

Full Length Research Paper

Biodiesel production from waste soybean oil biomass as renewable energy and environmental recycled process

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Alternative fuel is currently an important issue all over the world due to the efforts on reducing global warming which is contributed by the combustion of petroleum or petrol diesel. Biodiesel is non-toxic, biodegradable, produced from renewable sources and contributes a minimal amount of net green house gases, such as CO₂, SO₂ and NO emissions to the atmosphere. The study was carried out to produce biodiesel from waste/recycled oils to reduce the cost of biodiesel, waste and pollution. Some important variables such as volumetric ratio, types of reactants and catalytic activities were selected to obtain a high quality biodiesel fuel within the specifications of the American Standard for Biodiesel Testing Method (ASTM D 6751) and European Norm (EN 14214). The highest biodiesel yield was obtained (71.2%) under the conditions of 1:1 volumetric oil-to-methanol weight ratio, 0.5% NaOH catalyst at 50 °C reaction temperature and 320 rpm stirring speed. The results showed that biodiesel produced from different oil to methanol ratios, alcohol types and shaking time exhibited considerable differences. There was also a considerable difference of biodiesel yield produced by using methanol, ethanol and 1-butanol. The biodiesel yield increased in the order of 1-butanol < ethanol < methanol. There was a little difference in viscosity, acid value and chemical elements (Fe, Mg, Ca, Na, P etc.) at different parameters. The research showed that biodiesel obtained under optimum conditions from completely waste oil was of good quality and could be used as a diesel fuel which is considered as potential use of waste cooking oil. In addition, bioenergy could be renewed and environmental recycling process could be maintained potentially using waste soybean cooking oil.

Key words: Waste soybean oil, biodiesel, viscosity, acid value, element content.

INTRODUCTION

Biodiesel has recently attracted much attention all over the world because of its availability, renewability, non-toxicity, better gas emissions and its biodegradability. Biodiesel is typically produced by a reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-alkyl esters and glycerin, which is eventually removed. Biodiesel

consists of long-chain fatty acid esters (Haas et al., 2001; Abreu et al., 2004) produced by transesterification reaction of vegetable oils with short chain alcohols (Noureddini et al., 1998; Encinar et al., 2002, Harten, 2003). It is compatible with conventional diesel fuel and already used as a commercial fuel in Europe (Knothe et al., 2003; Dorado et al., 2003; Serdari et al., 1999). However, some chemical and physical properties of biodiesel can be affected by oxidation of the fuel during storage (Monyem et al., 2001). One drawback of biodiesel is that it is more prone to oxidation than petroleum-based fuels and in its advanced stages, can cause acidity in the fuel and form insoluble gums and sediments that can plug fuel filters (Monyem and Van Gerpen, 2001).

There is an interest in alternative energy sources since

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Abbreviations: TAN, Total acid number; FFAs, free fatty acids; FAME, fatty acid methyl esters.

the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. These sources were limited and would be exhausted in the near future. Historically, many biomass and agricultural derived materials have been suggested as alternative energy sources and the use of biodiesel as fuel presents a promising potential (Al-Widyan and Al-Shyoukh, 2002; Mushrush et al., 2001). This is due to its great contribution to the environment (Bagley et al., 1998) and to its role as a strategic source of renewable energy in substitution to diesel oil and other petroleum-based fuels (Wu and Foglia, 1998; Cardone et al., 2002).

Researchers have focused on different catalyst systems, different solvents and different acyl acceptors. Soybean oil has five fatty acids: approximately equal amounts of palmitic acid, oleic acid and linolenic acid (about 13% each), linoleic acid (approximately 55%) and stearic acid (approximately 4%). The average US production of soybean oil from 1993 to 1995 was 6.8 billion kg and in 2002, soybeans were harvested from more than 30 million ha across the United States, which accounts for 40% of the total world soybean output. This production capacity accounts for more than 50% of the total available biobased oil for industrial applications. A useful industrial application of soybean oil is in biodiesel blends. Kinney and Clemente (2004) reported that soybean oil-derived biodiesel possess enhanced biodegradation, increased flashpoint, reduced toxicity, lower emissions and increased lubricity.

Various oils (like algal oil, sunflower and plam oil) have been used in different countries as raw materials for biodiesel production owing to its availability (Hossain et al., 2008; Hossain and Boyce, 2009a). Although biodiesel cannot entirely replace petroleum based diesel fuel, there are at least five reasons that justify its development. It provides a market for excess production of vegetable oils, it decreases the dependence on imported petroleum, it does not contribute to global warming due to its closed carbon cycle, the exhaust emissions of carbon monoxide, unburned hydrocarbons and particulate emissions from biodiesel are lower than regular diesel fuel, when added to regular diesel fuel in an amount up to 20%, it can convert fuel into an acceptable fuel (Ayhau, 2009). Transesterification reaction is the most commonly applied technique to produce biodiesel. The objectives of this study were to compare the optimum conditions of fatty acid methyl ester (biodiesel production) and potential use of waste soybean cooking oil. In addition, identification of the quality (viscosity, acid number and metal content) of biodiesel produced was also done.

MATERIALS AND METHODS

Sunbeam Soya Oil

Soya cooking oil was bought from a hypermarket and fried for 2 h using the same sources in the University of Malaya cafeteria, Kuala

Lumpur, Malaysia.

Chemicals and reagents

The chemicals and reagents were obtained from the ABO lab, of the Institute of Biological Sciences Department, Faculty of Science, University of Malaya. The following chemicals were used: methanol (CH₃OH), ethyl ethanol (C₂H₅OH), 1-butanol (C₄H₁₀O), sodium hydroxide (NaOH) and potassium hydroxide (KOH) in pellet form and sodium sulfate in powder form. Other materials used included Double Ring 102 filter paper and aluminum foil.

Preparation of waste cooking oil

After frying, the waste cooking oil was collected from the University of Malaya cafeteria. Later, the waste cooking oil was filtered by filter paper to remove bit of food residues. The filtered clean cooking oil was then collected in a clean conical flask and used for the experiment.

Preparation of potassium and sodium alcoxide

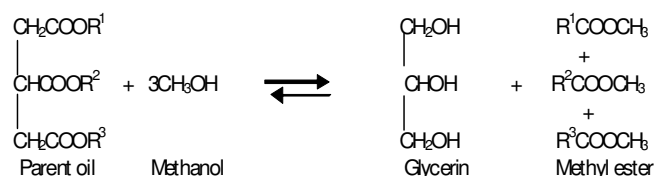
An appropriate volume of alcohol was measured and poured into a 500 ml conical flask. The catalyst in pellet form was weighed and mixed with alcohol. The mixture was then shaken for about 1 h until all the catalyst dissolved. Since alcohols would evaporate easily, the flask was covered with aluminium foil during shaking to reduce the loss of alcohol by evaporation. This covering can also prevent the alcoxide from absorbing water from the air.

Transesterification

Transesterification also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except that an alcohol is used instead of water (Murugesan et al., 2009). This has been widely used to reduce the viscosity of the triglycerides. The transesterification is represented as



If methanol is used in this process then it is called methanolysis. Methanolysis of triglycerides is represented as



Biodiesel preparation

The filtered oil was heated up to a temperature of 50°C in water bath to melt coagulated oil. It is important not to overheat the oil above 65°C, because at that temperature alcohol would boil away easily. The heated oil of 100 ml was measured and transferred into a conical flask containing catalyst-alcohol solution. The reaction was considered to start at this moment, since heated oil assisted the reaction to occur. The reaction mixture was then shaken by using shaker at a fixed speed for 2 h.

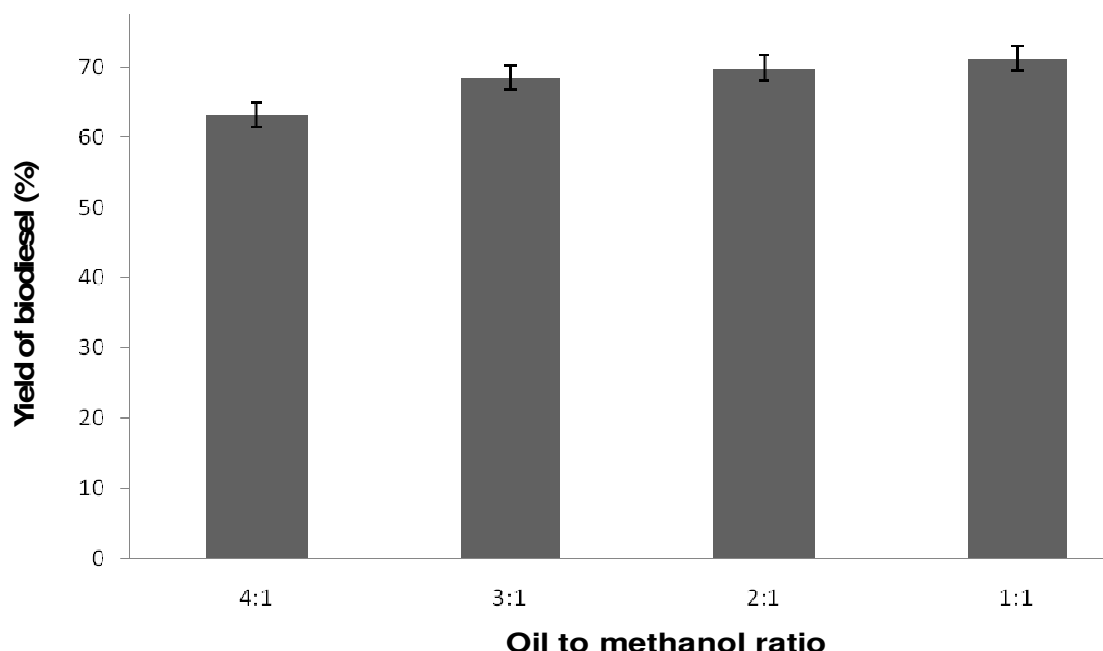


Figure 1. The effect of oil to methanol molar ratio on biodiesel production. Bars indicate mean \pm SE (n = 3).

Separation of biodiesel from by-products

The product of the reaction was exposed to open air to evaporate excess methanol for 30 min. The product was then allowed to settle down overnight. Two distinct liquid phases: crude ester phase at the top and glycerol phase at the bottom were produced in a successful transesterification reaction.

Purification of biodiesel by washing

The top ester phase (biodiesel) was separated from the bottom glycerol phase by transferring to a clean 250 ml conical flask. The biodiesel was then purified by washing with distilled water to remove all the residual by-products like excess alcohol, excess catalysts, soap and glycerine. The volume of distilled water added was approximately 30% of the biodiesel volume. The flask was shaken gently for 1 min and placed on the table to allow separation of biodiesel and water layers. After separation, the biodiesel was transferred to a clean conical flask. The washing process was repeated for several times until the washed water became clear. The clean biodiesel was dried in an incubator for 48 h, followed by using sodium sulphate. The final product was analyzed to determine its ester content (that is, purity of product) and also other equipments were used to determine related properties.

RESULTS

The effect of different oil to methanol molar ratio on biodiesel production

In this experiment, different oils to methanol molar ratio were used, for instance, 4:1, 3:1, 2:1 and 1:1. The reactions were carried out using 0.5% sodium hydroxide for 2 h at room temperature. Figure 1 shows the yield of

biodiesel from waste soybean oil by using different types of molar ratio of oil to methanol. The results show that increasing methanol to oil molar ratio increased the yield of biodiesel production. Oil to methanol molar ratio of 1:1 gave the optimum yield of biodiesel among them. The yield of biodiesel was 71.2% for 1:1 of oil to methanol molar ratio.

The effect of different alcohol types on biodiesel production

Different types of alcohol used affected the percentage of yield of biodiesel. Methanol, ethanol and butanol were used in this experiment. The reactions were carried out by using 0.5% NaOH, 1:1 oil to alcohol molar ratio for 2 h at room temperature. Figure 2 shows the yield of biodiesel from waste soybean oil by using different types of alcohol. The results show that methanol gave the best yield, followed by ethanol and butanol. For methanol, the yield of biodiesel achieved was 71.2%.

The effect of reaction time on biodiesel production

Reaction time was also a factor that can influence the yield of biodiesel. In this experiment, mixing times were chosen such as 2 and 6 h. The reactions were carried out by using 1:1 oil to methanol molar ratio and 0.5% of NaOH at room temperature. Figure 3 shows the yield percentage of biodiesel at 2 and 6 h of reaction times. From the results, 2 h of mixing time gave better yield when compared with 6 h. and gave 71.2%.

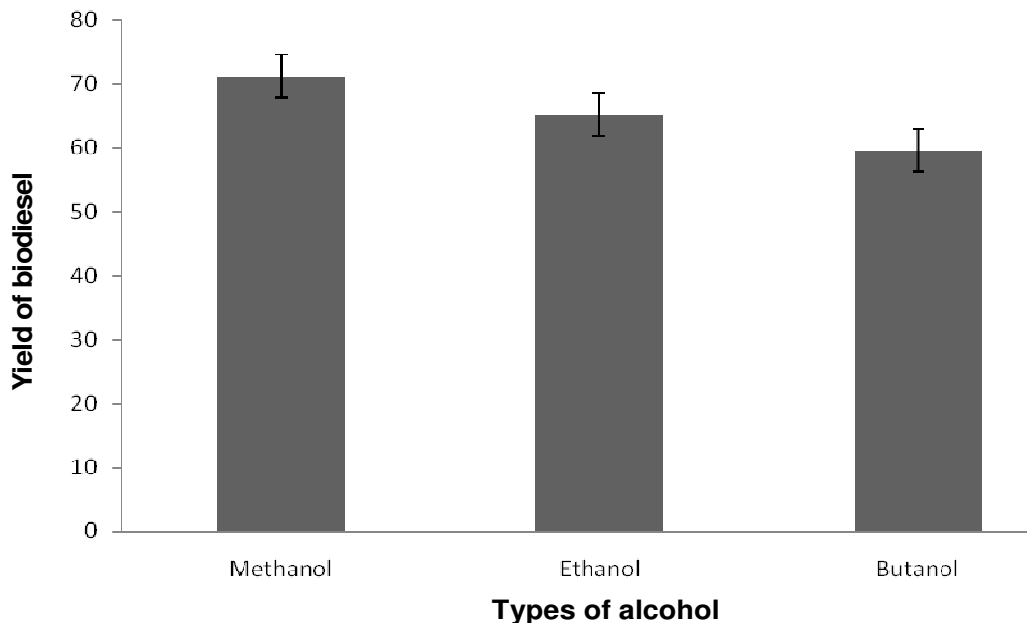


Figure 2. The effect of types of alcohol on biodiesel production. Bars indicate mean \pm SE (n = 3).

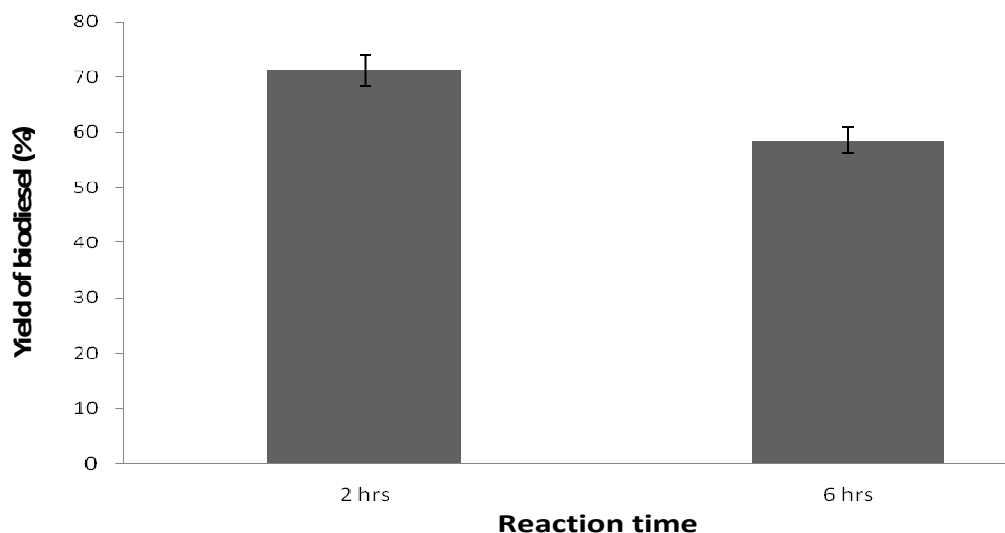


Figure 3. Effect of reaction times on biodiesel production. Bars indicate mean \pm SE (n = 3).

Viscosity measurement of biodiesel

One of the main purposes of the transesterification reaction was to reduce the viscosity of cooking oil in order to achieve the properties that is more suitable for its function as fuel. The standard range of viscosity for biodiesel in ASTM D6751 is 1.9 - 6.0 mm²/sec at 40°C. Figure 4 shows the viscosity of biodiesel produced from waste soybean oil in several of treatments. The viscosity was maintained the ASTM D6751 standard. The lowest viscosity was found in 1:1 oil to methanol ratio following 6 h shaking time.

Determination of the total acid number (TAN) value

Total acid number (TAN) indicates the level of free fatty acids (FFAs) present in biodiesel. TAN value lower than 0.5 mg KOH/g oil is ideal as fuel for vehicle. A high TAN value can have a strong solvency effect on rubber seals and hoses in the engine, thereby causing premature failure. It may also leave deposits, which can clog the fuel filter or drop fuel pressure. Figure 5 shows the result of TAN value of biodiesels produced using different reaction conditions. The TAN value of biodiesel was lower in 1:1 oil to methanol ratio, using methanol for 6 h shaking time

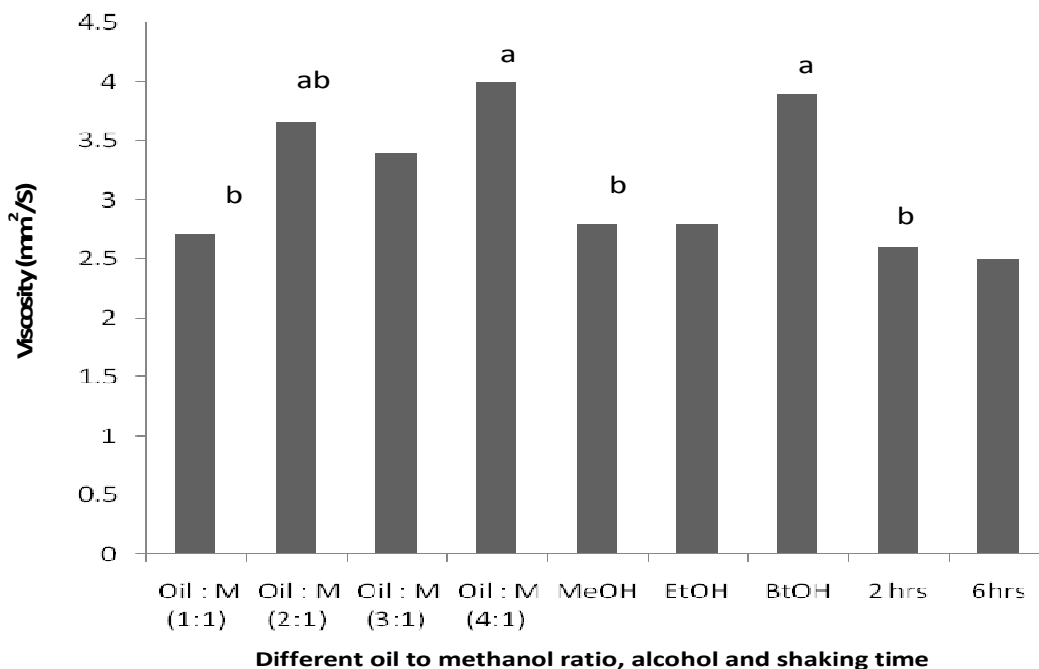


Figure 4. Biodiesel viscosity as affected by different types of parameter. Different letters indicate significant difference at 5% by LSD.

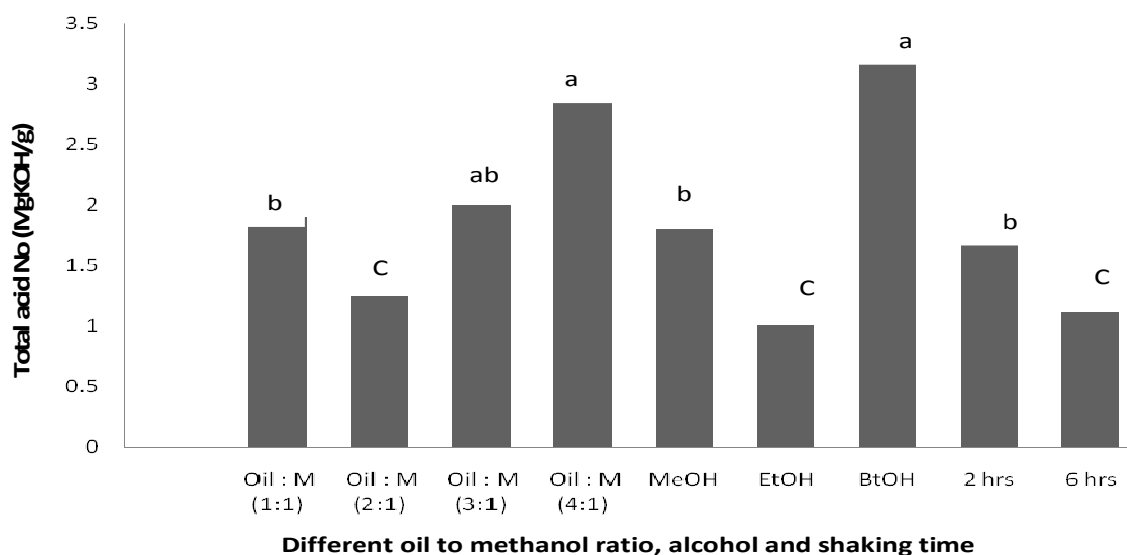


Figure 5. Biodiesel TAN value as affected by different types of parameter. Different letters indicate the significantly difference at 5% by LSD.

than other ratio of oil to methanol and butanol for 2 h.

Multi-element biodiesel analysis

Multi-element analyzer was used to measure wear debris and additives depletion. Table 1 shows the concentration of elements in biodiesels produced from different para-

eters. The concentrations of most of the elements in biodiesel produced from waste soybean oil were quite low generally. However, the concentration of argentums or silver was slightly high. Table 2 shows the standard value of viscosity and acid value. Figure 6 shows the biodiesel production and glycerin layer after shaking.

The elements measured in this study were iron, chromium, aluminium, copper, lead, tin, nickel, manganese,

Table 1. Element contents (ppm) in biodiesels produced from different alcohol to oil molar ratios.

Elements	Ratios				Shaking time		MeOH	EtOH	BtOH
	1:1	1:2	1:3	1:4	2 h	6 h			
Fe	1	0.5	1.5	1	0.7	0.5	0.5	0.4	0.5
Al	0	0	0	0.5	0.5	0.5	0.4	0.5	0.3
Cu	0.5	1	0.5	1	1.5	1	2	3	2
Pb	0.5	0	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sn	4	2	4.5	7	0	0	0	0	0
Ni	3	2.5	3	3.5	2.5	2.5	2.5	2.5	2.5
Ag	6.8	6.5	8.5	5.4	9	9	0	0	0
Mo	2	1	2	3	0.5	0.5	9	7	8
Zn	0	0	0.5	0.5	0.6	0.5	0.5	0.5	0.5
P	3.5	3.5	0	3	0	0	0.3	0.5	0.2
Ca	2	2	2.5	2	6.5	6.5	0	0	0
Mg	1	1	1	1	2	2	5	6.5	6
Si	1.5	5.5	3.5	4	2.0	2.5	0	0	0
Na	4.3	6.2	4	3.5	5.9	8.9	2	1	2

Mean: (n =3).

Table 2. Parameters for the quality of biodiesel (Meher et al., 2006).

Parameters	Austria (ON)	Czech republic (CSN)	France (journal official)	Germany (DIN)	Italy (UNI)	USA (ASTM)
Viscosity at 40°C (mm ² /s)	3.5 - 5.0	3.5 - 5.0	3.5 - 5.0	3.5 - 5.0	3.5 - 5.0	1.9 - 6.0
Acid number (mg KOH/g)	≤ 0.8	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.8

titanium, argentine, molybdenum, zinc, phosphorus, calcium, barium, magnesium, silicon, sodium, boron and vanadium. The result showed that the concentrations of all the elements were lower than 5 ppm, except argentine and sodium. However, these were under standard.

DISCUSSION

The effect of different oil to methanol molar ratio on biodiesel yield

From the results, it can be seen that 1:1 oil to methanol molar ratio gave the higher ester yield compared with 4:1, 3:1, 2:1 and 1:1 oil to methanol molar ratio. Oil to methanol molar ratio of 4:1 gave the lowest yield of biodiesel. The idea in increasing the oil to methanol molar ratio, means alcohol amounts were elevated and the fatty acid methyl esters (FAME) yield increased. To maximize the fatty ester yield, it is needed to drive the transesterification reaction to shift to the product that is ester and glycerin. Therefore, it is a need to increase the concentration of reactant such as alcohol amount, so that the reactions would be more favorable to generate FAME yield. Many researchers found that less alcohol would cause the transesterification to be incomplete. Many of

them found that the optimum oil to methanol molar ratio would be 1:6. With that molar ratio, one can get a higher ester yield if other reaction conditions are optimum. However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps to drive the equilibrium to back left, lowering the yield of esters (Murugesan et al., 2009).

The effect of different alcohol types on biodiesel production

From the results obtained, methanol gave the best fatty ester yield, followed by ethanol and the least was butanol. There are many reasons behind it. Firstly, methanol is simpler in terms of chemical structure, thus the transesterification reaction is more likely to occur. On the other hand, butanol is more complex in terms of chemical structure, therefore it is more difficult for transesterification to occur.

Secondly, the base catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. In the case of methanolysis, formation of emulsions quickly and easily breaks down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these



Figure 6. Biodiesel produced from waste soybean oil. Lower layer indicates glycerin and upper layer indicates biodiesel ester..

emulsions are more stable and severely complicate the separation and purification of esters.

The effect of different reaction times on biodiesel production

From the results, 2 h reaction time gave better ester yield than 6 h reaction time. Some researchers found that every reaction got a certain time to complete the reaction. For transesterification of triglyceride to ester, it takes about 90 to 120 min to complete the conversion. The longer the reaction time, the more the hydrolysis of ester would occur. It might produce many free fatty acids at the end, and these FFAs would participate in soap formation, thus reducing the biodiesel yield.

Analysis of biodiesel viscosity

From the results obtained, biodiesel viscosities were surprisingly higher than the ASTM standard. Average of biodiesel viscosities was $3 \text{ mm}^2/\text{s}$ at 40°C . However, the ASTM D6751 standard limit in $1.9 - 6.0 \text{ mm}^2/\text{s}$ at 40°C . Higher viscosity may be due to the long storage time. Actually, it was stored biodiesel produced for a few months before we analysed it with viscometer.

Few researchers found that the longer the storage time of biodiesel, the higher the viscosity value. During storage, the viscosity of ethyl esters increases owing to the formation of oxidized polymeric compounds that can lead to the formation of gums and sediments that clog filters (Bouaid et al., 2009). Eventually, it increases the viscosity of biodiesel in stored condition. It was reported that

kinetic viscosity of biodiesel from waste cooking oil was 5.3 and 1.9 - 4.1 mm^2/s at 313 K in commercial biodiesel fuel (Demirbas, 2008)

Analysis of biodiesel TAN value

Based on results it was reported that the average total acid number from all biodiesel samples were around 1 - 2. However, the ASTM D664 stated that the maximum of TAN value is 0.50. Higher acids content may be caused by the same problem, which was the storage time. Again, acids can be formed when traces of water cause hydrolysis of the esters into alcohol and acids (Bouaid et al., 2009). As expected, the acid number increases with an increase in peroxides because the esters first oxidize to form peroxides which then undergo complex reactions, including a split into more reactive aldehydes which further oxidize into acids.

Analysis of biodiesel element composition

Biodiesel from waste soybean cooking oil had considerably lower Fe, Cu, Pb, Ca, Na, K concentration than pure soy cooking oil. Most of the elements (Fe, Cr, Pb, Cu, Ag, Mg, Ca, Na, Zn, Si and P) fulfilled the requirement of the standard method specification as well (ASTM D 6751 and EN 14214 methods). Hossain and Boyce, (2009b) reported the same result as their previous research results.

From the results, average concentration of various element within biodiesel produced are generally lower as was expected. However, only argentums or silver were a little bit higher but still under standard.

Conclusion

The results showed that methanol was the best alcohol for this reaction condition. The highest triglyceride conversion rate of 72.7% was achieved after 2 h of reaction at 50°C, with a 1:1 molar ratio of methanol to waste soybean oil and a 1.0 wt% catalyst of sodium hydroxide. The optimal values of these parameters for achieving maximum conversion of oil to esters depends on the chemical and physical properties of these oils. Sufficient reaction time should be allowed to ensure complete conversion of triglycerides into esters. However, excess reaction time did not promote the conversion but favors the reverse reaction of transesterification which resulted in a reduction in the ester yield. In addition, the overall results showed that it was effective to produce good quality of biodiesel from waste oil which could be used for diesel engine.

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