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BIODIESEL PRODUCTION FROM WASTE SUNFLOWER COOKING OIL AS AN ENVIRONMENTAL RECYCLING PROCESS AND RENEWABLE ENERGY

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Abstract

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Comparison of the optimum conditions of alkaline-catalyzed transesterification process for biodiesel production from pure sunflower cooking oil (PSCO) and waste sunflower cooking oil (WSCO) through transesterification process using alkaline catalysts was studied. To obtain a high quality biodiesel fuel that comply the specification of standard methods (ASTM D 6751 & EN 14214), some important variables such as volumetric ratio, types of reactants and catalytic activities were selected. The highest approximately 99.5% biodiesel yield acquired under optimum conditions of 1:6 volumetric oil-to-methanol ratio, 1% KOH catalyst at 40єC reaction temperature and 320 rpm stirring speed. Result showed that the biodiesel production from PSCO and WSCO exhibited no considerable differences. The research demonstrated that biodiesel obtained under optimum conditions from PSCO & WSCO was of good quality and could be used as a diesel fuel which considered as renewable energy and environmental recycling process from waste oil after frying.

Key words: Biodiesel, Transesterification, Sunflower oil, Waste cooking oil

Introduction

Biodiesel is advised for use as an alternative fuel for conventional petroleum-based diesel chiefly because it is a renewable, domestic resource with an environmentally friendly emission profile and is readily biodegradable (Zhang et al., 2003) . The amount of greenhouse gas emissions, generating energy from renewable resources is being possessed a high priority gradually to decrease both over-reliance on imported fossil fuels (Blanco-Canqui and Lal, 2007). In accordance with the US Standard Specification for Biodiesel (ASTM 6751), biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats (Vicente et al., 2007) . It has similar physico-chemical properties of conventional fossil fuel and can consequently, entirely or partially substitute fossil diesel fuel in compression ignition engines (Pasqualinoa, 2006).

The high viscosity and poor volatility are the major limitations of vegetable oils for their utilization s fuel in diesel engines. Because high viscous vegetable oils deteriorate the atomization, evaporation and air-fuel mixture formation characteristics leading to improper

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combustion and higher smoke emission. Moreover this high viscosity generates operational problems like difficulty in engine starting, unreliable ignition and deterioration in thermal efficiency. Converting to biodiesel is one of the options to reduce the viscosity of vegetable oils (Paugazhabadivu et al., 2005).

The current feed stocks of production of biodiesel or mono-alkyl ester are vegetable oil, animal ft and micro algal oil. In the midst of them, vegetable oil is currently being used as a sustainable commercial feedstock. Among more than 350 identified oil-bearing crops, only sunflower, safflower, soybean, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines (Demirbas, 2006). Sunflower (*Helianthus annus*) is one of the leading oilseed crops cultivated for the production of oil mainly used for human consumption and can also been considered as an important crop for biodiesel production (Niotou et al., 2008). Among them, vegetable oils are now being used as a sustainable commercial feedstock. Paradoxically, the higher cost of solid vegetable oil affects the production cost of biodiesel. However, large amount of waste cooking oil is produced from restaurants, eatering establishments and food industries, etc, every year. Having probability of contaminating environmental water, discarding of this waste cooking oil can be challenging (Hubera et al., 2007). One possible solution and simultaneously generate economical profit.

The most studied process to obtain biodiesel from feed stocks is transesterification of triglycerides with low molecular weight alcohols catalyzed by homogenous catalysts (Aranda et al., 2007). Apply of base catalysts may cause problems due to the side saponification reaction which creates soap and consumes catalyst. These problems occur because of higher content of fatty acids and water in used cooking oil (Issariyakul et al., 2007). Notwithstanding these drawbacks, transesterification process using base catalyst has some benefits like low production cost, faster reaction speed and mild reaction conditions (Aranda et al., 2007). Recent researches have concentrated on heterogeneous catalysts for decrease of the processing costs related to homogeneous calcium carbonate rock, EST-4 and EST-1 catalysts and Na/NaOH/г-Al_2O_3 (Trakarnpruk and Porntangjitlikit, 2008).

The first objective of this study aims to compare the optimum conditions of fatty acid methyl ester (FAME) or biodiesel production from pure and waste sunflower oil through transesterification process using alkaline catalyst. In this work, the quality of biodiesel from both solid and used edible palm oil has been also analyzed and compared.

Materials and Methods

Materials

Pure Sunflower cooking oil (PSCO) was purchased from local grocery shop. The waste cooking sunflower oil (WSCO) was obtained from restaurants next to University of Malaya campus. To remove impurities the WSCOs were filtered under vacuum pressure (11 bar) Potassium hydroxide, sodium hydroxide, magnesium sulfate anhydrous, methanol, ethanol was purchased from SYSTERM/ Classic Chemicals Sdn Bhd, Malaysia.

Transesterification reaction

The transesterification reaction performed at different volumetric ratio of oil to methanol, varying from 4:1, 3:1, 1:3, 1:4 and 1:6 at 40єC and 350 rpm. The reaction time was kept constant at 3 hours for all experiments. Two types of catalysts have been used – NaOH and KOH at a range of 0.5 -2.0% wt. of oil. After transesterification reaction the biodiesel was separated from glycerol using separating funnel and finally washed with 5% water followed by magnesium sulfate anhydrous to remove the water. Several basic variables, namely, catalyst type and concentration, methanol to oil ratio and reaction temperature of transesterification were investigated as they play a significant difference in biodiesel produced (Ma and Hanna, 1999).

Biodiesel analysis

Several parameters have been analyzed by specific method to verify whether the products fulfill the specification of standard methods (ASTM D 6751 & EN 14214). An atomic emission (AE) specification multi-element oil analyzer (VIOA) was used to determine the group I metals (Na, K), group II metals (Ca, Mg) and phosphorus content. Viscosity was measured in mml/s at 40є C using houillon viscometer (France) with ISL software version 2.1. Total value was measured using titration method.

Result and Discussion

Two important properties of PSCO & WSCO are compiled in Table 1. The acid values expose the low amount of free fatty acids (FFA) in both types of oils. In contrast, WSCO has significantly high viscosity than PSCO. Both oils can be utilized as fuel in diesel engines, but the main barrier to employ the oil as fuel is its high viscosity (Table 1) which creates troubles in atomization of the fuel spray and function of the fuel injectors. The results also show that viscosity and acid value of WSCO are significantly higher than pure one. In two recent studies (Turkan and Kalay, 2006; Oliveira and Rosa, 2006), it has been found that almost 90% of the total fatty acids of commercial sunflower oil are composed of two double bonds containing oleic acids. Oliveira and Rosa (2006) have reported that the percentages of these two free fatty acids in sunflower oil are 23.9% and 66.1% consecutively.

Table 1
Determination of acid value and viscosity of PSCO and WSCO

Properties	PSCO	WSCO
Acid value, mg KOH/g oil	0.1	1.6
Viscosity, mm²/s at 40ºC	5.8	9.5

Effect of volumetric ratio

Methanol, ethanol, propanol, butanol and amyl alcohol can be used in the transesterification reaction, amongst these alcohols methanol is applied more frequently as its cost is low and it is physically and chemically advantageous (polar and shortest chain alcohol) over the other alcohols (Demirbas, 2005). According to Demirbas (2007), in contrast, ethanol is also preferred alcohol for using in the transesterification process compared to methanol since it is derived from agricultural products and is renewable and biologically less offensive in the environment. The effect of volumetric ratio of methanol and ethanol to oil was studied. Results exhibit that highest biodiesel yield is nearly 99.5% at 1:6 oil/methanol (Figures 1 and 2). In comparison, biodiesel yield using methanol continuously increases with the raise of methanol molar ratio. Conversely, in Figure 2, despite a decrease in 3:1 oil/ethanol (83% biodiesel yield) the trend shows similarity with methanol/oil molar ratio yield. In this case yield at 3:1 oil/ethanol is lower than yield at 4:1 oil/ethanol most probably as a result of emulsification during separating and washing process. Notwithstanding this exception, in overall results provide evidence that increase of both type of alcohol ratio improve the yield of biodiesel. The further study such as effect of catalyst was performed applying methanol as yield

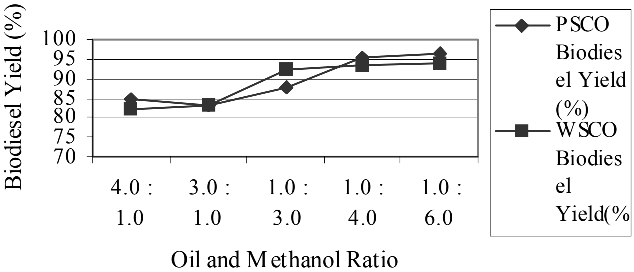

Fig. 1. Effect of volumetic ratio of sunflower oil to methanol (MeOH) on biodiesel yield (Reaction conditions: temperature = 40°C, catalyst KOH = 1 wt. %, RPM = 350, reaction time = 180 min)

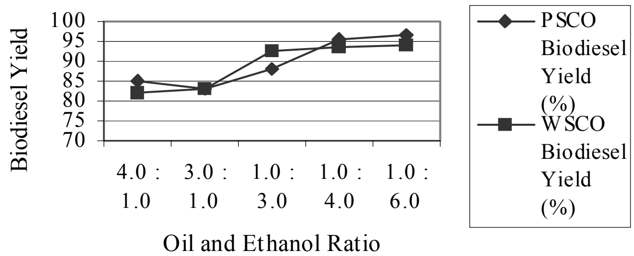

Fig. 2. Effect of volumetric ratio of sunflower oil to ethanol (EtOH) on biodiesel yield (Reaction conditions: temperature = 40°C, catalyst KOH = 1 wt. %, RPM = 350, reaction time = 180 min)

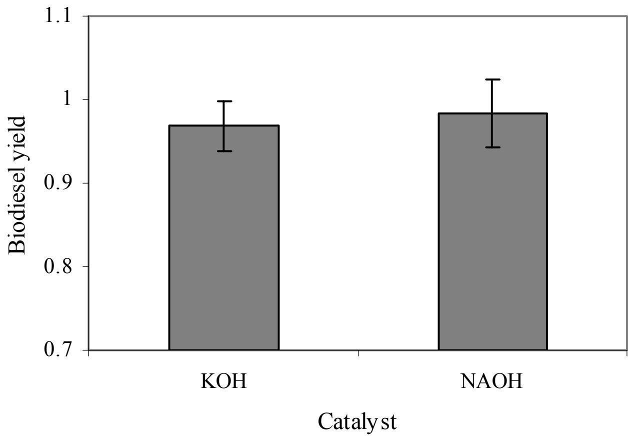

Fig. 3. Effect of different catalysts on ester yield (Reaction conditions: temperature = 40°C, oil: methanol = 1:6, catalyst = KOH, RPM = 350, reaction time = 120 min). Vertical bars indicate SE (n = 3)

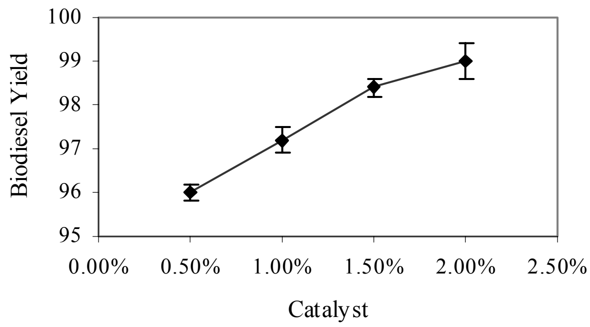

Fig. 4. Effect of catalyst concentration (Reaction conditions: temperature = 40°C, oil: methanol = 1:6, catalyst = KOH, RPM = 350, reaction time = 120 min). Vertical bars indicate SE (n = 3)

using this alcohol (oil: methanol = 1:6) has achieved the highest percentage.

Previous study (Knothe et al., 1996) shows that production of biodiesel from waste frying vegetable oil used catalyst potassium hydroxide with the reaction carried out at ambient pressure and temperature, the conversion rate of 80 to 90% were achieved and in two steps the ester yield were 99%. From Figure 3, it can be seen that highest biodiesel yield (98.4%) has been achieved using NaOH at 40^0C. Paradoxically, during separating washing of biodiesel the emulsification phenomena have been observed. Although the basic catalysts are the most common as the process using them is quicker and the reaction conditions are moderated (Freedman. et al., 1984), these catalysts have some drawbacks: they must be neutralized giving rise to wastewaters and can not be reutilized, they create difficulties to separate the methyl esters (biodiesel) by formation of stable emulsions, the byproduct glycerol is obtained as an aqueous solution of comparatively low purity and the reaction becomes very sensitive to the presence of water and free fatty acids (Arzamendia et al., 2007). In this study it has been observed that this emulsification can be alleviated reducing shaking intensity during washing and separation of biodiesel from glycerol. In spite of higher yield, using NaOH causes more emulsion than KOH and makes complicated to separate biodiesel from glycerin. For this reason, KOH has been screened as a catalyst to study the effect of catalyst concentration and above discussed effect of molar ratio on biodiesel yield. In Figure 4, The biodiesel yield shows a continuous rise from about 96% to 99% when the catalyst KOH concentration increases from 0.5% wt to 2.0% wt, but the yield production is not significant.

Analyzing biodiesel achieved under optimum condition

As above conferred, both pure and waste cooking sunflower oil can be consumed as fuel in diesel engines, but the main obstacle to use the oil as fuel is its high viscosity (consecutively 5.8 mmI/s and 9.5 mmI/s at 40єC; Tables 1 and 2) which create problems in atomization of the fuel spray and operation of the fuel injectors. The obtained free fatty acid alcohol esters or biodiesel from both oil through transesterification process have lower viscosity of 4.1 – 4.5 mmI/s at 40єC (Table 2).

The biodiesel samples produced under optimum condition of 1:6 volumetric oil-to-methanol molar ratio, 1% KOH catalyst and 40єC reaction temperature were analyzed concerning some significant specifications as fuel in diesel engine. These results are shown in Table 2. Most of these properties fulfill the restrictions of biodiesel standard in ASTM D 6751 and EN 14214. In contrast biodiesel obtained from WSCO has slightly higher acid value (0.44 mg KOH/

Table 2
Characteristics of produced biodiesels in contrast with standard value

Property	Unit	Standard method	Value according to standard method	Biodiesel (PSCO)	Biodiesel (WSCO)
Viscosity	mm²/s at 40ºC	ASTMD 6751	1.9–6.0	5.8	9.5
Acid number	mgKOH/g oil	ASTMD 6751	0.50 max	0.1	0.44
Group ı metals(Na+ K)	mg/kg	EN 14214	5.0 max	2.5	2.8
Group ıı metals(Ca+ Mg)	mg/kg	EN 14214	5.0 max	3.1	2.6
Phosphorus content	mg/kg	EN 14214	10.0 max	5.7	3.1

g oil) than biodiesel produced from PSCO (0.1 mg KOH/g oil). Additionally two types of the biodiesel show virtually similar viscosity. Viscosity is the most essential property of diesel fuel because it influences the wear rate of engine components (Kalam and Madjuki, 2002). Additionally, it can be observed from Table 2 that PSCO biodiesel has considerably higher phosphorus concentration than the other one and none of these fulfills requirement of the standard method specification as well.

Conclusion

The optimum conditions for biodiesel production from WSCO & PSCO have been studied. Result shows optimal condition of sunflower oil biodiesel productions are 1:6 volumetric oil-to-methanol molar ratio, 1 wt. %KOH at 40^0C reaction temperature. This study has provided evidence that waste cooking sunflower oil may be employed as a substantial source of biodiesel as fuel in diesel engines. Because, the produced biodiesel is of good quality within the array of standard method specifications and the production yield is apt. up to approximately 99% under optimum conditions. Moreover, this research represented that the production of biodiesel from PSCO & WSCO has no significant differences. Advance research is ongoing to reduce the production cost by developing a method to decrease the emulsification during base-catalytic transesterification and aqueous-washing of the product and readily recovery of glycerin byproduct. Biodiesel from used cooking sunflower oil could be used as a diesel fuel which considered as renewable energy and environmental recycling process from waste oil after frying.

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