Optimization of fractional freezing process for bioethanol purification

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Abstract. A new bioethanol purification method namely fractional freezing (FF) has been introduced to replace the conventional distillation and adsorption methods which require a higher energy and cost demand. The FF process was conducted in a cylindrical crystallizer equipped with a digital stirrer. Response surface methodology (RSM) was applied to optimize the process, and to investigate the effect of coolant temperature and freezing time towards the efficiency of the process which is represented by effective partition constant (K) and purification efficiency (Peff). Subsequently, a validation experiment was conducted to validate the predicted optimum conditions given by RSM. From the result, the optimum and comparative value of K (0.28) and Peff (31.74) were found at coolant temperature of -17°C and 65 min freezing time, with error for both responses less than 10% from prediction.

1. Introduction

Conventional fossil fuels such as oil, coal and natural gas are currently the main supplier for global energy demand [1]. This phenomenon has become a major concern in modern society due to the shortage of fossil fuel sources. Therefore, renewable source of energy and fuels such as biofuels have been studied recently by researchers to overcome this problem. Bioethanol has been classified as the most favorable alternative fuel for both short and long terms use [2]. The main advantage of bioethanol as compared to other alternative fuels is that it can be easily integrated as a sole fuel or as an additive in fuel blends in an existing fuel system without the needs of any modification of the engines. Furthermore, its blend with gasoline or other biofuel as an additive resulted in a rise of fuel octane level thus producing a fuel that burns completely and reducing the emission of carbon monoxide and other pollutants [2-5]. Bioethanol can also be classified as a carbon neutral sources of energy since carbon dioxide being absorbed by the raw materials for bioethanol production is offset by carbon dioxide released from bioethanol combustion [3, 4]. At present, bioethanol is the most prevailing biofuel, with a sharp increase in its global production over the last 25 years. According to Licht [6], worldwide production capacity of bioethanol has reached over 115 billion liters per year in 2015. There are various types of raw biomaterials used to produce bioethanol such as corn, sugarcane and lignocellulosic biomass. Basically, these biomaterials will undergo several pretreatment steps before being fermented to yield the desired bioethanol [1]. However, the produced bioethanol will commonly be in diluted form where further purification steps are needed to produce bioethanol that
meets the standard requirement of a biofuel [7]. As bioethanol-water mixture will form a binary azeotropic mixture at 78.1°C with purity of 95.63 wt%, an energy demanding, and complicated separation process is needed to reach the target purity of bioethanol. According to Frolkova and Raeva [8], there are a number of available purification techniques of bioethanol, such as distillation, pervaporation, adsorption, pressure swing distillation, extractive distillation, azeotropic distillation, and hybrid methods that combines the other options [7, 8]. These existing purification methods were reported to require higher energy and overall cost.

As compared to the other purification techniques, fractional freezing is believed to be the best option since distillation and pervaporation requires higher amount of energy to boil the target solution for the purpose of purifying it. The energy used in the processes is at least equal to the heat vaporization of the complete pure product that will be separated. On the other hand, adsorption demands a complicated selection of adsorbent surface types as well as of pore size distribution to avoid the containment of impurities onto the product [9]. Fractional freezing (FF) process has been introduced and adopted from the application of freeze concentration or freeze crystallization concept. FF is a process that separate two miscible organic compounds to its constituent components, based on the difference in freezing point of each component [10]. In crystallization process, the equilibrium condition is only possible at the melting point of the liquid. The alteration of this equilibrium condition could be achieved by introducing supercooling to the liquid. Supercooling which is also known as undercooling, is the process of lowering the temperature of a liquid or a gas below its freezing point without it becoming a solid. In the presence of seed ice or ice nucleus, a liquid below its standard freezing point will be able to crystallize. FF is indeed a very effective purification process since one of the two components that has a lower melting point will crystallize first. Thus, the separation of the two components can be easily achieved [11]. The effectiveness of the purification process is normally described by the purity level of the ice formed, as well as the purity of the purified component. Based on literature, fractional freezing is capable to produce a high purity of crystal [12]. Furthermore, the energy required by FF is relatively low as compared to evaporation involved in distillation since the latent heat of fusion involved in FF is much lower than the latent heat of vaporization involved in evaporation [13]. FF is also suitable to purify component with high volatility since no heating process is involved. Therefore, fractional freezing is believed to be able to offer a better system in order to make purification of bioethanol a more efficient process, in terms of its product quality as well as energy requirement. In this study, the fractional freezing of bioethanol was conducted in a cylindrical crystallizer equipped with a digital stirrer. Next, optimization of the FF process was conducted by assessing its performance, represented by effective partition constant ($K_{eff}$) and purification efficiency ($P_{eff}$) via Response Surface Methodology (RSM) at different coolant temperature and freezing time. It is essential in most research studies especially in engineering and analytical chemistry to optimize a process in order to determine the conditions of the design parameters, at which the response attains its optimum value [11].

2. Materials and Methods

2.1. Materials
Diluted bioethanol with bioethanol-water ratio of 1:5 was used as the target solution to be purified [4]. Bioethanol with 96% purity was purchased from Avantis Laboratory Supply, Ipoh, Malaysia. This liquid mixture is assumed as a model solution that represents the product of fermentation process to yield bioethanol [11]. On the other hand, 50% (v/v) of ethylene glycol-water solution was used as a coolant to supply cooling energy to the system. Ethylene glycol is normally applied in heat transfer processes which involve a very low temperature range. The ethylene glycol with 99% purity was also purchased from Avantis Laboratory Supply, Ipoh, Malaysia.
2.2. Fractional freezing apparatus
The experimental setup of the fractional freezing process consisted of a 1.5 liter cylindrical crystallizer, a refrigerated waterbath (DC-2030, Ningbo, China), a digital stirrer (Eurostar 40 digital, IKA, Malaysia), retort stands, and refractometer (Milwaukee, USA). The main apparatus of the system is cylindrical crystallizer as it provides the place for crystallization to occur. The refrigerated waterbath was used to store the coolant, at which the desired readings of coolant temperature were controlled (-16 to -20 °C). Retort stands with clamps were used to hold the crystallizer while it is immersed into the waterbath. In order to provide a well-mixed liquid mixture, a digital stirrer was used to stir the diluted bioethanol at 50 rpm. Finally, a refractometer was used to measure the purity of bioethanol produced at the end of the experimental run. Figure 1 shows the experimental setup for the fractional freezing process.

![Digital stirrer](image1)
![Cylindrical crystallizer](image2)
![Retort stand](image3)
![Refrigerated waterbath](image4)

**Figure 1.** Experimental setup for the FF process.

2.3. Experimental design
The optimization process for fractional freezing of bioethanol was conducted based on central composite design (CCD) which is the best design that applies response surface methodology (RSM) [11]. The optimization process was carried out through STATISTICA software (version 8.0) to find the optimum value for each tested operating parameter. There are four major steps in the applications of RSM as an optimization technique. First, the independent variables of major effects on the system as well as the dependent variables were selected through screening studies followed by the restriction of the experimental region. In this study, the independent variables are coolant temperature and freezing time, while dependent variables are effective partition constant ($K$) and purification efficiency ($P_{eff}$). Second, the type of experimental design was chosen to carry out the experimental run according to the designated value of set of factors or variables. Third, the obtained experimental data was treated statistically or mathematically through the fit of a polynomial function (model). Fourth, the model’s fitness was evaluated before the optimum values for each studied variable was obtained.

In this study, the low, middle and high levels for the range of process parameter involved are tabulated in table 1. A total of 10 experiments were run to optimize the designed system. The arrangement of experimental runs through CCD in this study was produced based on the 2k factorial
design with two factors and one block, in which 10 combinations of parameter were executed including two replication at the center point to evaluate the error. Each experiment was performed in duplicate. The substitution of the selected parameters into the model enabled a calculation for a predicted response. Equation (1) shows the mathematical model to predict the response.

\[
Y = \beta_0 + \sum_{j=1}^{4} \beta_j X_j + \sum_{j=1}^{4} \beta_{jj} X_j^2 + \sum_{i<j} \beta_{ij} X_i X_j
\]  

(1)

where \(Y\) is the predicted response value, \(\beta\) is the regression coefficient which is a weighting factor that has been calculated by the statistical program to fit the experimental data and \(X\) is an experimental factor that influences the process.

| Table 1. Range of process parameters. |
|--------------------------------------|
| Parameter                             | Range and Levels |
|                                      | -α    | -1    | 0     | +1    | +α    |
| Coolant Temperature, \(X_1\) (°C)     | -20   | -19   | -18   | -17   | -16   |
| Freezing Time, \(X_2\) (min)         | 50    | 60    | 70    | 80    | 90    |

2.4. Experimental procedure

The diluted bioethanol mixture with bioethanol-water ratio of 1:5 was prepared and precooled at 10°C in a cold room to maintain the low temperature during the freezing process. The waterbath containing ethylene glycol–water solution was switched on to reach the desired coolant temperature. As the coolant temperature reached the desired reading, the cylindrical crystallizer was immersed into the refrigerated waterbath while being supported by two retort stands. Then, the diluted bioethanol solution was then fed into the crystallizer. At this time, the digital stirrer was switched on at a prescreened speed of 50 rpm to mix the mixture. The diluted bioethanol liquid mixture was left in the crystallizer for crystallization to occur.

At the designated time, the stirring process was stopped, and the crystallizer was removed from the refrigerated waterbath. For sample collection purpose, the unfrozen (purified) bioethanol was first collected before the frozen crystals was thawed. The volume of the crystal layer and the purified bioethanol were then measured and the samples of both were collected. The collected samples were then analyzed to check the concentration of bioethanol by using refractometer (Milwaukee, USA). The procedures were repeated at different coolant temperature and freezing time following the design of experiment, where the runs were carried out in duplicates to obtain an accurate result.

2.5. Evaluation of process efficiency

Effective partition constant (\(K\)) has been used prominently in assessing the performance of freeze crystallization process from several aspects of application [14]. Abstractly, \(K\) value stands for a ratio of solute in ice and liquid phase, as indicated in the following equation (2).

\[
(1 - K) \log \frac{V_L}{V_o} = \log \frac{C_o}{C_L}
\]

(2)

where \(C_o\) is defined as the initial component concentration in liquid mixture (mgL\(^{-1}\)), \(C_L\) is concentration of purified liquid (mgL\(^{-1}\)), \(V_L\) is volume of purified liquid (mL) and lastly \(V_o\) is defined as volume of the liquid mixture (mL). Value of \(K\) should vary from 0 to 1, where lower value indicates higher efficiency.
On the other hand, the purification efficiency \((P_{\text{eff}})\) that represents the raise in the concentration of the purified liquid component in accordance to the amount of target component trapped in the crystal is also defined as the effectiveness of the separation process through fractional freezing. Purification efficiency can be calculated as equation (3) below [15]:

\[
P_{\text{eff}} = \left( \frac{C_L - C_o}{C_o} \right) \times 100
\]

3. Result and discussion

3.1. Ice formation through fractional freezing

During the freezing process, ice crystal layer (water) had been successfully formed on the inner wall of the crystallizer, thus proving the ability of fractional freezing in separating components of the bioethanol liquid solution. This is due to the higher freezing point of water (0°C) as compared to bioethanol (-114°C). Figure 2 shows the close-up view of the ice crystal layer formed in the crystallizer.

![uncrystallized layer](image1)

![crystal layer](image2)

**Figure 2.** Ice crystal formed

3.2. Model Adequacy Check

Based on the RSM, all 10 of the designed experiments and results of response \(K\) and \(P_{\text{eff}}\) for each run are tabulated in table 2. The response, \(K\) and \(P_{\text{eff}}\) were correlated with two independent variables studied by using multiple regression analysis with second order polynomial. The empirical mathematical model of the predicted \(K\) \((Y_1)\) and \(P_{\text{eff}}\) \((Y_2)\) as a function of \(X_1\) and \(X_2\) and their interaction using linear and quadratic regression coefficient of main factors and linear-by-linear regression coefficients of interaction was derived and represented in the following equations. Equation (4) and equation (5) represent the predicted effective partition constant and purification efficiency respectively.

\[
Y_1 = 5.809 + 0.64X_1 - 0.0078X_2 + 0.0202X_1^2 + 0.00016X_2^2 + 0.00066X_1X_2
\]

\[
Y_2 = -385.511 - 41.9X_1 + 0.563X_2 - 1.136X_1^2 - 0.006X_2^2 - 0.014X_1X_2
\]

The coefficients with one factor represent the effect of the factor itself while the coefficients with two factors indicate the effect and interaction between the two factors. The quadratic effect of the factor can be seen in coefficients with second order terms. The positive and negative signs in the equations signify parallel and adverse effect of the factors to the responses respectively [16].
Table 2. Design of experiment and response for $K$ and $P_{eff}$

| Run | $X_1$ (°C) | $X_2$ (min) | $K$  | $P_{eff}$ (%) |
|-----|------------|-------------|------|---------------|
| 1   | -15        | 70          | 0.315| 16.399        |
| 2   | -16        | 50          | 0.317| 17.475        |
| 3   | -16        | 90          | 0.454| 16.733        |
| 4   | -18        | 42          | 0.309| 25.347        |
| 5   | -18        | 70          | 0.303| 29.334        |
| 6   | -18        | 70          | 0.303| 29.334        |
| 7   | -18        | 98          | 0.501| 25.977        |
| 8   | -20        | 50          | 0.545| 25.414        |
| 9   | -20        | 70          | 0.562| 25.878        |
| 10  | -20        | 90          | 0.577| 26.854        |

The coefficient of determination ($R^2$) had been analyzed to evaluate the adequacy of the fit model by using the same software. $R^2$ represent the validity of the model generated. According to the regression model, the value of $R^2$ for $K$ and $P_{eff}$ are 0.949 and 0.960, respectively. This value indicates that 94.9% of the sample variation for $K$ and 96% of the sample variation for $P_{eff}$ could be attributed to the independent factors. Hence in this case, the obtained value of $R^2$ indicates that there was a good agreement between the observed and the predicted value of response $K$ and $P_{eff}$ obtained from the model. The predicted value for the responses for each run can also be obtained from the regression model as tabulated in table 3 and table 4. Additionally, figure 3 and figure 4 show the variation of the experimental data against the predicted value of $K$ and $P_{eff}$, respectively. The figures indicate that majority of the predicted values for both response $K$ and $P_{eff}$ from the regression model falls very near to the line plotted. This result can be expected from the good values of $R^2$ of both responses.

Figure 3. Observed value versus predicted value of response $K$. 
Figure 4. Observed value versus predicted value of response $P_{eff}$.

Table 3. Observed and Predicted $K$ for each run.

| Run | Observed $K$ | Predicted $K$ | Residual |
|-----|--------------|---------------|----------|
| 1   | 0.315        | 0.340         | -0.025   |
| 2   | 0.317        | 0.279         | 0.038    |
| 3   | 0.454        | 0.441         | 0.013    |
| 4   | 0.309        | 0.353         | -0.044   |
| 5   | 0.303        | 0.303         | -0.000   |
| 6   | 0.303        | 0.303         | -0.000   |
| 7   | 0.501        | 0.509         | -0.008   |
| 8   | 0.545        | 0.506         | 0.039    |
| 9   | 0.562        | 0.588         | -0.026   |
| 10  | 0.577        | 0.564         | 0.013    |
3.3. Analysis of variance (ANOVA)

The suitability of the generated prediction models was further evaluated by using the analysis of variance (ANOVA) method. Table 5 and table 6 show the ANOVA analysis of the quadratic model for response $K$ and $P_{eff}$, respectively. The method requires one to observe the $F$-value which portrays the ratio of mean square regression to the mean square residual. In order to consider the prediction model as appropriate, the calculated $F$-value should be greater than the tabulated value for 95% confidence level. The tabulated $F$-values for $K$ (14.846) and $P_{eff}$ (19.450) have already exceeded the tabulated $F$-value for 95% confidence level (6.2561) at more than two times. Hence, the prediction mathematical model is considered to have a good or satisfactory agreement to the experimental data obtained for both $K$ and $P_{eff}$ responses.

### Table 5. ANOVA table for prediction model of $K$ response.

| Sources     | Sum of Squares of Error (SS) | Degree of Freedom (DF) | Mean Squares (MS) | $F$-value |
|-------------|------------------------------|------------------------|-------------------|-----------|
| Regression (SSR) | 0.12284                     | 5                      | 0.024570          | 14.846    |
| Residual    | 0.006619                     | 4                      | 0.001655          | -         |
| Total (SST) | 0.129468                     | 9                      | -                 | -         |
| $R^2$       | 0.949                        | -                      | -                 | -         |

### Table 6. ANOVA table for prediction model of $P_{eff}$ response.

| Sources     | Sum of Squares of Error (SS) | Degree of Freedom (DF) | Mean Squares (MS) | $F$-value |
|-------------|------------------------------|------------------------|-------------------|-----------|
| Regression (SSR) | 220.2417                    | 5                      | 44.0483           | 19.450    |
| Residual    | 9.0586                       | 4                      | 2.2647            | -         |
| Total (SST) | 229.3003                     | 9                      | -                 | -         |
| $R^2$       | 0.960                        | -                      | -                 | -         |
After the prediction model has been proven to be appropriate or valid, the variables which significantly affect the selected responses were then identified. Table 7 and table 8 shows the arranged multiple regression results, which later would be used to assess the significance of each factor in the model.

**Table 7. Regression analysis for K response.**

| Factor   | Coefficient Estimation | Standard Error | F       | p    |
|----------|------------------------|----------------|---------|------|
| $X_1$    | 0.635918               | 0.175038       | 37.048  | 0.004|
| $X_1^2$  | 0.020156               | 0.004756       | 17.958  | 0.013|
| $X_2$    | -0.007790              | 0.011341       | 14.660  | 0.019|
| $X_2^2$  | 0.000160               | 0.000048       | 11.272  | 0.028|
| $X_1X_2$ | 0.000656               | 0.000508       | 1.666   | 0.266|

**Table 8. Regression analysis for $P_{eff}$ response.**

| Factor    | Coefficient Estimation | Standard Error | F       | p    |
|-----------|------------------------|----------------|---------|------|
| $X_1$     | -41.900                | 6.47545        | 54.648  | 0.002|
| $X_1^2$   | -1.136                 | 0.17596        | 41.663  | 0.003|
| $X_2^2$   | 0.006                  | 0.00176        | 10.506  | 0.032|
| $X_1X_2$  | -0.014                 | 0.01881        | 0.526   | 0.509|
| $X_2$     | 0.563                  | 0.41957        | 0.139   | 0.728|

The factor or variable with the highest $F$-value and the lowest $p$-value is considered as the most significant factor, while the other factors are arranged in descending order of significance, from the most significant to the less significant factor. Based on the confidence level fixed for the ANOVA analysis applied, the influence of factor is considered significance if the $p$-value is less than 0.05. Based on the analysis, both response $K$ and $P_{eff}$ give almost the same result. The factor that gives the most significant effect to both responses is the linear term of $X_1$ (coolant temperature) with $F$-value of 37.04819 at $p$-value 0.003683 for response $K$ and $F$-value of 54.64790 at $p$-value 0.001786 for response $P_{eff}$. This is followed by three other factors which are quadratic of coolant temperature ($X_1^2$), linear term of freezing time ($X_2$) and quadratic of freezing time ($X_2^2$) in descending order of significance for response $K$. On the other hand, for $P_{eff}$ response, only two other factors are considered significance which are quadratic of coolant temperature ($X_1^2$) and freezing point ($X_2^2$).

**3.4. Response surface contour plot analysis**

The effects of the two process variables or factors on the response of $K$ and $P_{eff}$ were also observed by plotting a three-dimensional (3D) surface plot of the response against the two selected factors. A perfect interaction between the process variables is portrayed by an elliptical contour plot. Next, a two dimensional (2D) fitted response profile known as contour plot was observed in which a suitable range for the plotted variables that would yield the best value for the $K$ and $P_{eff}$ values are suggested. Figure 5(a) and figure 5(b) show the 3D and 2D surface plots of $K$ as a function of coolant temperature and freezing time.
Figure 5. Surface (a) and contour (b) plots of $K$ value as a function of coolant temperature ($^\circ$C) and freezing time (min).

It can be seen from the figure that the $K$ value starts to decrease from 30 min to 60 min of freezing time. However, further freezing the solution at above 60 min has turned the trend of $K$ value where it starts to increase. Generally, longer freezing time could provide higher purification efficiency to the FF process. As the freezing process started, the degree of crystallinity of the formed ice layer is still low with the presence of dendrites structure. By providing longer freezing time, the ice layer grows thicker, leaving the unfrozen solution in a state approaching the saturation level [17]. In this analysis, 60 min is sufficient to give the highest efficiency of the process, portrayed by the lowest $K$ value and the highest $P_{eff}$ value obtained. However, too long freezing time might shift the trend of impurities (bioethanol component) concentration in the ice caused by the saturation of impurities in the concentrate [18]. This situation can be explained by the growth of ice layers which nearly occupied the space inside the crystallizer especially after 60 min of concentration process.

On the other hand, operating the process below coolant temperature of -17 °C resulted in an increase in $K$ value, which indicates lower separation efficiency of the PFC process. As mentioned by Ramos et al. [19] heat transfer within the wall of crystallizer and the coolant for the crystallization process could be enhanced by low temperature of the coolant. Or in other words, low surface temperature could provide the needed initial supercooling for the ice nucleation. This phenomenon explains clearly the decrease in $K$ value as the coolant temperature decreased from -14 °C to -17 °C, portraying the increase in process efficiency. In this analysis, the process reached the highest efficiency at -17 °C where the lowest $K$ value was obtained. However, further lowering of the coolant temperature could also cause impurities (bioethanol component) inclusion in the ice crystal [20]. Higher temperature difference between the crystallizer wall and the entering solution resulted in higher ice growth rate [21]. If the crystal growth rate is faster than the impurities outward movement at this condition, then a part of the impurities might get entrapped within the ice crystal formed. As a result, the purity of ice produced becomes lower caused by impurities contamination [20]. The range of coolant temperature and freezing time that produce the lowest value of $K$ are from -16°C to -18°C and from 50 min to 70 min, respectively.

Next, figure 6(a) and figure 6(b) illustrate the 3D and 2D surface plot of $P_{eff}$ as a function of coolant temperature and freezing time. From the figure, the value of $P_{eff}$ increases as the coolant temperature decrease and freezing time increase. However, the value of $P_{eff}$ starts to decrease as the freezing time exceed 70 min, as well as the coolant temperature goes below -19 °C. This is due to the high rate of solute inclusion in the ice formed during this condition. The best range of coolant
temperature and freezing time for response $P_{\text{eff}}$ are between -17°C to -19°C and 60 min to 80 min, respectively.

![Figure 6](image)

**Figure 6.** Surface (a) and contour (b) plots of $P_{\text{eff}}$ value as a function of coolant temperature (°C) and freezing time (min).

### 3.1. Optimum operating conditions and validation

As the optimum value for both process parameters between the response $K$ and $P_{\text{eff}}$ is close to one another, a validation experiment was carried out by operating the FF process at the average values of the optimum condition between the two response parameters. The average optimum values for coolant temperature and freezing time were -17 °C and 65 min, respectively. Table 9 shows the optimum condition, predicted and validation values for both response $K$ and $P_{\text{eff}}$. Based on this table, the values of prediction and validation for both responses are close enough to each other with error less than 10%, thus concluding that the optimization method used could satisfactorily predict each response according to the investigated independent variables, based on the model produced. The optimum condition of fractional freezing for bioethanol purification was obtained at coolant temperature of -17°C and 65 min of freezing time.

Although the optimum $K$ value obtained through this study was exceptionally good (0.282), the optimum $P_{\text{eff}}$ obtained (31.736%) was not able to beat the purification efficiency by the conventional methods like adsorption (50.9%) and pervaporation (85%). Therefore, further modification of the current fractional freezing process will be needed to yield a better separation efficiency. One of the recommendations for future research work is to construct a multiple fractional freezing process as well as to develop a continuous FF process which could efficiently purify solution with high crystal productivity. Furthermore, different setup of FF process could widen the scopes of research in terms of parameters involved. For example, in continuous process, solution movement could possibly affect the process efficiency as it affects the heat transfer within the FF process [11].

### Table 9. Regression analysis for $P_{\text{eff}}$ response.

| Response | $X_1$ (°C) | $X_2$ (min) | Prediction | Validation |
|----------|------------|-------------|------------|------------|
| $K$      | -17        | 65          | 0.260      | 0.282      |
| $P_{\text{eff}}$ | -17        | 65          | 30.206     | 31.736     |
4. Conclusion

In conclusion, this study has proved that fractional freezing (FF) process has a good potential to be applied in the purification of bioethanol, which may replace the conventional existing methods. The process offers a new alternative of purification method that has never been explored especially in Malaysia. Response surface methodology was used to predict the optimum process variables (coolant temperature and freezing time) for purification of bioethanol. By using response surface and contour plots, the optimum set of operating variables can be pictured graphically, in order to achieve the desired purification levels for bioethanol. Therefore, it was recommended that the intermediate range of coolant temperature and freezing time will result in a higher purification efficiency. Based on the optimization data and analysis, the high efficiency of the FF process was achieved at coolant temperature of -17°C and freezing time of 65 min with $K$ and $P_{ef}$ of 0.282 and 31.736, respectively. These values have been validated through experiment with error for both responses less than 10% from prediction.

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