Response Surface Methodology in Optimization of Separation Process for Methylal /Methanol Based on Process Simulation of Extractive Distillation

W. Weerachaipichasgul, A. Chanpirak, P. Kittisupakorn

***Abstract*—Continuous extractive distillation is widely used to separate the mixture of methylal and methanol. The selection of separation agent (entrainer) for extractive distillation of binary mixture is usually based on the analysis of relative volatility diagrams of components as residue curve map (RCM). Tetra-ethylene-glycol as entrainer is possible to obtain high purity of methylal in the extractive distillation process. A practical method to propose the design of the extractive distillation column (EDC) has been obtained by response surface methodology (RSM) with the study of the effect of factors and their interactions on the requirement of energy consumption and methylal purity. The reboiler heat duty of EDC is directly related to mass reflux ratio, entrainer feed stage, temperature of entrainer, and entrainer to feed ratio. While the purity of methylal is related to the entrainer feed stage only. The optimal operation for EDC can be found by using the point prediction of RSM that is sufficient and efficient.**

***Index Terms*—Azeotropic mixture, Extractive distillation, Optimization, Response surface methodology**

I. Introduction

THE most common process for a thermal separation technology is distillation which is performed based on the different boiling point. Distillation is the important unit operations that need highly energy consumption. To isolate the azeotropic mixture, there are many techniques such as membrane pervaporation, pressure swing distillation, azeotropic distillation, and extractive distillation [1-3]. In the chemical industrial, extractive distillation is most frequently used because of a greater variety of entrainers and a wider range of operation conditions. Moreover, the feed of entrainers may be controlled by heat and material balances [4].

Methylal (Dimethoxymethane, DMM) is a colorless liquid, a presence of 42 % oxygen by weight, 100% miscible with diesel, and low soot in the combustion. As a result, methylal can be used to be additive in the diesel fuel to reduced gas pollutants [5-6]. Normally, Methylal is synthesized by the reversible reaction of methanol and formaldehyde or paraformaldehyde with heterogeneous acidic catalyst. To overcome the restrictions of chemical equilibrium, an excess of methanol is fed to the reactor [7-9]. Therefore, the mixture of methanol and methylal occurs in the production. However, methylal and methanol form a minimum-boiling azeotropic mixture at atmospheric pressure with 94.06 wt.% methylal [10]. Thus, conventional distillation cannot apply to separate completely the mixture of methylal and methanol.

Extractive distillation is widely used for separation of azeotropes. The most important step is to choose an entrainer (low toxicity, easy recovery, thermal stability, high boiling point, high relative volatility between key components, and high capacity) [10]. There are several researchers investigate the different entrainers to separate the mixture of methanol and methylal such as dimethylformamide (DMF), the mixture of DMF and ionic liquid, and ethylene glycol [10]. Although the selectivity of methylal to methanol of DMF is higher than that ethylene glycol, the ethylene glycol has a low toxicity [11].

The consideration of the toxicity level, ethylene glycol has a considerable toxicity level while the other entrainers is non-toxic. Therefore, the development should drive for safety process. Tetra-ethylene-glycol can be potential entrainer to substitute ethylene glycol such as in the ethanol process industries [12]. To intensify the separation of methylal and methanol, it is necessary to identify new entrainer such as tetra-ethylene-glycol.

The purpose of this work is to design an extractive distillation process to separate methylal by using tetra ethylene-glycol as entrainer. The residue curve maps (RCMs) for the methylal/methanol/ tetra-ethylene-glycol are essential graphical tools for demonstration the potential effect of tetra-ethylene-glycol that can eliminate the azeotropic mixture of methylal and methanol. Moreover, the steady state design involves the selection of the appropriate thermodynamic model and the study of the effect of the main design variables to give the methylal is higher than 99.9%.

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II. Steady State Design

A. Residue Curve Map

The extractive distillation process considered in this study is simulated based on commercial software (Aspen plus). The NRTL activity model is selected as the property package in the simulation using the built-in binary interaction parameters in the simulator. Residue curve map (RCM) is used to design and analyze for distillation boundaries and tie lines in the ternary phase diagram. The residue curve map of methylal/methanol/tetra-ethylene-glycol system at 1 atm as showed in Fig.1, tetra-ethylene glycol gives a good performance to modify the vapor-liquid equilibrium curve from an unstable node (the binary azeotrope) to a stable node.

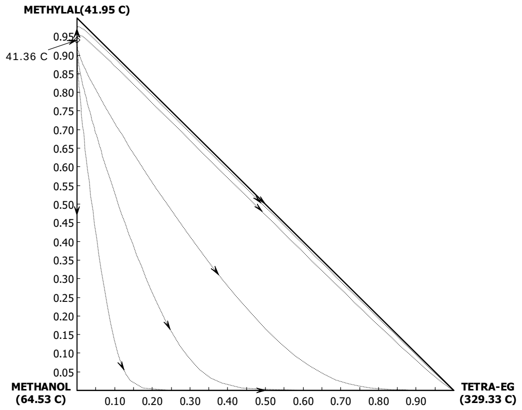

Fig. 1. Residue curve map for the system methylal/methanol/tetra-ethylene-glycol at 1 atm

B. Process Design

The process flowsheet of the extractive distillation as showed in Fig. 2, that has two columns, one for extractive separation and another for solvent recuperation. The azeotropic mixture (F) and the entrainer (E) streams are fed to extractive distillation column (EDC), where the desired compound takes place to the top of the extractive distillation column. The bottom product of the extractive distillation column feeds to the entrainer recovery column, where the solvent is separated from methanol and is recycled to the extractive distillation column.

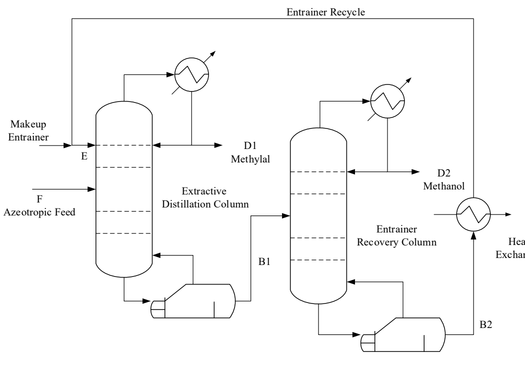

Fig. 2. Typical process flowsheet for the purification of methylal using distillation

In this paper, the excess methanol is fed into the reversible reaction to shift the equilibrium reaction to the right-hand side. Hence the mixture in the production stream combines with methanol, methylal, and water. After pretreatment, water is removed from the feed stream of the extractive distillation process. In order to optimize, the feeding rate is fixed flow rate at 100 kg/h, and temperature at 40°C, respectively. Moreover, mass fraction of methylal methanol are 94.06 wt. % and 5.94 wt. %, respectively. Feed stream is connected to EDC of 15 trays at the tray 8.

III. Response Surface Methodology

Response surface methodology (RSM) is one of statistical methods that can be helpful for optimization processes. RSM is applied to predict the relative significance of several variables [13].

Central composite design (CCD) is a standard RSM design that is applied to find the optimal condition in the extractive distillation column. The desired model response of the independent variables is obtained by using RSM and regression analysis. The predicted optimal condition is given

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

where $\hat{y}$ is the predicted response x_i is the levels of the independent variables, i, j, ij, and ii is the linear coefficient, the quadratic coefficient, the interaction effect, and the squared effect, respectively. Moreover, ε is the random error, and β is the regression coefficients of the independent variables [13].

The interaction between the process parameters and response is investigated by using Analysis of variance (ANOVA). To fit the polynomial model, the quality of this model is inspected by R^2 and statistical significance is evaluated by P-value. Moreover, the predicted optimal operating conditions are presented in 3D plot.

In general, the variables in the polynomial model are not necessarily having the same dimension which makes it difficult to compare their coefficients. Therefore, the variables are coded, all vary between the same minimum and maximum values (-2 and 2). In this work, there are four levels per factor to study and the coded variables are shown in Table I

TABLE I
VARIABLES AND SIMULATION DOMAIN FOR EDC

Factor	Level				
	-2	-1	0	1	2
Reflux ratio (RF)	0.5	3	5.5	8	10.5
Entrainer feed stage (ES)	1	3	5	7	9
Entrainer to Feed ratio (E/F)	1.5	2	2.5	3	3.5
Temperature of Entrainer (Temp (E))	45	80	115	150	185

To obtain the best model, ANOVA is used to analysis. A quadratic model of RSM is applied to simulate data as followed by the eliminating the term to find statistically insignificant. The model summary statistic demonstrates the high coefficient of determination R^2 (>0.9) and a P-value lower than 0.05 to suggest the models for product purity and energy consumption of the extractive distillation column

IV. Results and Discussion

The results from the design of the extractive distillation column is discussed. The data obtained from simulations are investigated for reboiler duty and product purity of methylal. The results for all operation conditions proposed by the RSM design are shown in Table II.

TABLE II
SIMULATIONS GENERATED FOR THE EXTRACTIVE DISTILLATION COLUMN

No	Rf	E/F	Es	Temp (E)	% Methylal	Q_r (MJ/hr)
1	8(1)	7(1)	2(-1)	80(-1)	99.626	305.799
2	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
3	3(-1)	3(-1)	2(-1)	80(-1)	100.000	146.307
4	8(1)	3(-1)	2(-1)	150(1)	99.999	273.363
5	5.5(0)	5(0)	2.5(0)	45(-2)	99.998	252.672
6	5.5(0)	5(0)	3.5(2)	115(0)	100.000	229.142
7	5.5(0)	5 (0)	2.5(0)	115(0)	99.999	216.238
8	5.5(0)	5(0)	1.5(-2)	115(0)	99.975	204.818
9	3(-1)	7(1)	3(1)	150(1)	99.987	120.516
10	8(1)	3(-1)	2(-1)	80(-1)	99.998	303.856
11	8(1)	7(1)	2(-1)	150(1)	99.706	274.894
12	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
13	5.5(0)	5(0)	2.5(0)	185(2)	100.000	176.524
14	8(1)	3(-1)	3(1)	150(1)	100.000	278.023
15	8(1)	7(1)	3(1)	80(-1)	99.900	324.254
16	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
17	5.5(0)	5(0)	2.5(0)	45(-2)	99.998	252.672
18	3(-1)	7(1)	3(1)	80(-1)	99.986	166.242
19	3(-1)	7(1)	3(1)	150(1)	99.987	120.516
20	3(-1)	3(-1)	3(1)	80(-1)	100.000	166.214
21	3(-1)	3(-1)	3(1)	150(1)	100.000	120.484
22	10.5(2)	5(0)	2.5(0)	115(0)	99.979	373.921
23	5.5(0)	5(0)	1.5(-2)	115(0)	99.975	204.818
24	5.5(0)	5(0)	2.5(0)	185(2)	100.000	176.524
25	8(1)	7(1)	3 (1)	80(-1)	99.900	324.254
26	5.5(0)	5(0)	2.5 (0)	115(0)	99.999	216.238
27	5.5(0)	5(0)	2.5 (0)	115(0)	99.999	216.238
28	5.5(0)	5(0)	2.5 (0)	115(0)	99.999	216.238
29	8(1)	7(1)	3(1)	150(1)	99.932	278.363
30	8(1)	3(-1)	2(-1)	80(-1)	99.998	303.856
31	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
32	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
33	3(-1)	3(-1)	3(1)	150(1)	100.000	120.484
34	5.5(0)	9(2)	2.5(0)	115(0)	97.756	223.583
35	3(-1)	7(1)	3(1)	80(-1)	99.986	166.242
36	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
37	8(1)	7(1)	2(-1)	150(1)	99.706	274.894
38	5.5(0)	1(-2)	2.5(0)	115(0)	54.751	121.423
39	8(1)	3(-1)	3(1)	150(1)	100.000	278.023
40	5.5 (0)	5 (0)	3.5 (2)	115(0)	100.000	229.142
41	3(-1)	3(-1)	2(-1)	80(-1)	100.000	146.307
42	3(-1)	3(-1)	2(-1)	150(1)	100.000	115.820
43	5.5(0)	1(-2)	2.5(0)	115(0)	54.751	121.423
44	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
45	8(1)	7(1)	2(-1)	80(-1)	99.626	305.799
46	10.5(2)	5(0)	2.5(0)	115(0)	99.979	373.921
47	0.5(-2)	5(0)	2.5(0)	115(0)	99.869	58.768
48	8(1)	7(1)	3(1)	150(1)	99.932	278.363
49	3(-1)	7(1)	2(-1)	150(1)	99.968	115.890
50	3(-1)	7(1)	2(-1)	80(-1)	99.951	146.417
51	8(1)	3(-1)	3(1)	80(-1)	100.000	323.754
52	0.5(-2)	5(0)	2.5(0)	115(0)	99.869	58.768
53	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
54	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
55	3(-1)	7(1)	2(-1)	80(-1)	99.951	146.417
56	5.5(0)	5(0)	2.5(0)	115(0)	99.999	216.238
57	3(-1)	7(1)	2(-1)	150(1)	99.968	115.890
58	8(1)	3(-1)	2(-1)	150(1)	99.999	273.363
59	3(-1)	3(-1)	2(-1)	150(1)	100.000	115.820
60	8(1)	3(-1)	3(1)	80(-1)	100.000	323.754
61	5.5(0)	9(2)	2.5(0)	115(0)	97.756	223.583
62	3(-1)	3(-1)	3(1)	80(-1)	100.000	166.214

The results of ANOVA analysis for all response are shown in Table III. A high R^2 coefficient confirms that a satisfactory match of quadratic model to simulate the data. In this work, data of methylal purity cannot be explained by the model; on the other hand, data of heat duty have the variation in the process data only 0.03% that the response cannot be explained by the model. Moreover, the F-value are much higher than 5 and P-value is lesser than 0.05, implying that the model terms are statistically [13].

TABLE III
ANOVA ANALYSIS FOR RESPONSE

Source	%Methylal		Q_r (MJ/hr)	
	F-value	P-value	F-value	P-value
Model	4.850	0.000	135.520	0.000
Linear	4.350	0.004	465.210	0.000
x_1 :Rf	0.000	0.980	1728.910	0.000
x_2 :Es	17.520	0.000	21.010	0.000
x_3 :E/F	0.000	0.976	10.010	0.003
x_4 :Temp (E)	0.000	0.995	100.930	0.000
Square	12.580	0.000	8.420	0.000
x_1^2	1.550	0.220	1.180	0.284
x_2^2	40.760	0.000	27.220	0.000
x_3^2	1.600	0.213	1.380	0.246
x_4^2	1.610	0.211	0.690	0.409
Interaction	0.000	1.000	0.450	0.843
$x_1 \bullet x_2$	0.000	0.965	0.010	0.913
$x_1 \bullet x_3$	0.000	0.979	0.000	0.946
$x_1 \bullet x_4$	0.000	0.995	0.000	0.988
$x_2 \bullet x_3$	0.000	0.974	0.010	0.941
$x_2 \bullet x_4$	0.000	0.994	0.000	0.987
$x_3 \bullet x_4$	0.000	0.997	2.660	0.110
R^2	59.07%		97.58%	
Adjust R^2	46.48%		96.86%	
Pred R^2	18.43%		95.18%	

Independent terms the interactions are statistically significant if the P- value is lesser than 0.05. In Table III, ANOVA analysis results indicate the reboiler heat duty of EDC is directly related to mass reflux ratio (Rf), entrainer feed stage (Es), and mass of the entrainer to feed ratio (E/F). While the purity of methylal is related to Es only. The overall equation for the model relating the reboiler heat duty of EDC of code factors is given by

$$\begin{aligned} Qr = {} & 7.26992 + 28.3674x_1 + 27.2506x_2 - 2.40788x_3 - 0.270574x_4 \\ & + 0.301736x_1^2 - 2.26865x_2^2 + 8.17924x_3^2 + 0.00118310x_4^2 \\ & + 0.0509445x_1 \bullet x_2 - 0.126974x_1 \bullet x_3 - 3.92468e^{-4}x_1 \bullet x_4 \\ & - 0.172217x_2 \bullet x_3 - 5.41133e^{-4}x_2 \bullet x_4 - 0.216664x_3 \bullet x_4 \end{aligned} \quad (2)$$

The graphic analysis of the response surface and contour plot for the reboiler heat duty of EDC and the purity of methylal are illustrate in Fig.3 and Fig. 4, respectively. The interaction between parameters that affect the heat duty are presented in Fig. 3 (a) – Fig. 3 (l). Moreover, the effect of the interaction between parameters for and product purity are presented in Fig. 4 (a) – Fig. 4 (l).

Results demonstrate that for each response, different parameters and interactions are important; for optimization of EDC, all parameters should be considered simultaneously. The optimal condition of all factors can be found the optimization of energy consumption and product purity by using the point prediction of RSM. The optimum values of parameters are shown in Table IV and the

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response for the optimal condition to predict the point option by RSM is presented in Fig.5. The optimized entrainer feed is on stage 2.54, which should be on stage 3.

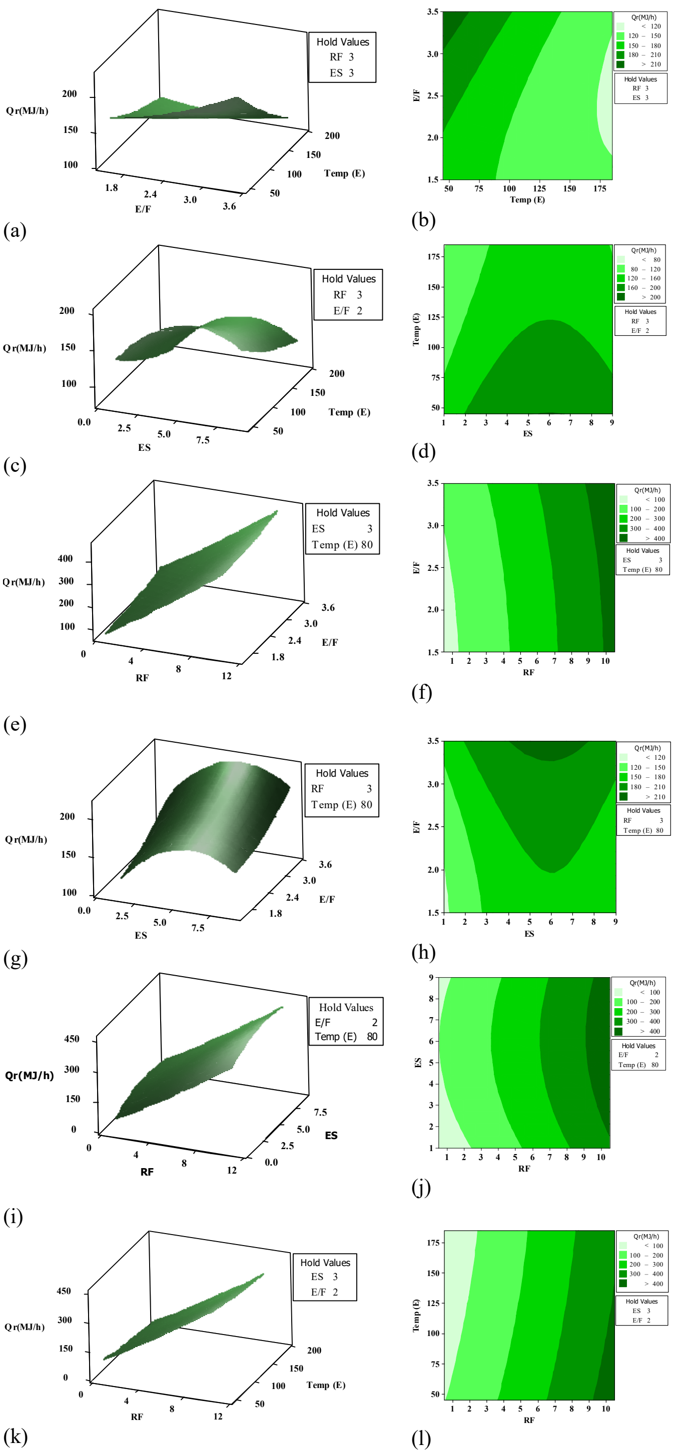

Fig. 3. Response surface for heat reboiler duty connecting of the entrainer to feed ratio (E/F) and temperature of entrainer (Temp (E)) (a),(b); the entrainer feed stage (Es) and temperature of entrainer (Temp (E)) (c),(d); reflux ratio (RF) and entrainer to feed ratio (E/F) (e), (f); entrainer feed stage (Es) and reflux ratio (RF) (i), (j); reflux ratio (RF) and temperature of entrainer (Temp (E)) (k),(l).

TABLE IV
OPTIMUM PARAMETER OF EDC

Rf	Es	E/F	Temp (E)
0.5	2.54 (3)	1.5	45

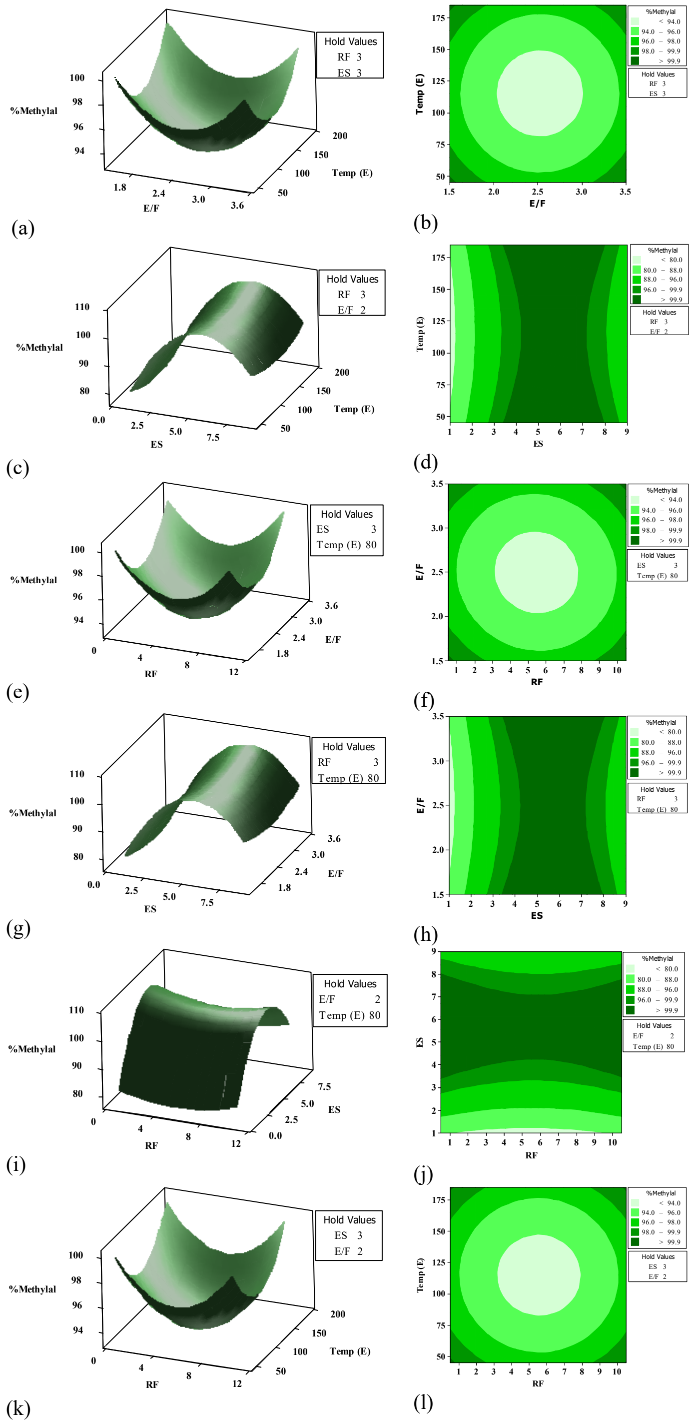

Fig. 4. Response surface for purity of methylal connecting of the entrainer to feed ratio (E/F) and temperature of entrainer (Temp (E)) (a),(b); the entrainer feed stage (Es) and temperature of entrainer (Temp (E)) (c),(d); reflux ratio (RF) and entrainer to feed ratio (E/F) (e), (f); entrainer feed stage (Es) and reflux ratio (RF) (i), (j); reflux ratio (RF) and temperature of entrainer (Temp (E)) (k),(l).

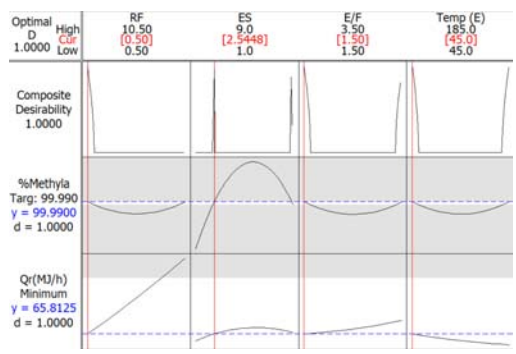

Fig. 5. The optimum value of all parameters

Moreover, the final design for the extractive distillation process that consists of the recovery entrainer column and condition to operation are presented in Fig. 6. The extractive distillation process, the feed of azeotropic mixture is on stage 8 and the position and temperature of tetra-ethylene-glycol stream are on stage 3 and 45 °C, respectively. In EDC, methylal (99.99 wt. %) is withdrawn into the overhead and the bottom stream (the mixture of tetra-ethylene-glycol and methanol) is connected to entrainer recovery column on stage 2.

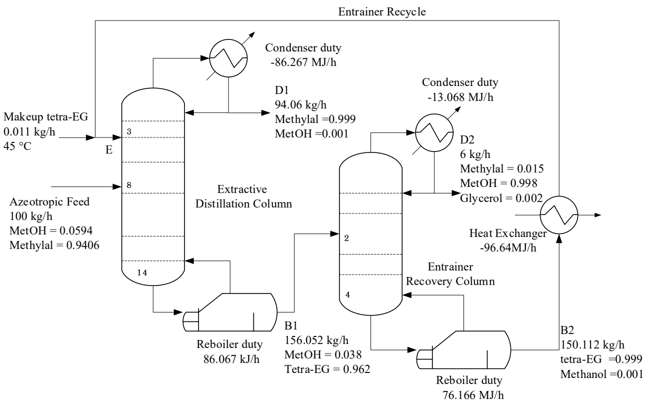

Fig. 6. Final flowsheet design for the extractive distillation process to separate methylal-methanol system

V. CONCLUSION

In this work, the separation of methylal and methanol by extractive distillation is intensified by tetra-ethylene-glycol as entrainer. For this system, NRTL model in the commercial simulator (Aspen plus) is used to simulate. The residue curve map (RCM) of the methylal / methanol / tetra-ethylene-glycol is prior analysis. Tetra-ethylene-glycol as entrainer is possible to obtain high purity of methylal in the extractive distillation process. A practical method to propose the design of the extractive distillation column (EDC) has been obtained by response surface methodology (RSM) with the study of the effect of factors and their interactions on the requirement of energy consumption and methylal purity. The reboiler heat duty of EDC is directly related to mass reflux ratio (Rf), entrainer feed stage (Es), temperature of entrainer (Temp(E)), and entrainer to feed ratio (E/F). While the purity of methylal is related to Es only. To obtain the optimal operating conditions, sensitivity analysis of the EDC has been studied by RSM that is sufficient and efficient for design the extractive distillation system.

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