

DESIGN EXTRACTIVE DIVIDING WALL DISTILLATION COLUMN BASED ON RESPONSE SURFACE METHODOLOGY USING PROPYLENE-GLYCOL (PG) AS AN ENTRAINER, SEPARATE THE MIXTURE OF METHYLAL AND METHANOL

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Abstract

The primary drawback of traditional extractive distillation (to separate an azeotropic mixture) lies in its energy efficiency. Consequently, the design of an extractive dividing wall distillation column (EDWC) to separate an azeotropic mixture (methylal and methanol) by using propylene glycol (PG) as an entrainer has been studied. The optimal design of the EDWC was based on the central composite design (CCD) method in the response surface methodology (RSM) to identify the important parameters that affect the product purity of methylal, methanol, and energy consumption. Moreover, the optimal parameters to achieve the desired values of product quality and energy consumption could be calculated by the RSM optimizer. According to the simulation results, the feed stages of the mixture and entrainer, with their interaction parameters, had the greatest impact on the product qualities and amount of energy. The purity of methylal was influenced by the distillate rate of the main column, and the reflux ratio, as well as their interaction. On the other hand, the distillate rate of the main and prefractionator columns had the most significant effect on the purity of methanol. The important operation parameters in EDWC for heat duty in a reboiler were the link between the reflux ratio and the vapor split ratio. The reboiler heat duty of 118,768.76 kJ/h (saving 44.24 %) allowed for the separation of methylal and methanol at 99.99 wt.% and 94.75 wt.%, respectively. Subsequently, PG can be employed to segregate methyl and methanol using EDWC.

Keywords: Azeotropic mixture, Central composite design, Extractive dividing wall distillation column, Propylene glycol, Response surface methodology.

1. Introduction

Distillation is a popular separation method in the chemical and petrochemical industries, accounting for more than 90% of all fluid separations. The main disadvantage of the distillation process is its low thermodynamic efficiency (approximately 95% of energy consumption for substance isolation), which accounts for about 3% of global energy consumption [1]. Energy prices are well known to have an impact on economic growth. In addition, there is a growing awareness of the environmental crisis. Saving energy consumption not only benefits the economy, but it also benefits the environment by lowering emissions associated with energy combustion.

The aim of improving the design of the intensified distillation process is to reduce energy consumption and reduce the cost of capital. Dividing-wall distillation columns (DWCs) represent an enhanced form of the distillation process that offers potential energy savings of approximately 30-40% when compared to conventional distillation methods [2-4]. Using a dividing wall column (DWC) makes it easier to join two separate columns together, which creates a single shell. The implementation of this technique involves the placement of a vertical wall within the axial section.

Extractive dividing wall distillation columns (EDWCs) are used to separate azeotrope and/or low-relative-volatile liquid mixtures. They can save 10-20% of the energy and 40% of the capital cost compared to the traditional extractive distillation process (two columns) [3, 5, 6].

Methylal, also known as dimethoxymethane (DMM), is widely utilized in various chemical industries due to its advantageous properties such as favourable solubility, low viscosity, low surface tension, and transparent liquid state [7]. Additionally, methylal demonstrates the potential to serve as an additive in diesel fuel with the aim of enhancing engine performance, providing corrosion protection, and mitigating issues related to pollutant emissions [8]. The synthesis of methylal can be achieved through a reversible reaction involving methanol and formaldehyde, facilitated by a heterogeneous acidic catalyst.

The limited chemical equilibrium of methylal production results in a restricted yield. By introducing an excess of the reactant, methanol, the equilibrium will be shifted towards the product side [7, 9]. Nevertheless, methylal cannot be highly purified from this mixture using a conventional distillation column. The main cause of this is the azeotropic mixture of methanol and methylal that forms at atmospheric pressure (minimum boiling azeotrope).

In industrial settings, the extractive distillation system is commonly employed for the efficient separation of methylal from a mixture of methylal and methanol. This is primarily attributed to the system's utilization of a diverse range of entrainers and the ability to operate under a wider range of conditions. In the extractive distillation process, an entrainer is introduced with the purpose of increasing the relative volatility. This phenomenon occurs due to the entrainer exhibiting a higher affinity for the heavy component in comparison to the light component. The light and heavy components can be obtained from the upper and lower sections of the distillation column, respectively.

Several variables are considered while choosing an entrainer for this specific application: low toxicity, easy recovery, thermal stability, high boiling point, high

relative volatility between important components, and high solvent capacity. Because of its high selectivity and efficiency, dimethyl formamide (DMF) is a popular organic entrainer for methylal separation from methanol. However, as a solvent, DMF does not have any eco-friendly qualities. Additional organic entrainers, such as ethylene glycol, cyclohexanol, and glycerol, have been investigated in order to identify a new and unique entrainer [9-14].

Propylene glycol was used as the entrainer to separate the mixture of methylal and methanol, based on the selectivity standard. Furthermore, propylene glycol exhibits a remarkably low level of toxicity and is environmentally benign [15]. To get rid of the azeotropic combination, a propylene glycol feasibility study needs to look at how the mixture acts by using thermodynamic analysis of phase diagrams, more specifically residue curve mappings (RCMs) [13].

The efficiency of the separation process for the mixture of methylal and methanol can be improved by using propylene glycol as the entrainer for designing the EDWC appropriately. Because of the increased number of parameters involved, the design of divided-walled columns is more complicated than the design of conventional distillation. These parameters include the number of trays in each section, the ratio of liquid to vapor in the spits, the placement of the feed tray, and the side product.

For the column design, it is necessary to optimize all of these factors at once because of their interdependencies. Statistical methodologies show great potential for conducting process optimization studies. While there are numerous program simulations in the chemical industry, there is a lack of research on the correlation between input factors and output response, as well as the impact of interactions among input variables on the output response.

Relationships between output responses and independent input factors into the polynomial model can be studied generally using response surface methodology (RSM), which is based on central composite design (CCD). In addition, the optimal conditions can be estimated in order to create the experiments and simulated processes that are based on CCD [1, 3, 12-14, 16-18].

The aim of this work is to design EDWC by using propylene glycol (PG) as an entrainer in the methylal and methanol separation processes. The study applied response surface methodology (RSM) based on central composite design (CCD) to analyse the effects of various process parameters (the number of stages in the main column and prefractionator, the location of the mixture and entrainer feed stages, the distillate rate of the main column and prefractionator, the mass reflux and vapor split ratios, and the entrainer temperature).

The data (simulation results) are based on Aspen Plus, followed by applying RSM to identify the trends of each parameter and finding the optimal conditions to give the maximum product purity and minimize energy consumption in the reboiler of EDWC.

2. Model Simulation

The combination of methylal and methanol, when subjected to atmospheric pressure, forms an azeotropic mixture with a minimum boiling point of 41.03 °C (94.06 wt.% methylal and 5.88 wt.% methanol). In the process of extractive

distillation, propylene glycol (PG) serves as an entrainer to separate an unstable node consisting of methylal and methanol into a stable node [13]. In this work, the Non-Random Two Liquid (NRTL) model is used in the commercial program (Aspen Plus v.11) to establish the binary interaction parameters because the NRTL model can be predicted into non-ideal systems at low pressure (< 10 bar), including azeotropic behaviour [19].

2.1. Column configuration

The process design of EDWC cannot be simulated directly by using a commercial process simulator. Hence, the primary objective in the design of the EDWC is to transform two traditional columns into a single column with the same functionality. The main column on the left side and the prefractionator (rectifying column) on the right side of the column have diving walls that separate them. Moreover, the reboiler is shared in the main column with the prefractionator, as shown in Fig. 1(a).

The general arrangement for the equivalent diagram of the extractive dividing wall distillation system is illustrated in Fig. 1(b). The internal wall of the column is connected to the upper edge of the separating wall, preventing the liquid from the main column from descending into the prefractionator. As a result, the liquid split at the top of the dividing wall is absent. In contrast, the vapor is transferred from the main column to the prefractionator that is located at the wall location when it is at the bottom of the diving wall.

The feed stream (F) is a mixture of methylal and methanol, and the entrainer stream (E) is propylene glycol (PG). The entrainer feed is located above the feed stream. As the heavy component (methanol) was taken out and sent to the stripping part of the main column with the entrainer, its vapor pressure and volatility went down in the rectifying part of the column. This brought a high concentration of methanol vapor into the prefractionator. This makes it easy to separate the methanol vapor from the entrainer.

As a result, the light component, which is methylal (P1), is removed from the top of the main column, and the methanol (P2) is discharged from the top of the prefractionator. In addition, the recovery entrainer can be achieved at the bottom of the column and then circulated to the main column during the process. However, some entrainers would be lost in the process, and then the make-up stream of the entrainer would be installed to balance the stream of the entrainer (E).

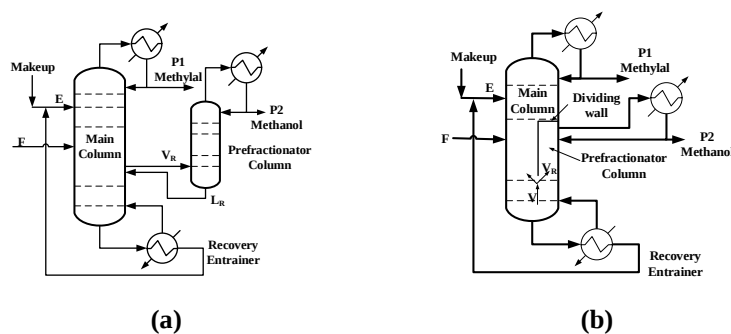


Fig. 1. (a) Equivalent Diagram for EDWC, (b) General arrangement for EDWC.

In order to achieve specifications greater than 99.9 wt.% of methylal, maximum methanol purity, and the lowest energy requirement in the reboiler, design parameters included the number of stages of the main column and prefractionator, the location of the feed stage of the mixture and entrainer, the distillate rate of the main column and prefractionator, mass reflux and vapor split ratios, and the temperature of the entrainer. The feed mixture settings for this study included a flow rate of 100 kg/h with 94.12 wt.% methylal and 5.88 wt.% methanol at a temperature of 30 °C. The feed of the entrainer influenced the purity of products and reboiler heat duty [11, 20].

Then the flow rate of the entrainer was 100 kg/h, and the entrainer-to-feed mass ratio was 1. The EDWC system has been operated with a total condenser and a partial reboiler. The operational parameters of the EDWC were a preliminary study to specify the initial conditions and their outcomes, which are documented in Table 1 [21].

Table 1. Operation conditions for the separation of methylal and methanol mixture using PG as an entrainer in the EDWC.

Parameters	
Number of stages in the main column	52
Number of stages in the prefractionator	12
Feed stage of mixture	35
Feed stage of entrainer	4
Distillate rate	
- main column (kg/h)	94.2
- prefractionator (kg/h)	6.5
Mass reflux ratio	5
Vapor split ratio	0.22
Entrainer temperature (°C)	30
Results	
Mass fraction	
- methylal	0.999
- methanol	0.892
- propylene glycol	1
Reboiler duty (kJ/h)	2.48×10^5

2.2. Response surface methodology

Response surface methodology (RSM), which is able to forecast the relative relevance of many effect variables, has been utilized in a significant number of studies to investigate the interaction between the output responses (dependent variables) and the unique input variables (independent variables). The RSM can be used to solve an optimization problem involving the process parameters for a multi-objective. A central composite design (CCD) is a type of experimental design used in response surface methodology (RSM). It involves a series of mathematical and statistical tools to design experiments. The desirable reactions can be assessed.

$$\hat{y} = \alpha_0 + \sum_{i=1}^k \alpha_i x_i + \sum_{i=1}^k \alpha_{ii} x_i x_i + \sum_{i=1}^k \sum_{j=1, j \neq i}^k \alpha_{ij} x_i x_j + \varepsilon \quad (1)$$

where $\hat{y}$ is the desirable response, x_i and x_j are the independent variables, α_0 , α_i , α_{ii} and α_{ij} are the regression factors of the independent variables that can be estimated through optimization procedure regarding the available data set for constant, linear,

quadratic, and interaction terms, respectively. Moreover, ε is the random error, and k is the study factors number.

ANOVA is a method to analyse the interaction between individual input variables and output response. The model is presented in the polynomial formation that demonstrates the effects of the interaction variables on the response by three-axis response surfaces and two-axis plots. Plausibility of the quadratic model can be checked by the value of the R^2 ($R^2 > 0.9$ and $\text{Adj-}R^2 > 0.9$) and P-value (P-value < 0.05) to predict the optimal conditions [17]. The quality of the model has been evaluated by measuring the $\text{Adj-}R^2$, which quantifies the extent to which the model predicts the variation in the data. The R^2 value is enhanced by removing inconsequential items, whereas the $\text{Adj-}R^2$ value is improved by adding terms [14, 17, 22]. To indicate the model quality, the difference between the $\text{Adj-}R^2$ and R^2 values should be less than 0.20 [23, 24].

3.Results and Discussion

The RSM method, which was split into two parts, had cut down on the simulation run for the steady-state design of the EDWC for methylal and methanol with a propylene-glycol system. There were 9 factors to predict the output responses by using the RSM based on the CCD method (156 runs consisting of 128 factorial points, 18 axial points, and 10 center points). The strong correlation between the several variables made it difficult to use regression models to accurately predict the response. Hence, it could partition the model into two components (structural and operational) in order to minimize the interplay of variables.

Table 2 presents the determined range of variables from the preliminary simulation runs. All parts were determined as the optimal parameters to achieve the specification of 99.9 wt.% methylal, maximum purity of methanol, and minimum energy requirement in the reboiler. To reduce the interaction of variables, the optimal structure parameters (number of stages in the main column (x_1), prefractionator (x_2), mixture feed stage (x_3), and entrainer feed stage (x_4)) were first determined. There were 31 simulation runs for four variables.

And then, keeping structural parameters constant, the operation variables (distillate rate of the main column (x_5), distillate rate of the prefractionator (x_6), reflux ratio (x_7), vapor split ratio (x_8), and entrainer temperature (x_9)) as 5 variables (32 simulation runs) were determined to be the optimal parameters.

Table 2. Variables code levels for EDWC.

Independent Variables	Value of Coded level		
	Low (-1)	Central (0)	High (1)
x_1 : Number of stages in the main column	50	52	54
x_2 : Number of stages in the prefractionator	4	5	6
x_3 : Feed stage of mixture	23	24	25
x_4 : Entrainer feed stage	12	14	16
x_5 : Distillate rate of main column	94.1	94.2	94.3
x_6 : Distillate rate of prefractionator column	6.4	6.6	6.8
x_7 : Reflux ratio	3	4	5
x_8 : Vapor split ratio	0.09	0.10	0.11
x_9 : Entrainer temperature	60	100	140

3.1. Structural parameters optimization

In this section, the results of the design and optimization of the number of stages (main column and prefractionator) and the position of the feed trays (mixture and entrainer) were investigated. The obtained data from the simulation for the purity of methylal and methanol and the heat duty were considered. The ANOVA results were shown in Table 3 that the quadratic model fit the data well ($R^2 > 90\%$, F-value > 5 , and P-value < 0.05) [14]. The R^2 values of the regression models, as shown in Table 3, were found to be 98.60% for purity of methylal ($\hat{y}_{1,1}$), 99.63% for purity of methanol ($\hat{y}_{1,2}$), and 92.43% for reboiler heat duty ($\hat{y}_{1,3}$).

The Adj- R^2 values for methylal purity, methanol purity, and reboiler heat duty were 97.37%, 98.16%, and 96.54%, respectively. In this case, the regression model for the reboiler heat duty was the least accurate.

However, the high values of R^2 and Adj- R^2 ($> 90\%$), as well as the difference of less than 20%, indicated an accurate match between the results [14]. Therefore, the regression models demonstrated high accuracy in identifying the response variables presented in Eqs. (2)-(4).

$$\begin{aligned}\hat{y}_{1,1} = & 0.8697 + 1.5 \times 10^{-4}x_1 - 2.9 \times 10^{-4}x_2 + 1.06 \times 10^{-2}x_3 \\ & - 8.5 \times 10^{-4}x_4 - 8 \times 10^{-6}x_1^2 - 3.1 \times 10^{-5}x_2^2 - 2.81 \times 10^{-4}x_3^2 \\ & - 1.02 \times 10^{-4}x_4^2 + 3.1 \times 10^{-5}x_1x_2 + 3.1 \times 10^{-5}x_1x_3 \\ & - 1.6 \times 10^{-5}x_1x_4 - 6.2 \times 10^{-5}x_2x_3 + 3.1 \times 10^{-5}x_2x_4 \\ & + 1.56 \times 10^{-4}x_3x_4\end{aligned}\quad (2)$$

$$\begin{aligned}\hat{y}_{1,2} = & 0.981 - 3.21 \times 10^{-3}x_1 - 2.6 \times 10^{-3}x_2 + 1.01 \times 10^{-2}x_3 \\ & - 2.68 \times 10^{-2}x_4 + 5 \times 10^{-6}x_1^2 + 2.1 \times 10^{-5}x_2^2 \\ & - 7.29 \times 10^{-4}x_3^2 - 9.64 \times 10^{-4}x_4^2 + 1.25 \times 10^{-4}x_1x_2 \\ & + 1.25 \times 10^{-4}x_1x_3 - 6.3 \times 10^{-5}x_1x_4 - 2.5 \times 10^{-4}x_2x_3 \\ & + 1.25 \times 10^{-4}x_2x_4 + 2 \times 10^{-3}x_3x_4\end{aligned}\quad (3)$$

$$\begin{aligned}\hat{y}_{1,3} = & 237708 + 356x_1 - 707x_2 - 56x_3 + 903x_4 - 2.52x_1^2 + 72.0x_2^2 \\ & + 18.2x_3^2 + 28.32x_4^2 - 4.2x_1x_2 - 4.4x_1x_3 + 2.17x_1x_4 + 8.4x_2x_3 \\ & - 4.2x_2x_4 - 63.6x_3x_4\end{aligned}\quad (4)$$

In Table 3, the feed stage of the mixture (x_3) and the entrainer (x_4) had a major effect on the purity of the products (methylal ($\hat{y}_{1,1}$) and methanol ($\hat{y}_{1,2}$)) and the reboiler heat duty ($\hat{y}_{1,3}$). Moreover, the number of prefractionator stages (x_2) had a small effect on the reboiler heat duty ($\hat{y}_{1,3}$). Moreover, the interaction between the location of the feed stage of the mixture and the entrainer influenced the purity of methylal and methanol, as well as the reboiler heat duty, as shown in Figs. 2-4.

Increasing the distance between the location of the feed stages of the mixture and the entrainer could improve the quality of methylal and methanol, as shown in Figs. 2 and 3. Because the mixture (methylal and methanol) and the entrainer (PG) had more space to contact each other, the relative volatility between the methylal and methanol was reduced. The increased difference in location between the feed stages of the mixture and the entrainer could enhance the quality of methylal and methanol, as presented in Figs. 2 and 3, respectively, because of the increasing time to contact between the mixture (methylal and methanol) and the entrainer (PG).

Moreover, reducing the space between the feed stages of the location of the mixture and the entrainer reduced the reboiler heat duty, as shown in Fig. 4. This was because the reboiler heat duty used less energy to reach the vapor-liquid equilibrium on each plate in the column. If the feed stages of the mixture and entrainer had a high difference in location, the heat duty of the reboiler needed to increase.

The distance between the feed stages of the mixture and the entrainer was needed to evaluate the optimal condition to give the product purity of methylal greater than 99.9 wt.% and maximum methanol purity with minimum energy consumption in the reboiler by using the RSM optimizer's multi-objective optimization method.

Table 3 ANOVA analysis for responses of structural parameters.

Source	$\hat{y}_{1,1}$		$\hat{y}_{1,2}$		$\hat{y}_{1,3}$	
	F-value	P-value	F-value	P-value	F-value	P-value
Model	80.45	0.000	305.19	0.000	60.83	0.000
x_1	0.89	0.36	0.31	0.584	0.08	0.786
x_2	0.89	0.36	0.31	0.584	9.09	0.008
x_3	200	0.000	782.4	0.000	149.97	0.000
x_4	747.56	0.000	3160.96	0.000	621.31	0.000
x_1^2	0.6	0.451	0.01	0.940	0.27	0.608
x_2^2	0.6	0.451	0.01	0.940	13.92	0.002
x_3^2	48.26	0.000	7.14	0.017	0.89	0.36
x_4^2	100.68	0.000	199.41	0.000	34.41	0.000
x_1x_2	1.33	0.265	0.47	0.503	0.11	0.747
x_1x_3	1.33	0.265	0.47	0.503	0.12	0.738
x_1x_4	1.33	0.265	0.47	0.503	0.11	0.740
x_2x_3	1.33	0.265	0.47	0.503	0.11	0.748
x_2x_4	1.33	0.265	0.47	0.503	0.11	0.749
x_3x_4	33.33	0.000	120.18	0.000	24.25	0.000
Coefficient of determination						
% R^2	98.6		99.63		92.49	
% Adj- R^2	97.37		98.16		96.54	

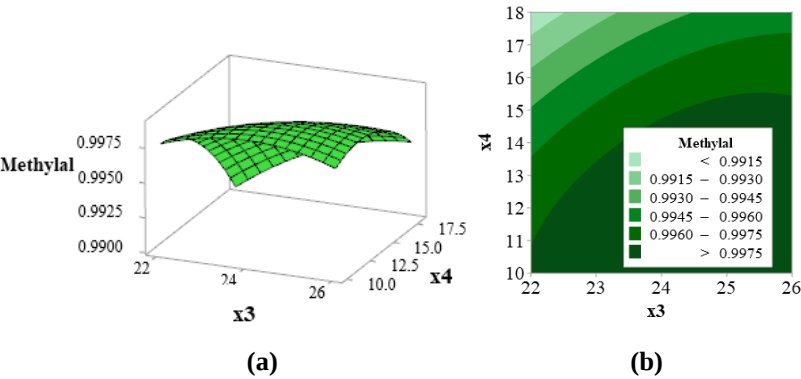


Fig. 2. Effect of the interaction for structural parameter of EDWC for methylal purity of x_3 and x_4 at the holding values of x_1 and x_2 is 52 and 5, respectively. (a) Surface plot; (b) Contour plot.

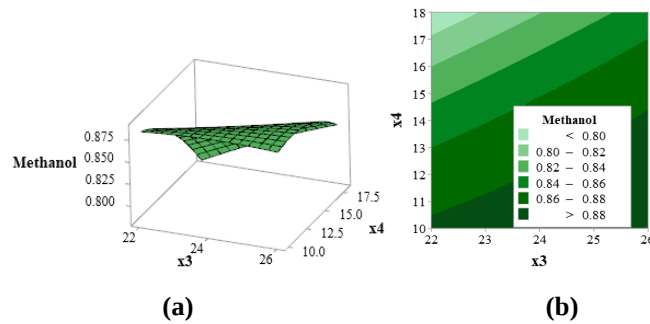


Fig. 3. Effect of the interaction for structural parameter of EDWC for methanol purity of x_3 and x_4 at the holding values of x_1 and x_2 is 52 and 5, respectively. (a) Surface plot, (b) Contour plot.

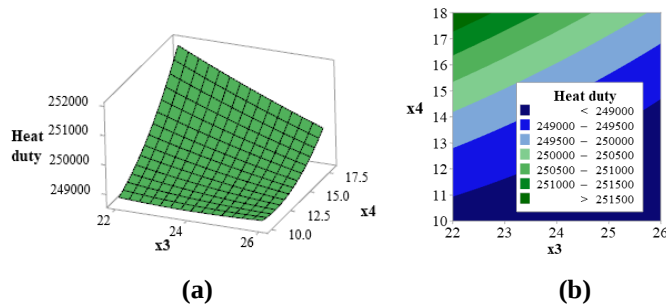


Fig. 4. Effect of the interaction for structural parameter of EDWC for heat duty (kJ/h) of x_3 and x_4 at the holding values of x_1 and x_2 is 52 and 5, respectively. (a) Surface plot, (b) Contour plot.

For multi-objective optimization, the RSM optimizer could be generated, as illustrated in Fig. 5. The suggested simulation method had the highest attractiveness value (nearly 1), with x_1 (number of stages in the main column) = 56, x_2 (number of stages in the prefractionator) = 5, x_3 (mixture feed stage) = 25, and x_4 (entrainer feed stage) = 11. The purity of methylal was more than 99.9 wt.%, the methanol purity was 88.77 wt.%, and the reboiler heat duty was 2.487×10^5 kJ/h. In this section, methylal purity could achieve the desired target. As part of the operational parameter optimization, the maximum methanol purity and the minimum reboiler heat duty were repeated to be calculated 333.

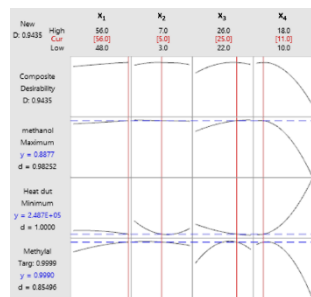


Fig. 5. RSM Optimizer results for a structural parameter of EDWC.

3.2. Operational parameters optimization

After studying the optimal structural parameters, there were five operational process parameters for optimization in CCD to achieve the purpose of this work. These were the distillate rates of the main column (x_5) and prefractionator (x_6), the reflux ratio (x_7), the vapor split ratio (x_8), and the entrainer temperature (x_9). The levels of the parameters were presented in Table 2. To obtain the optimal operating parameters for the EDWC, two dependent parameters (methanol ($\hat{y}_{2,2}$), and heat duty ($\hat{y}_{2,3}$)) were analyzed. The results of the quadratic models were as follows:

$$\begin{aligned}\hat{y}_{2,2} = & -354 + 7.2x_5 + 8.79x_6 - 1.46x_7 - 194x_8 + 4.87 \times 10^{-2}x_9 \\ & - 3.6 \times 10^{-2}x_5^2 - 9.1 \times 10^{-3}x_6^2 - 3.86 \times 10^{-3}x_7^2 - 11.1x_8^2 \\ & - 1 \times 10^{-6}x_9^2 - 9.37 \times 10^{-2}x_5x_6 + 1.63 \times 10^{-2}x_5x_7 + 2x_5x_8 \\ & - 5 \times 10^{-3}x_5x_9 - 0.00937x_6x_7 + 1x_6x_8 + 2.5 \times 10^{-4}x_6x_9 \\ & + 0.2x_7x_8 - 5 \times 10^{-5}x_7x_9 + 0.00469x_8x_9\end{aligned}\quad (6)$$

$$\begin{aligned}\hat{y}_{2,3} = & 349583430 - 6798736x_5 - 9838774x_6 - 1957614x_7 \\ & + 202617229x_8 - 49888x_9 + 32801x_5^2 + 10096x_6^2 + 500x_7^2 \\ & + 4035035x_8^2 + 0.251x_9^2 + 103345x_5x_6 + 20538x_5x_7 \\ & - 2069549x_5x_8 + 514x_5x_9 + 10335x_6x_7 - 1032915x_6x_8 \\ & + 256x_6x_9 - 206689x_7x_8 + 51.6x_7x_9 - 5168x_8x_9\end{aligned}\quad (7)$$

The analysis of the ANOVA for all responses was presented in the R^2 and Adj- R^2 values, F-value, and P-value, as shown in Table 4. The R^2 value of 97.34% and the Adj- R^2 value of 92.49% for methanol purity, as well as the R^2 value of 99.54% and the Adj- R^2 value of 98.71% for reboiler heat duty, indicated a significant similarity between the quadratic model value and the experimental value (simulated data). This study demonstrated that the regression models for methanol purity and reboiler heat duty were precise because R^2 and Adj- R^2 were greater than 90%.

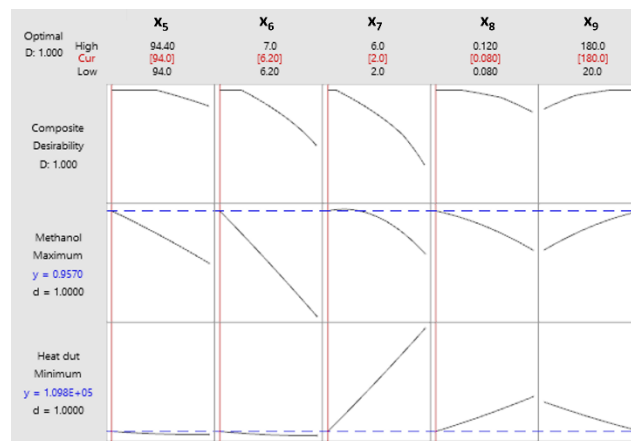
The input variables (distillate rate of the main column and prefractionator, reflux ratio, vapor split ratio, and entrainer temperature) had a greater impact on the output variables. Especially for the reboiler heat duty, the values of R^2 and Adj- R^2 were higher than the structural parameters. Moreover, the p-values of the model and each parameter indicated the statistically significant model and the effect of parameters and interactions on parameters.

In Table 4, the ANOVA results demonstrated that the purity of the methanol and the reboiler heat duty were affected by both single parameters and the interactions between operating parameters. The influencing variables for the purity of methanol were the distillate rates of the main column (x_5) and the prefractionator (x_6). The product purity depended on the withdrawal of the distillate products (main column and prefractionator), which affected the reflux ratio (x_7) and the vapor split ratio (x_8) and had a direct impact on the heat duty of the reboiler.

All interactions between operating parameters affected the reboiler heat duty. In Fig. 6, a composite desirability of 1, the settings were optimal for achieving good results for all the responses, resulting in a methanol purity of 95.7% wt. and the heat duty of the reboiler of 1.098×10^5 kJ/h, which operated under the conditions of the distillate rates of the main column, the prefractionator ratios of reflux and vapor split, and the entrainer temperature being 94.174 kg/h, 6.20 kg/h, 2, 0.08, and 180 °C, respectively.

Table 4 ANOVA analysis for responses for operational process parameters.

Source	$\hat{y}_{2,2}$		$\hat{y}_{2,3}$	
	F-value	P-value	F-value	P-value
Model	20.1	0.000	119.38	0.000
x_5	15.35	0.002	2.14	0.171
x_6	355.13	0	3.72	0.08
x_7	4.74	0.052	2298.93	0
x_8	0.99	0.341	19.65	0.001
x_9	0.99	0.341	4.35	0.061
x_5^2	0.09	0.77	0.27	0.617
x_6^2	0.09	0.77	0.4	0.539
x_7^2	10.16	0.009	0.62	0.449
x_8^2	0.84	0.378	0.4	0.539
x_9^2	0.84	0.378	0.4	0.542
$x_5 x_6$	1.31	0.277	5.75	0.035
$x_5 x_7$	0.98	0.343	5.68	0.036
$x_5 x_8$	1.49	0.248	5.77	0.035
$x_5 x_9$	1.49	0.248	5.69	0.036
$x_6 x_7$	1.31	0.277	5.75	0.035
$x_6 x_8$	1.49	0.248	5.74	0.035
$x_6 x_9$	1.49	0.248	5.63	0.037
$x_7 x_8$	1.49	0.248	5.75	0.035
$x_7 x_9$	1.49	0.248	5.74	0.035
$x_8 x_9$	1.31	0.277	5.75	0.035
Coefficient of determination				
% R^2	97.34		99.54	
% Adj- R^2	92.49		98.71	

**Fig. 6.** RSM Optimizer results for operational parameters of EDWC.

Here, the Aspen Plus software simulated the ideal design settings in the EDWC, as shown in Fig. 7. The main column has 56 stages, which included the condenser and reboiler, and the prefractionator had 4 stages (40-44). The mixture of methylal and methnol was fed to stage 25, while the recovered PG (entrainer) was mixed with a small make-up feeding to stage 11. Before introducing the recovered PG into the EDWC column, a heat exchanger was required to lower the recovery entrainer stream to 180 °C.

The distillate flow rates of the main column and prefractionator column were 94 kg/h and 6.2 kg/h, respectively. Moreover, the reflux ratio was 2, and the vapor-spilt ratio was 0.08. According to the operating parameters, the products purity of was methylal and methanol were 99.99 wt.% and 94.75 wt.%, respectively, and the purity of the recycled entrainer was 100 wt.% PG. The energy consumption for the reboiler in the EDWC was 118,768.76 kJ/h. The comparison of the simulation, the errors of the products concentration and reboiler heat duty was slightly different with the optimal results in the RSM optimizer.

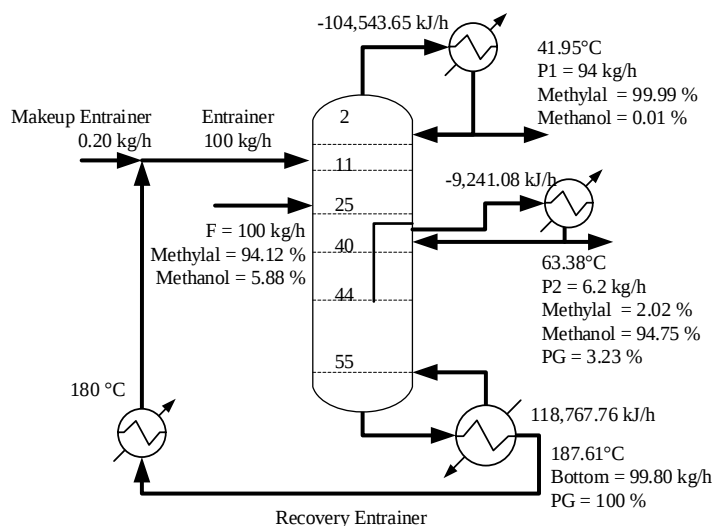


Fig. 7. Final flowsheet design for the extractive dividing wall distillation column for methylal-methanol system with entrainer as PG.

The total energy consumption in the conventional extractive distillation column (CEDC) was greater than that in the EDWC [5, 8, 21]. In Fig. 8, the specific comparison between different entrainers is shown. The various types of entrainers used in extractive distillation process could impact both the purity of the distillation products and the overall energy consumption in the reboiler.

It was found that the purity of methylal and methanol in the CEDC was slightly different in the EDWC when using the DMF as an entrainer. By using propylene glycol (PG) as an entrainer in the CEDC to achieve the purity of methylal to 99.9 wt.%, the total energy consumption in the reboiler needed more energy to boil up the PG than DMF as entrainer because the boiling point of PG was higher than DMF.

However, using PG as an entrainer reduced the total energy consumption in the EDWC by 44.24% compared to the CEDC. Although using PG as an entrainer in the reboiler of EDWC required an additional 0.48% energy compared to using dimethylformamide (DMF) as the entrainer, DMF proved to be an unsuitable entrainer due to its significant toxicity and adverse environmental impact [10]. Thus, PG served as a substitute entrainer to enhance the separation process of methylal and methanol in EDWC, thereby improving thermodynamic efficiency.

The liquid composition profiles in the main column and the prefractionator column were displayed in Fig. 9. From the condenser, which was stage 1, all the way up to the reboiler, which was stage 56, the stages were numbered. When the entrainer and mixture were fed on stages 11 and 25, respectively, the methylal content increased to 99.99 wt.%, as shown in Fig. 9(a). In the lower section, PG composition rapidly increased to 1. Methanol was extracted from the prefractionator on stage 40, and its concentration increased to 94.75 wt.%, according to the data presented in Fig. 9(b).

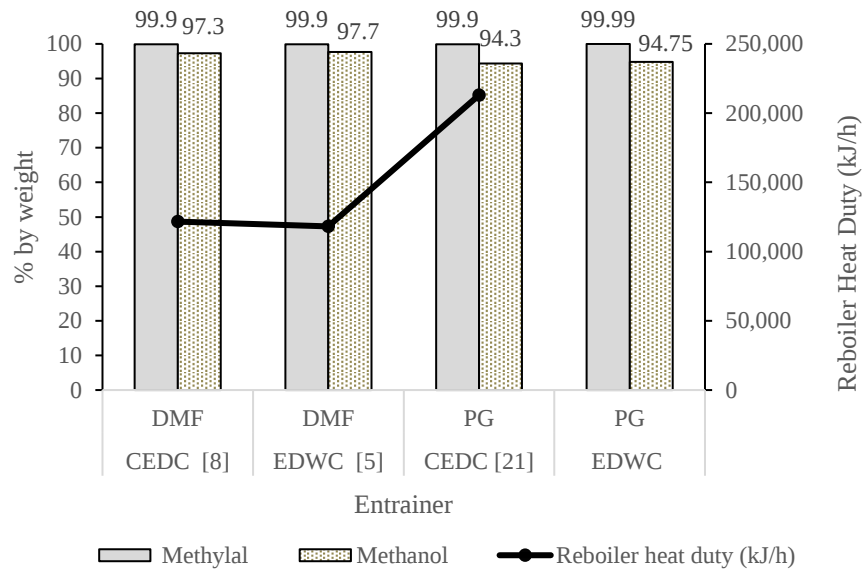


Fig. 8. Comparison of the process simulation results.

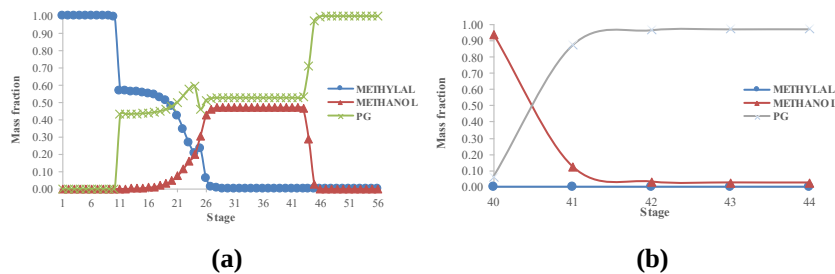


Fig. 9. Liquid composition profiles in methylal-methanol-PG system for the EDWC. (a) Main column, (b) Prefractionator.

4. Conclusions

The development of an extractive dividing wall column (EDWC) for the separation of a mixture of methylal and methanol utilized propylene glycol (PG) as an entrainer. The design of the column was based on the central composite design (CCD) in response surface methodology (RSM). The CCD approach could be used to calculate the ideal structure and operating conditions for the separation process

in EDWC in order to achieve the desired compositions and minimize energy usage. Furthermore, the study examined the impact of factors and their interactions on both product quality and energy consumption.

Important structural parameters in EDWC design for achieving the desired product purity and energy consumption were the number of prefractionator stages, the location of the feed stage of the mixture and the entrainer, and the interaction action between these two points. The purity of the methyl also had an impact on the reflux ratio and the main column's distillate rate, as well as their interaction. On the other hand, the distillate rate of the main and prefractionator columns indicated the purity of methanol.

The most essential operational parameter in EDWC was the relationship between the reflux ratio and the vapor split ratio. This was related to the heat duty in a reboiler. It was also possible to find the optimal EDWC process parameters and get the pure product while keeping the reboiler heat duty as low as possible (99.99 wt.% methylal, 94.75 wt.% methanol, and 118,768.76 kJ/h (saving energy 44.24%)). This was possible because the RSM predicted the output response so well.

The main column stages were 56 (including the reboiler and condenser), whereas the prefractionator column stages were 4. The combination feeding of the mixture of methylal and methanol was fed to stage 25, while the entrainer feeding took place at stage 11. The main column and prefractionation column had distillate flow rates of 94 kg/h and 6.2 kg/h, respectively. The reflux ratio was 2.0, the vapor split ratio was 0.08, and the entrainer temperature was 180 °C.

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