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OPTIMISATION OF PROCESS PARAMETER CONDITIONS FOR BIODIESEL PRODUCTION BY REACTIVE EXTRACTION OF JATROPHA SEEDS

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Abstract

Biodiesel can be produced by reactive extraction of jatropha seeds to reduce the cost and processing time associated with conventional methods. In this study, the relationship between various parameters of reactive extraction of jatropha seeds is investigated. The effect of processing time, the moisture content of jatropha seeds and hexane to oil weight ratios are examined to determine the best performance for biodiesel yield. Response surface methodology was used to statistically evaluate and optimise the process parameter conditions. It was found that the biodiesel production achieved an optimum biodiesel yield of 73.7% under the following conditions: processing time of 160 min, moisture content of jatropha seeds of 1% and hexane to oil weight ratio of 7.2.

Keywords: Biodiesel, Co-solvent hexane, Jatropha seed, Moisture content, Processing time, Reactive extraction.

1. Introduction

Biodiesel is one of the promising possible sources to substitute for conventional diesel fuel and produces favourable effects on the environment. It is presently making a global transition from a research and demonstration concept to commercial production. One of the challenges to widespread biodiesel adoption is its cost

Nomenclatures

X_1	Processing time, min
X_2	Moisture content of jatropha seed, %
X_3	Hexane to oil weight ratio

Abbreviations

ANOVA	Analysis of variance
DF	Degree of freedom
DOE	Design of experiments
GC-MS	Gas chromatography-mass spectrofotometry
RSM	Response surface methodology

compared with petroleum diesel fuel. The relative high price of biodiesel arises from the high cost of the refined edible oils that are predominant feedstocks for fuel production [1]. There are several non-edible oil seed species which could be used as a feedstock for biodiesel production such as jatropha (*Jatropha curcas*), karanja (*Pongamia pinnata*), rubber tree (*Hevea brasiliensis*) and castor (*Ricinus communis*). Among these, jatropha is a multipurpose species with many attributes and considerable potential. The jatropha plant has been attracting attention for its easy adaptability to tropical and subtropical climates in marginal and non-agricultural areas. The land area for jatropha planting is increasing because this plant can be used to reclaim land, and prevent and control erosion. In addition, the presence of phorbol esters makes jatropha oil unsuitable for food and feed applications [2].

There are several ways to produce biodiesel, and the most common way is transesterification of oils with short chain alcohol to fatty acid alkyl esters in the presence of a catalyst. Alcohols such as methanol, ethanol, 1-propanol and butanol have been used for biodiesel production [3]. The transesterification reaction can be catalysed by a homogeneous catalyst such as sodium hydroxide, potassium hydroxide and sulphuric acid; or a heterogeneous catalyst such as enzymes, alkaline transesterification earth metal reaction compounds and anion exchange resins [4]. Enzymes-catalysed processes such as using lipase as a catalyst do not produce side reactions, however, the lipases are still very expensive for industrial scale production and it requires a three-step process to achieve a high conversion [5]. An acid-catalysed process is useful when a high amount of free fatty acids is present in the vegetable oil, but the reaction time is very long even at the boiling point of alcohol, and a high molar ratio of alcohol is needed. Base catalysts are usually preferred over acid catalysts because of the higher reaction rates and lower process temperatures required as compared to the acid-catalysed process [6]. A batch transesterification process is the most common method for producing biodiesel. It has suffered several disadvantages compared to continuous processes such as requiring larger reactor volumes, resulting in higher capital investment. A continuous process has been developed to reduce higher procurement costs and also to enhance mixing of the reactants in order to improve the reaction rates [7].

The conventional methods for biodiesel production from oil seeds involves the following steps: oil extraction, purification (degumming, dewaxing, deacidification, dephosphorisation, dehydration, etc.), and subsequent esterification or transesterification. These multiple biodiesel processing steps constitute over 70% of the total cost of biodiesel production if refined oil is used as the feedstock [8]. Due to investment and energy cost savings, and the possibility of overcoming thermodynamic limitations imposed by reversible reactions or kinetic restrictions in irreversible reactions, recently, simultaneous processes of reactive extraction that combine reaction and separation operations in one unit have received much attention. Reactive extraction differs from the conventional biodiesel production process in that the oil-bearing material is brought into contact with the alcohol directly instead of reacting with pre-extracted oil. In this process, alcohol acts both as a reagent for transesterification and a solvent for extraction. As a consequence, a higher amount of alcohol is required compared to conventional processes. On the other hand, reactive extraction eliminates the requirement of two separate processes of oil extraction and transesterification reaction, thus reducing processing time, cost, and the amount of solvent required [9,10]. Dussan et al. [11] also reported that reactive extraction increases yield and selectivity in a system with multiple reactions, reduces recycle streams and formation of waste streams, and facilitates purification of products that are difficult to separate by conventional processes.

Meanwhile, response surface methodology (RSM) is an important tool for analysing and evaluating the relationship between the responses and independent variables and searching for optimal process parameters of desirable responses. RSM was widely applied in the reactive extraction process by many researchers. Shuit et al. [10] investigated reactive extraction of jatropha seed to biodiesel using a sulphuric acid catalyst. The optimum biodiesel yield of 98.1% obtained at a reaction temperature of 60°C, methanol to seed ratio of 10.5 mL/g, sulphuric acid of 21.8 %-w and reaction period of 10h. Pradhan et al. [12] reported that the production of biodiesel from castor seed achieved an optimum biodiesel yield of 88.2% at the following reaction conditions: methanol to oil molar ratio of 225:1, catalyst KOH concentration of 1%-w, reaction temperature of 55 ^{o}C, and mixing intensity of 350 rpm. Sulaiman et al. [13] reported the use of reactive extraction of solid coconut waste for biodiesel production. Based on RSM, the optimum biodiesel yield of 88.5% was found under the following conditions: 2%-w of KOH catalyst, 700 rpm of mixing intensity and 62°C reaction temperature.

The central composite design (CCD) and the Box–Behnken design (BBD) are the most commonly selected designs in RSM. The CCD contains a cube part which is a full factorial allowing determination of main and interaction effects, and a star design (α) for quantifying the main and quadratic effects. Meanwhile, the BBD contains rotated lower-dimensional designs, and globular three-level designs. The BBD offers much less flexibility than the CCD [14]. However, the BBD is useful for optimising a small number of variables at few levels. In addition, the BBD is an important alternative for avoiding time-consuming experiments [15]. Thus, BBD is extensively applied in various applications such as amine absorption processes [16], supercritical fluid extraction [17] and microwave-assisted transesterification [18].

In the present study, the use of a reactive extraction process for biodiesel production from jatropha seed is presented. The main objective of this study is to examine the effect of process parameters, i.e. processing time, moisture content of jatropha seed and co-solvent concentration (hexane to oil weight ratio). RSM comprising a Box-Behnken design will be used to optimise the process parameters of the reactive extraction of jatropha seed to produce biodiesel.

2. Experimental

2.1. Reagents and Materials

The jatropha seed was kindly provided by a local farm around Banda Aceh, Indonesia. The hexane of 99.9% purity was purchased from Fisher Scientific. The methanol used throughout this study was of technical grade. All chemicals were used without further purification.

2.2. Experimental Procedure

Jatropha seed was firstly blended and sieved to a size of <1 mm. Then, it was repeatedly weighed and dried in the oven at 76 °C until a constant weight was achieved. The dried seed was then sieved again to obtain fine particles of <0.355 mm in size.

A catalyst of sodium hydroxide of 0.9 g was dissolved in 400 mL of methanol, and then the mixture was placed in a 1000 mL round bottom flask and placed in a constant temperature water bath. The mixture was heated to the desired temperature of 45^{o}C, using a heated circulating water bath. After the desired temperature was achieved, 42 g of ground and sieved jatropha seed with the specified moisture content was transferred to the round bottom flask and the reaction was carried out at the desired temperature for the specified processing time. The mechanical stirring experiment with agitation speed of 600 rpm was performed for the reaction system. The schematic apparatus for reactive-extraction of jatropha seed was shown in Fig. 1.

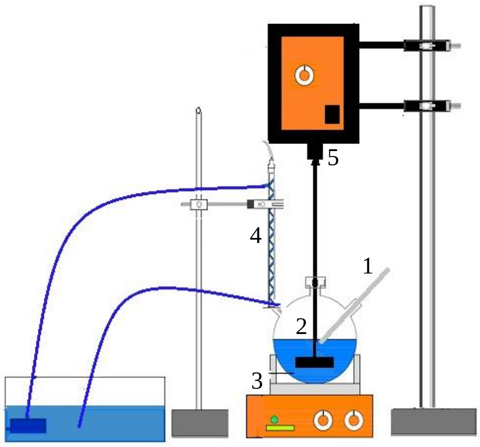

Fig. 1. Schematic apparatus for reactive-extraction of jatropha seed: 1 - thermometer, 2 - reaction mixture, 3 - water bath, 4 – condenser, 5 - agitation motor

After reaction for the desired processing time, the solid residue was separated from the liquid using vacuum filtration. The solid residue was washed repeatedly with methanol to recover any product that adhered to the seed and the excess methanol was removed using a rotary evaporator. Two layers of liquid were formed after evaporation. The upper layer contained the ester phase, while the bottom layer contained the glycerol phase. After separation using a separating funnel, the upper layer was weighed and stored in a sealed vial ready for gas chromatography-mass spectrofotometry (GC-MS) analysis.

2.3. Product Analysis

The chemical composition of biodiesel was analysed by a gas chromatograph coupled with a mass spectrometer detector (GC-MS, Model QP 2010 Plus, Shimadzu Japan). Helium was used as a carrier gas. The sample components were identified by matching their mass spectra with those from the library database.

The experimental results were reported in terms of biodiesel yield determined by Eq. (1):

$$\text{Biodiesel yield} = \frac{\text{Weight of biodiesel}}{\text{Weight of oil in jatropha seeds}} \times 100\% \qquad (1)$$

The amount of oil in the jatropha seed was measured by a Soxhlet extractor with hexane as solvent according to ISO 659-1988. After the extraction process, the hexane was removed using a rotary evaporator, and the amount of extracted oil was measured. The oil content in jatropha seed was found to be 23.3%. Meanwhile, the moisture content of the jatropha seeds was determined using the oven method [19].

2.4. Experimental Design

The effect of process parameters on the yield of biodiesel was studied using Design of Experiments (DOE). The DOE selected was RSM using Design Expert version 6.0.6 (Stat-Ease, Inc.) software. To optimise the reaction parameters of reactive extraction of jatropha seed, a Box-Behnken with a three-level-three-factor design that addressed processing time (X_1), moisture content of jatropha seed (X_2) and hexane to oil weight ratio (X_3) was selected. Table 1 indicates the independent variables and their levels used in the response surface design. A single factor experiment was conducted to determine appropriate the ranges of independent variables to be used in design of experiments.

Table 1. Independent variables and their levels used in the response surface design

Independent variables	Factor levels		
	-1	**0**	**1**
Processing time, X_1 (min)	60	120	180
Moisture content, X_2 (%)	1	3	5
Hexane to oil weight ratio, X_3 (-)	6.3	7.6	8.9

The experimental data were analysed by the response surface regression procedure to fit to the following second-order polynomial equation of Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^{3}\beta_i X_i + \sum_{i=1}^{3}\beta_{ii} X_i^2 + \sum_{i=1}^{2}\sum_{j=i+1}^{3}\beta_{ij} X_i X_j \quad (2)$$

where Y is the response (% yield); β_0, β_i, β_{ii} and β_{ij} are the intercept, linear, quadratic and interaction constant coefficients, respectively; and X_i, X_j are the independent variables. All experimental data regression and analysis was performed with the analysis of variances (ANOVA).

3. Results and Discussion

3.1. Single factor experiment

Figure 2 shows the effect of process parameters on yield of biodiesel. As shown in Fig. 2(a), the variation of processing time had a great effect on yield of biodiesel. The experiments were carried out with 1% of jatropha seed moisture content and 7.6 of hexane to oil weight ratio. An upward trend with an increase in the reaction time was noticed. This indicated that jatropha oil was extracted from seed and then the oil was transformed to biodiesel. Yield of biodiesel increases remarkably with increasing processing time within 120 min, and kept almost constant above 120 min. It is suggested that there is only a little oil obtained in the extracting liquor when the reaction had processed more than 120 min. This might also indicate that the transesterification reaction reached equilibrium condition, thus, further proceeds the reaction that may lead to reverse of reaction to reactant side and reduce the biodiesel content [14].

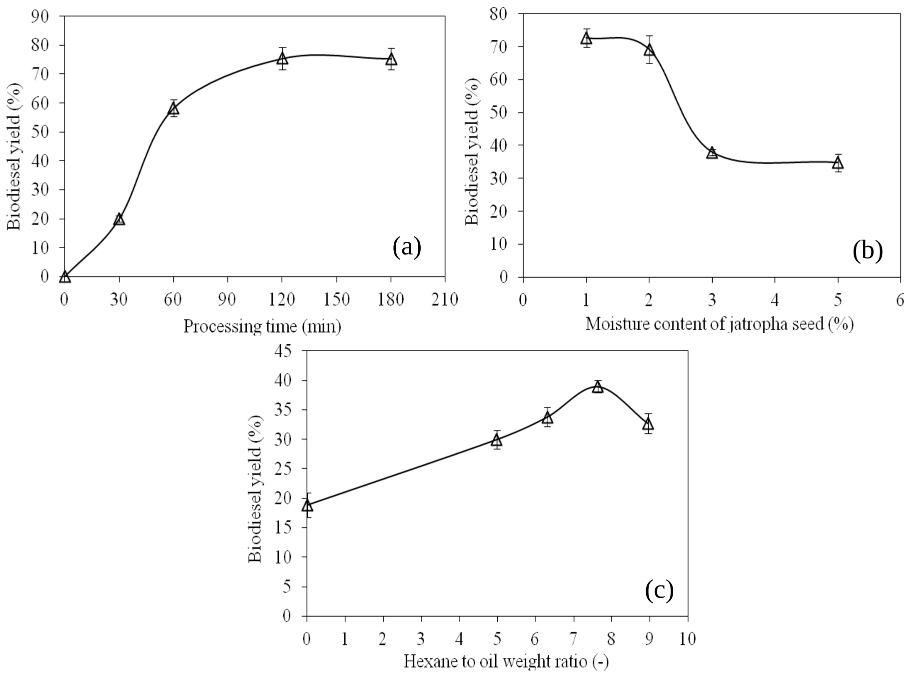

Fig. 2. Effect of process parameters on yield of biodiesel

Meanwhile, as shown in Fig. 2(b), the yield of biodiesel increases with decrease of moisture content of jatropha seed. The experiments were conducted with 120 min of processing time and 7.6 of hexane to oil weight ratio. The presence of water greatly affected alkali-catalysed transesterification by making the reaction partially change to saponification and leading to soap formation [4, 15]. Also, Haas [16] noted that water inhibits transesterification reactions since it competes with the alcohol (reactant), thereby transforming the required ester transfer reaction into ester hydrolysis, and leading to formation of free fatty acids.

The influence of the cosolvent of hexane to oil weight ratio on the yield of biodiesel obtained is presented in Fig. 2(c). The experiments were carried out with 120 min of processing time and 3% of jatropha seed moisture content. In a transesterification system, the mass transfer between the two phases of oil and alcohol becomes a significant factor that affects the reaction rate due to immiscibility of the oil and alcohol phases. Methanol extracts some amount of material from the seed but very little is triglyceride since methanol is a very polar solvent, whereas most triglycerides are non-polar long chain hydrocarbon molecules. Based on this fact, a cosolvent of hexane could be added to enhance the miscibility of the phases and speed up the reaction rate [10]. As shown in Fig. 2(c), biodiesel yield is improved when compared to the system without cosolvents. A suitable amount of hexane, however, must be added to achieve an optimum biodiesel yield. The biodiesel yield reaches its optimum at a hexane to oil weight ratio of 7.6. When the hexane to oil the weight ratio of was lower than 7.6, biodiesel yield decreased because of the immiscibility of methanol and oil. On the other hand, beyond a hexane to oil weight ratio of 7.6, the transesterification rate also decreases due to a dilution effect of the excess of hexane. Excessive addition of hexane into the reaction system also could increase the operating cost. Qian et al. [17] reported that the optimum loading amount of hexane to oil weight ratio was found to be 3:1 in an alkali-catalysed transesterification process of jatropha oil prepared by two-phase solvent extraction of jatropha seed.

3.2. Statistical Analysis and Model Fitting

Based on the observations from single factor experiments, the range of each independent variable (processing time, moisture content of jatropha seed and hexane to oil weight ratio) that influence biodiesel yield were selected. The experimental parameters, ranges and levels of the independent variables investigated in this study, and the results on the basis of the Box-Behnken experimental design are shown in Table 2. All of the 17 designed experiments were conducted and the results analysed by multiple regression. Five duplicates are included at the centre of the design. The predicted values were obtained from the model fitting technique and were seen to be sufficiently correlated to the observed values. The following quadratic model equation (in coded factors) that correlates the yield of biodiesel to various process parameters is given by Eq. (3).

$$Y = 38.92 + 4.85X_1 - 18.27X_2 - 1.05X_3 - 2.20X_1X_2 + 0.55X_1X_3 + 1.90X_2X_3 - 5.16X_1^2 + 13.74X_2^2 - 4.06X_3^2 \quad (3)$$

Statistical analysis of the model was performed to evaluate the ANOVA and check the adequacy of the empirical model. The results of ANOVA for fitting the quadratic response surface model by a mean square method are summarised in Table 3. The coefficients of the response surface model as provided by Eq. (3) were also evaluated. The significance of each of the coefficients are checked from *p*-values (probability of error value), which also indicate the interaction strength of each parameter. According to Table 3, the *p*-value of the model is less than 0.0001, demonstrating high significance in predicting the response values and the suitability of the model. The high *F*-value (*F* model = 54.59) with very low probability value indicated the high significance of the fitted model. Table 3 presents the significance of all coefficients established by *p*-values.

Table 2. Experimental Design Matrix and Results

Processing time, A (min)	Moisture content, B (%)	Hexane to oil weight ratio, C (-)	Biodiesel yield (%)
60	3	6.3	26.1
120	3	7.6	38.9
180	3	8.9	34.4
120	3	7.6	38.9
120	3	7.6	38.8
60	5	7.6	24.0
180	5	7.6	32.3
180	1	7.6	75.4
120	1	6.3	70.6
60	3	8.9	26.6
60	1	7.6	58.3
120	3	7.6	39.0
120	5	8.9	30.4
120	5	6.3	32.4
180	3	6.3	31.7
120	1	8.9	61.0
120	3	7.6	39.0

Table 3. ANOVA for response surface quadratic model

Source	Sum of squares	DF	Mean square	*F*-value	*p*-value
Model	3836.21	9	426.25	54.59	<0.0001
A-Processing time	188.18	1	188.18	24.10	0.0017
B-Moisture content	2671.8	1	2671.80	342.21	<0.0001
C-Hexane to oil weight ratio	8.82	1	8.82	1.13	0.3231
AB	19.36	1	19.36	2.48	0.1593
AC	1.21	1	1.21	0.15	0.7055
BC	14.44	1	14.44	1.85	0.2160
A^2	112.11	1	112.11	14.36	0.0068
B^2	794.9	1	794.90	101.81	<0.0001
C^2	69.4	1	69.40	8.89	0.0205
Residual	54.65	7	7.81		

The low value of the coefficient of variation (CV = 6.81%) indicated that the results of the fitted model are reliable. The quality of the model fit was evaluated by the coefficient of determination (R^2), this value being calculated to be 0.986 for the response, indicating that the developed model equation successfully captured the correlation between the process parameters to the yield of biodiesel. The adjusted coefficient of determination (R^2Adj.) value reconstructs the expression with all the significant terms included. The value of the adjusted coefficient of determination (R^2 Adj. = 0.968) is also very high, supporting the significance of the model. As the fitted model Eq. (3) provides a good approximation to the experimental condition, the model is used to find the values of the process parameters for optimum yield of biodiesel.

It can be observed that the variable with the largest effect on biodiesel yield is the linear term of moisture content of jatropha seed (X_2) followed by the quadratic term of moisture content of jatropha seed (X_2^2), linear term of processing time (X_1), quadratic term of processing time (X_1^2) and quadratic term of hexane to oil weight ratio (X_3^2) (see Table 3). However, the linear term of hexane to oil weight ratio (X_3) and all the interaction terms (X_1X_2, X_1X_3 and X_2X_3) are found to be insignificant (p>0.05). Regression analysis of the experimental data also shows that processing time and moisture content of jatropha seed has significant positive and negative linear effects respectively on biodiesel yield. Both processing time and moisture content of jatropha seed are found to have strong linear effects of 4.85 and -18.27, respectively on biodiesel yield (Eq. 3).

3.3. Optimisation of Process Parameter Conditions

The graphical representation of the regression Eq. (3), and the contour plot are presented in Fig. 3. Two variables within the experimental range were depicted in one 2D surface plot. The shape of the surface plot indicated different interaction between the variables.

Contour plots of Figs. 3(a) and (b) show that the moisture content of jatropha seed has a significant effect on biodiesel yield. As moisture content of jatropha seed decreases, biodiesel yield increases for all ranges of processing time and hexane to oil weight ratio. Results also show that low moisture content of jatropha seed irrespective of processing time and hexane to oil weight ratio would give a high biodiesel yield. Higher processing times up to 130 min would give higher biodiesel yield ranging from 34 to 65% at moisture content of jatropha seed lower than 4% (Fig. 3(a)). Hexane to oil weight ratio, however, does not give any significant contribution to the biodiesel yield. It was observed that hexane to oil weight ratio does not have a positive effect on biodiesel yield, when processing time was held constant at 120 min (Fig. 3(b)). Figure 3(c) shows that when holding moisture content of jatropha seed at its centre point of 3%, the processing time is recommended to be kept at 140-160 min with hexane to oil weight ratio at 7.2-7.5 in order to achieve a high biodiesel yield.

The optimal values of the selected variables are obtained by solving the regression equation of Eq. (3). This model is used to find the value of the process parameters that gives the optimum yield of biodiesel. The predicted optimal value, obtained from the model equation for reactive extraction of jatropha seed to produce biodiesel are time of process of 160 min, moisture content of of jatropha seed of 1% and hexane to oil weight ratio of 7.2. The model predicts that the maximum yield of biodiesel that can be obtained under these optimum conditions is 73.7%.

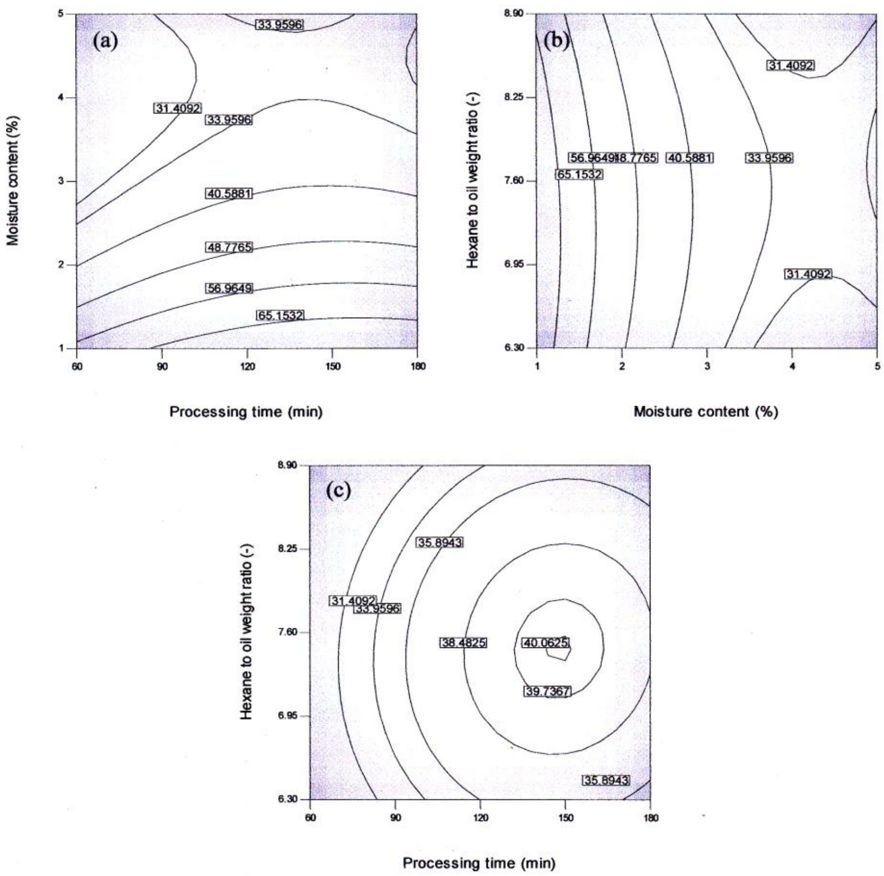

Fig. 3. Contour plots showing the effects of experimental factors on biodiesel yield: (a) processing time and moisture content at hexane to oil weight ratio of 7.6, (b) moisture content and hexane to oil weight ratio at processing time of 120 min, and (c) processing time and and hexane to oil weight ratio at moisture content of 3%.

3.4. Verification of Predictive Model

The suitability of the model equation for predicting optimum response value was tested under the optimum conditions. These set conditions were used to validate experimentally and predict the values of the response using the model equation. The biodiesel yield of 71.7±1.9% obtained from the real experiments is very close to the model prediction, indicating that the model is adequate for the reactive extraction of jatropha seed. Predicted and experimental values of the response under optimum conditions is shown in Table 4.

Table 4. Predicted and experimental values of the response under optimum conditions

Optimum condition			Biodiesel yield (%)	
Processing time (min)	Moisture content (%)	Hexane to oil weight ratio	Predicted	Experimental (N=3)
160	1	7.2	73.7	71.7±1.9%

3.5. Properties of biodiesel

The biodiesel obtained from each experiment is very similar with an appearance of a clear yellow liquid. The composition of the biodiesel was analysed by GC-MS. The fatty acid methyl ester composition of the biodiesel obtained is given in Table 5. The biodiesel mainly consists of four fatty acid methyl esters of methyl oleate, methyl linoleate, methyl palmitate and methyl stearate. Methyl palmitoleate and methyl linolenate are present in small amounts. In addition, it can be concluded that the composition of the biodiesel is similar to the fatty acid composition of jatropha oil as the source of the biodiesel. The data obtained is comparable with the results of other researchers [24,25]. The variation in the percentage of fatty acid composition of the biodiesel might be due to the diverse agro-climatic conditions for jatropha cultivation.

Table 5. Fatty acid methyl ester composition of biodiesel

Component	Composition (%)		
	This study	**Wang et al. [24]**	**Berchmans and Hirata [25]**
Methyl palmitate	14.9	13.4	14.9
Methyl palmitoleate	1.6	0.9	1.1
Methyl stearate	7.5	7.2	3.85
Methyl oleate	39.1	43.5	32.5
Methyl linoleate	35.1	33.6	47.4
Methyl linolenate	0.9	0.1	-

The acid value, viscosity and density of the biodiesel obtained after reactive extraction are presented in Table 6. It can be seen that all specified properties are in the acceptable ranges according to Indonesian National Standards (*Standar Nasional Indonesia*, SNI 04-7182-2006). Meanwhile, the viscosity and density of the biodiesel are in line within the range specified in the EN 14214 biodiesel standards. However, the acid value is slightly higher than 0.50 mg KOH/g. According to EN 14214, a further purificaton process such as neutralisation, is recommended to reduce the biodiesel acidity before being used in diesel engines.

Table 6. Properties of biodiesel

Property	Unit	Value		
		This study	**EN 14214**	**SNI 04-7182-2006**
Acid value	mg KOH/g oil	0.52	< 0.5	< 0.8
Viscosity at 40 ^{o}C	mm^2/s	4.7	3.5-5.0	2.3-6.0
Density at 15 ^{o}C	kg/m^3	860	860-900	850-890

4. Conclusions

RSM with a Box-Behnken design was employed to statistically evaluate and optimise the process parameters of processing time, moisture content and hexane to oil weight ratio for biodiesel production by reactive extraction of jatropha seed. According to ANOVA, the effects of processing time and moisture content were significant. Quadratic models fitted the responses of biodiesel yield for predicting the responses. The optimum biodiesel yield of 73.7 % was obtained using processing time of 160 min, moisture content of jatropha seed of 1% and hexane to oil weight ratio of 7.2. GC-MS results showed that methyl oleate was the highest component in the biodiesel.

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References

1. Zhang, Y., Dube, M.A., McLean, D.D.; and Kates, M. (2003). Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology*, 89(1), 1-16.
2. Kartika, I.A., Yani, M., Ariono, D., Evon, Ph.; and Rigal, L. (2013). Biodiesel production from jatropha seeds: Solvent extraction and in situ transesterification in a single step. *Fuel*, 106, 111-117.
3. Lateef, F.A., Onukwuli, O.D., Okoro, U.C., Ejikeme, P.M.; and Jere, P., (2014). Some physical properties and oxidative stability of biodiesel produced from oil seed crops. *Korean Journal of Chemical Engineering*, 31(5), 725-731.
4. Atadashi, I.M., Aroua, M.K., Aziz, A. R. A.; and Sulaiman, N.M.N. (2012). The effects of water on biodiesel production and refining technologies: A review. *Renewable and Sustainable Energy Reviews*, 16(5), 3456.
5. Wang, D., Xu, Y.; and Shan, T. (2008). Effects of oils and oil-related substrates on the synthetic activity of membrane-bound lipase from *Rhizopus chinensis* and optimization of the lipase fermentation media. *Biochemical Engineering Journal*, 41(1), 30-37.
6. Shyamsundar, M., Shamshuddin, S.Z.M.; and Sahu, J.N. (2013). Catalytic synthesis of biodiesel from pongamia glabra over zirconia and its modified forms. *Korean Journal of Chemical Engineering*, 30(12), 2186-2190.
7. Azhari, Ghazi, T.I.M., Resul, M.F.M.G., Yunus, R.; and Yaw, T.C.S. (2008). Preliminary design of oscillatory flow biodiesel reactor for continuous biodiesel production from jatropha triglycerides. *Journal of Engineering Science and Technology*, 3(2), 138 - 145.
8. Zeng, J., Wang, X., Zhao, B., Sun, J.; and Wang, Y. (2009). Rapid in situ transesterification of sunflower oil. *Industrial & Engineering Chemistry Research*, 48(2), 850-856.
9. Kaul, S., Porwal, J.; and Garg, M.O. (2010). Parametric study of Jatropha seeds for biodiesel production by reactive extraction. *Journal of the American Oil Chemists' Society*, 87(8), 903-908.
10. Shuit, S.H., Lee, K.T., Kamaruddin, A.H.; and Yusup, S. (2010). Reactive extraction of Jatropha curcas L. seed for production of biodiesel: Process optimization study. *Environmental Science and Technology*, 44(11), 4361–4367.
11. Dussan, K.J., Cardona, C.A., Giraldo, O.H., Gutiérrez, L.F.; and Pérez, V.H. (2010). Analysis of a reactive extraction process for biodiesel production

using a lipase immobilized on magnetic nanostructures. *Bioresource Technology*, 101(24), 9542-9549.

12. Pradhan, S., Madankar, C.S., Mohanty, P.; and Naik, S.N. (2012) Optimization of reactive extraction of castor seed to produce biodiesel using response surface methodology. *Fuel*, 97, 848–855.
13. Sulaiman, S., Aziz, A.R.A.; and Aroua, M.K. (2013). Reactive extraction of solid coconut waste to produce biodiesel. *Journal of the Taiwan Institute of Chemical Engineers*, 44(2), 233-238.
14. Langhans, L. (2000). Designs for response surface modelling-quantifying the relation between factors and responses, Tranter, R.L. (Ed.), Design and Analysis in Chemical Research, CRC Press, Sheffield.
15. Montgomery, D.C. (2005). Design and Analysis of Experiments, 6th ed. John Wiley &Sons, Inc., New Jersey.
16. Nuchitprasittichai, A.; and Cremaschi, S. (2011). Optimization of CO_2 capture process with aqueous amines using response surface methodology. *Computers and Chemical Engineering*, 35(8), 1521– 1531.
17. Khajeh, M. (2011). Optimization of process variables for essential oil components from *Satureja hortensis* by supercritical fluid extraction using Box-Behnken experimental design, *Journal of Supercritical Fluids*, 55(3), 944–948.
18. Liao, C.-C.; and Chung, T.-W. (2013). Optimization of process conditions using response surface methodology for the microwave-assisted transesterification of Jatropha oil with KOH impregnated CaO as catalyst. *Chemical Engineering Research and Design*, 91(12), 2457-2464.
19. Haas, M.J., Scott, K.M., Foglia, T.A.; and Marmer, W.N. (2007). The general applicability of in situ transesterification for the production of fatty acid esters from a variety of feedstocks. *Journal of the American Oil Chemists' Society*, 84(10), 963–970.
20. Lee, H.V., Yunus, R., Juan, J.C.; and Taufiq-Yap, Y.H. (2011). Process optimization design for jatropha-based biodiesel production using response surface methodology. *Fuel Processing Technology*, 92(12), 2420-2428.
21. Bikou, E., Louloudi, A.,; and Papayannakos, N. (1999). The Effect of Water on the Transesterification Kinetics of Cotton Seed Oil with Ethanol. *Chemical Engineering & Technology*, 22(1), 70-75.
22. Haas, M.J. (2005). Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. *Fuel Processing Technology*, 86(10), 1087-1096.
23. Qian, J., Shi, H.; and Yun, Z. (2010). Preparation of biodiesel from *Jatropha curcas* L. oil produced by two-phase solvent extraction. *Bioresource Technology*, 101(18), 7025-7031.
24. Wang, R., Song, B., Zhou, W., Zhang, Y., Hu, D., Bhadury, P.S.; and Yang, S. (2011). A facile and feasible method to evaluate and control the quality of *Jatropha curcus* L. seed oil for biodiesel feedstock: Gas chromatographic fingerprint. *Applied Energy*, 88(6), 2064-2070.
25. Berchmans, H.J.; and Hirata, S. (2008) Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresource Technology*, 99(6), 1716-1721.