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Research paper

Transesterification of *Moringa Oleifera* Seed Oil by Sodium Silicate Catalyst Using Different Co-Solvents

Puvaniswaran K. Moorthi [1]*, Preeti Shrivastava [2], Soundarajan Krishnan [3]

[1]Biocon Sdn. Bhd., Malaysia
[2]School of Science and Engineering, Manipal International University, Malaysia
[3]Department of Chemical Engineering, Manipal International University, Malaysia
**Corresponding author E-mail: puva_10@yahoo.com*

Abstract

Biodiesel is a renewable energy source which is derived as an alternate fuel for diesel engine. It is produced by transesterification process. *Moringa oleifera* seed oil has been extracted using n-hexane by solvent extraction method. The high flashpoint of Moringa oleifera oil is a beneficial safety feature so that it can safely be stored at room temperature. The study examines the production of biodiesel using *Moringa oleifera* seed oil with sodium silicate as catalyst and different co-solvents. The biodiesel produced from *Moringa oleifera* seed oil exhibits high yield using diethyl-ether as co-solvent with 60°C as the reaction temperature and 1 hour as the reaction time. Furthermore, the optimum ratio of methanol to oil is 7:1 and the amount of catalyst required to produce highest yield is 0.30 g. Moreover, the optimum ratio of methanol to co-solvent is 1:1 ratio. It has been found that the saponification value and free fatty acid are 170.2 mg of KOH/ g of oil and 0.33 %, respectively. The moisture content of biodiesel is 0.04% with higher calorific value when compared to diesel and vegetable oil. The pH and cloud point of biodiesel recorded are 7.37 and 18°C, respectively. All these values have been found to be within the range of American Standard for Testing Material for biodiesel. Only the acid value has fallen outside the ASTM limits. Hence, it can be concluded that biodiesel produced from *Moringa oleifera* seed oil has the potential to be an alternate fuel and the energy of the future.

Keywords: *Biodiesel; Co-solvent; Moringa olifera seed oil; Sodium silicate; Transesterification.*

1. Introduction

In the past few decades, efforts have been taken for the production of alternate renewable energy sources due to large consumption as well as depletion of conventional fuel [1]. The need for biodiesel has been growing rapidly because of its non-toxic and biodegradable characteristics [2]. Biodiesel has less harmful emissions of carbon monoxide and oxides of Sulphur, resulting in decreased greenhouse effect. Biodiesel has the potential to play vital role in the energy sector. It is usually obtained by the transesterification of oils or fats using alcohol as solvent. *Moringa oleifera* oil is an attractive means by which biodiesel can be produced. It can be extracted from ground *Moringa oleifera* seeds with n-hexane as solvent using soxhlet apparatus. *Moringa oleifera* oil has high cetane number greater than 60, which is among the highest reported for a biodiesel fuel. The heterogeneous transesterification is the best method to be selected for the production of biodiesel. This is because it produces biodiesel of high purity in a short time. The use of catalyst can increase the rate of reaction which is essential for the process to take place in shorter period. One major challenge of heterogeneous catalyst is that it requires activation at very high temperatures every time, in order to open the active sites. The *Moringa oleifera* oil has high content of oleic acid and cetane number, and it prevents oxidative degradation [3].

2. Materials and Method

2.1. Materials

The main raw material used for biodiesel production in this study is *Moringa oleifera*. It is easily available in the market. The chemicals which have been used in this research study are of AR Grade for methanol, diethyl-ether, acetone, cyclo-hexane, sodium sulfate, sodium hydroxide, ethanolic potassium hydroxide and sodium chloride. Sodium silicate and iso-propanol are of LR Grade. Phenolphthalein is 0.1% alcoholic solution.

2.2. Oil extraction procedure

The seeds were bought at the market according to the quantities needed. The good seeds were selected and the damaged ones discarded. The seeds were cleaned and de-shelled to avoid any contamination. The seeds were dried using microwave at 70°C to 85°C to remove any moisture content and cooled to room temperature [4]. After cooling, the seeds were ground using mortar and pestle, prior to solvent extraction. 30 g of ground seeds were put into a porous thimble and placed in a soxhlet extractor and n-hexane was used as the solvent. The ratio of ground seeds to solvent was kept as 1:25. The solvent extraction was carried out for 6 to 8 hours at 40°C to 60°C [4]. The mixture of oil and solvent were separated by means of water bath at 85°C. The main purpose of heating was to remove excess solvent from the extracted oil at

70^{o}C by refluxing [4]. The crude oil was stored outside in the closed glass jar for the transesterification process.

2.3. Transesterification process

100 g of M*oringa oleifera* oil was mixed with 20 ml of acetone as co-solvent in a 250 mL round-bottomed flask. The sodium silicate was heated at 400^{o}C for two hours to remove moisture and any organic contaminants from the catalyst [5]. Then, sodium silicate was added to the mixture of oil and acetone, and heated while stirring, using a magnetic stirrer. 0.35 g of sodium silicate was added to methanol. The co-solvent to methanol ratio of 1:1 was used. The mixture was stirred at 300 to 400 rpm for about two to four minutes. The molar ratio of oil to methanol used was 1:5 and prepared separately in different flask. The methanol solution was quickly poured into the flask which contained the mixture of oil and co-solvent prepared separately. At first the mixture became cloudy and soon separated into two layers. The temperature was 50^{o}C. After 1 hour, the reaction was stopped and the mixture was poured into a separating funnel. The separation was done one to two hours after the transesterification reaction was initiated. The mixture separated into two different layers. The glycerin being denser than biodiesel settled to the bottom while the biodiesel remained at the top. The stopcock of the separating funnel was opened and the glycerin was allowed to drain into a small beaker. The reaction was carried out using different molar ratio of oil to methanol such as 1:6, 1:7 and 1:8 for different co-solvents namely, diethyl-ether, acetone and cyclo-hexane, and also with blank solution as control.

The biodiesel was purified by dry purification process using sodium sulfate as the absorbent. Then, the upper layer from the separating funnel was washed with saturated NaCl solution and by distilled water to separate glycerol and soap. The unpurified biodiesel was heated and stirred slowly until it reached 65^{o}C. The anhydrous sodium sulfate was added to remove residual water in the methyl ester product. The biodiesel later was filtered to remove the adsorbent and subjected to characterization [6].

3. Results and discussion

3.1. *Moringa oleifera* seed oil characterization

Table 1 shows the physio-chemical properties of *Moringa oleifera* seed oil. The percentage yield of oil was 40% which was the maximum yield reported [7]. The oil which was extracted from *Moringa oleifera* seed had a pleasant odour with cream yellow colour. The saponification value of oil was 180.1 which was in agreement with the FAO/WHO standards [8]. The free fatty acid of freshly extracted *Moringa oleifera* seed oil was below the range of FAO/WHO standards which was 4.5. It was a good indicator because high free fatty acid could cause soap formation during alcoholysis from its by-product. However, the acid value of seed oil was higher than the values stated for edible oil by FAO/WHO standards [8].

Table 1: The Physio-chemical Properties of *Moringa oleifera* Seed Oil Extracted Compared with FAO & WHO Standards

Physio-chemical properties		*Moringa oleifera* seed oil	FAO/WHO standards
Physical properties			
Organoleptic	Yield (%)	40	Organoleptic
	Odour	Agreeable	
	Colour	Cream yellow	
Appearance at room temperature	Transparent liquid		
Chemical properties			
Acid value (mg KOH/g)	4.5		4
Saponification value (mg of KOH/g of oil)	180.1		181.2 ± 2.60
Free fatty acid (%)	4.5		5.78-7.28

3.2. Transesterification of Biodiesel

The percentage yield of biodiesel can be calculated by Equation (1):

$$\%\ yield\ of\ biodiesel = \frac{Volume\ of\ biodiesel\ produced}{Total\ volume\ of\ product\ obtained} \times 100 \qquad (1)$$

The use of co-solvent in transesterification process resulted in higher yield of biodiesel. It also functioned as a reaction medium and binder between triglycerides and alcohol to allow contact between the two polar feedstock and increase the mutual solubility of methanol and *Moringa oleifera* seed oil, and the mixing intensity between them. This resulted in higher reaction yield, less soap formed, shorter time of reaction separation, and washing. The diethyl-ether gave highest % yield of biodiesel when compared to the other three co-solvents studied because it enhanced the miscibility of methanol as co-solvent with *Moringa oleifera* seed oil. Moreover, it also had less glycerin formation which was 8 ml with most biodiesel formed compared to solvent which was used. Data in Table 2 shows the comparison of co-solvents used for transesterification process.

Table 2: Effect of Different Co-solvents and Blank on %Yield of Biodiesel (Catalyst Loading = 0.3 g; Methanol to Oil Ratio = 7:1)

	Blank	Diethyl-ether	Acetone	Cyclo-hexane
Volume of biodiesel produced (ml)	98	120	106	100
Volume of glycerin produced (ml)	12	8	12	13
%yield of biodiesel	78	88	79	77

As it can be observed in Table 3, with a 5:1 molar ratio, the conversion of biodiesel achieved was 77% after 1 hour. The % yield of biodiesel increased as the molar ratio increased, with maximum yield of 85% with a molar ratio 7:1. Nevertheless, further increase in molar ratio to 8:1 did not enhance the yield of biodiesel, since a lower value of 80% was obtained. This was because for higher molar ratios, the separation of glycerol was difficult, as excess ethanol hindered the decantation. The yield of di- to monoglycerides was favorable with excess of alcohol. Since the concentration kept increasing during the concentration, there was possibility of slight recombination of esters and glycerol to monoglycerides [9]. Accordingly, the molar ratio of alcohol to oil was one of the most important variables affecting the biodiesel yield, and although the stoichiometric ratio for transesterification required three moles of alcohol and one mole of triglyceride, an excess of oil was used in practice.

Table 3: Effect of Ratios of Methanol to Oil on %Yield of Biodiesel with Di-ethyl ether as Co-solvent

Ratio of methanol to oil	5:1	6:1	7:1	8:1
Volume of biodiesel produced (ml)	100	105	118	110
Volume of glycerin produced (ml)	13	12	10	12
% yield of Biodiesel	77	79	85	80

Table 4 shows the effect of sodium silicate amount on % yield of biodiesel. The maximum yield was attained with the catalyst loading of 0.30 g. For higher values, the yield was lower. When there was large free fatty acid content, the addition of more sodium silicate or other alkali catalyst decreased the acidity and avoided deactivation. The formation of emulsion increased the viscosity and led to the formation of gels when the addition of catalyst was excessive [9]. The glycerol separation hindered and reduced the actual biodiesel yield. This was because it was necessary to remove it from the reaction at the end to prevent other unwanted reaction taking place.

Table 4: Effect of Catalyst Loadings on % Yield of Biodiesel with Diethyl-ether as Co-solvent and Methanol to Oil Ratio of 7 : 1

Catalyst Loading (g)	0.20	0.25	0.30	0.35
Volume of biodiesel produced (ml)	100	105	118	110
Volume of glycerin produced (ml)	13	12	10	12
% yield of biodiesel	77	79	85	80

The reaction temperature can heavily influence the reaction rate and also the yield of biodiesel because intrinsic rate constant are strongly dependent on temperature. Table 5 shows the effect of reaction temperatures on % yield of biodiesel. The reaction rate was higher at high temperature than a low temperature. However, once the maximum temperature was attained, the reaction was unfavorable and decreased the biodiesel yield. It was found that biodiesel yield decreased as the reaction temperature increased above 60°C. This was because the boiling point of methanol was 65°C. Once the temperature was higher than this, it vaporized the alcohol and resulted in much lesser yield. The interaction between temperature and catalyst concentration led to lesser biodiesel yield. This was because solubility of reactant at higher temperature reduced the separation between methyl ester and glycerol phase leading to decrease in yield of biodiesel.

Table 5: Effect of Reaction Temperatures on % Yield of Biodiesel with Catalyst Loading of 0.30 g, Di-ethyl ether as Co-solvent and Methanol to Oil Ratio of 7 : 1

Temperature (°C)	40	50	60	70
Volume of biodiesel produced (ml)	110	113	119	100
Volume of glycerin produced (ml)	13	13	10	11
% yield of biodiesel	78	79	85	80

When the ratio increased from 1:0.25 to 1:1.25, % biodiesel yield increased until it achieved its optimum level of 1:1, then it started to drop down significantly. This explained that higher amount of solvent than methanol could decrease the reaction rate and yield of biodiesel. This was probably because of the optimum level, the co-solvent acted as a barrier between the reactant methanol and the oil molecules, and resulted in dilution effect on the reagents. The data in Table 6 explained % yield of biodiesel.

Table 6: Effect of Ratios of Methanol to Co-solvent on % Yield of Biodiesel with Catalyst Loading of 0.30 g, Di-ethyl ether as Co-solvent and Methanol to Oil Ratio of 7 : 1 with Temperature of 60°C

Ratio of methanol to co-solvent	1 : 0.25	1 : 0.5	1 : 1	1 : 1.25
Volume of biodiesel produced (ml)	109	111	121	100
Volume of glycerin produced (ml)	14	10	10	12
% yield of biodiesel	77	80	85	78

Co-solvent was used to improve the miscibility of alcohol and oil during trans-esterification chemical reaction. The excessive addition of co-solvent into the reaction system decreased the trans-esterification rate, due to a dilution effect on the reagents [10]. The presence of co-solvent made the system homogeneous. The biodiesel conversion with co-solvent was higher when compared to the one without co-solvent, as evident in Table 7.

Table 7: Effect of Co-solvent on % Yield of Biodiesel

	With co-solvent	Without co-solvent
Volume of biodiesel produced (ml)	122	105
Volume of glycerin produced (ml)	10	12
% yield of biodiesel	85	79

3.3. Biodiesel characterization

The biodiesel produced had 0.33% FFA. The standard value of FFA is stated to be below 0.5% [11]. It has been known that biodiesel with FFA content higher than 0.5% decreased the engine performance since it produced soap. It showed that the oil was less likely to undergo oxidation since the value was below the range given. Furthermore, the value was lower than the standard one and no pre-treatment was required.

The pH value indicated the alkalinity or acidity in biodiesel. The pH value recorded was slightly alkaline. This was because sodium silicate (Na_2SiO_3) leached into the biodiesel. The biodiesel produced using sodium silicate was required to undergo separation process using water washing to separate Na_2SiO_3. This proved that Na_2SiO_3 supported the transesterification of oil into biodiesel which caused biodiesel with alkaline characteristics. The pH value of biodiesel recorded was 7.37 which was slightly more than neutral.

The cloud point is the temperature of the fuel at which small, solid crystals can be observed as the fuel cooled. The pour point referred to the lowest temperature at which there is movement of the fuel when the container is tipped. The cloud point of biodiesel from *Moringa Oleifera* seed oil was recorded as 16°C. The cloud point of biodiesel produced was slightly higher [12]. This was because of high content of saturated ester which possessed higher melting point. It seemed to compensate the cold flow properties of biodiesel determined by the amount of melting component and not their nature.

The purity level of biodiesel had strong effects on its fuel properties. The main problem faced with long-term storage of biodiesel was mainly hydrolytic and oxidative degradation. Hydrolytic degradation consisted of hydrolysis of biodiesel when water was present in the reaction medium. The maximum moisture content of standard biodiesel was said to be 0.05% [13]. The average moisture content of biodiesel was 0.04 % and it does not require treatment.

The saponification value indicated average molecular weight of fatty acid content as glyceride in oil. The high saponification value indicated that oils are normal triglycerides and very useful for the production of liquid soap and shampoo. The presence of high percentage of fatty acids can also indicate high saponification values. This led to soap formation and the separation of products would be exceedingly difficult. This could lead to low yield of biodiesel. The average value of saponification value of biodiesel was 170.2 mg of KOH/g of oil.

The acid value of oil was used as a measure of quality. The acid value of oil must not be too high, as this denoted an excessively high content of Free Fatty Acid (FFA). The presence of free fatty acid influenced fuel aging due to hydrolytic cleavage of ester bond. The European and American Standards specify maximum values of 0.5 and 0.8 mg of KOH/g, respectively. The average acid value was 0.43 mg of KOH/g which is within the range of ASTM.

The best was to measure the chemical energy of fuel by heat of combustion. Heat of combustion is usually denoted as net calorific value and gross calorific value. Net heat value is also known as Lower Heating Value (LHV) and gross heat value as Higher Heating Value (HHV) [13]. As for biodiesel, as the solution was heated up and the temperature was recorded with every 30 seconds of intervals and the theoretical temperature obtained. Therefore, the actual boiling temperature of biodiesel obtained was 80℃. In Figure 1, it indicated that as the time increased, the temperature also gradually increased, as it approached 14 and 15 min, it was an optimum temperature for biodiesel, and then after 16 min, the cooling process began. The calorific value obtained for biodiesel was found to be 45.98 mJ/kg.

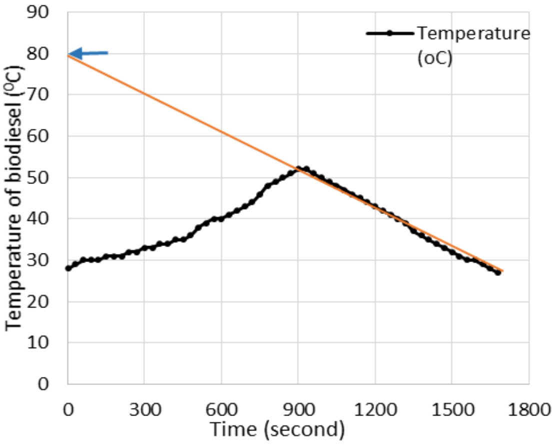

Fig. 1: The actual combustion point of biodiesel from heating and cooling plot

While conducting the experiment for diesel, it was carried out in a fume chamber due to safety precautions. As the diesel was being heated, the time taken was observed. The actual temperature determined for diesel was 70℃ and the calorific value obtained was 35.11 MJ/kg. Figure 2 shows the actual boiling point temperature for the diesel based on the intersection. As diesel is highly viscous, therefore, the optimum temperature was achieved fast. Comparing both, the highest actual temperature obtained was for biodiesel, followed by diesel. It indicated that biodiesel was less viscous and diesel was highly viscous. Biodiesel was determined to have the highest calorific value when compared to diesel. The higher the combustion rate, the higher the calorific value obtained.

The higher heating value is one of the most vital properties of a fuel. The oxygen content of biodiesel improved the combustion process and decreased its oxidation potential. This was because the combustion efficiency of biodiesel was higher than that of diesel. Thus, the higher heating value was an important property to define the energy content and thereby, the efficiency of fuels. Moreover, the results also showed that the longer the carbon chain of biodiesel, the higher its calorific value [14]. Therefore, it could be concluded that biodiesel from *Moringa Oleifera* seed oil had larger amount of long methyl ester chain with the highest calorific value.

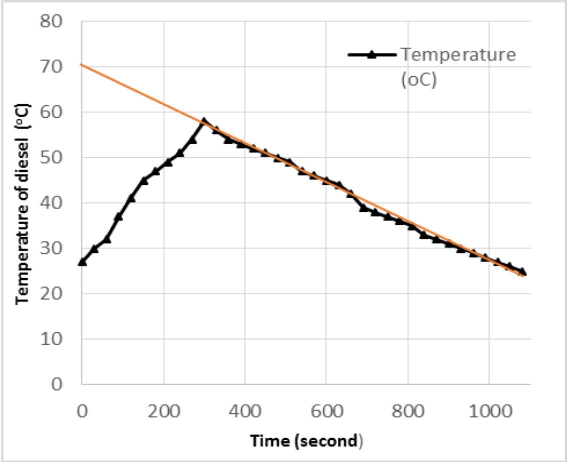

Fig. 2: The actual combustion point of diesel from heating and cooling plot

4. Conclusion

This study basically dealt with the effect of co-solvent activity during the transesterification of *Moringa oleifera* seed oil to produce biodiesel. *Moringa oleifera* seed oil exhibited good physiochemical properties with low free fatty acid and acid value, thereby exhibiting the potential to be used as feedstock for the production of biodiesel. Among the three co-solvents studied, diethylether was found to perform well. The maximum yield of biodiesel was obtained using different parameters under the transesterification process. The parameters such ratio of oil to methanol, temperature, catalyst loading and ratio of methanol to solvent were investigated. The optimum reaction conditions for the transesterification of *Moringa oleifera* seed oil were found to be reaction temperature of 60ºC, molar ratio of methanol to oil of 7:1, 0.30 g of catalyst, molar ratio of solvent to methanol of 1:1 and reaction time of 1 h. These conditions gave the highest yield of biodiesel by volume. The biodiesel had higher calorific value when compared to diesel. The moisture content was within the range and does not require pre-treatment.

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