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Simplex Lattice Design Method for the Optimization of Non-Edible Oils Mixture Composition as Feedstock for Biodiesel Synthesis Using Reactive Distillation

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Abstract. The diminished of fossil fuel becomes a critical issue today. Thus, it is essential to develop alternative energy resources which are renewable and environmental friendly. Among the prospective alternative is biodiesel. Biodiesel (fatty acid methyl ester) is produced by combining vegetable oils with alcohol via transestefication reaction. To avoid conflict between food and energy needs, the uses of non-edible oils as raw material is suggested. Commonly, biodiesel synthesis employs a single type of vegetable oil feed-stock. The dependency on a certain feed-stock could cause an increasing price due to the high demand and low supply. Thus, it is beneficial to apply diversification by employing multiple feed-stocks or mixture of non-edible oils as biodiesel feedstocks. However, the best composition of the multiple feed-stocks is needed to obtain the optimum yield of biodiesel. In this work, mixture of non-edible oils, i.e. jatropha, nyamplung (*Calophyllum inophyllum L.*) seed, and used cooking oils were applied as biodiesel feedstocks. Non-edible oils are cheap but have high free fatty acid (FFA). The high FFA is not favorable for the alkaline-catalyzed transesterification since it will cause undesired saponification reaction and lower biodiesel yield. Hence, pretreatment to reduce FFA content is crucial prior to transesterification. In this work, esterification of FFA in vegetable oils mixture (jatropha, nyamplung, and used cooking oils) with methanol using reactive distillation in the presence of $SnCl_2$ catalyst was conducted as pretreatment step of biodiesel production. Various compositions of the oils mixture were employed. To determine the best formulation of feed-stocks, Simplex Lattice Design Method (SLDM) was used for the optimization of non-edible oils mixture composition as feedstock for biodiesel synthesis using reactive distillation. The prediction using SLDM was validated with the experimental data. It was found that the optimal composition of oil mixture was the mixture contains 37.291 v/v% jatropha oil + 37.709 v/v% nyamplung oil + 25 v/v% used cooking oil. This composition of feedstocks revealed the FFA conversion of 85.93% (prediction) and 86.03% (experiment). The desirability value was 0.937 which indicated the validity of the SLDM optimization method. The esterified oil mixture was then underwent transesterification reaction to produce biodiesel. The yield of biodiesel demonstrated 99.65 % purity and density of 884 kg/m^3.

1. Introduction

Fuel oil is indispensable in this modern as energy source for transportation, power plant, domestic activity, industry, and so on. Thus, the world dependency on fuel supply is high. Currently, the most utilized fuel is fossil based fuel. However, fossil fuel is a kind of non-renewable energy resource and the depleting reserves of fossil fuel turns into a critical issue in this decade. Besides, combustion and burning of fossil fuel also results in an environmental problem, especially in term of climate change. An abundant carbon dioxide emission produced by the vehicle or machine powered by fossil fuel will be entrapped in the atmosphere for a long time, enhancing the carbon dioxide concentration and leading to the world's temperature. This condition will cause climate change which provides negative impact to the ecosystem. Therefore, it is essential to develop alternative energy resources which have renewable characteristic and environmental friendly. Among the prospective renewable energy to replace or substitute fossil fuel is biofuel. *Biofuel is* energy resources derived from renewable plant and animal materials. Biofuel includes bioethanol, biodiesel, biogas, bio-oil, and green diesel [1].

To date, the most potential and economical biofuel for diesel machine is biodiesel. Biodiesel is priority is some country such as Indonesia. In Indonesia, the development of biodiesel as renewable energy resource is stated in the Regulation of the President of Republic of Indonesia Number 5 (2006) and presented in the Blueprint of the National Energy Management, formulizing the development of biodiesel technology for a period of 20 years (2005 – 2025) [2].

Biodiesel or fatty acid methyl ester (FAME) is produced by combining vegetable oils or animal fats with short chain alcohol, such as methanol or ethanol through transestefication reaction. In Indonesia, the most used feed-stocks for biodiesel production are crude palm oil (CPO) and jatropha oil. However, the employment of CPO as edible oil for biodiesel raw material will cause side problem in terms of the conflict between food and energy need. The huge consumption on CPO for biodiesel production potentially initiates the problem on food security. Therefore, utilization of non-edible oil is more suggested [3].

Jatropha oil is a type of non-edible oil, which is more suitable to be consumed as biodiesel feedstocks. In spite of this, dependency on one type of feed-stocks will bring about the fluctuation of such the commodity price. Even, the price could tend to increase when there is high disparity between the jatropha oil's demand and its market supply. This unbalanced situation will imply the higher price this kind of vegetable oil due to the limited supply availability. Thus, to avoid the problem caused by the low supply and high demand of a certain vegetable oil, it is beneficial to apply diversification strategy on biodiesel feed-stocks. In this case, utilization of multiple feed-stocks or mixture of non-edible vegetable oils as raw material for biodiesel production is a prospective alternative [4].

There are several future non-edible vegetable oils for biodiesel production. In Indonesia, there are nyamplung (*Calophyllum inophyllum L.*) seed oil, rubber-seed oil, *k*emiri sunan (*Aleurites trisperma Blanco*) oil, waste cooking oil, etc. The combination of various types of non-edible oils as feedstocks for biodiesel is interesting to ensure the security and stable price of vegetable oils raw material. However, the best composition of the multiple feed-stocks is needed to obtain the optimum yield of biodiesel. Thus, this research studied the optimization of non-edible oils mixture composition which is utilized as biodiesel raw material. Non-edible oils usually cheap but have low quality and high free fatty acid (FFA). The high amount of FFA content is not favorable in the transesterification reaction between vegetable oils and alcohol in the presence of alkaline catalyst since it will cause saponification as undesired side reaction, consume the catalyst, and lower biodiesel yield. Hence, pretreatment to reduce the FFA content in the vegetable oils feedstock is crucial prior to the main transesterification reaction. In this work, esterification of FFA in vegetable oils mixture with methanol in the presence of solid acid catalyst (tin (II) chloride) using reactive distillation was conducted. FFA was converted into methyl ester to decrease the FFA content in the feedstock and in the same way added the amount of methyl ester (biodiesel) [5].

Continuous process using reactive distillation process was applied for biodiesel production since this technology provides many advantages. Reactive distillation is frontier intensification process in biodiesel production since it integrates reaction and separation in one unit column. Hence, it offers benefit compared to sequential process, namely: 1) reduces equipment investment and operating cost, 2) decreases consumption of utility, 3) results in higher conversion and selectivity, and 4) possibility to shift equilibrium towards product formation. On the other hand, catalyst employed in this FFA esterification is tin (II) chloride solid acid catalyst ($SnCl_2.2H_2O$). This catalyst can result in high conversion in esterification reaction and easily to separate from the reaction mixture [5].

In this work, combination of jatropha, nyamplung seed, and waste cooking oils were used as feedstocks of biodiesel production using reactive distillation process. Various compositions of the oils mixture were employed. Since the mixture of vegetable oils have high FFA, then esterification reaction of non-edible oil feedstock was conducted to reduce the FFA prior to transesterication reaction. To determine the best formulation of feed-stocks, Simplex Lattice Design Method (SLDM) of Design Expert Software was used for the optimization of non-edible oils mixture composition. The prediction using SLDM was validated with the experimental data of FFA esterification reaction using reactive distillation in the presence of tin (II) chloride catalyst. The best formulation of feed-stocks is the composition of crude jatropha oil (CJO), crude nyamplung seed oil (CNO), and waste cooking oil (CJO) which provides best conversion of reaction (FFA reduction). The optimal composition of feedstock was furthermore employed for biodiesel production trough transesterification reaction in the presence of NaOH catalyst in reactive distillation column.

2. Methods

2.1. Materials

Raw materials utilized in this study was a mixture of non-edible oils consisting crude jatropha oil (CJO), crude nyamplung seed oil (CNO) and waste cooking oil (WCO). WCO oil was obtained from home industry in Kebumen, Jawa Tengah, Indonesia with the density, FFA content, and molecular weight of 0.954 g/mL, 1.32%, and 865.24 g/gmol, respectively. CJO with density, FFA content, and molecular weight of 0.940 g/mL, 9.4%, and 868.3074 g/gmol, respectively, was supplied by PT Jatropha Green Energy, Kudus, Indonesia. CNO with the density, FFA content, and molecular weight of 0.97 g/mL, 16.14%, and molecular weight of 884.8144 g/gmol was provided by Koperasi Jarak Lestari, Cilacap, Indonesia. Methanol (99 %v/v) and solid acid catalyst tin (II) chloride (99% purity) were obtained from Merck. The average molecular weight of the oil mixture was 884.2100 g/gmol.

2.2. Experimental Work of Esterification Reaction.

Prior to the esterification reaction, degumming process using 20% phosphoric acid was carried out to remove gum from the oils. Esterification reaction of the mixture of non-edible oils and methanol was then conducted in reactive distillation column as described in the previous work [6]. The reaction was performed at constant temperature of 60°C and molar ratio of oil to methanol of 1:60. Catalyst employed in this work was tin (II) chloride with the amount of 5% w/w oil. Analysis of FFA conversion was performed using titrimetric analysis [7]. The initial oil mixture composition on the feed-stock was varied. Oil feed-stock composition variation was determined using Design Expert Software by applying Simplex Lattice Design Method. Based on this method, the different initial formulation of oil feed-stocks composition on 100 mL total mixture basis is depicted in Table 1. The feed-stocks formulation revealed the FFA content ranging from 8.42 to 12.26%.

Table 1. Experimental Design of Initial Oil Feed-Stock Composition

Run	CJO (mL)	CNO (mL)	WCO (mL)
1.	51.9	31.9	16.2
2.	27.5	50.0	22.5
3.	49.6	25.4	25.0
4.	70.5	10.0	19.5
5.	77.3	12.8	10.0
6.	40.0	50.0	10.0
7.	43.1	40.4	16.5
8.	35.0	40.0	25.0
9.	69.2	20.8	10.0
10.	59.9	15.1	25.0
11.	59.8	23.6	16.6

2.3. Optimization and Validation.

Optimization was carried out based on the data of reaction conversion of FFA (the decreasing of FFA content on the esterification reaction) on various oil feed-stocks composition. Simplex Lattice Design Method (SLDM) was applied for optimization process to determine the most appropriate composition of feedstock which provided the best FFA reduction through esterification reaction using reactive. Optimization was then validated by comparing the FFA reduction prediction using design expert software with the experimental data. The best composition was then used for biodiesel synthesis through transesterification reaction. Ethyl ester content in biodiesel produced from transesterification reaction was instrumentally determined using Gas Chromatography-Mass Spectroscopy (GC-MS).

3. Result and Discussion

3.1. Esterification Reaction

The FFA Esterification reaction of the non-edible oil mixture was accomplished based on the experimental design, in which the feed-stocks composition was determined using SLDM in Design Expert Software. The FFA conversion of each experiment was demonstrated in Figure 1. The FFA conversion achieved in this work was ranging from 70-85%, in which the FFA content could be reduced from 8.24-12.26% to 1-2%.

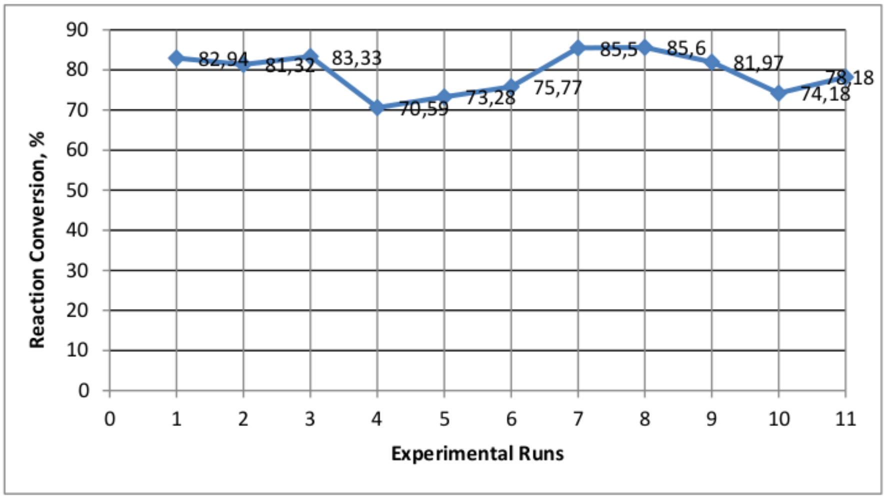

Figure 1. Conversion of Esterification Reaction at Reaction Temperature of 60°C, Ratio Molar of Oils to Methanol of 1:6, and Tin (II) Chloride Catalyst Concentration of 5% w/w oil for Various Feed-Stock Composition

3.2. *Response Analysis*

Each Response variable subsequently went through Analysis of Varians (ANOVA). The ANOVA model for variable analysis selected in this work was the model suggested by Design Expert Software 10.0, which provided highest level and significance. Based on ANOVA (Table 2), it was revealed that the selected model for each oil mixture respose was quadratic model. This model has shown the highest value of R^2 (0.944) compared to the other models. This model also demonstrated significance with the p value of $p < 0{,}0001$ ($< 0{,}05$). The ANOVA revealed that the CJO dan CNO provided significant effect on the response of FFA conversion. Lack of Fit (F-Value) was 4.46 (>0.05) indicating insignificant Lack of Fit. Insignificant value of Lack of Fit is a requirement for a good model since it indicates the suitability of the response data with the model [8].

Table 2. Method Analysis for the Response of FFA Reduction of Non-Edible Oil Mixtures

Response	Model	Significance ($p<0.05$)	Information
AB	Quadratic	0.7807	Insignificant
AC	Quadratic	0.0716	Insignificant
BC	Quadratic	<0.0001	Significant

A = Waste Cooking Oil (WCO)
B = Crude Jatropha Oil (CJO)
C = Crude Nyamplung Seed Oil (CNO)

Design Expert Software 10.0 also offers facility of normal plot residual which indicates whether the residual (the difference between the actual response and the predicted response value) fulfills the normal line/ straight line [9]. The residual plot was shown in Figure 2.

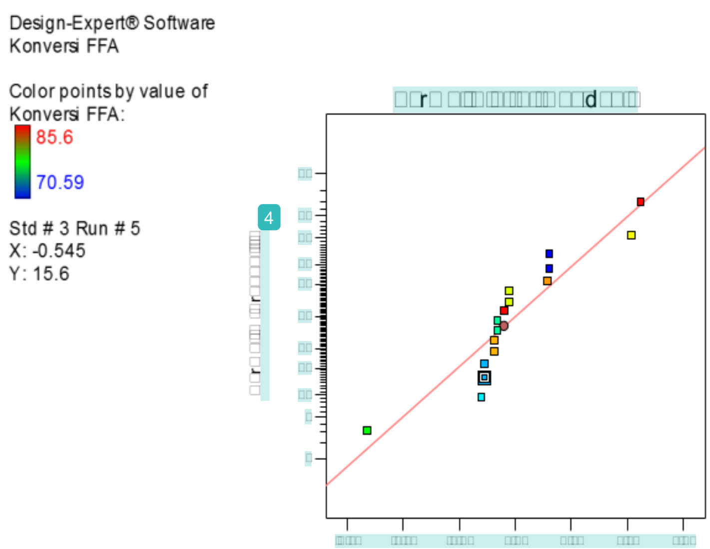

Figure 2. Residual Normality Response of FFA Reduction

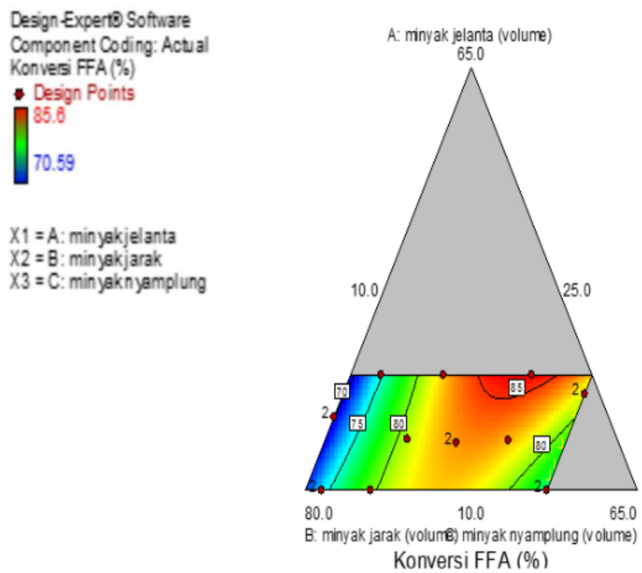

Figure 3. Contour Plot of Response Test of FFA Conversion

Contour plot in Figure 3 denotes how the combination of composition component affects the response of FFA conversion. The different colour on the contour plot specifies the value of FFA conversion. Blue colour indicates the response of the lowest conversion (70.59%). Red colour shows the response of the highest conversion (85.6%). The lines consisting of dots on the contour plot demonstrates the combination of the three components with the different composition which results in the similar yield. The surface shape of the interaction relationship between these components is depicted more clearly on the three-dimensional graph shown in Figure 4. The result of response analysis was then combined to obtain optimum composition of CJO, CNO, and WCO which yields the best FFA conversion.

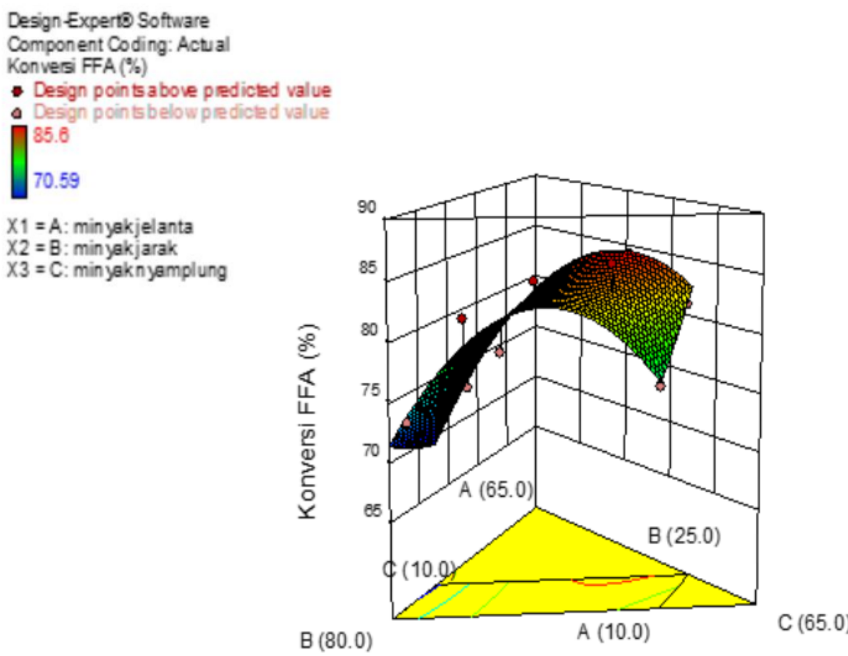

Figure 4. The Three Dimensional Response Test on the FFA Conversion

3.3. *Response Analysis*

Optimization was performed using Simplex Lattice Design Method (SLDM). This Method is able to carried out optimization according to the variable data and response measurement data inputted. Output of the optimization step is the recommendation of the new optimal formulation of the oil mixture. The optimal formulation is the composition which demonstrated the maximum desirability value. Desirability value is the function value for optimization purpose, indicating the ability of the program to fulfill the need based on the criteria specified on the final product.

In this work, optimization was conducted by determining the criteria (goal) of the desired FFA conversion which was ranging from 70.59% to 100%, thus the final FFA content resulted by the esterification reaction achieved the value as low as possible. Optimization using SLDM brought about the optimum FFA conversion of 85.938% with the formulation as shown in Table 3 and the desirability value of 0.937. The closer value of desirability to 1.0 denotes the reliability of the program to develop the desired result [11].

Table 3. Hasil Formula Optimum dari Metode *Simplex Lattice Design*

Composition	Prediction (mL)
CJO	37.291
CNO	37.709
WCO	25

The predicted value as shown in Table 3 was furthermore validated using experiment. Validation was carried out by evaluating the difference of the reaction conversion obtained by the predictive program and the empirical value obtained by experimental work for the similar non-edible oils feed-stock composition. The proximity between the predictive and empirical value indicates the validity of the model as demonstrated in Table 4.

Table 4. Comparison Between Predictive and Experimental Data of FFA Conversion Using the Optimal Composition of Feed-Stocks

Optimal Composition	Predictive FFA Conversion	Experimental FFA Conversion (Validation)
37.291 mL CJO + 37.709 mL NCO + 25 mL WCO	85.938%	86.03%

The validated optimum composition was then utilized as the feed-stocks for the transesterification reaction to produce biodiesel using reactive distillation process at the temperature of 60°C, molar ratio of oil to methanol of 1:6, and catalyst concentration of 1% NaOH catalyst [6]. Biodiesel produced contained 99.65% alkyl ester based on GC-MS analysis. The density of product was 884 kg/m^3, which meets the biodiesel standard.

4. Conclusion

Optimal composition of non-edible oil mixture which consists of crude jatropha oil, nyamplung seeds oil, and waste cooking oil can be predicted using Simplex Lattice Design Method (SLDM). The optimization resulted in the best composition of 37.291 mL CJO, 37,709 mL CNO, and 25 mL WCO which revealed in the optimum FFA conversion of 86.03%. Biodiesel produced after the oil mixture underwent transesterification reaction has the density of 884 kg/m^3 and alky ester content of 99.65%.

Acknowledgement

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