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Optimization of Biodiesel Production from Mixed Jatropha curcas–Ceiba pentandra Using Artificial Neural Network-Genetic Algorithm: Evaluation of Reaction Kinetic Models

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Biodiesel production from non-edible vegetable oil is one effective way to anticipate the problems associated with fuel crisis and environmental issues. In this study, artificial neural network and genetic algorithm based Box Behnken experimental design used to optimize the parameters of the biodiesel production for mixed of *Jatropha curcas–Ceiba pentandra* oil such as methanol to oil ratio, agitation speed and catalyst concentration. Based on the results, the optimum operating parameters for the transesterification of the oil mixture J50C50 are as follows: methanol-to-oil ratio: 40 %v/v, agitation speed: 1,794 rpm and the catalyst concentration: 0.68 % wt. This process is carried out at constant temperature and time of 60 °C and 2 h. The theoretical yield predicted under this the highest yield for the J50C50 biodiesel with a value of 93.70 %. The model developed was validated by applying the optimum values to three independent experimental replicates with a 93.56 %. Comparison between the predicted values to the actual value with a small error percentage indicates that the regression model was reliable in predicting the conversion at any given conditions within the ranges studied. Moreover, the activation energy of 24.421 kJmol^{-1} and frequency factor of 1.88 x 10^2 min^{-1} was required for the transesterification process. The fuel properties of the biodiesel were measured according to ASTM D 6751 and EN14214 standards and found to be within the specifications.

1. Introduction

Today, fossil fuels have an important role in supplying global energy needs. Approximately 80 % of the total global energy needs derived from fossil fuels. Biodiesel is sustainable and renewable sources which is considered to have the potential to meet the energy needs and answer these concerns (Fazal et al., 2012). Biodiesel can be produced from a variety of sources which include edible oils, non-edible oils, waste oils as well as animal fats (Mofijur et al., 2013). To minimize production costs, *Jatropha curcas* (J*. curcas*) oil is one of the common non-edible feedstocks for biodiesel production since J. *curcas* has an oil yield of around 1590 kg per hectare (Silitonga et al., 2011). J*. curcas* belongs to the *Euphorbiaceae* family. Transesterification of J*. curcas* oil results in biodiesel with high fatty acid methyl ester (FAME) content up to 97 % (Rabiah Nizah et al., 2014). Other non-edible oil is *Ceiba pentandra* (C. *pentandra*) which is the Malvaceae family. C*. pentandra* fibre also contains about 36 – 64 % cellulose. From the studies, it is known that has a saturated fatty acid content of 17.15 % and 76.32 % of unsaturated fatty acids in the oil C. *pentandra* (Vedharaj et al., 2013). The production of biodiesel from oil seeds can be obtained through extraction, purification and transesterification. Optimization of the production parameters using artificial neural network (ANN) combined with genetic algorithms are employed simultaneously to optimize the two responses (Mohammad Fauzi et al., 2014). The aim of this research is to increase production and produce biodiesel that is optimal from a *J. curcas–C. pentandra* crude oil mixture. Some reaction parameters in the transesterification process is generated by Box-Behnken experimental design (ie. Methanol-to-oil ratio, catalyst concentration and speed agitation). Furthermore, these parameters on the optimization using artificial neural network (ANN) to obtain the optimum conditions. A kinetic study was also

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conducted and the reaction rate constant (k) and activation energy (EA) at various temperatures were determined. Fuel properties of the biodiesel were determined and compared with ASTM D 6751 specifications.

2. Materials and methods

2.1 Material

In this study, crude J. *curcas* were purchased from Kebumen, West Java Indonesia. While crude oil of C. *pentandra* purchased from Probolinggo, East Java Indonesia. All reagents used are methanol (99.9 % purity), sulfuric acid (H_2SO_4, purity> 98.9 %), Phosphoric acid (H_3PO_4, 20 %) and potassium hydroxide pellets (KOH purity 99 %). The Whatman filter paper size of 150 mm (filter Fioroni, France) was purchased from Metta Karuna Enterprise (Kuala Lumpur, Malaysia).

2.2 Methods

2.2.1 J. *curcas*- C.*pentandra* oil mixture and degumming process

In this study, the oil used is a mixture of crude *J. curcas* and *C. pentandra* oil with their respective percentage is 50 % or abbreviated by J50C50. Selection this composition is based on the previous study which stated that the J50C50 oil mixture is suitable to be converted into biodiesel. J50C50 also has some properties are better than other mixtures, such as low acid value, kinematic viscosity and density (Dharma et al., 2016). A J. *curcas* 50 % and C. *pentandra* 50 % was mixed, the oil is separated from the gums through degumming process. J. *curcas* and C. *pentandra* oil was preheated at 60 °C for 15 min. After that, 2 vol.% phosphoric acid (H_3PO_4, 20 % concentration) was added to the crude oil is heated at 60 °C and a speed of 800 rpm for 30 min. Following by a separation process used a funnel for at least 4 h. These gums are separated from the oil and washed several times with distilled water at 40 °C. The residue water in oil evaporated with a vacuum pump for 30 min to avoid oil oxidation.

2.2.2 Esterification

In this process, the mixture of crude oil degumming proceeds much as 200 mL with 30 % methanol to oil molar ratio and 1 % (v/v) H_2SO_4 was added to oil temperature of 60 ºC for 3 h at 1,200 rpm stirring speed. Once the reaction was complete, the product was poured into a separating funnel to separate the excess alcohol, H_2SO_4 and dirt was presented in the upper layer. The bottom layer was separated and settled for 4 h. Then, esterified oil was heated at 60 ºC in a rotary evaporator under vacuum for 1 h to remove extra methanol and water in oil.

2.2.3 Transesterification process

Esterified oil from J50C50 mixture was measured and preheated to the temperature of 60 °C by using a heating circulator. Alkaline catalyst (KOH) is diluted with methanol and then added to the hot oil and then stirred continuously for 2 h, the temperature was maintained at 60 °C. Upon completion of the reaction period, biodiesel precipitated separating funnel for 6 h to separate the glycerol from biodiesel. The bottom layer containing the dirt, excess methanol and glycerol were pulled off. The oil was imported into a rotary evaporator to remove the remains of methanol. Then, oil was washed with distilled water several times to remove impurities entrained glycerol. In this process, 50 % (v/v) of distilled water at 50 °C was sprayed over the surface of the ester and stirred slowly. The bottom layer was removed and the top layer was inserted into the flask. Furthermore, the oil evaporated to remove water and methanol extra by using a vacuum pump at 60 °C and filtered with a filter paper.

2.3 Design experiment

A Box-Behnken was employed in these modelling J50C50 studies with artificial neural network (ANN) provided in Design Expert software package version 9.0.4.1 (Stat-Ease Inc., Minneapolis, MN, USA) software was applying to design the experiment (DOE), the methanol-to-oil ratio *(A),* speed agitation *(B)*, and catalyst concentration *(C)*. The coded and uncoded levels of independent variables the Box-Behken for transesterification of J50C50 step is showed in Table 1.

2.4 Artificial Neural Network (ANN) Modeling

In this study, a three layer feed forward was employed and the hyperbolic tangent sigmoid *(tansig)* transfer function used from input to hidden layer. While the purelin transfer function applied from hidden layer to output. The tansig and the purelin transfer function are expressed as Eq(1) and (2) as below:

$$\tan sig\ (x) = \frac{2}{(1+ e^{-2x})} - 1 \quad (1)$$

$$A = purelin\ (x) = x \quad (2)$$

The back propogation with *Levenberg–Marquard* was ANN consists to three layers as input layers with four input (methanol to oil molar ratio, catalyst concentration, and speed agitation), hidden layers with the optimum number of neurons and single output variable. The configuration of a single hidden layer shown in Figure 1. The ANN was trained until the minimum mean square error (MSE) reached and average correlation coefficient (R) were closed or equal to 1. The performance of well trained and tested ANN were used for modeling the GA to predict the acid value for esterification process and the methyl ester yield for transesterification process at various combination of independent parameters.

Table 1: The Box-Behken coded and uncoded independent variable

Factor	Units	Level		
		−1	0	+1
Methanol to oil ratio (A)	mol/mol	30	50	70
Speed agitation (B)	rpm	800	1300	1800
Catalyst concentration (C)	wt. %	0.50	1.25	2.00

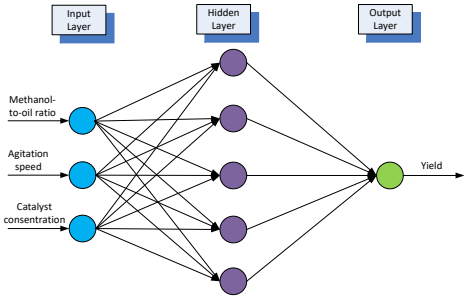

Figure 1: The configuration of a single hidden layer with five neurons

2.5 Kinetic modeling

The Arrhenius equation can be written as Eq(3):

$$k(T) = k = Aexp(-Ea/\breve{R}\,T) \tag{3}$$

where A and Ea are the Arrhenius parameters which stand for frequency factor or pre-exponential coefficient (min^{-1}) and activation energy (J/mol) respectively. $\breve{R}$ is the gas constant (8.314 J/mol K) and T is the absolute temperature (K). By taking the natural logarithm Eq(4) can be expressed as Eq(4):

$$\ln k = \ln A - \frac{Ea}{\breve{R}\,T} \tag{4}$$

To determine the rate of reaction per unit time, r, the following basic equation was used;

$$r = \frac{da}{dt} = k(T)f(a) \tag{5}$$

Expanding the equation, assuming that a simple *n*th order kinetic relationship holds for the conversion dependent term, $f(a)$, such that $f(a) = (1-a)^n$, Eq(6) can be written as;

$$r = \frac{da}{dt} = k(1-a)^n \tag{6}$$

In order to determine the value of k, integral method is used to solve Eq(6). Rearranging and integrating Eq(7), Eq(8) is obtained as;

$$[(1-(1-a)^{1-n})/1-n] = kt(for\ n \neq 1) \tag{7}$$

Thus, a plot of $[(1-(1-a)^{1-n})/1-n]$ versus *t* $(for\ n \neq 1)$ should result in a straight line of slope *k* for the proper value of *n.* The criterion used to determine the acceptable value of *n* is that when the plot $[(1-(1-a)^{1-n})/1-n]$ versus *t* $(for\ n \neq 1)$ give the best straight line for all reaction temperature studied.

3. Results and discussion

3.1 Design experimental using the Box-Behnken

Experimental as well as predicted values obtained for yield value responses at the design points are shown in Table 2. All the three variables are shown in both coded and uncoded (actual) form. Design Expert with the Box-Behnken experimental design was used to generate 17 test parameters of the three independent variables such as the methanol-to-oil ratio (A), speed of agitation (B), and catalyst concentration (C). The coded and uncoded levels of independent variables were used for transesterification of J50C50 which generated 17 experimental runs.

Table 2: The Box-Behnken experimental design results for transesterification of J50C50 oil mixture

No. Experiment	*A* Methanol (%)	*B* Speed (rpm)	*C* Catalyst (%)	Yield (wt.%) experiment	Yield (wt.%) predicted
1	70	1,300	2.00	81.27	81.09
2	50	1,300	1.25	92.10	92.06
3	30	1,300	0.50	93.30	93.47
4	70	1,300	0.50	93.07	92.67
5	70	1,800	1.25	90.84	91.37
6	50	1,300	1.25	92.01	92.06
7	30	1,300	2.00	81.36	81.75
8	50	1,300	1.25	91.96	92.06
9	50	1,800	2.00	82.51	82.15
10	30	800	1.25	91.19	90.66
11	50	1,800	0.50	92.92	92.79
12	50	800	0.50	92.01	92.36
13	50	1,300	1.25	91.75	92.06
14	70	800	1.25	89.29	89.33
15	50	800	2.00	79.59	79.71
16	30	1,800	1.25	91.54	91.49
17	50	1,300	1.25	92.88	92.06

3.2 Physicochemical properties of J. *curcas*, C. *pentandra* and J50C50 biodiesels

The physicochemical properties of the J50C50 biodiesel are tabulated in Table 3. The properties were determined according to the procedures outlined in the ASTM D6751 and EN14214 standards. The kinematic viscosity at 40 °C of the J50C50, J. *curcas* and C*. pentandra* biodiesel is found to be 4.296, 4.577 and 4.744 mm^2/s, respectively, which is within the range specified in the ASTM D6751 and EN 14214 standards (1.9 – 6.0 mm^2/s and 3.5 – 5.0 mm^2/s). In contrast, the kinematic viscosity at 40 °C for diesel is 2.96 mm^2/s, which indicates that diesel has higher fluidity compared to the J50C50biodiesel. The density at 15 °C of the J50C50, J. *curcas* and C*. pentandra* biodiesel is found to be 866.9, 876.2 and 885.7 kg/m^3, respectively, which is dependent on the fatty acid composition and purity of the biodiesel (Martínez et al., 2014). Increased density of biodiesel causes increased viscosity, which can affect the operation of the fuel injection system due to the delivery of a slightly greater mass of fuel in the volume metering equipment (Demirbas, 2008). The acid value of the J50C50, J*. curcas* and C. *pentandra* biodiesel is 0.042, 0.046 and 0.051 mg KOH/g. A high acid value is undesirable since it can result in severe corrosion of the fuel supply system and internal combustion engine resulting from degradation of the fuel in service. The calorific value of the J50C50, J. *curcas* and C*. pentandra* biodiesel is found to be 40.212, 39.461 and 39.469 MJ/kg. The J50C50 biodiesel has a calorific value which is slightly higher than the calorific value of biodiesels derived from individual J*. curcas* and C*. pentandra* oils. The oxidation stability at 110 °C of the J50C50, J. *curcas* and C. *pentandra* biodiesel is found to be 6.23, 14.01 and 1.76 hours, respectively. Hence, the J50C50 biodiesel has an oxidation stability which is a compromise between the J*. curcas* and C*. pentandra* biodiesels. However, the oxidation stability at 110 °C of the J50C50 biodiesel is still far from that for diesel which has an oxidation stability of 15.2 h. Based on the results shown in Table 3, it can be deduced that there is a need to improve the physicochemical properties of the J50C50 biodiesel and this can be achieved by optimizing the operating parameters of the transesterification process (Martínez et al., 2014).

3.3 ANN model analysis

Artificial neural network (ANN) based on experimental work was carried out to create a models of used to yield of biodiesel. Utilization of facilities available toolboxes for ANN modelling was considered a simple way to get accurate results. Selection of hidden neurons number was made to obtain the value of MSE (minimum) and R

Table 3: Comparison of the physicochemical properties of J50C50 biodiesel before optimization with diesel

Property	Unit	Diesel[a]	ASTM D6751	EN 14214	J. *curcas*	C. *pentandra*	J50C50
Viscosity	mm^2/s	2.96	1.9–6.0	3.5–5.0	4.577	4.744	4.296
Density	kg/m^3	846.1	880	860–900	876.2	885.7	866.9
Flash point	°C	75.5	100–170 min.	>120	125.5	120.5	120.5
Calorific value	MJ/kg	45.361	−	35	39.461	39.469	40.212
Acid value	mg KOH/g	0.017	0.05 max	0.05 max	0.046	0.051	0.042
Oxidation stability	hour	15.2	3 min	6 min	14.01	1.76	6.23

(maximum). In this study, several parameters such as methanol-to-oil ratio, agitation speed, and the percentage of catalyst is used as an input parameter, while the yield becomes output parameter. The model used to predict and optimize biodiesel production developed independently. In order to test the performance of this model, 17 patterns are used, in which 65% of the pattern (11 patterns) are used for training. It should be noted that 17.5% of the pattern (3 patterns), each of which is used for testing and validation. The number of patterns used in training, testing and validation is similar to a study conducted by Mohammad Fauzi et al, which uses 70% of the data for the training process and the rest is used for testing and validation. They also found that the optimum response to the results and conversion was 83, 4% (Mohammad Fauzi et al., 2014). Comparisons of experimental versus predictions for performance parameters could be seen in Figure 2. ANN prediction was done for biodiesel production yielded a correlation coefficient (R) is 0.9982. A mistake during the learning process or the root-mean square error (RMSE) for performance parameters is 0.2812. Results of analysis using ANN prediction looked to have found a relative error of less than 5 % where the value was still within the margin of error is acceptable. The optimization is done using genetic algorithms also produce optimum conditions for some parameters such as methanol-to-oil molar ratio at 40 % v / v, agitation speed is 1794 rpm and the catalyst concentration was 0.68 wt %. The results showed that the yield of biodiesel derived reached 93.70 %.

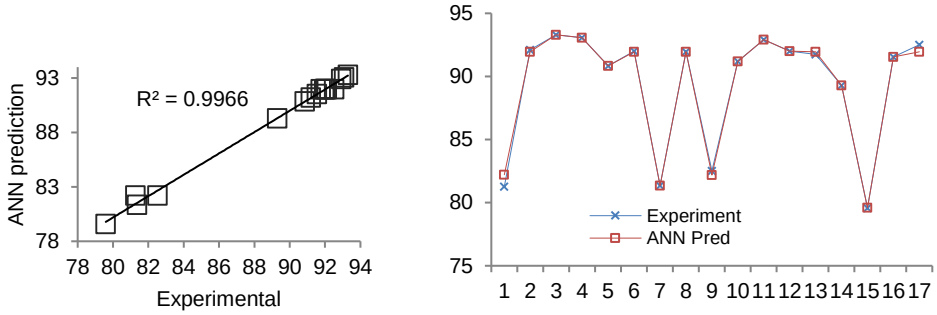

Figure 2: Comparison of ANN predicted with measured data for engine analysis

3.4 Kinetic modeling analysis

Study kinetic for some variations in temperature and time on the transesterification process J50C50 oil at the optimum condition is generated by using ANN namely methanol-to-oil molar ratio at 40 % v/v, agitation speed is 1794 rpm and the catalyst concentration was 0.68 wt % can be seen in Figure 3. The increase in the rate of reaction seen directly proportional to the rise in temperature of 323-333 ^{o}K and increase the processing time of 60 – 120 min. Seen that the biodiesel yield reached a fairly high percentage at a temperature of 333 K and 120 min reached 93.56 %. Tendency of increase in biodiesel yield produced basically obey the Arrhenius law.

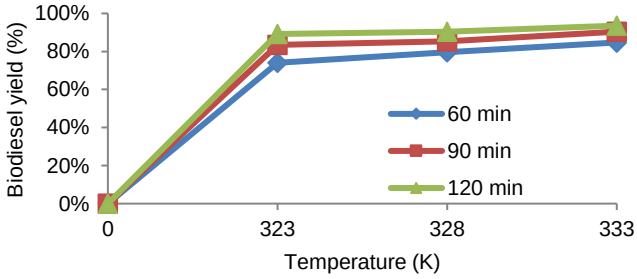

Figure 3: Various reaction temperatures versus time in optimum condition

3.5 Fuel properties of optimized J50C50 biodiesel

Based on the results shown in Table 4 it is evident that there is a marked improvement in the physicochemical properties of the J50C50 biodiesel after optimization and fulfils the specifications given in the ASTM D6751 and EN 14214 standards for biodiesel.

Table 4: Physicochemical properties of the J50C50 biodiesel after optimization

Property	Unit	J50C50 biodiesel
Kinematic viscosity at 40°C	mm^2/s	3.985
Density at 15°C	kg/m^3	830.2
Flash point	°C	198
Pour point	°C	0.5
Cloud point	°C	0.5
Cold filter plugging point	°C	-2.0
Calorific value	MJ/kg	40.937
Acid value	mg KOH/g	0.028
Oxidation stability at 110°C	h	10.24
FAME content	%m/m	99.1
Cetane index	–	58

4. Conclusion

This study investigated the effect of process parameters biodiesel production from J. *curcas*–C. *pentandra* oil mixture to obtain optimum biodiesel yield. Artificial neural networks and genetic algorithms based Box Behnken experimental design used to optimize the operating parameters of the transesterification process are methanol-to-oil molar ratio, agitation speed and catalyst concentration. Based on the results, the optimum operating parameters for the transesterification of J50C50 oil mixture are as follows: the ratio of the methanol-to-oil: 40 % v/v, agitation speed: 1,794 rpm and catalyst concentration: 0.68 wt %. This process is carried out at constant temperature and 60 °C and 2 h. The theoretical results predicted below the highest yield for biodiesel J50C50 with a value of 93.70 %. The kinetic study performed to validate the model by applying the optimum values for triplicates independent experiments with 93.56 %. Comparison between the predicted values to the actual value with a small error percentage indicates that the regression model is reliable in predicting conversion to any conditions provided in the range studied. In addition, the activation energy produced was 24.421 kJ mol^{-1} and the frequency factor is 188 min^{-1} required for the transesterification process. The physicochemical properties of the optimized J50C50 biodiesel fulfil the requirements given in the ASTM D6751 and EN 14214 standards.

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