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Research paper



Potential Feedstock of Rubber Seed Oil for Biodiesel Production

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Abstract

Biodiesel can help to reduce the world's dependence on fossil fuels and which also has significant environmental benefits. Biodiesel is a mixture of fatty acid methyl esters (FAME) obtained via transesterification of vegetable oils or animal fats with an alcohol. The rubber seed oil (RSO) is chosen as a potential non-edible vegetable oil for the production of biodiesel. The oil was extracted from the seed by using pressurized liquid extraction (ASE). The percentage rubber seed oil extracted from 2.6 kilograms rubber seed was obtained 35%. The acid value of RSO has reduced from 52.3 mg KOH/g to 0.8 mg KOH/g while FFA% value has reduced from 35% to 1.18% after acid esterification was applied to RSO. The oil was proceed with base transesterification where the triglycerides from the oil were converted into FAME. The optimization of transesterification process was performed in order to determine the optimum conditions that give the highest FAME yield. Result shows that optimum conditions of the transesterification of rubber seed oil were 1:6 of oil to methanol mass ratio ,30 wt% KOH catalyst, 60 ^{o}C reaction temperature and 60 minutes reaction time, that offering the highest biodiesel yield of 96%.

Keywords: *Rubber Seed Oils, Transesterification, Accelerated Solvent Extraction, Optimisation, Biodiesel*

1. Introduction

Biodiesel is defined by the American Standard Testing Material (ASTM) as a liquid fuel that composed of the fatty acid alkyl ester of the long chain fatty acid derived from vegetable oil and animal fat. The current motivation towards the production of biodiesel is the conservation of fossil fuels as well as concerns over environmental problems. Considerable attention and effort has been given in producing alternative renewable energy like biodiesel which is also known as fatty acid methyl ester (FAME) [1]. FAME is an alternative biofuel produced through the esterification of Free Fatty Acids (FFAs) with methanol and transesterification of triglycerides [2]. Besides that, biodiesel possesses all the favorable characteristics of diesel and is renewable, biodegradable, non toxic and 'carbon neutral' since no net amount of carbon is released to the atmosphere.

Generally there are four major types of feedstock available for the biodiesel production including oil seed (vegetable oil), animal fats, algae and different low quality material such as waste cooking oil, greases and soap stock [3]. Most of the raw material has been derived from edible or non-edible oil of vegetable resources including rubber seed, rapeseed, soybean, palm oil, Jatropha curcas L., sunflower, algae and waste oil cooking [4]. Edible oil has been used for feedstock, and if used it to produce biodiesel it can create unsteadiness of the food supply. That is why it can be replaced by using non-edible and economical feed stocks such as rubber seed. Rubber seed can be considered as the appropriate feedstock for sustainable biodiesel production due to it is a non-edible sources, unused for anything else and rubber seed biodiesel has an economical value and proficient for biodiesel production. The oil content in rubber seed is between 40% and 50% [5,6-8]. Besides, Malaysia in one of the major rubber producing country in the world, according to Association of Natural Rubber Producing countries with an estimated rubber seed production in Malaysia to be 1.2 million metric tons. A common method used to extract the oil from the rubber seeds is solvent extraction. Accelerated solvent extraction (ASE) is an automated extraction technique that uses elevated temperature and pressure to expedite the removal of oil from the seeds [9] Once the oil is extracted, the weight percent of oil in the seeds can be determined, and the composition of the oils can be studied.

This paper is aimed to produce biodiesel from rubber seed oil via transesterification process. Rubber seed oil will be extracted using ASE technique as mentioned in previous study[10]. In addition, this paper also aimed to reduce the FFA% value in the rubber seed oil (RSO) to 1 % using acid-catalyst esterification method before proceed to production of biodiesel. On top of that, optimization on parameter reaction such as methanol mass ratio(w/v), catalyst loading (wt.%), reaction time and temperature will be carried out.

2. Experimental

2.1 Extraction of Rubber Seed Oil

Dried sample of rubber seed was ground into a particle size in the range of 2 – 5 mm. A cellulose filter was placed at the bottom of the extraction cell (100 ml cell). 15 g of rubber seed was added in the cell. The samples consisting of 15 g milled seeds were mixed with diatomaceous earth (1:4) in a 100 ml Dionex stainless-steel cell. The diatomaceous earth was put on top of the sample in order to remove moisture, disperse the sample matrix and neutralize mineral acids. The head space of the cell was left around 1/5 of the

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cell length and next the extraction cell was assembled. The extraction cell was then placed into the ASE system. Next, the method conditions as shown in Table 1.0 were set on the ASE system.

Table 1.0: ASE conditions

Accelerated Solvent extraction set up	
Temperature	100 ^{o}C
Time	10 min
Static Time	15 min
Flush volume	60%
Purge Time	60 s
Solvent	n-Hexane
Static Cycle	1

After the extraction process completed, the extracts were transferred to a round bottom flask and undergo evaporation process using rotary evaporator in order to remove solvent. The extracted rubber seed oil was weighed and the percentage of oil content was calculated using the following equation:

$$\%\ \boldsymbol{Oil\ Content} = \frac{\boldsymbol{Weight\ of\ extracted\ oil\ (g)}}{\boldsymbol{Weight\ of\ sample\ (g)}} \times \mathbf{100}\%$$

2.2 Acid Esterification Process

Acid esterification is a chemical reaction in which triglycerides (rubber seed oil) react with lower alcohol such as methanol in the presence of an acid catalyst and reduced the high amount of free fatty acids [11]. Esterification was performed at atmospheric pressure in a 500 ml three-necked round bottom flask equipped with a reflux condenser and a magnetic stirrer. The flask was heated with hot plate and a thermometer was inserted to measure the reaction temperature. 60 ml of RSO was poured in the flask and heated to about 50 oC.The preheated oil was added with 300 ml methanol (6: 1 of methanol: oil molar ratio) and 0.3 g (0.5 wt/v%) 1 M sulphuric acid for a few minutes. At atmospheric pressure, the mixture was heated and stirred continuously for 30 minutes. The product was poured into a separating funnel for separating the excess alcohol and lower layer was separated for next process.

2.3 Acid Value Determination

A standard solution of 0.01 N KOH was used as titrant. Firstly, 50 ml 2-propanol and 50 ml toluene were placed in a 250 ml Erlenmeyer flask. Both solutions were used as a solvent to dissolve the oil. 1 gram of rubber seed oil was added into the mixture solution (toluene + 2-propanol) then 3 drops phenolphthalein indicator was added. Titration was done using 0.01 N KOH in a 100 ml burette and the mixture solution, drop by drop until the colour of solution turns into pink. The volume of KOH solution needed for the colour changes was recorded then used to calculate acid and FFA value by using formulas below:

Acid value = $= \frac{\boldsymbol{V \times N \times Mw}}{\boldsymbol{W}}$, where

V – Volume of KOH (ml) used in titrating the sample for the colour changes.
N – Normality of the KOH solution
Mw – Molecular weight of KOH (56.1 g/mol)
W – Weight of the oil sample (g)
After the resultant oil FFA value was reduced to less than 1%, next step transesterification process to produce biodiesel was proceed.

2.4 Base Transesterification Process

About 50 g of RSO was added in a three neck round bottom flask connected to a reflux condenser and heated using hot plate. Then, 100 ml methanol (2:1 of methanol: oil molar ratio) and 15 g (30 wt.%) 0.1 M KOH catalysts were mixed into the mixture. Next, the mixture was heated at 60 ^{o}C and at atmospheric pressure for 60 minutes at 1000 rpm stirring. In order to optimize the transesterification process in production of biodiesel from RSO, the process had determined the effect of oil: methanol mass ratio, reaction tempeature, reaction time and the catalysts loading. The manipulated variable conditions were specified as shown in Table 1.

Table 1: Process parameter for base transesterification

Parameter	Variable Conditions			
Oil to methanol mass ratio (w/v)	1 : 2	1 : 4	1 : 6	1 : 8
Catalyst loading (wt.%)	1 : 10	1 : 20	1 : 30	1 : 40
Temperature (^{o}C)	40	50	60	70
Reaction time (min)	30	60	90	120

Further analysis continued with identification of biodiesel produced using GC-FID. Finally, the FAME yield (%) of the biodiesel products was calculated by using equation below [12]:

$$\boldsymbol{FAME\ yields}\ (\%) = \frac{\boldsymbol{weight\ of\ biodiesel\ produced}}{\boldsymbol{weight\ of\ oil}} \times \mathbf{100}\%$$

2.5 GC-FID Analysis

Qualitative analysis of the FAME was performed by Agilent Technologies Gas Chromatography equipped with Flame Ionization Detector (GC-FID) and 30m x 250µm x 0.25µm HP5-MS capillary column. A sample preparation was applied to the FAME product before it could injected into the column of GC-FID for analysis.The GC-FID analysiscontinued with standard mixture of FAME using same GC set up repoted in [13].

3. Results and Discussion

3.1 Extraction Of Oil From Rubber Seed

Accelerated Solvent Extraction (ASE) was used to extract the oil from rubber seed. Hexane act as solvent was pumped into an extraction cell containing the sample, which was then brought to an elevated temperature and pressure. Then, the extract was transferred from the heated cell to a bottle inside the chamber. The oil from rubber seed was extracted using ASE used three different method conditions as shown in Table 3 in order to determine the best conditions to provide highest yield of oil. About 90 grams of rubber seed was used for oil extraction in each method conditions. The total oil content (wt.%) was calculated from weight of extracted oil divided by weight of rubber seed and the results were tabulated in Table 3.

Table 3: The % yield of oil for three different ASE conditions

	Method 1	Method 2	Method 3
Static time	10 min	15 min	20 min
Extracted oil	21.98 g	32.45 g	31.33 g
Oil yield (w/wt.%)	24 %	36 %	34.8 %

It was found that static time was significantly effects on the yield of extracted oil. Static time is extraction time of sample inside the cell, where the sample was soaked with solvent under high temperature and pressure. As shown in Table 3, the static time was varied from 10 min, 15 min and 20 min and the percentage of oil obtained was 24%, 36% and 34.8% respectively. Method 2 with static time of 15 minutes was the best conditions for rubber seed oil extraction because it produced the highest yield of oil (36 w/wt.%). However, method 3 operated with longer static time which was 20 minutes did not improve the yield of oil because only 34.8% of yield was obtained. Therefore, 15 minutes of static time was the best ASE condition to produce high percentage of rubber seed oil (RSO) yield. The best condition was then used for further extraction process. After extraction process completed,

hexane that used as solvent was removed from the oil using rotary evaporator until concentrated RSO was obtained.

3.2 Acid esterification process

Esterification process was considered as the pre-treatment to reduce the acid value and FFA value in the RSO sample. Separation of two immiscible layers which were ester and water occurred due to difference density. Since the ester product was located at the bottom, it had higher density than the water. The esterification reaction was reversible reaction. The esterification was successfully done when two layers were formed. The pre-treatment of RSO with acid catalyzed esterification was successfully reduced the acid value of RSO from 52.3 to 0.8 (mg KOH/g). Therefore, the transesterification process can be performed since the acid value of RSO was reduced less than 1 mg KOH/g.

3.3 Optimization Of Transesterification Process For Biodiesel Production.

3.3.1 Effect of oil to methanol mass ratio (w/v) on yield of biodiesel.

As shown in Figure 2, it was found that the biodiesel yield significantly increased from 87.6% to 95% with increase in molar ratio from 1:2 to 1:6. But, further increase in molar ratio to 1:8, the yield of biodiesel was drop to 90%. The result shows the maximum yield of biodiesel was achieved at the mass ratio of 1:6 with 95% yield. Meanwhile, further increase in mass ratio, it found there was no any improvement in the conversion efficiency, instead a decrease of biodiesel yield was observed. The yield of biodiesel reduced because of the excess of methanol that could interfere with the separation of ester product and by-products by increasing the solubility of glycerol. Besides, the excess of methanol could drive the equilibrium of ester product and glycerol into by-product.

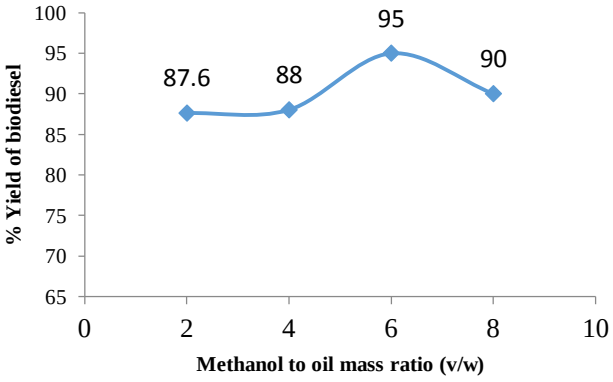

Figure 1: Effect of methanol: oil (v/w) mass ratio

In addition, according to [14], at higher molar ratios alcohol may hinder the glycerol separation and bring difficulties in heating the reaction mixture. On the other hand, [14] stated that high methanol to oil ratio had a significant effect on the yield of biodiesel. Previous study claimed that with increasing molar ratio of methanol to oil, OH group present in the alcohol reacts with triglycerides and lead to hydrolysis reaction. This phenomena resulting decreased the biodiesel yield due to form formation. The interaction between temperature with methanol to oil ratio changes the biodiesel yield greatly.

Thus, higher amount of alcohol was required to give the best conversion of biodiesel from RSO. However, when the amount of alcohol was too high, it gave adverse effect on the yield of biodiesel. Therefore, when the transesterification of RSO with parameters constant at 60 oC of reaction temperature, 60 minutes reaction time, and 30 wt.% catalyst loading; 1:6 of oil to methanol molar ratio was the optimum ratio that offering the highest biodiesel yield with 95% yield. This result was supported with the study by [2,4] whereby both studies found that the maximum yield of biodiesel from RSO was achieved at the mass ratio of 1:6 with 96% yield. They stated that the molar ratio of 6:1 of methanol to oil gave the best conversion.

3.3.2 Effect of catalyst loading (wt.%) on yield of biodiesel

Figure 3 shows the effect of catalyst loading on yield of biodiesel. It was found that catalyst loading 30 wt.% was the optimum due to high percentage of biodiesel yield (96.1%). The results show the yield of biodiesel increases when the amount of catalyst increases from 10 to 30 wt.%, but slightly decreased when the amount of catalyst exceeded to 40 wt.%.The maximum yield of biodiesel obtained was 96.1% at 30 wt.% catalyst loading, which increased from initial yield of 86.9% and 92.3% at catalyst loading of 10 and 20 wt.% respectively. However, further increase in catalyst loading to 40 wt.% was decreased the yield of biodiesel to 93.8%.

Previous study found that the maximum yield of biodiesel from rubber seed oil was 82.68% at 3.5 wt.% of 1 M KOH catalyst loading and with increasing the catalyst amount, the product yield was declined [13]. They reported that the decrease in biodiesel yield with increase in catalyst loading (above 3.5 wt.%) can be attributed to soap formation during the reaction which in turn ultimately affects the yield adversely. The resulting soaps do not only lower the conversion of ester, but also cause other problems associated with phase separation.

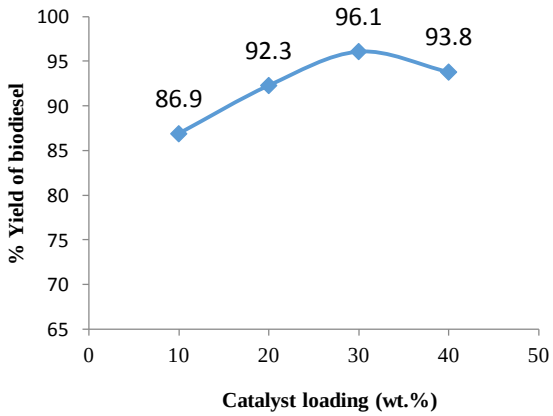

Figure 2: Effect of catalyst loading

In this study, the amount of catalyst required to give the best conversion of biodiesel from RSO was 30 wt.% of 0.1 M KOH. However, when the amount exceed 30 wt.%, it gave adverse effect on the yield of biodiesel. Therefore, when the transesterification of RSO with parameters constant at 60 oC of reaction temperature, 60 minutes reaction time, and 1:6 of oil to methanol mass ratio; 30 wt.% catalyst loading was the optimum that offering the highest biodiesel yield with 96.1% yield.

3.3.3 Effect of reaction time on yield of biodiesel

The optimum reaction time during transesterification process for the biodiesel production was determined by performing reactions up to 2 hours. In order to identify the perfect reaction time for RSO to achieve the highest yield of biodiesel, four various time reaction were studied which were 30, 60, 90 and 120 minutes. Whereas, other parameter conditions were kept constant; 1:6 of oil to methanol mass ratio, 30 wt.% catalyst loading and 60 oC reaction temperature. Figure 4 shows the effect of reaction time on the yield of biodiesel.

It was found that yield of biodiesel was increased drastically from 76.6% to 96% with the increasing of duration of reaction from 30 to 60 minutes respectively. However, the yield of biodiesel was produced consistently when the reaction time increased until 120 minutes. Therefore, 60 minutes was sufficient enough for RSO to complete the conversion into biodiesel during transesterification process. Longer time reaction would not significantly affect the yield of biodiesel. This result was supported by study from [13] that revealed 60 minutes of reaction was sufficient for the completion of the transesterification where they achieved the maximum biodiesel yield which was 90.1%.

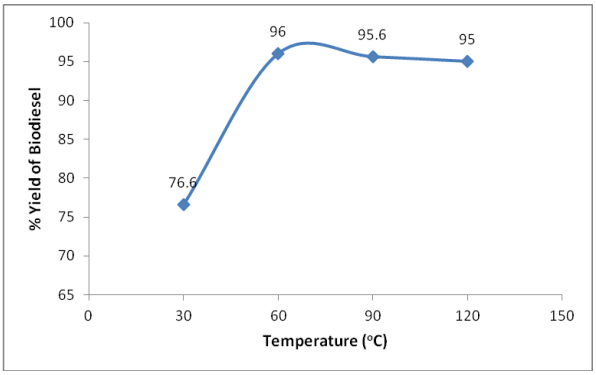

Figure 3: Effect of reaction time

3.3.4 Effect of temperature on yield of biodiesel

The effect of temperature on yield of biodiesel was studied at four temperature which were 40 oC, 50 oC, 60 oC and 70 oC while other parameters condition were kept constant at 1:6 of oil to methanol mass ratio, 30 wt.% of catalyst loading and 60 minutes of reaction time. Figure 5 shows the effect of reaction temperature on the yield of biodiesel.

It was found that the maximum biodiesel yield of 96.8% was observed at the reaction temperature of 60 oC, which increased from the yield of 85.6% and 90.3% at temperature of 40 oC and 50 oC respectively. Higher temperature improves the efficiency of transesterification, which in turn enhances the RSO conversion to biodiesel. The result was similar with previous study where they found the optimum temperature for RSO to produce highest yield of biodiesel (96.9% and 96% respectively) was 60 oC [2,6].

However, increasing the temperature above 60 oC did not improve the biodiesel yield, in fact the yield significantly reduced to 92% when temperature increased to 70 oC. According to [5], this is due to methanol evaporation at temperature higher than 64.7 oC is where the boiling point of methanol and hence oil to methanol cannot be maintained to achieve a desirable reaction then the yield was decreased. Besides, [2] also stated that at higher temperature of 65 oC, there was substantial loss of moisture leading to oil degradation that caused the decreased in the yield.

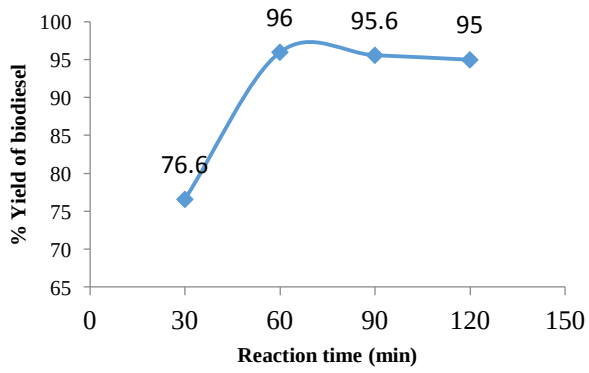

Figure 4: Effect of reaction temperature

4. Conclusions

The percentage yield of rubber seed oil in 2.6 kilograms rubber seed was found 35%. The optimum conditions of the transesterification of rubber seed oil were 1:6 (w/v) of oil to methanol mass ratio, 30 wt.% KOH catalyst, 60 oC reaction temperature and 60 minutes reaction time, that offering the highest biodiesel yield with average 96% yield.

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