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Biodiesel fuel production from soybean oil waste as agricultural bio-resource

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Abstract

The study was conducted to investigate the optimum conditions for biodiesel formation from pure (virgin) soybean cooking oil (PSCO) and waste soybean cooking oil (WSCO) coming after alkaline transesterification process in combination with methanol, ethanol and 1-butanol. Some important variables such as volumetric ratio, types of reactants and catalytic activities were selected to obtain a high quality biodiesel fuel with the specification of American Society for Testing and Materials (ASTM D 6751) and European Norm (EN 14214). The highest biodiesel yield (99.6%) was obtained under optimum conditions of 1:6 volumetric oil-to-methanol weight ratio, 1% KOH catalyst at 40º C reaction temperature and 320 rpm stirring speed. The results showed that biodiesel yield from PSCO and WSCO exhibited no considerable differences. But there was 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 a bit difference in viscosity, acid value and chemical elements (Ca, Na, P, Fe, Cu, Pb, Mg etc.) between PSCO and WSCO. The research investigated that biodiesel obtained under optimum conditions from PSCO and WSCO was of good quality and could be used as a diesel fuel which considered as potential use of waste cooking oil.

Keywords: Biodiesel, butanol, corn oil, transesterification, waste oil.

Abbreviation: PSCO: Pure soybean cooking oil, WSCO: Waste soybean cooking oil, EN: European Norm, ASTM: American Society for Testing and Materials

Introduction

New alternative and renewable fuel (biodiesel, bioethanol) has received a considerable attention recently due to the occurrence of oil depletion, global warming and the greenhouse effect. Biodiesel is a good alternative energy which is one of the most promising energy sources (Demirbas, 2005). 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 is non-toxic, biodegradeable, produced from renewable sources and contributes a minimal amount of net green house gases, such as CO_2 and NOx emissions and sulfur to the atmosphere (Bouaida et al., 2007). 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). The high viscosity and poor volatility are the major limitations of vegetable oils for their utilization as fuel in diesel engines. Because high viscous vegetable oils deteriorate the atomization, evaporation and air-fuel mixture formation characteristics leading to improper 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). Oilseed crop (like palm oil, sunflower) has been considered as biodiesel production because of providing a positive energy return compared with the energy used to produce the fuel (Hossain, et al., 2009a; Kallivroussis et al., 2002). The current feedstocks of biodiesel production or mono-alkyl ester are vegetable oil, animal fat 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, soybean, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines (Demirbas and Kara, 2006). The higher cost of solid vegetable oil affects the production cost of biodiesel (Niotou et al., 2008). However, large amount of waste cooking oil was produced from restaurants, catering establishments and food industries every year. Having probability of contaminating environmental water, discarding of this waste cooking oil can be challenged (Hubera et al., 2007). Application of base catalyst may cause problem due to the side saponification reaction which creates soap and consumes catalyst in palm oil and sunflower (Hossain, et al., 2009b). These problems occur because of higher content of fatty acids and water in used cooking oil (Hossain et al., 2009b). Recent researches have concentrated on heterogeneous catalysts for increasing of biodiesel yield (Hossain et al., 2008) and decreasing of the processing costs related to homogeneous catalysts (Na/NaOH/KOH/γ-Al_2O_3) (Trakarnpruk and Pornta- ngjitlikit, 2008). The objectives of this study were to compare the optimum conditions of fatty acid methyl ester (FAME) or biodiesel production and potential use of waste corn cooking

Table 1. Measurement of acid value and viscosity of pure soybean cooking oil (PSCO) and waste soybean cooking oil (WSCO). SE ± (n =3).

Oil type	Acid value of FAME (mgKOH/g oil)	Viscosity of FAME (cSt at 40°C)
PSCO	0.43±0.01	4.14±0.05
WSCO	0.46±0.02	4.38±0.04

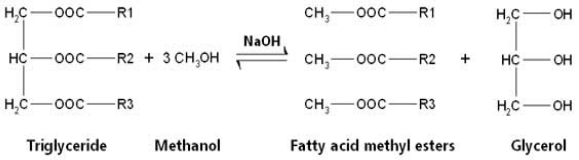
oil compared to virgin oil through transesterification process using alkaline catalyst. In addition, toanalyze and compare the quality (viscosity and acid number) of biodiesel from both pure and waste cooking soybean oils.

Materials and methods

Materials

Pure (virgin) soybean cooking oil (PSCO) was purchased from local UOA shopping Mall, Kuala Lumpur, Malaysia. The waste cooking soybean oil (WSCO) was obtained from restaurants at the University of Malaya campus. The WSCO was filtered to remove impurities under vacuum pump, pressure (160psi/11bar) Potassium hydroxide, sodium hydroxide, magnesium sulfate anhydrous, methanol, ethanol were purchased from Biochem Lab. Sdn Bhd, Kuala Lumpur, Malaysia.

Transesterification reaction



Transesterification reaction was occurred using different types of alcohol performed at volumetic ratio 1:6 of oil to methanol, oil to ethanol and oil to 1-butanol using KOH catalyst. Transesterification reaction took place using methanol and ethanol and butanol at different volumetric ratio of oil to methanol, ranging from 4:1, 3:1, 1:3, 1:4 and 1:6 at 40º C and 320 rpm. The reaction time was maintained 3 hours constantly for all experiments. Two types of catalysts, NaOH and KOH have been used to come about the transesterification reaction at 1.0% (w/v) concentration having volumetric ratio 1:6 of oil to methanol. The KOH has been used at a concentration of 0.5, 1.0, 1.5, and 2.0 % (w/v) of oil having volumetric ratio 1:6 of oil to methanol. 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. Catalyst type and concentration, methanol to oil ratio and reaction temperature of transesterification were investigated as they played a significantly difference in biodiesel produced (Ma and Hanna, 1999).

Biodiesel analysis

Parameters have been analyzed by specific method to verify whether the products fulfill the American Standard of Biodiesel Testing Methods (ASTM D 6751) and European Norm for Biodiesel (EN 14214). Viscosity was determined in Cst at 40º C using houillon viscometer (France) with ISL software version 2.1. Total acid value was measured using titration method. An atomic emission (AE) specification multi-element oil analyzer (MOA) was used to determine the Na, K, Ca, Mg, P, Fe, Cr, Pb, Ag, Sn, Al, Zn and Si content. Data were analyzed statistically. Standard error (SE) and least significant difference (LSD) test were employed.

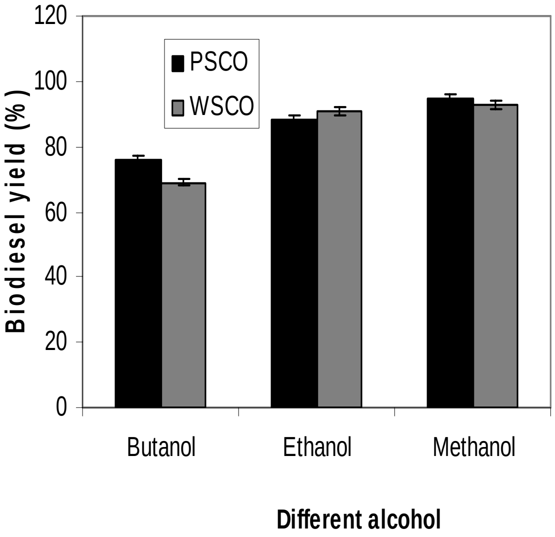


Fig 1. Biodiesel yield in different alcohol types. Biodiesel yield (Reaction conditions: temperature = 40°C, %, RPM = 320, reaction time = 180 minutes).

Result and discussion

Effect of different alcohols

The effects of different alcohols like methanol, ethanol and 1-butanol in transesterification process were observed. The result investigated that transesterification of virgin soybean cooking oil and waste soybean cooking oil using methanol gave the highest biodiesel yield (Fig.1). The biodiesel yield increased in the order of 1-butanol < ethanol < methanol (Fig. 1).

Properties of pure and waste palm cooking oil

Viscosity and acid value of PSCO & WSCO were shown in Table 1. The acid values exposed on the low amount of free fatty acids (FFA) in both types of oils. The results also investigated that viscosity was higher in WSCO than in PSCO. However, acid value was lower in PSCO than in WSCO. It had been found that almost 90% of the total fatty acids of commercial sunflower oil were composed of two double bonds containing oleic acids (Turkan and Kalay, 2006; Oliveira and Rosa, 2006). Oliveira and Rosa (2006) reported that the perce-

Table 2. Characteristics of biodiesel with standard methods (ASTM D 6751 and EN 14214).

Property of FAME	Unit	Standard Method[a]	Value according to standard method
Viscosity	cSt at 40°C	ASTM D 6751	1.9 - 6.0
Acid number	mgKOH/g oil	ASTM D 6751	0.50 max
Group I metals (Na^+ K)	mg/l	EN 14214	5.0 max
Group II metals (Ca^+ Mg)	mg/l	EN 14214	5.0 max
Phosphorus content	mg/l	EN 14214	10.0 max

ASTM: American Standard for Biodiesel Testing Method, EN: European Norm

ntages of these two free fatty acids in sunflower oil were 23.9% and 66.1% consecutively. Table 2 shows standard value of biodiesel given by ASTM D 6751 & EN 14214 methods.

Effect of volumetric ratio

The effect of volumetric ratio of methanol and ethanol to oil was investigated. The results exhibited that the highest biodiesel yield was nearly 99.5% at 1:6 oil/methanol (Fig. 2) and 98.0% at 1:6 oil/ethanol (Fig. 3). In comparison, biodiesel yield using methanol continuously increased with the raise of methanol volumetric ratio. In figure 3 the trend showed similarity with methanol/oil to ethanol/oil volumetric ratio yield. The yield was higher at 1:6 oil/methanol and oil/ethanol than other ratios (4:1, 3:1, 1:3 and 1:4). It might be due to the increase of methanol or ethanol volume in the transesterification reaction (Fig. 2 and 3). Notwithstanding, this exception in overall results, provided the evidence that increase of both types of alcohol ratios improved the yield of biodiesel. The further study such as effect of catalysts (KOH and NaOH) was performed applying methanol. By using this alcohol (oil: methanol = 1:6) the highest percentage of yield had achieved in PSCO using KOH and NaOH catalysts (Fig. 4). It has been observed that after the increase of a certain concentration of catalyst (KOH) biodiesel yield decreased (Fig. 5). Methanol, ethanol, propanol, butanol and amyl alcohol could be used in the transesterification reaction, amongst these alcohols methanol was applied more frequently as its cost was low and it was physically and chemically advantageous (polar and shortest chain alcohol) over the other alcohols (Demirbas, 2005). According to Demirbas (2007), in contrast, ethanol was also preferred alcohol for using in the transesterification process compared to methanol since it was derived from agricultural products and was renewable and biologically less offensive in the environment. Knothe et al., (1996) reported that production of biodiesel from waste frying vegetable oil using potassium hydroxide catalyst with the reaction carried out at ambient pressure and temperature, the conversion rate of 80 to 90% was achieved and the ester yield was 99% (Hossain et al., 2009a). It can be seen that the highest biodiesel yield (99.5%) has been achieved using KOH at 40^0C (Fig. 4). In spite of higher yield, using KOH caused more emulsion than NaOH and made 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 volumetric ratio on biodiesel yield. The biodiesel yield showed a little increase from 0.5-1.5% and decreased from 2.0% wt but the yield production was not significant (Fig. 4). During separation of biodiesel washing the emulsification phenomena have been observed slightly. The basic catalysts were the most common as the process using the

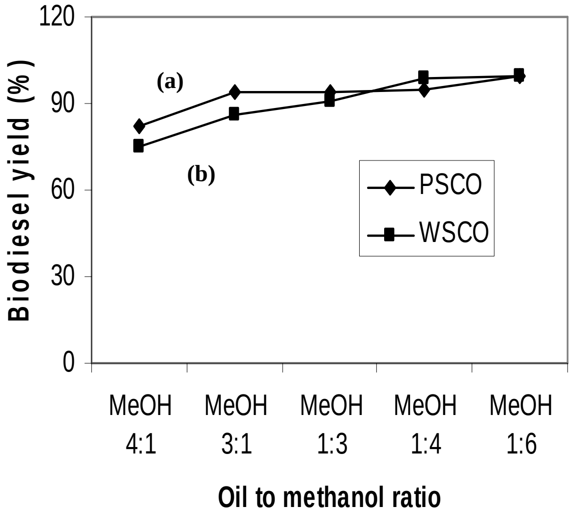


Fig 2. Effect of volumetic ratio of oil to methanol (MeOH) on biodiesel yield (Reaction conditions: temperature = 40°C, catalyst KOH = 1 wt. %, RPM = 320, reaction time = 180 minutes). Different letters (a, b) showed difference at 5% level of significant by Least significant difference (LSD) test.

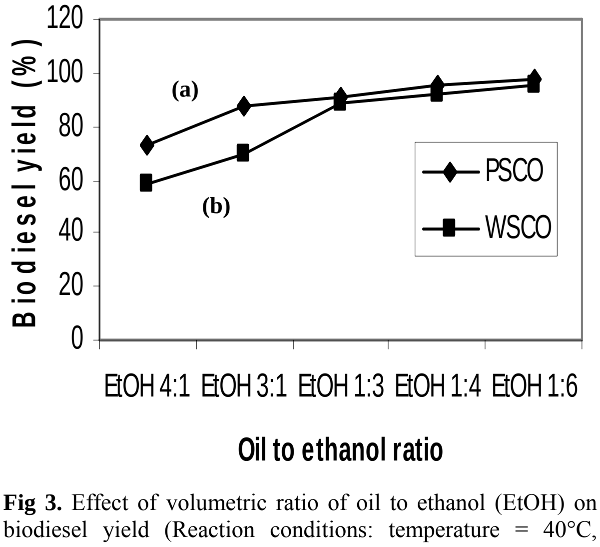


Fig 3. Effect of volumetric ratio of oil to ethanol (EtOH) on biodiesel yield (Reaction conditions: temperature = 40°C, catalyst KOH = 1 wt. %, RPM = 320, reaction time = 180 minutes). Different letters (a, b) showed difference at 5% level of significant by Least significant difference (LSD) test.

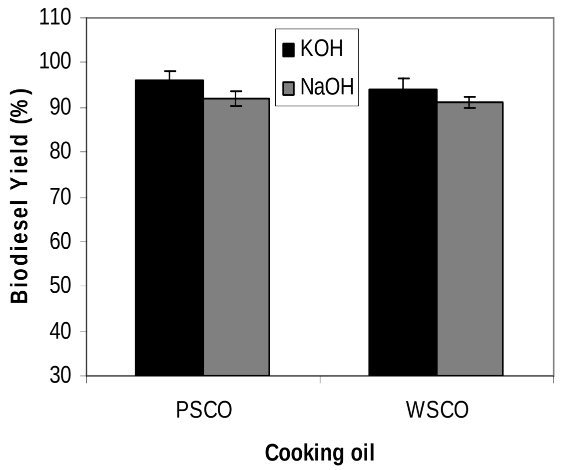


Fig 4. Effect of different catalysts on ester yield (Reaction conditions: temperature = 40°C, oil: methanol = 1:6, catalyst = KOH, RPM = 320, reaction time = 180 minutes). Vertical bars indicate SE (n = 3).

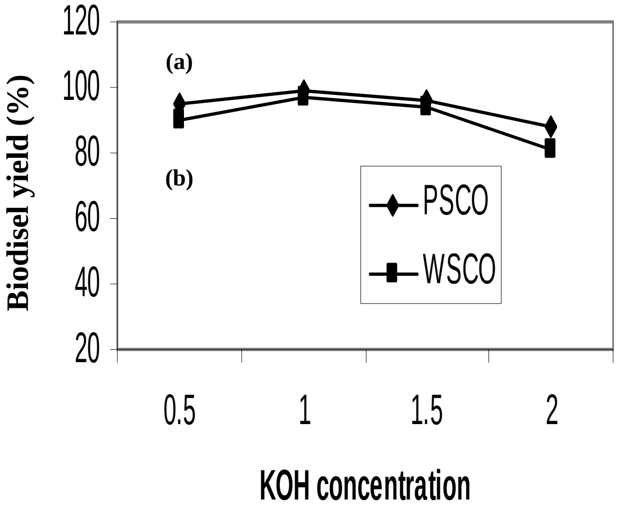


Fig 5. Effect of catalyst concentration (Reaction conditions: temperature = 40°C, oil: methanol = 1:6, catalyst = KOH, RPM = 320, reaction time = 180 minutes). Different letters (a, b) showed difference at 5% level of significant by Least significant difference (LSD) test

reaction conditions (Freedman et al., 1984). It has been created difficulties to separate the methyl esters (biodiesel) by formation of stable emulsions in the study. These catalysts have little drawback, they could be neutralized rising to waste water and could not be reutilized. Hossain el al., (2009b) also found bit emulsion in biodiesel produced by Sunflower oil. Arzamendia et al., (2007) reported the same result that the byproduct (glycerol) was obtained as an aqueous solution of comparatively low purity and the reaction became very sensitive to the presence of water and free fatty acids. In the study, it has been observed that this emulsification could be alleviated reducing shaking intensity during washing and separation of biodiesel from glycerol.

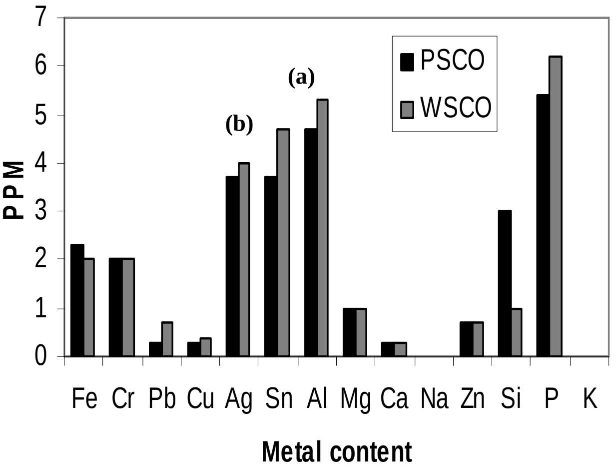


Fig 6. Metal content of biodiesel produced under optimum condition in contrast with standard value. Group I metals (Na $^{+}$ K), Standard method, EN 14214 (5.0mg/kg max.)Group II metals (Ca $^{+}$ Mg), Standard method, EN 14214 (5.0mg/kg max.), P content Standard method, EN 14214 (10.0mg/kg max.). Trace amount or no interfere of Zn, Cu, Mn, Fe, CO, Pb,Cr metal. Standard method, EN 14214. Different letters (a, b) showed difference at 5% level of significant by Least significant difference (LSD) test.

Analyzing biodiesel achieved under optimum condition

The obtained free fatty acid alcohol esters or biodiesels from both oil applying transesterification process have lower viscosity of 4.1–4.5cst at 40º C (Table 2). As above discussion, both PSCO and WSCO could be consumed as fuel in diesel engines, but the main obstacle to use the oil as fuel is its high viscosity which creates problems in atomization of the fuel spray and operation of the fuel injectors. However, results showed better performance in this research. The biodiesel samples produced maintaining optimum condition of 1:6 volumetric oil-to-methanol volumetric ratio, 1% KOH catalyst and 40º C reaction temperature were analyzed concerning some significant specifications as fuel in diesel engine. These results were shown in Fig. 4 and 5. Most of these properties fulfilled the restrictions of biodiesel standard in ASTM D 6751 and EN 14214. In contrast biodiesel obtained from WSCO has slightly higher acid value (0.46 mg KOH/g oil) than biodiesel produced from PCCO (0.43 mg KOH/g oil). Additionally two types of the biodiesel showed virtually similar viscosity. Viscosity is the most essential property of diesel fuel because it influences the wear rate of engine components (Kalam and Masjuki, 2002). Additionally, it can be observed from Fig. 6 that biodiesel from WSCO had considerably lower Fe, Cu, Pb, Ca, Na, K concentration than PSCO (Fig. 6). 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 & EN 14214 methods).

Conclusion

Optimal conditions of soybean oil biodiesel produced were 1:6 oil-to-methanol volumetric ratio, 1% wt KOH at 40^0C reaction temperature. The study provided evidence that waste cooking soybean oil might be employed as a substantial source of biodiesel as fuel in diesel engines. Because, the produced biodiesel was of good quality within the array of standard method specifications and the production yield was up to approximately 99.6% under optimum conditions. Moreover, this research indicated that the production of biodiesel from PSCO & WSCO had a bit significant differences and also the research highlighted that waste cooking oil could be used potentially by following this innovation.

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