

Full Length Research Paper

Impacts of alcohol type, ratio and stirring time on the biodiesel production from waste canola oil

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The use of alternative fuels in order to reduce the environmental impacts of diesel emissions has been extensively investigated. Trends in the regional use of biomass-derived fuels, such as alcohols, biodiesel and agricultural residues as a proposed control initiative against elevated carbon monoxide levels in urban areas have expanded to a global scale. Waste cooking oil is considered as the most suitable material due to its readily-availability and cost-effectiveness. In this study, the transesterification of waste canola cooking oil was carried out using lower alcohol to oil molar ratios to study its feasibility. Some important variables such as volumetric ratio, types of reactants and shaking time were selected to obtain a high quality biodiesel fuel with the specification of American Standard for Biodiesel Testing Material (ASTM D 6751) and European Norm (EN 14214). The highest biodiesel yield was obtained (49.5%) under conditions of 1:1 volumetric oil-to-methanol weight ratio, 0.5% NaOH catalyst at 55 °C reaction temperature and 250 rpm stirring speed. The results showed that biodiesel production from different oil to methanol ratio, alcohol types and shaking time exhibited considerable differences. There was also a considerable difference of biodiesel yield produced by methanol, ethanol and 1-butanol. The biodiesel yield increased in the order of 1-butanol < ethanol < methanol. There was little difference in viscosity, acid value and chemical elements (Fe, Mg, Ca, Na, P etc.) at different parameters. The result showed that the optimal combination which could give highest production of biodiesel was transesterification, carried out for 2 h by using methanol to oil molar ratio of 1:1, catalyzed by 0.5% sodium hydroxide and produced biodiesel can be used as fuel in diesel engine.

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

INTRODUCTION

Environmental issues are the driving forces for the development of alternative energy sources, since the burning of fossil fuels causes various environmental problems including global warming, air pollution, acid precipitation, ozone depletion, forest destruction, and emission of radioactive substances (Dincer, 2000). The alternative energy source of fossil fuels includes hydro, wind, solar, geothermal, hydrogen, nuclear, and biomass (Demirbas, 2005). Among these alternative energy sources, biofuels derived from biomass are considered as the most pro-

promising alternative fuel sources because they are renewable and environmental friendly.

Biomass and agricultural derived materials have been used as alternative energy sources and the use of biodiesel as fuel is a promising potential being a market that grows rapidly (Al-Widyan and Al-Shyoukh, 2002; Mushrush et al., 2001; Harten, 2003, Hossain et al., 2009). This is due to its great contribution to the environment and to its role as a strategic source of renewable energy in substitution to diesel oil and other petroleum-based fuels (Wu et al., 1998; Cardone et al., 2002; Bagley et al., 1998; Monyem et al., 2001; Hossain et al., 2009).

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

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Table 1. Variable and fixed parameters used in this study.

| Variable parameters | Fixed parameters |
|----------------------------|---------------------------------|
| Alcohol to oil molar ratio | Types of alcohol: Methanol |
| 1 : 1 | Types of catalyst: NaOH |
| 1 : 2 | Amounts of catalyst: 0.5% |
| 1 : 3 | Reaction time: 2 h |
| 1 : 4 | Mixing intensity: 250 rpm |
| Types of alcohol | Alcohol to oil molar ratio: 1:1 |
| Ethanol | Types of catalyst: NaOH |
| Methanol | Amounts of catalyst: 0.5% |
| Butanol | Reaction time: 2 h |
| | Mixing intensity: 250 rpm |
| Reaction time | Alcohol to oil molar ratio: 1:1 |
| 2 h | Types of alcohol: Methanol |
| 6 h | Types of catalyst: NaOH |
| | Amounts of catalyst: 0.5% |
| | Mixing intensity: 250 rpm |

esters and glycerin, which is removed. Biodiesel consists of long-chain fatty acid esters (Hass 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). It is compatible with conventional diesel fuel and already serves as a commercial fuel in Europe (Knothe et al., 2003; Dorado et al., 2003; Serdari et al., 1999).

The use of biodiesel has drawn attention in the last decade as it is a renewable, biodegradable, and nontoxic fuel, and has been industrially produced from vegetable oils (Hossain et al., 2009a) in North America and Europe and from waste edible oils in Japan and Malaysia (Shimada et al., 1999; Hossain et al., 2009b). Oilseed rape (*Brassica* and related species, Brassicaceae) is now the second largest oilseed crop in the world, providing approximately 13% of the world's supply and occupying approximately 2% of the world's croplands (Leff et al., 2004). The name 'canola' was adopted in 1979 as a registered trademark of the Canadian Canola Association and referred to as rapeseed cultivars that produce seed oils with less than 2% erucic acid (22:1) and defatted meals with less than 30 $\mu\text{mol/g}$ of aliphatic glucosinolates (Shahidi, 1990). The world's canola commerce is mainly supplied by two species, *Brassica napus* L. and *Brassica rapa* L. which can produce seeds containing 40% or more oil. Among all species of *Brassica*, *B. napus* L. is the most productive species under cultivation (Pua and Douglas, 2004). Rapeseed now serves as the main feed-stock in European countries for biodiesel production (Wardle, 2003).

The objective of this study is to investigate the biodiesel production from waste canola cooking oil by using

amount of alcohol lesser than the theoretical amount according to stoichiometric equation and the parameters that optimize this transesterification.

MATERIALS AND METHODS

The canola cooking oil purchased from hypermarket was used for frying to produce waste cooking oil. The waste cooking oil was then collected in a plastic bottle. After collection, the waste cooking oil was filtered with filter paper to remove food residues. The filtered cooking oil was then collected in a clean conical flask and used for experiments.

Preparation of sodium and potassium alcocide

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 (Table 1). Since alcohols would evaporate easily, the flask was covered with aluminium foil during shaking to prevent the evaporation of alcohol. This covering can also prevent the alcocide from absorbing water from the air.

Transesterification

This process is similar to hydrolysis, except that alcohol is employed instead of water. The stoichiometry of this reaction shows that 3 moles of alcohol react with 1 mole of triglyceride to give 3 moles of fatty acid ester and 1 mole of glycerine (Figure 1). The reaction rate of transesterification can be accelerated by using catalysts.

Biodiesel preparation

The filtered oil was heated up to a temperature of 60°C in water bath to melt coagulated oil. The heated oil of 100 mL was poured into the conical flask containing catalyst-alcohol solution, and this moment was taken as the starting time of the reaction. The reaction mixture was then shaken by using shaker at a fixed speed of 250 rpm (Table 1). When the reaction reached the preset reaction time, shaking was stopped.

Separation of biodiesel from by-products

The product of reaction was exposed to open air to evaporate excess methanol for 30 min. The product was then allowed to settle overnight to produce two distinct liquid phases: crude ester phase at the top and glycerol phase at the bottom. There are a few methods to separate these 2 layers, including using the separating funnel and removing the biodiesel using pipette. The latter was used in this experiment.

Biodiesel purification

The crude ester phase was separated from the bottom and glycerol phase was transferred to a clean conical flask. The biodiesel produced contains some residues including excess alcohol, excess catalyst, soap and glycerine. It was purified by washing with distilled water to remove all the residual by-products. The volume of water added was approximately 30% (volume) of the biodiesel. The flask

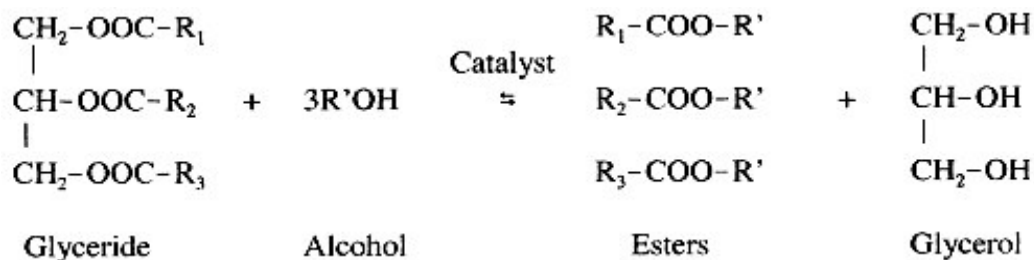


Figure 1. Transesterification reaction (Ma and Hanna, 1999).

Table 2. Element contents (ppm) in biodiesels produced from different alcohol to oil molar ratios. Same letters are not significantly difference at 5% by LSD.

| Elements | Ratios | | | | Shaking time 2 (ppm) | 6 h (ppm) | MeOH (ppm) | EtOH (ppm) | BtOH (ppm) |
|----------|--------------|--------------|--------------|-----|-------------------------|--------------|---------------|---------------|---------------|
| | 1:1 (ppm) | 1:2 (ppm) | 1:3 (ppm) | 1:4 | | | | | |
| Fe | 1 | 0.5 | 1.5 | 1 | 0.7 | 0.5 | 1 | 0.7 | 0.5a |
| Al | 0 | 0 | 0 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.4a |
| Cu | 0.5 | 1 | 0.5 | 1 | 1.5 | 2 | 1 | 1.0 | 2b |
| Pb | 0.5 | 0 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.4 | 0.5a |
| Sn | 4 | 2 | 4.5 | 7 | 0 | 0 | 7 | 0 | 0 |
| Ni | 3 | 2.5 | 3 | 3.5 | 2.5 | 2.5 | 3.5 | 2.0 | 2.5b |
| Mn | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ag | 8.8 | 6.5 | 2.5 | 7.4 | 9 | 6 | 7.4 | 7.0 | 8.2d |
| Mo | 2 | 1 | 2 | 3 | 0.5 | 0.5 | 3 | 0.5 | 0.5a |
| Zn | 0 | 0 | 0.5 | 0.5 | 0.6 | 0.5 | 0.5 | 0.6 | 0.5a |
| P | 3.5 | 3.5 | 0 | 3 | 0 | 0 | 3 | 0 | 0 |
| Ca | 2 | 2 | 2.5 | 2 | 6.5 | 6.5 | 2 | 6.5 | 6.5c |
| Mg | 1 | 1 | 1 | 1 | 2 | 2 | 1 | 1 | 2b |
| Si | 1.5 | 5.5 | 3.5 | 4 | 2.0 | 2.5 | 4 | 2.0 | 2.5b |
| Na | 4.3 | 6.2 | 4 | 3.5 | 5.4 | 8.4 | 3.0 | 5.4 | 7.4d |

was shaken gently for 1 min and placed on 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 incubator for 48 h, followed by using sodium sulphate. The final products were analyzed to determine related properties including viscosity, total acid numbers (TAN) and element contents.

Experiments were carried out to study different parameters affecting biodiesel production, including alcohol to oil molar ratio, types of alcohol and reaction time. In each experiment, the parameters being studied were changed while other parameters were fixed. The experiments are summarized in Table 2.

RESULTS

Biodiesel yields

The effect of different methanol to oil molar ratios on biodiesel yields was investigated. The volume of waste

cooking oil used in this study was 100 mL for each sample, thus the percentage of biodiesel produced was equivalent to the volume of biodiesel produced. From Figure 2, the highest biodiesel yield of 49.5% was obtained when the methanol to oil molar ratio was 1:1, and the methanol to oil molar ratio of 1:4 gave the lowest biodiesel yield of 18%. Generally, the biodiesel yields decreased with decreasing methanol to oil molar ratios.

The second parameter for optimization of biodiesel production using lower alcohol to oil molar ratios being investigated was the types of alcohol. In this study, methanol, ethanol and butanol were used. As shown in Figure 3, the highest biodiesel yield of 49.5% was obtained when methanol was used for transesterification of waste cooking oil, followed by ethanol which gave biodiesel yield of 23.5%. The transesterification employing butanol gave the lowest biodiesel yield, which was 19.5%.

The last parameter investigated the mixing times of

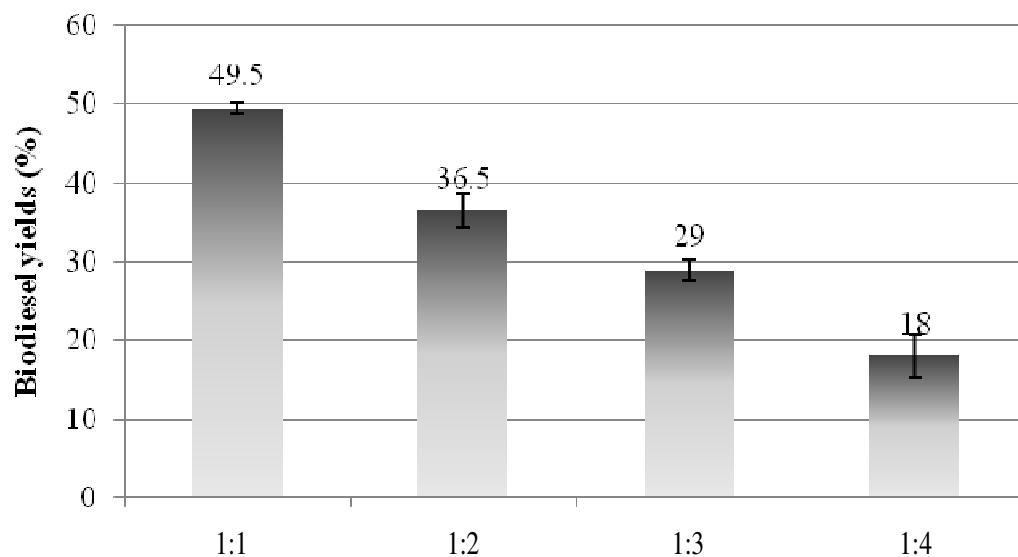


Figure 2. The effect of different methanol to oil molar ratios on biodiesel yields. Mean±SE (N = 3).

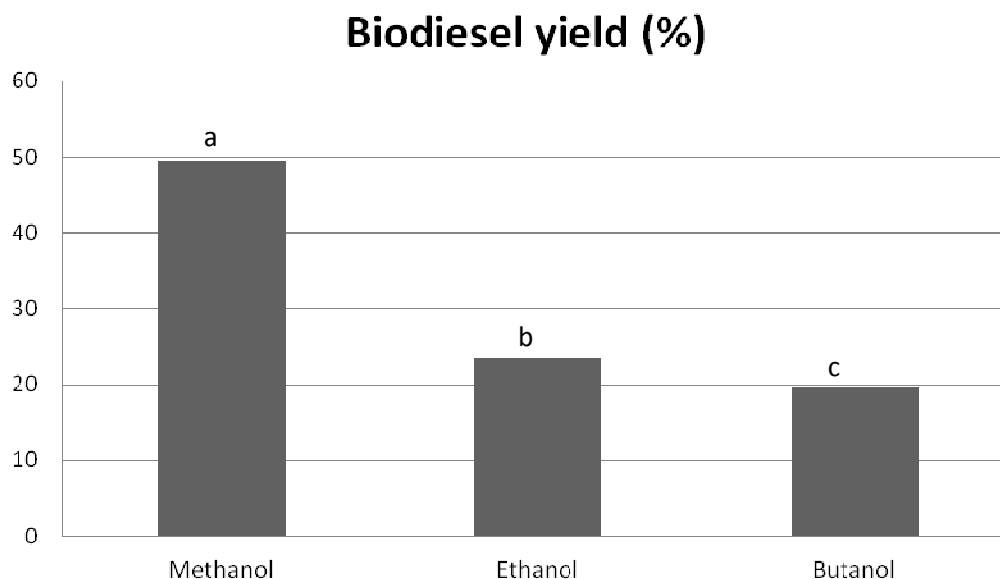


Figure 3. The effect of different types of alcohol on biodiesel yields. Same letters are not significantly difference at 5% by LSD. Mean±SE (N = 3).

transesterification. As shown in Figure 4, the biodiesel yield was higher for mixing time of 2 h, which was 49.5% compared to 27.5% by using mixing time of 6 h. It might be due to the excess shaking and reaction time was not considered as optimum level of biodiesel production. Due to more mixing time, fatty acid could be affected to result in conversion of the fatty acid to more methyl ester; and soap could be formed during biodiesel washing. That was why mixing time of 6 h influenced the yield of biodiesel

than it was when drastically reduced.

Biodiesel analysis

Viscosity determination

The result showed that the biodiesel with lowest viscosity was obtained when the methanol to oil molar ratio of 1:2

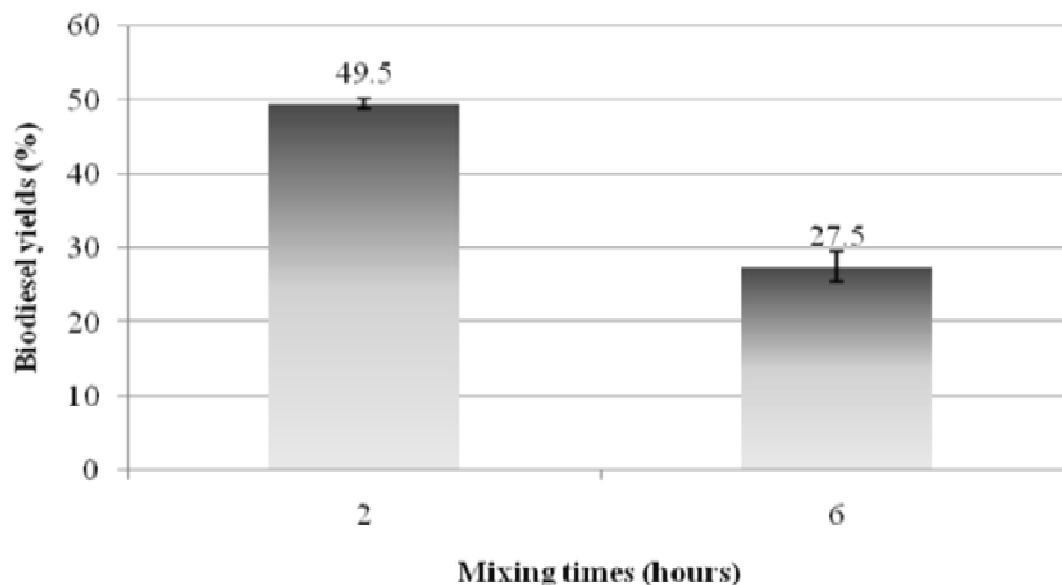


Figure 4. The effect of different mixing times on biodiesel yields. Mean \pm SE (N = 3).

Table 3. The acid value and viscosity in different parameters has been shown. Same letters are not significantly difference at 5% by LSD.

| Study No. | Variable parameters/treatments alcohol to oil molar ratio | Acid value viscosity (mgKOH/g of oil) (mm ² /s) |
|-----------|--|---|
| 1 | 1 : 1 | 0.10a 2.5a |
| | 1 : 2 | 0.60a 2.7a |
| | 1 : 3 | 01.2ab 3.5b |
| | 1 : 4 | 01.3b 2.0a |
| 2 | Types of alcohol | |
| | Ethanol | 1.0a 2.7a |
| | Methanol | 0.9a 2.6a |
| | Butanol | 1.0a 4.1bc |
| 3 | Reaction time | |
| | 2 h | 0.9a 4.0c |
| | 6 h | 1.0a 3.7bc |

was used, and the methanol to oil molar ratio of 1:4 gave the standard biodiesel viscosity will be the standard biodiesel viscosity (Table 3).

As shown in Table 3, the biodiesel produced through butanolysis has the highest viscosity value followed by ethanol which produced biodiesel. The biodiesel produced through methanolysis gave the biodiesel with lowest viscosity. Sodium hydroxide-catalyzed transesterification carried out for 2 h gave biodiesel with higher viscosity compared to that carried out using mixing time of 6 h.

Total acid number (TAN) determination

The result of TAN analysis showed that the TAN values of most samples were useful for engine use. It had been seen that most of the TAN values of biodiesel followed the American Standard for Biodiesel Testing Material (ASTM D 6751) and European Norm (EN 14214) by which biodiesel could be identified as safety fuel for the use of diesel engine (Table 4). The average TAN value derived from the data was the lowest (0.1 mg KOH/g) at the ratio of 1:1, methanol to oil.

Table 4. Parameters for the quality of biodiesel standard (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 |

Multi-element analysis

The elements measured in this study were iron, chromium, aluminium, copper, lead, tin, nickel, manganese, titanium, argentum, molybdenum, zinc, phosphorus, calcium, barium, magnesium, silicon, sodium, boron and vanadium (Table 3). The result showed that the concentrations of all the elements were lower than 5 ppm, except argentum and sodium.

DISCUSSION

Biodiesel yield

The result showed that the biodiesel yields of all the samples were low, with a maximum average value of 49.5%. This result was expected since the amounts of alcohol used in this study were much lower than the theoretical optimum amount. One of the most crucial factors resulting in the low biodiesel yield was the soap formation. In this study, the raw material used for biodiesel production was waste cooking oil, which contained a large amount of free fatty acids. These free fatty acids react with the alkaline catalysts to form soap. High soap formation would lead to formation of gels, which subsequently traps a large amount of esters within the glycerin layer and leads to the loss of biodiesel (Stavarache et al., 2005). Besides that, soap dissolves in the glycerol layer since it contains one polar end. The dissolved soap increases the solubility of biodiesel in the glycerol and further decrease the recovery of biodiesel (Vicente et al., 2004). After transesterification, the washing step is necessary to purify the biodiesel. The pre-sence of soap reduces the biodiesel yield in this step since it leads to the formation of emulsions which hinders the purification of biodiesel. This is because the soap present in the esters phase tends to accumulate at the interfacial region between two immiscible ester and water layers.

Optimization of biodiesel production

Effect of alcohol to oil molar ratios on biodiesel yields

According to the stoichiometric equation of transesteri-

fication, 3 moles of alcohol would react with 1 mole of triglyceride to give 3 moles of fatty acid ester and 1 mole of glycerine. In other words, an alcohol to oil molar ratio of at least 3:1 is required for complete reaction. Many researchers have reported an alcohol to oil molar ration of 6:1 to be the optimal ratio, while Leung and Guo (2006) reported that the maximum biodiesel production was obtained at a molar ratio of 7:1 in transesterification of used frying oil. In this study, the alcohol to oil molar ratios used were much lower than the above mentioned optimal ratios to study the feasibility of using low alcohol to oil molar ratios. In biodiesel production using waste cooking oils as raw materials, the main costs of materials are the costs of alcohol and catalyst. Since catalyst is required only in minute amounts, the primary cost would be only for alcohol. Therefore, if the use of alcohol can be reduced without significantly reducing the production of biodiesel, the biodiesel production cost would be lowered and the process would be more cost-effective. The result showed that the biodiesel yields were low for all four ratios used, and the yields decreased with decreasing methanol to oil molar ratio. Singh et al. (2006) suggested that higher methanol to oil molar ratios was better than lower ratios in terms of soap formation.

Effect of types of alcohol on biodiesel yields

Based on the result obtained, the amounts of biodiesel produced by using different types of alcohol decreased in the following order: Methanol > Ethanol > Butanol. This result obtained was slightly different with the finding of Nye et al. (1983). They reported that methanol was the alcohol that can give the highest biodiesel yield, followed by butanol and then ethanol. According to Meher et al. (2006), the production of biodiesel by using ethanol in alkali-catalyzed transesterification is more difficult than that by using methanol. This is due to the formation of stable emulsion during ethanolysis. For methanolysis, the emulsions formed would break down easily to form a lower glycerol rich layer and upper methyl ester rich layer. While in ethanolysis, the emulsions formed are more stable due to the presence of larger non-polar group in ethanol, making the separation and purification of biodiesel more difficult (Zhou et al., 2003). This explained why the biodiesel yield from ethanolysis was lower than methanolysis in this study. Although methanol is the most suitable alcohol for alkali-catalyzed biodiesel

production, the reported result obtained from biodiesel production catalyzed by lipase suggested otherwise. Mittelbach (1990) reported that the ethanol- and butanol-catalyzed transesterification gave much higher yields than methanol-catalyzed transesterification. The same result was also reported by Abigor et al. (2000).

Effect of mixing times on biodiesel yields

According to many researchers, the biodiesel yields are directly proportional to the reaction times. In other words, the biodiesel yields increase with increasing reaction times. However, the result showed that the biodiesel yields were higher when reaction time of 2 h was used. This anomalous result may be resulted from the higher soap formation when longer reaction time was used. Thus, the rate of soap formation was also increased. This explanation arose from the observation that more soap was observed in biodiesels prepared by using reaction time of 6 h, compared to biodiesels prepared using 2 h.

Biodiesel analysis

Biodiesel derived from vegetable oil is subjected to make deterioration through hydrolytic and oxidative reactions due to the presence of double bonds (Mittelbach and Gangl, 2001). The oxidation through contact with air during production and storage is one of the most prominent factors contributing to the deterioration of biodiesel. Thus, biodiesel is unsuitable for long-term storage (Knothe and Dunn, 2003).

Thompson et al. (1998) investigated the extent of deterioration of rape methyl ester and rape ethyl ester under different storage conditions. They found that the acid values and viscosity of biodiesels increased over time. The increase of acid values is caused by the hydrolysis of biodiesel to free fatty acids during storage. The formation of oxidized polymeric compounds during storage also makes the viscosity of biodiesel to increase (Mittelbach and Gangl, 2001).

The viscosity and TAN values of biodiesel produced are proportional to those of raw material, which means that the oil with higher viscosity and TAN values of produced biodiesel. According to Felizardo et al. (2006), the viscosity and acidity of oil might increase during frying. The result of viscosity and TAN tests showed that all the biodiesels produced exhibit bit higher viscosity and TAN values. The poor quality of biodiesels produced may also have resulted from the inappropriate washing step. It was reported that warm water was much more effective at removing soap and free glycerin from the ester than cold water (Canakci and Gerpen, 2003). Nabi et al. (2006) stated that washing biodiesel with hot distilled water can give rise to pure biodiesel with better quality, and the best temperature for water was 50°C which

resulted in biodiesel with 99% of purity. Predojević (2008) reported two new methods for purification of biodiesel, washing using silica gel and 5% phosphoric acid. Both of these methods were shown to be more effective than washing biodiesel with hot distilled water.

Viscosity

Formation of soap would cause increase in the viscosity of biodiesel (Demirbaş, 2003). Therefore high soap formation rate might be the main reason causing high viscosity values of biodiesels in this study but still under standard. Another reason that might be responsible for the high viscosity values is the storage time. Mittelbach and Gangl (2001) studied the stability of biodiesel made from used frying rapeseed oil stored at 20 - 22°C under different storage conditions. They found that the viscosities of biodiesels increased slightly after a storage period of 170 days, from a value of 4.55 cSt at day 0 to values ranging from 4.6 to 4.85 cSt at day 170.

The overall viscosity values of biodiesels produced in this study have slightly exceeded the ASTM limit of biodiesel, with a maximum value of 53 cSt. Some of the researchers also reported the production of biodiesel with high value of viscosity. For example, production of biodiesel with viscosity as high as 30.8 cSt was reported by Siler-Marinkovic and Tomasevic (1998) in an acid-catalyzed transesterification of sunflower oil.

There were not many literatures which correlate the viscosity of biodiesel to the parameters affecting the transesterification. Sinha et al. (2008) studied the effect of various parameters on the viscosity of the biodiesel produced through transesterification of rice bran oil. They found that the methanol to oil ratio did not cause significant variation in the viscosity of biodiesel. The methanol to oil molar ratios used by Sinha et al. (2008) are more than or equal to the theoretical optimal amount, ranging from 6:1 to 15:1. Therefore all of the transesterification processes proceeded to almost completion without soap formation, and produced biodiesels with similar viscosity.

In the determination of effect of catalyst concentration on the viscosity of biodiesel, Sinha et al. (2008) used catalyst concentrations ranging from 0.5 - 1.25%. Their result showed that all the biodiesels produced have similar viscosities and the values were lower than the ASTM limit of 5 cSt, except for biodiesel produced using 0.5% sodium hydroxide. The last parameter studied by Sinha et al. (2008) was the reaction time. They reported that different reaction times did not affect the viscosity of bio-diesel significantly. In this study, even though the soap formation was higher in biodiesel produced through 6 h transesterification compared to that produced through 2 h, the viscosity test showed that the former has a lower viscosity value.

Nye et al. (1983) reported that the alkali-catalyzed

transesterification employing methanol gave biodiesel with lowest viscosity of 7.38 cSt at 25°C, while ethanolysis and butanolysis gave biodiesel with viscosity values of 18.5 and 16.5 cSt respectively. Encinar et al. (2005) reported that the methanolysis of used frying oil catalyzed by potassium hydroxide gave biodiesel with better properties compared to sodium hydroxide. Similar result was also reported by Tomasevic and Siler-Marinkovic (2003). The result of this study showed similarity with the findings of these researchers in which biodiesel produced using potassium hydroxide has lower viscosity compared to that produced using sodium hydroxide.

Total acid number (TAN)

In this study, the TAN values of most samples were little bit higher than ASTM standard. These samples might be less chemical reactive or contain excessive acid value, which means that the acid contents of these samples were either too low to be detected or too high. Tomasevic and Siler-Marinkovic (2003) reported that alcohol to oil molar ratio has no influence on the acid value of biodiesel. They also reported that molar ration of alcohol to oil was not a factor for influencing total acid number in the biodiesel. Hossain et al. (2010) observed that reaction and storage time were a key factor for the increasing and decreasing of TAN in the biodiesel.

The acid value mainly depends on the kinds of oil used as raw materials. It was also reported that the acid numbers of the biodiesel were influenced by reaction times, in which increasing reaction times would cause increase in the value of acid number (Mahajan et al., 2007). Vicente et al. (2004) carried out alkali-catalyzed transesterification of refined sunflower oil. Their result showed that the acid values for biodiesels produced using sodium hydroxide were higher than those produced using potassium hydroxide.

Besides from viscosity, Mittelbach and Gangl (2001) also studied the changes of biodiesel TAN values associated with a pro-longed storage period. They found that the values of acid number increased from 0.35 mg KOH/g to values ranging from 0.38 - 0.54 mg KOH/g after a storage period of 170 days. In this study, the average TAN value of biodiesels produced was 1.3 mg KOH/g in 1:4 methanol to oil molar ratio which is much higher than the limit values of 0.5 - 0.8 mg KOH/g.

Multi-element analysis

The presence of metals in the biodiesel is undesirable, as this may cause various problems, including promoting biodiesel degradation (Schober and Mittelbach, 2005), corrosion of engine, operability problems, environmental pollution and subsequent negative effects on human health. The elements whose quantities in biodiesel need

to be controlled are sodium (Na) and potassium (K), which originate from the catalyst in biodiesel production, and phosphorus (P), which originate from the raw materials. The maximum permissible concentrations of Na and K in biodiesel are 5 mg kg⁻¹, while P is 10 mg kg⁻¹ (Korn et al., 2007). Apart from these elements, the levels of other elements such as magnesium (Mg), calcium (Ca), copper (Cu), iron (Fe), and zinc (Zn) should also be regulated.

The metals in biodiesel can catalyze oxidation, especially highly-reactive species such as copper and zinc (McCormick et al., 2005). However the effect of presence of metals on oxidative stability is relatively less prominent compared to the effect exerted by presence of double-bonds (Knothe and Dunn, 2003). Burning of biodiesel containing lead causes lead deposition in the motor parts, which lead to engine corrosion.

Metals such as potassium, sodium, magnesium, and calcium present in biodiesel lead to injector, fuel pump, piston and ring wear, engine deposits, and filter plugging (McCormick et al., 2005). Other metals such as copper and iron strongly increase the rate of gum formation, as nickel and zinc, but to a lesser extent (Teixeira et al., 2007). The release of poisonous heavy metals such as lead to environment from vehicle is the main source of lead in human blood.

It entered the human body through the inhalation of air or food chain. Lead is toxic and can cause various problems in engine (Goyer, 1993). As a result, the concentration of lead in fuels should be controlled within a safe level. Therefore these biodiesels are safe to be used. The metals present in the biodiesel can be removed by using chelators such as citric acid in order to attain desired concentrations. The chelators would chelate the metals so that it can be removed by filtration (Gerpen et al., 2004).

Conclusion

Based on the study of the alkaline transesterification of waste canola oil and few parameters affecting its efficiency, the following conclusions can be made:

- i) The optimal combination which can give highest production of biodiesel was transesterification carried out for 2 h by using methanol to oil molar ratio of 1:1 catalyzed by 0.5% sodium hydroxide.
- ii) The production of biodiesel employing methanol to oil molar ratio of 1:1 was feasible in terms of biodiesel yield since the 6 times reduction of alcohol volume used only resulted in the 2 times decrease of biodiesel yield.
- iii) In terms of biodiesel quality, the biodiesels produced generally standard viscosity and a little higher TAN values, and standard metal content except Sn and Ag contents. Therefore produced biodiesel can be suitable to use as fuel in diesel engine.

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