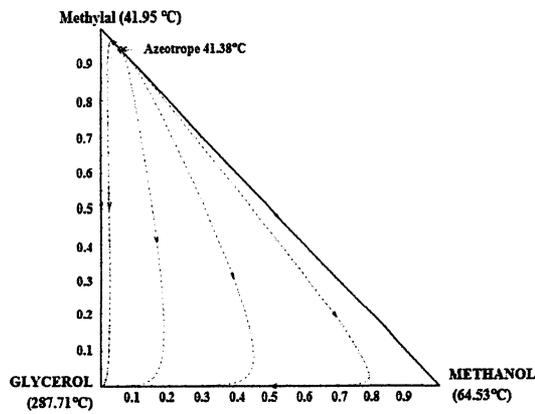
2. Model Simulation

Azeotropes point of the methylal-methanol mixture at 41.38 °C atmospheric pressure with 94.06 wt % methylal has been studied. Binary interaction parameters are estimated by the property package based on the Non-Random Two Liquid (NRTL) activity model in commercial software (Aspen Plus). In extractive distillation system, an unstable node in the vapor-liquid equilibrium of methylal/methanol can converts to a stable node by entrainer that determines by using residue curve map (RCM). The different entrainers as dimethylformamide (DMF), and glycerol as can eliminate the azeotropic mixture (methylal/methanol) at 1 atm that are presented in Fig. 1. The intersection of the vertical axis of the isovolatility curve of glycerol quite closed to methylal corner, as well as that of DMF. Therefore, DMF can be substitutes by glycerol.

Extractive distillation system includes the extractive distillate (ED) column and recovery distillate (RD) column as shown in Fig. 2. The mixture stream (F) is fed to the column of ED with a stream of entrainer (E), where methyl will be withdrawn to the top stream (D1) and the mixture of methanol and glycerol as in the bottom stream (B1) stream of the ED column is separated into the RD column. While methanol will be taken place to the top (D2) of RD column, glycerol will be withdrawn from the bottom of RD column (B2) to recirculate back to the column of ED. However, some entrainer losses in the D1 and D2 streams, as a result, the makeup stream of entrainer needs to balance in the system. In this work, the feed flow of methylal and methanol are 94.12 kg/h and 5.88 kg/h, respectively with 25 °C and 1 atm. The specification of methylal is 0.999 by weight to obtain from the top of ED column and mass fraction of methanol is greater than 0.95 that is withdrawn from the top of RD column. Both columns have a total condenser and a partial reboiler. The main variables in the extractive distillation system such as stage number, mass reflux ratio, entrainer to feed mass ratio, feed stage of mixture and entrainer, and temperature of entrainer, are influent to the energy consumption and methylal purity in the ED column. The operating pressure in the ED column is fixed at 1 atm. On the other hand, the operating pressure in the column of RD is fixed at 0.2 atm to avoid the thermal degradation of glycerol [17, 18].



(a). Methylal/Methanol/DMF system.



(b). Methylal/Methanol/Glycerol system.

Fig. 1. Residue curve map (RCM) at 1 atm.

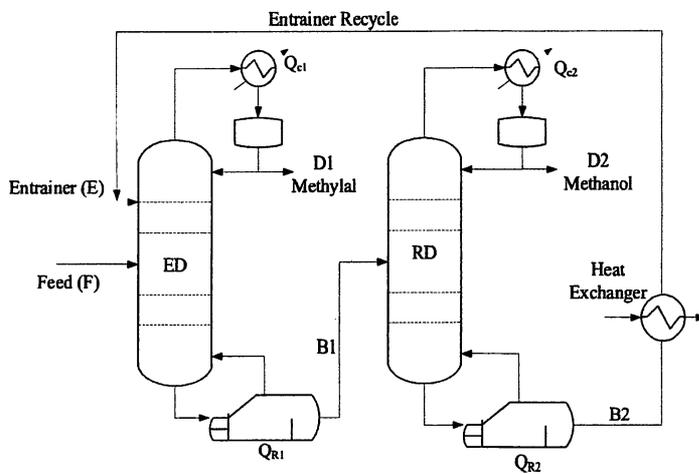


Fig. 2. Extractive distillation system.

2.1. Response surface methodology

Response surface methodology (RSM) is a statistical technique to analyse the relations between the output response and individual input variables. Central composite design (CCD) is a standard RSM design that can be helpful to optimize the process design. The desired response modelling to several independent variables is related to the variables by linear and quadratic terms to formulate a simple model as given

$$\hat{y} = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i x_i + \sum_{i=1}^k \sum_{j=1, j < i}^k \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where \hat{y} is the predicted response which depends on k number of factors and x_i is the levels of the independent variables. β_0 , β_i , β_{ii} , and β_{ij} are constant, linear, interaction and square terms coefficients, respectively and ε is the random error term [16].

The investigation of the interaction between process parameters and responses is analysed by ANOVA. The quality of the polynomial model is inspected by R^2 and P-value. Also, the operational conditions are presented in the 3 D diagram to predict the optimal conditions. To obtain the quadratic model of RSM is simulated the data following by modifying to eliminate the term of statistically insignificant. The model summary statistic demonstrates the high coefficient of determination $R^2 > 0.9$ and P-value < 0.05 that suggest the model for the product quality and energy consumption of ED column. Multi-variables regression analysis is run by MINITAB.

To design the ED column, there are 6 factors consist of total stage number (Nt), the location of mixture feed (NF) and entrainer feed (NE), temperature of entrainer (ET), entrainer to feed mass ratio (E/F), and mass reflux ratio (Rf) to minimize the reboiler heat duty with specification of product purity. For six factors, there are 53 simulation runs (32 factorial points, 12 axial points, and 9 centre points runs) can be considered. To reduce the simulation runs, the design of process parameters in the ED column would be separated into 2 parts: optimal structural and operational parameters. The range of variables in the ED column are selected based on the preliminary simulation is shown in Table 1. The range for each parameter is chosen from the extreme values of these parameters.

Table 1. Operation conditions for the separation of methylal and methanol using glycerol as an entrainer in the extractive distillation system.

Parameters	ED column	RD column
Total number of stages	11	5
Feed stage		
- mixture	7	3
- entrainer	4	-
Pressure (atm)	1	0.2
Distillate rate (kg/h)	94	6
Mass reflux ratio	0.2	0.25
Entrainer to feed mass ratio	1	-
Temperature of entrainer (°C)	25	-
Mass fraction from the top stream of column		
- methylal	0.999	0.043
- methanol	0.002	0.957

- glycerol	trace	73 PPM
Mass fraction from the bottom stream of column		
- methylal	0.002	4 PPB
- methanol	0.055	4 PPM
- glycerol	0.943	1
Reboiler duty (kJ/h)	73,148.54	31,607.95

3. Results and Discussion

3.1. Structural parameters optimization

In this section, the total number of stages (x_1), location feed stage of mixture (x_2) and entrainer (x_3) in the EDC are parameters to improve the mass fraction of methylal (≥ 0.999 w/w) with minimum reboiler heat duty. The range of parameters is given in Table 2 and the overall operational conditions by RSM design are shown in Table 3. The response results from the design parameters are obtained by ANOVA analysis as shown in Table 4.

Table 2. Variables code levels for structural parameters of ED column.

Process factor	Simulation range	
	Low level (-1)	High level (1)
x_1 : Total number of stages (Nt)	10	12
x_2 : Location feed stage of mixture (NF)	7	9
x_3 : Location feed stage of entrainer (NE)	3	5

Table 3. Simulations generated for structural parameters of ED column.

No.	x_1 (Nt)	x_2 (NF)	x_3 (NE)	Methylal Purity	Heat Duty (kJ/h)
1	10(-1)	7(-1)	3(-1)	0.997	72,068.2
2	12 (1)	7(-1)	3(-1)	1.000	72,124.3
3	10 (-1)	9 (1)	3(-1)	0.982	71,567.4
4	12 (1)	9 (1)	3(-1)	0.998	72,092.0
5	10(-1)	7(-1)	5 (1)	0.995	72,008.5
6	12 (1)	7(-1)	5 (1)	0.998	72,095.3
7	10(-1)	9 (1)	5 (1)	0.981	71,547.7
8	12 (1)	9 (1)	5 (1)	0.997	72,068.7
9	9 (-2)	8 (0)	4 (0)	0.981	71,547.5
10	13 (2)	8 (0)	4 (0)	1.000	72,124.3
11	11 (0)	6 (-2)	4 (0)	0.998	72,095.0
12	11 (0)	10 (2)	4 (0)	0.982	71,567.1
13	11 (0)	8 (0)	2 (-2)	0.999	73,707.3
14	11 (0)	8 (0)	6 (2)	0.995	72,008.6
15	11 (0)	8 (0)	4 (0)	0.997	72,068.5
16	11 (0)	8 (0)	4 (0)	0.997	72,068.5
17	11 (0)	8 (0)	4 (0)	0.997	72,068.5
18	11 (0)	8 (0)	4 (0)	0.997	72,068.5
19	11 (0)	8 (0)	4 (0)	0.997	72,068.5
20	11 (0)	8 (0)	4 (0)	0.997	72,068.5

A high value of R^2 confirms to fitting value of quadratic model. F-values are much larger than 5 and the P-value of the model is less than 0.05, to indicate the terms of model that are significant [12-16].

In this case, the product purity of methylal ($y_{1,1}$) and the reboiler heat duty ($y_{1,2}$) of the ED column are directly related to the total number of stages (Nt) (x_1), location

of mixture feed stage (NF) (x_2), and an entrainer feed stage (NE) (x_3). The overall equation for the model relating the purity of methylal and the reboiler heat duty in the ED column of code factors are given by

$$y_{1,1} = 0.96332 + 1.475e^{-2}x_1 - 1.2568e^{-2}x_2 - 2.784e^{-3}x_3 - 1.636e^{-3}x_1^2 - 1.761e^{-3}x_2^2 - 1.1e^{-5}x_3^2 + 3.25e^{-3}x_1x_2 + 2.5e^{-4}x_2x_3 \quad (2)$$

$$y_{1,2} = 71238 + 913x_1 - 150x_2 - 1736x_3 - 76.5x_1^2 - 77.7x_2^2 + 179x_3^2 + 113x_1x_2 + 3x_1x_3 + 6x_2x_3 \quad (3)$$

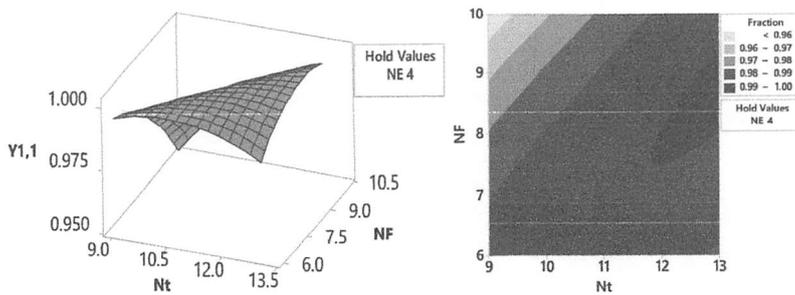
The effects of input parameters in ED column for distillate composition and reboiler heat duty are presented in Table 4. In this case, the purity of methylal in the ED column is directly related to the total number of stages (Nt) (x_1), the location of mixture feed (NF) (x_2), and the location of entrainer feed (NE) (x_3). Moreover, the effects of interaction parameter between x_1 and x_2 , and x_2 and x_3 are significant. The interaction parameters between x_1 and x_2 are more effective on the distillate composition than the interaction parameters between x_2 and x_3 because of the lower P-value and higher F-value. On the other hand, the reboiler heat duty in the ED column is related to the only entrainer feed stage. The effect of input parameters for structural column depend on the model of distillate product purity is greater than that the model of reboiler heat duty because of the higher value of R^2 .

The response of methylal purity in the ED column is related to the term between the total stage number of the ED column (x_1) and location of feed (x_2) as is shown in Fig. 3(a). Since the total stage number of the ED column is down and location of the mixture feed installed closer the condenser, methylal purity decreased. Figure 3(b) shows the methyl purity response in the ED column for the interaction parameters between the location of mixture feed stage (x_2) and the location of entrainer feed stage (x_3). It is found, methylal purity increased, where the location of entrainer feed stage is higher than the location of the mixture feed.

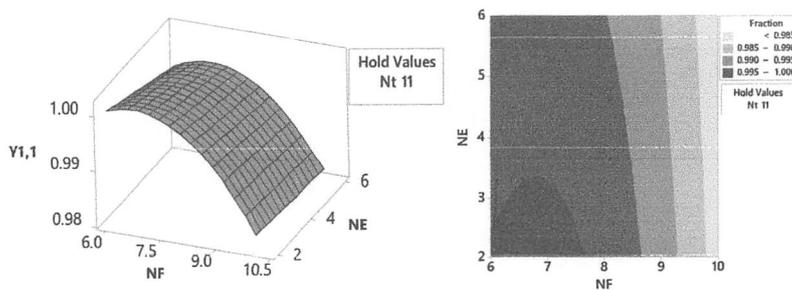
Table 4. ANOVA analysis for structural parameters of ED column.

Source	$y_{1,1}$		$y_{1,2}$	
	F-Value	P-Value	F-Value	P-Value
Model	2,945.32	0.000	3.81	0.024
Linear	6,592.14	0.000	5.49	0.017
x_1 : Nt	11,345.71	0.000	4.06	0.072
x_2 : NF	8,045.71	0.000	3.19	0.104
x_3 : NE	385.00	0.000	9.22	0.013
Square	1,353.33	0.000	5.54	0.017
x_1^2	2,115.92	0.000	1.74	0.216
x_2^2	2,451.53	0.000	1.80	0.210
x_3^2	0.10	0.756	9.54	0.011
Interaction	890.48	0.000	0.40	0.754
$x_1 \cdot x_2$	2,655.71	0.000	1.21	0.298
$x_1 \cdot x_3$	0.00	1.000	0.00	0.974
$x_2 \cdot x_3$	15.71	0.003	0.00	0.957

R ²	99.96 %	77.42 %
Adjust R ²	99.93 %	57.10 %



(a). Interaction between total stages number (N_t, x_1) and location of mixture feed stage (NF, x_2).



(b). Interaction between the location of entrainer feed stage (NE, x_3) and mixture feed stage (NF, x_2).

Fig. 3. Effect of the interaction for structural parameters for methylal purity.

The structural parameters of ED column can be achieved by RSM to predict the model of product purity and reboiler heat duty. The optimal number of stages, the feeding location of the mixture and entrainer are presented in Fig. 4. The composite desirability is 0.8848. The individual desirability indicates that the settings are more effective at product target (0.9999) than at minimum reboiler heat duty (0.78470). These results indicate the setting to achieve the results for response of mass fraction is more effective than the reboiler heat duty. As a result, the structural parameters in the ED column are more influential in the composition than in the heat duty. However, the structural parameters in the ED column for number of stages, the feeding location of the mixture and entrainer (integral number) are 12, 7, and 5, respectively, which can obtain the minimum reboiler heat duty for a given specification methylal purity. Although the optimal structural parameters in the ED column cannot give the target value of product, the reboiler heat duty can achieve to minimum value as presented in Table 3. Then, the mass reflux ratio (R_f), entrainer to feed mass ratio (E/F), and temperature of entrainer (ET) is presented in terms of operation parameters that need to calculate the conditions to obtain the minimum heat duty subject to target purity of methylal in the ED column at 0.999 w/w.

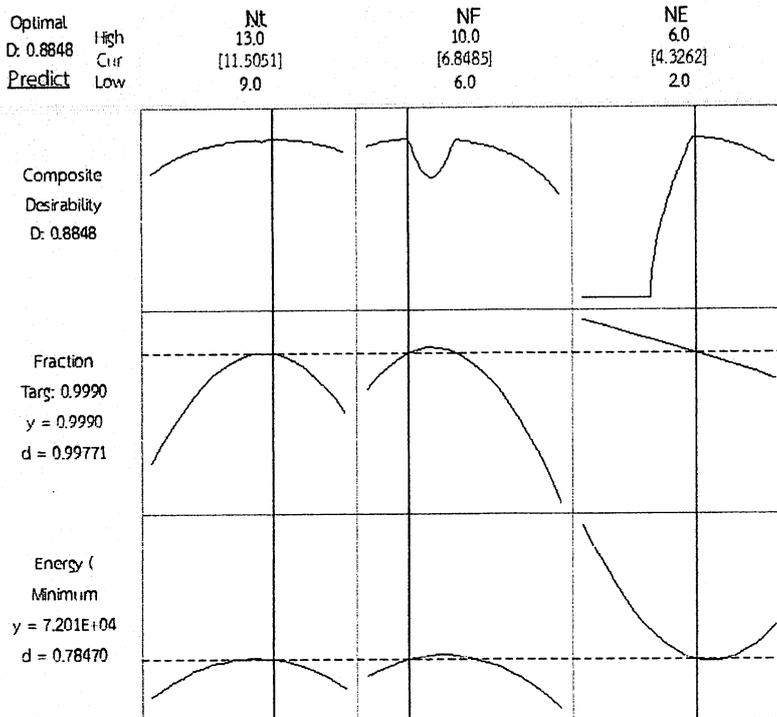


Fig. 4. Response optimization plot for structure parameters for ED column.

3.2. Operational parameters optimization

In the previous section, the number of trays, the feeding location of the mixture and entrainer are 12, 7, and 5, respectively. All factors of the operational variables would be influenced the product purity of methylal and reboiler heat duty. In CCD method, process variables are mass reflux ratio (Rf), entrainer to feed mass ratio (E/F), and temperature of entrainer (ET) use to predict the response given the minimum reboiler heat duty and the quality specification of methylal would be considered in this case.

Table 5. Variables code levels for operational parameters of ED column.

Process factor	Simulation range	
	Low level (-1)	High level (1)
x_4 : Temperature of entrainer (ET)	50	100
x_5 : Entrainer to feed mass ratio (E/F)	0.8	1.4
x_6 : Mass reflux ratio (Rf)	0.6	1.2

In this case, the levels of variables are listed in Table 5. Different operational parameters caused by changing the responses that are proposed by RSM design as is shown in Table 6. The model parameters and interaction on parameters are demonstrated the significant model by ANOVA analysis as is shown in Table 7.

Table 6. Simulations generated for operational parameters of ED column.

No.	x_4 (ET)	x_5 (E/F)	x_6 (Rf)	Methylal Purity	Heat Duty (kJ/h)
1	50(-1)	0.8(-1)	0.6(-1)	0.999	74,783
2	100 (1)	0.8(-1)	0.6(-1)	0.998	65,812
3	50(-1)	1.4 (1)	0.6(-1)	0.999	94,015
4	100 (1)	1.4 (1)	0.6(-1)	0.998	78,289
5	50(-1)	0.8(-1)	1.2 (1)	0.999	95,713
6	100 (1)	0.8(-1)	1.2 (1)	0.999	86,733
7	50(-1)	1.4 (1)	1.2 (1)	1.000	114,937
8	100 (1)	1.4 (1)	1.2 (1)	1.000	99,224
9	25 (-2)	1.1 (0)	0.9 (0)	1.000	100,230
10	125 (2)	1.1 (0)	0.9 (0)	0.999	75,492
11	75 (0)	0.5 (-2)	0.9 (0)	0.999	74,799
12	75 (0)	1.7 (2)	0.9 (0)	1.000	106,220
13	75 (0)	1.1 (0)	0.3 (-2)	0.997	67,248
14	75 (0)	1.1 (0)	1.5 (2)	1.000	109,145
15	75 (0)	1.1 (0)	0.9 (0)	0.999	88,226
16	75 (0)	1.1 (0)	0.9 (0)	0.999	88,226
17	75 (0)	1.1 (0)	0.9 (0)	0.999	88,226
18	75 (0)	1.1 (0)	0.9 (0)	0.999	88,226
19	75 (0)	1.1 (0)	0.9 (0)	0.999	88,226
20	75 (0)	1.1 (0)	0.9 (0)	0.999	88,226

The product purity of methylal ($y_{2,1}$) and reboiler heat duty ($y_{2,2}$) in the ED column are directly related to the temperature of entrainer (x_4), entrainer to feed mass ratio (x_5), mass reflux ratio (x_6). Interaction parameters between x_4 and x_6 , and x_5 and x_6 are significant parameters on the distillate purity of methylal ($y_{2,1}$) because the P-value is lower than 0.05 as is presented in Table 7. Moreover, the effect of interaction parameters between x_4 and x_5 is a significant to the reboiler heat duty ($y_{2,2}$). The overall equations for the model relating the purity of methylal ($y_{2,1}$) and energy consumption ($y_{2,2}$) in ED column of code factors are given by

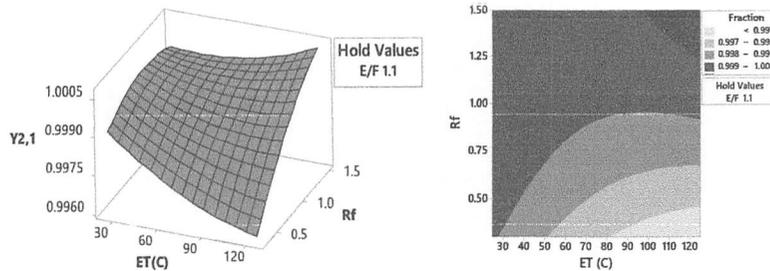
$$y_{2,1} = 1.00326 - 6.7e^{-5}x_4 - 4.44e^{-3}x_5 - 7.4e^{-4}x_6 + 1.263e^{-3}x_5^2 - 1.515e^{-3}x_6^2 + 3.3e^{-5}x_4x_5 + 2.778e^{-3}x_5x_6 \quad (4)$$

$$y_{2,2} = 34648 + 22.15x_4 + 29222x_5 + 35047x_6 - 0.1475x_4^2 + 0.6333x_5^2 - 92x_6^2 - 224.75x_4x_5 + 0.07x_4x_6 + 9x_5x_6 \quad (5)$$

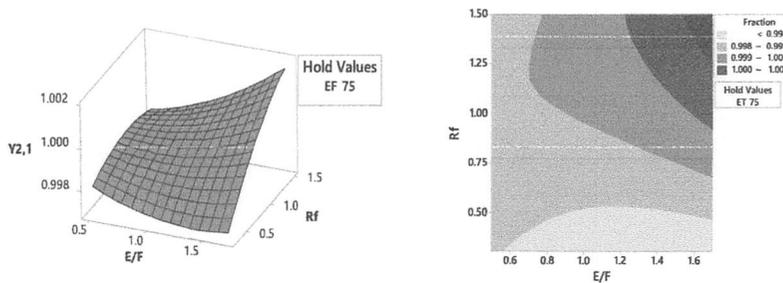
The interaction parameters in the response surface diagram between entrainer temperature (x_4), mass reflux ratio (x_6), and entrainer to feed mass ratio (x_5), mass reflux ratio (x_6) for distillate product composition in the ED column ($y_{2,1}$), are shown in Fig. 5. The results indicated; mass reflux ratio (x_6) is the most effect on distillate purity because of the least quantity of P-value for effect of x_6^2 . Moreover, increasing the temperature of entrainer (x_4), and the mass ratio of entrainer to feed (x_5) can improve the purity of methylal. Figure 6 shows the response surface diagram of the interaction parameters between entrainer temperature (x_4) and entrainer to feed mass ratio (x_5) to influence the energy consumption in the ED column. The energy supply of reboiler in the ED column for using the low temperature of entrainer is higher than that use the high temperature of entrainer. Moreover, the reboiler heat duty of the ED column increases because of the effect of increased the entrainer to feed mass ratio.

Table 7. ANOVA analysis for operational parameters of ED column.

Source	y _{2,1}		y _{2,2}	
	F-Value	P-Value	F-Value	P-Value
Model	37.13	0.000	166,927.67	0.000
Linear	86.43	0.000	496,008.97	0.000
x_4 : ET	31.43	0.000	270,473.41	0.000
x_5 : E/F	31.43	0.000	441,168.26	0.000
x_6 : Rf	196.43	0.000	776,385.24	0.000
Square	14.48	0.001	1,418.63	0.000
x_4^2	10.20	0.010	94.59	0.000
x_5^2	10.20	0.010	3,616.66	0.000
x_6^2	14.69	0.003	0.76	0.403
Interaction	10.48	0.002	3,355.43	0.000
$x_4 \cdot x_5$	0.00	1.000	10,066.28	0.000
$x_4 \cdot x_6$	15.71	0.003	0.00	0.975
$x_5 \cdot x_6$	15.71	0.003	0.00	0.963
R ²	97.09%		100%	
Adjust R ²	94.48%		100%	



(a). Interaction between mass reflux ratio (Rf, x_6) and entrainer feeding temperature (ET, x_4).



(b). Interaction between reflux ratio (Rf, x_6) and entrainer to feed ratio (E/F, x_5).

Fig. 5. Effect of the interaction for operational parameters for methylal purity.

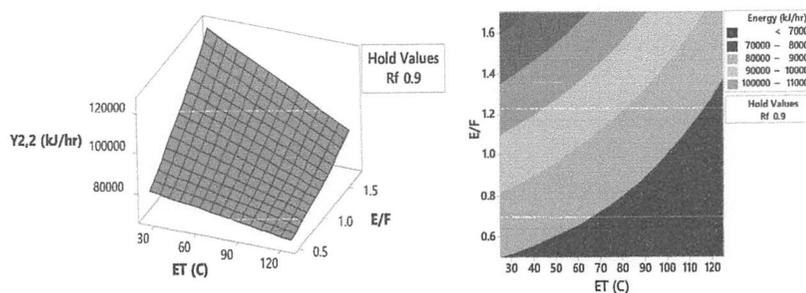


Fig. 6. Effect of the interaction for operational parameters between entrainer feeding temperature (ET, x_1) and entrainer to feed ratio ($E/F, x_2$) for reboiler duty.

The optimal parameters of entrainer temperature, entrainer to feed mass ratio, and mass reflux ratio are 121 °C, 0.5, and 0.9788, respectively to obtain the minimum energy requirement in the reboiler (73,293.4 kJ/h) for a specification mass fraction of methylal greater than 0.999 w/w. The design extractive distillation process needs to recover the entrainer. Before recovered glycerol drops into the ED column, the bottom stream of RD column is needed to reduce to be 121 °C by heat exchanger. Moreover, makeup stream of entrainer employs to balance the mass of entrainer that appears in the distillate stream RD column. Figure 7 illustrates the final optimal flowsheet to separate methylal-methanol-glycerol system with detail stream information, and heat duty. Since glycerol will be withdrawn from the bottom of RD column to recirculate back to the column of ED, some glycerol losses in the RD column. As a result, the makeup stream of glycerol needs to balance in the system (1.4×10^4 kg/h).

The simulation results demonstrate the mass composition of methylal at the top of ED column and methanol at the top of RD column are 0.999 w/w, and 0.957 w/w, respectively. Total energy consumption in the extractive distillation system is 95,762.4 kJ/h that combines with the reboiler heat duty in the ED column (73,293.4 kJ/h) and in the RD column (22,469 kJ/h). Moreover, total energy consumption in the extractive distillation system (ED column and RD column) is considered as presented in Table 8. Energy consumption in the reboiler of the ED column is higher than in the reboiler of the RD column. The use higher boiling point of entrainer can reduce the reboiler heat duty in the ED column and in the RD column. It is found that the energy consumption in the reboiler of ED column for using glycerol as entrainer is the least value. Although purity of methanol for using glycerol as entrainer is lesser than that ethylene glycol does, heat duty in the RD column for recovery glycerol is the lesser than that to recover ethylene glycol. Moreover, the reboiler heat duty for the RD column to recovery entrainer is high when the quantity of entrainer feed in the ED column is high.

The liquid compositions profiles in the ED column and RD column are presented in Fig. 8. In ED column, stages are counted from the condenser (stage 1) to reboiler (stage 12). Since the entrainer and mixture are fed at stages 5 and 7, respectively, methylal composition increases rapidly to 0.999 w/w and glycerol slip down quickly to zero, in the rectifying section, as is presented in Fig. 8(a). In the RD column, composition of glycerol increases rapidly to equal 1, and methanol falls to zero in the stripping section, as is presented in Fig. 8(b).

Table 8. Comparison of the process simulation results for the different entrainers.

Entrainers	Mass fraction		Reboiler heat duty (kJ/h)		Total heat duty (kJ/h)
	Methylal	Methanol	ED column	RD column	
DMF [9]	0.999	0.973	101,016	20,736	121,752
DMF+IL [9]	0.999	0.972	92,592	17,892	110,484
Ethylene glycol [10]	0.999	0.964	84,780	42,732	127,512
Cyclohexanol [11]	0.9992	0.9665	186,912	36,900	223,812
Glycerol	0.999	0.957	73,293.4	22,469	95,762.4

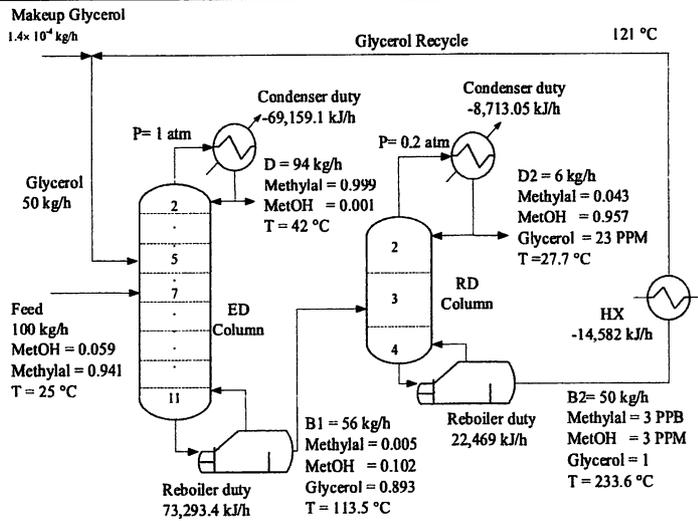


Fig. 7. Final flowsheet design for the extractive distillation process for methylal-methanol-glycerol system.

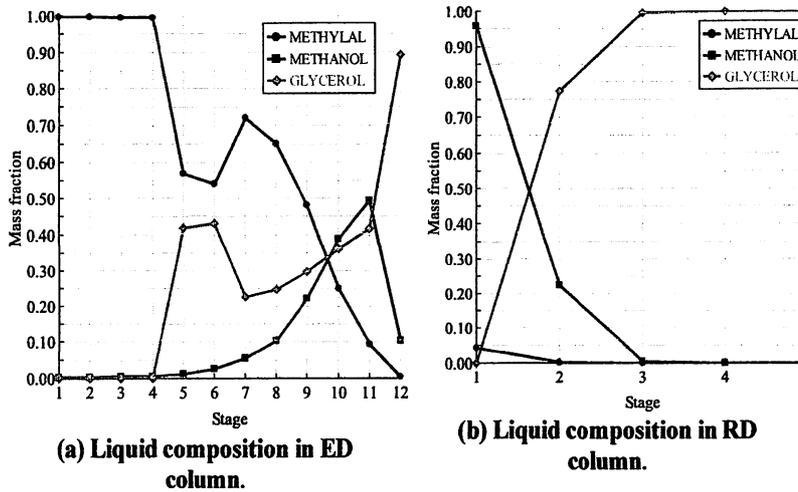


Fig. 8. Liquid composition and temperature profiles in methylal-methanol-glycerol system for the extractive distillation process.

4. Conclusions

In this work, the optimal parameters of structural and operational in the extractive distillation (ED) column to achieve the distillate product purity with minimum energy consumption in the reboiler had been studied based on response surface methodology (RSM). In this process, glycerol is an entrainer to separate the mixture of methylal and methanol in the ED column. Methylal purity is obtain from the top and the mixture of glycerol and methanol is withdrawn from the bottom. Purity of methylal is directly related to the total number of stages, the feeding location of mixture and entrainer, the mass reflux ratio, the entrainer to feed mass ratio, and the temperature of entrainer. Moreover, the interaction parameters between the total number of trays and feeding location of entrainer, the feeding location of mixture and entrainer, the mass reflux ratio and entrainer temperature, and the mass reflux ratio and entrainer to feed mass ratio influence on the purity of methylal. While reboiler heat duty is directly to the entrainer to feed mass ratio, the temperature of entrainer, and the mass reflux ratio, respectively. The interaction parameters between the entrainer temperature and entrainer to feed mass ratio influence on the reboiler heat duty in ED column. Moreover, the predicted results by the RSM provide good agreement with the simulated results to optimize the process parameters of ED column. The number of stages, the feeding location of the mixture and entrainer are 12, 7, and 5, respectively, and the temperature of entrainer, the entrainer to feed mass ratio, and the mass reflux ratio are 121 °C, 0.5, and 0.9788, respectively to obtain the minimum energy requirement in the reboiler of the extractive distillation column (73,293.4 kJ/h) with purity of methylal (0.999 w/w).

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