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Optimization on Pretreatment of Rubber Seed Oil Using Microwave-assisted Technique

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Recently, Rubber Seed Oil (RSO) has been considered as a promising potential oil source for biodiesel production. However, like other non-edible feedstocks, RSO contains a significant amount of high free fatty acids which affect the process of biodiesel production. In the present work, microwave-assisted esterification process was conducted as a pre-treatment step to reduce the high free fatty acid (FFA) content of RSO from 40.14% to less than 1%. Response surface methodology (RSM) involving central composite design (CCD) was employed in the design of experiments (DOE) and the optimization of esterification reaction. The optimum conditions were found at 60 °C, with methanol to oil molar ratio of 19.94:1, H₂SO₄ catalyst of 7.93 wt% and reaction time of 23 min. The result shows that methanol to oil molar ratio was the most influencing parameter towards the FFA reduction followed by temperature, whereas the catalyst loading and the reaction time both were observed to be insignificantly effective.

Key Words

Biodiesel, Rubber Seed Oil, Microwave technique

1. Introduction

Currently, there are different types of feedstock for biodiesel production including edible oils, non-edible oils, animal fats, and algae. Many issues such as food versus fuel controversy and environmental concerns have been raised in recent years over the use of edible oils¹⁾. Moreover, the price of biodiesel is far higher than fossil fuel due to the relatively high cost of edible oil feedstock. Hence, non-edible oils have been considered as a sustainable alternative resource for biodiesel production.

As a non-edible oil, Rubber Seed Oil (RSO) has been successfully used to produce biodiesel by many researchers^{2) ~ 4)}. Normally RSO has high free fatty acid (FFA) content. Thus, acid esterification process is required as a pre-treatment step to reduce FFA value to less than 1%. In order to increase the reaction rate of the process, intensification techniques like microwave, ultrasound or supercritical fluids have been developed and employed in biodiesel production. Recent studies have shown that microwave technique has significantly reduced the reaction

time and obtained higher yields in the production of biodiesel. As an electromagnetic irradiation (frequencies between 0.3 and 300 GHz), it is considered as an energy source which provides the energy directly to the material⁵⁾. In theory, microwave energy is transferred into materials by dipolar polarization, ionic conduction, and interfacial polarization mechanisms, causing localized and rapid superheating of the reaction materials⁶⁾. The whole volume of reactants which is exposed to microwave irradiation would be heated rapidly and evenly whereas in conventional heating the heating process is much slower and a large portion of energy is lost to the ambient. Therefore, microwave irradiation is a promising method, providing a quick and energy-efficient process for biodiesel production.

Suppalakpanya, K. *et al.*⁷⁾ used a commercial microwave oven to produce biodiesel by a two-step reaction. In the esterification step, the FFA value was decreased from 7.5 wt% to less than 2 wt%. The optimum conditions were found at a molar ratio of FFA to ethanol of 1:24 with 4% wt./wt. of H₂SO₄/FFA, a microwave power of 70 W and a reaction time of 60 min, whereas it took 240 min with conventional heating at 70 °C to obtain the same result. Kim, D. *et al.*⁸⁾ studied the energy efficiency of microwave-accelerated esterification with a heterogeneous

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catalyst. More than 90% conversion of the esterification was achieved at 60 °C, 20:1 molar ratio of methanol to oil and 5 wt% sulfated zirconia as the catalyst with 20 min of microwave heating, while a reaction time of 130 min was needed to obtain the similar conversion by conventional heating. In addition, the electric energy consumed by microwave heating was only 67% of estimated minimum heat energy demand due to the significant reduction in reaction time.

To the best of the author's knowledge, microwave technique applying in the acid esterification process for pre-treatment of RSO has not been reported in the previous literature. The aim of this research is to study the optimization of esterification process by using response surface methodology (RSM). The relationship between four parameters including methanol to oil molar ratio, catalyst concentration, temperature and reaction time, was also investigated.

2. Experimental

2.1 Materials

RSO was supplied by Kinetics Chemicals (M) Sdn. Bhd. Malaysia. All the other chemicals and reagents such as sulfuric acid (98%), methanol (99.8%) and potassium hydroxide pellet were purchased from Merck Chemicals.

2.2 Acid esterification setup and procedure

Fig. 1 shows the Microwave synthesis reactor (CEM MARS 6, USA), working at a frequency of 2.45 GHz with two magnetrons (1800 W).

All batch microwave experiments were conducted in a 500 ml three-necked round bottomed-flask equipped with a reflux condenser for preventing methanol loss. The maximum power set up for this type of glass was 500 W.

Fig. 1 Microwave system setup

The temperature was measured and automatically controlled via a fiber optic temperature probe with its tip immersed into the medium. The line graph illustrating the microwave power output throughout each run was also displayed on the screen. In each run, a 30 g of oil was weighed into the flask. A specific amount of methanol and sulfuric acid was added and the mixture was allowed to be stirred thoroughly for 2 min before irradiation. The esterification process under microwave irradiation then occurred for a specific time depending on the experimental plan. During the reaction, the mixture was agitated by a magnetic stirring bar at 900 rpm.

After the completion of the reaction, the sample was collected into a separating funnel and allowed to stand for 6 h for phase separation. The lower layer which contained the esterified oil was washed with warm de-ionized water to remove impurities. Following that, a rotary evaporator was used to eliminate the remaining methanol and water. The sample was then dried over anhydrous Na_2SO_4 and filtered by using filter paper. Ultimately, FFA concentration of the product was determined according to AOCS-Cd 3d-63 method⁹. This method is based on the titration of FFA with potassium hydroxide solution in the presence of phenolphthalein indicator. The acid value of the oil was calculated using the Eq. (1)

$$\text{Acid value} = \frac{(A - B) \times M \times 56.1}{m}, \text{ mg KOH/g oil} \quad (1)$$

Where, A is the volume of titrant solution used in the titration of the sample, mL. B is the volume of titrant solution used in the titration of the blank, mL. M is the molarity of the titrant solution, mol/L. m is the mass of the sample, g.

The FFA content is defined as the amount of fatty acids (in weight percent) in an oil. It is determined using the Eq. (2)¹⁰

$$\text{FFA} = \frac{\text{Acid value}}{1.99}, \% \quad (2)$$

In this study, the initial FFA value of RSO feedstock was found to be 40.14%. In order to avoid saponification, acid esterification process was applied to reduce FFA content of RSO from 40.14% to less than 1%. Four different parameters including methanol to oil molar ratio, catalyst concentration, temperature and reaction time were investigated for their effects on the process by using RSM. The reaction parameters and their ranges are shown in Table 1. Design Expert software 7.0 was utilized to create the experiment plan based on central composite design (CCD). Center points were designated as 0, the low and high factors were coded as -1 and +1 respectively while the axial factors were coded as -2 and +2.

Table 1 Parameters of acid esterification

Process parameters	-2	-1	0	+1	+2
Methanol to oil(mol:mol)	6.59	10	15	20	23.41
Catalyst amount (wt.%H ₂ SO ₄ /RSO)	4.95	7	10	13	15.05
Temperature (°C)	45	49	55	61	65
Time (min)	11.6	15	20	25	28.4

3. Results and Discussion

Table 2 shows the design of experiment (DOE) created by Design Expert software 7.0 as well as the experiment results. Each run was performed twice and the results were averaged. In all cases, the two results agreed within 5% error.

In this study, RSM was employed to determine the optimum operating conditions that resulted in the minimum FFA value of the esterified oil. Necessary calculations were performed by Design Expert software 7.0 for building a regression model to predict the FFA value and searching for optimum conditions. As a result, the second-order polynomial model selected for the response of FFA

concentration in terms of coded factors is attained in Eq. (3)

$$\begin{aligned} \text{FFA}(\%) = & 1.98 - 2.34A - 0.17B - 0.60C - 0.43D + 0.14AB \\ & + 0.46AC + 0.33AD + 0.26BC - 0.82BD + 0.28CD \\ & + 0.90A^2 + 0.089B^2 - 0.098C^2 - 0.050D^2 \end{aligned} \quad (3)$$

Statistical analysis of variance (ANOVA) was used to evaluate the adequacy of the fitted model and the significance of the individual variables that affect the model. The ANOVA of the derived model is presented in Table 3. In the ANOVA, the statistical significance of the regression model was assessed by the p value. The obtained p value was 0.0018 (much less than 0.05), implying a good significance for the regression model. The R-squared, also known as the coefficient of determination, is a statistical measure of how close the data are to the fitted regression line. The high R-squared of 0.9710 indicates that the quadratic model was well fitted to the actual data.

The optimization procedure was performed and the optimum conditions were identified at 60 °C, 19.94:1 molar ratio of methanol to oil, 7.93 wt% H₂SO₄ catalyst for 23 min of reaction time. At these conditions, the FFA content obtained from the model was 0.67%. Three tests were carried out at the optimum conditions to validate the selected conditions and the actual FFA value was found to be $0.79 \pm 0.02\%$. It can be concluded that the experiment results were in good agreement with the predicted values.

The influences of parameters are compared in the perturbation plot (Fig. 2). The steepest curve shows the most influencing variable corresponding to the investigated regions. The plot indicates that methanol to oil molar ratio is the most influencing variable, followed by temperature whereas catalyst concentration and reaction time were found to have the least influence. In terms of the reaction time, although a significantly faster reaction was attained by the aid of microwave, there was only a marginal increase in the FFA conversion when the reaction time was increased.

Table 2 Design of experiments and experiment results

Run	A Methanol:oil mol:mol	B Catalyst wt. %	C Temp °C	D Time min	Response FFA wt. %
1	20	13	49	15	1.32
2	15	10	55	20	1.67
3	20	7	61	25	0.81
4	10	13	61	25	2.45
5	10	7	49	15	6.80
6	20	13	61	15	0.90
7	15	10	55	20	1.64
8	6.59	10	55	20	8.82
9	15	10	55	28.41	1.48
10	15	10	65.09	20	1.15
11	15	10	55	20	1.68
12	15	4.95	55	20	2.89
13	15	10	55	11.59	2.93
14	15	10	55	20	1.63
15	10	13	49	25	3.58
16	15	10	44.91	20	2.99
17	15	10	55	20	2.45
18	20	7	49	25	1.14
19	23.41	10	55	20	0.95
20	15	15.05	55	20	2.31
21	10	7	61	15	3.53

Table 3 Statistical analysis of variance (ANOVA)

Source of variation	Sum of squares	Degree of freedom	Mean squares	F value	P value
Model	75.78	14	5.41	14.35	0.0018
Residual	2.26	6	0.38		
Total	78.04	20			
R-squared =0.9710		Adj R-squared =0.9033		Adeq Precision=15.163

Fig. 2 Perturbation plot

Table 4 describes the comparison in optimum conditions for RSO between microwave and conventional methods. According to the table, the FFA conversion of 98% was achieved in 23 min with the assistance of microwave while it took 60 and 90 min to reach 98.6% and 98% respectively of FFA conversion in the conventional method^{2) 4)}. At optimum condition, although a higher amount of methanol was required since it was the most important factor, the catalyst concentration was reduced comparing to conventional method. Besides, it was observed that the complete product separation in conventional method normally required 12 h⁴⁾ which was around 6 h in the current study. This may be attributed to that methanol did not only act as a polar solvent, which easily absorbs microwave energy but also involved in attaining a faster separation process. Furthermore, total energy consumption for the esterification would be 0.192 kWh with the maximum power consumed for microwave heating was 500 W. Due to significant shorter reaction time and

less energy loss to the environment, the overall energy used by microwave method would much lower than the conventional method. The study reveals that the application of microwave technique offers a fast, simple and energy efficient route to the esterification process of RSO with the advantages of enhancing the reaction rate and of improving the separation process.

4. Conclusion

The acid esterification process using microwave technique has successfully reduced the high FFA content of Rubber Seed Oil from 40.14% to $0.79 \pm 0.02\%$. The optimum condition was found at a temperature of 60 °C, methanol to oil molar ratio of 19.94:1, H₂SO₄ catalyst of 7.93 wt% with a reaction time of 23 min. Four varying factors were investigated in the optimization study using Response Surface Method. According to the result, methanol to oil molar ratio was the most influencing variable in FFA reduction while catalyst concentration was the least effective factor.

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References

- Atabani, A. E.; Silitonga, A. S.; Ong, H. C.; Mahlia, T. M. I.; Masjuki, H. H.; Irfan Anjum Badruddin; Fayaz, H., *Renew Sustain Energy Rev*, **18**, 211-245 (2013)
- Chuah, L.F.; Bokhari, A.; Yusup, S.; Klemeš, J. J.; Abdullah, B.; Akbar, M. M., *Arab J SciEng*, **41**, 2515 (2016)

Table 4 Comparison of process variables with previous studies for esterification process of RSO

Parameters	Microwave	Conventional method	
	This work	Chuah, L.F. <i>et al.</i> ²⁾	Junaid, A. <i>et al.</i> ⁴⁾
Methanol:oil (mol:mol)	19.94:1	10:1	15:1
H ₂ SO ₄ catalyst (wt.%)	7.93	10.74	10
Temperature (°C)	60	65	45
Time (min)	23	60	90
FFA conversion (%)	98	98.6	98

- 3) Bokhari, A.; Chuah, L. F.; Yusup, S.; Klemes, J. J.; Kamil, R. N. M., *Bioresource Technology*, **199**, 414-422 (2016)
 - 4) Junaid, A.; Yusup, S.; Bokhari, A.; Kamil, R. N. M., *Energ Convers Manage*, **78**, 266-275 (2014)
 - 5) Motasemi, F.; Ani, F. N., *Renew Sustain Energy Rev*, **16**, 4719-4733 (2012)
 - 6) Gude, G. V.; Patil, P.; Martinez-Guerra, E.; Deng, S.; Nirmalakhandan, N., *Sustain Chem Process*, **1**, 5 (2013)
 - 7) Suppalakpanya, K.; Ratanawilai, S. B.; Tongurai, C., *Fuel*, **89**, 2140-2144 (2010)
 - 8) Kim, D.; Choi, J.; Kim, G.-K.; Seol, S. K.; Ha, Y.-C.; Vijayan, M.; Jung, S.; Kim, B. H.; Lee, G. D.; Park, S. S., *Bioresource Technology*, **102**, 3639-3641 (2011)
 - 9) Firestone, D., Ed., AOCs Official Method Cd 3d-63: Acid Value, 2015
 - 10) Chuah, L. F.; Bokhari, A.; Yusup, S.; Klemes, J. J.; Abdullah, B.; Akbar, M. M., *Arab J SciEng*, **41**(7), 2515-2526 (2014)
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