

Comparative Biodiesel Production Potential of Food Waste Oils as Renewable Energy Source

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The present study aimed at the production of biodiesel from used soybean, sunflower and canola cooking oil. These oils are used in food processing industry and at retails for deep frying. Waste cooking oil,due to its readily-availability and cost-effectiveness is considered as the most appropriate candidate for the production of biodiesel. Lipase mediated transestrification for the production of fatty acid methyl ester (FAME) of waste cooking oils needs optimization of some important variable such as type of alcohol, temperature, reaction time and oil to alcohol ratio. The best combination for maximum production of biodiesel through transesterification, was achieved at reaction temperature 50 °C, by using methanol to oil ratio of 1:6 and optimal reaction time of 2 h. The biodiesel conversions from soybean (93 %), sunflower (90 %) and canola (57.5 %) were obtained when oil to alcohol ratio was 1:6. The FT-IR spectroscopy was used to assess biodiesel composition.

Keywords: Biodiesel, Waste cooking oil, Transestrification, FTIR.

INTRODUCTION

The expected depletion of natural energy resources within a century has compelled to seek renewable energy sources. In recent time, bio-energy resources, including biodiesel has attracted globally attention due to increasing demand and environmental concerns^{1,2}. Burning of fossil fuel causes numerous ecological problems including global warming, air pollution, acid precipitation, ozone depletion, forest destruction, and emission of radioactive substances³. For the development of alternative energy sources environmental issue is driving force^{4,5}. Biodiesel is one of the most well-known renewable energy resources, produced from transesterification of triacylglycerols (TAG), with short chain alcohol yielding monoalkyl esters [fatty acid methyl esters (FAMEs) and fatty acid ethyl esters (FAEEs)] of long-chain fatty acids and glycerol^{6,7}.

Transesterification of waste oils can be carried out chemically or enzymatically⁸. However, drawback of chemical methods has placed immense importance on development of alternate technologies such as lipase mediated transesterification for the production of fatty acid methyl ester⁹. Among more than 350 potential sources of unidentified oils the edible vegetable oils include cotton seed, ground nut, palm, rape seed, soybean, sunflower, peanut, coconut, *etc.* similarly non-edible sources include jatropha, pongamia, neem, rubber seed, mahua, silk cotton tree, jojoba and castor oil has been used as worldwide¹⁰⁻¹². Higher cost of vegetable oil affects the production cost of biodiesel¹³. However, every year large quantity of waste cooking oil is produced from food industries, restaurants and catering establishments. Recovering and disposal of this waste oils is challenging task. This non-recovery can potentially contaminate green waters and create other environmental problems¹⁴. The use of waste cooking oil as biodiesel feedstock reduces the cost of biodiesel production ¹⁵ since the feedstock costs constitutes approximately 70-95 % of the overall cost of biodiesel production¹⁶. Hence, the use of waste cooking oils and non-edible oils should be given higher priority over the edible oils as biodiesel feedstock.

The objective of this study was to compare some critical parameters and potential use of soybean, sunflower and canola waste oil for the lipase mediated biodiesel production. The variation in biodiesel composition depending on waste oil used.

EXPERIMENTAL

The soybean, sunflower and waste canola cooking oil were taken after being used in deep frying. Food residues were removed from the waste cooking oil using filter paper. This filtered waste cooking oils was then collected in a conical flask or bottle and used for the experiment. **Transesterification reaction:** Lipase (Novozyme, Denmark) as used for synthesis of fatty acid methyl ester. The solution was prepared by crushing and dissolving 0.2 g of the enzyme in 10 mL of 0.1 M Na-phosphate buffer (pH 7.0). For transesteri-fication reaction 7 mL of alcohol, 8 mL of hexane followed by 0.2 mL of 10 % lipase solution (pH 7) and 2 g of waste cooking oil were added into the individual 125 mL Erlenmeyer flask. This reaction mixture was incubated at 45 °C at 200 rpm for 5 h.

Biodiesel purification: After shaking the product was kept for 16 h to separate it into two clear phases: glycerol at the lower layer was drained out and crude esters at the upper layer were produced in a successful transestrification reaction. Glycerol was separated from reaction mixture by centrifugation at 6000 rpm for 15 min. Purification of biodiesel was carried out by washing with distilled water to remove impurities like unreacted alcohol, excess catalyst; soap and glycerol until it become clear. The final product was analyzed to determine its ester contents.

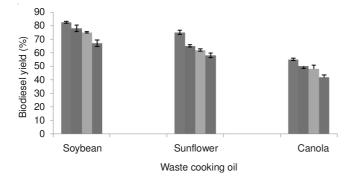
The % yield was determined using following formula:

$$Yield (\%) = \frac{Weight of biodiesel}{Weight of cooking oil} \times 100$$

Analysis of fatty acid methyl ester: Biodiesel samples were analyzed using attenuated total feflectance-Fourier transform infrared (ATR-FTIR) spectroscopy using NicoletTM380 FTIR spectrometer (equipped with standard KBr beam splitter) and deuterated triglycine sulfate detector along with the Smart ARKTM ATR accessory. FT-IR spectrum of the biodiesel was obtained between 4000-400 cm⁻¹. A minimum of 32 scans was signal-averaged with a resolution of 2 cm⁻¹.

RESULTS AND DISCUSSION

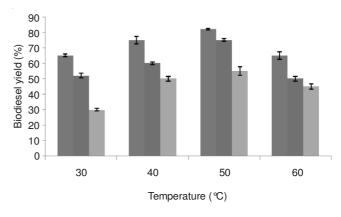
Effect of different alcohols on transesterification of waste oils: The effect of different alcohols like methanol, ethanol, *n*-propanol and *n*-butanol were analyzed for the transesterification of waste soybean, sunflower and canola cooking oil. Different types of alcohol decreased in the following order: methanol > ethanol > *n*-propanol > *n*-butanol (Fig. 1). Based on the result obtained, methanol gave the best fatty acid methyl ester using waste cooking oil. However, maximum biodiesel production (93 %) was obtained from the waste soya bean cooking oil.



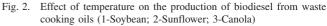
■ Methanol ■ Ethanol ■ *n*-Propanol ■ *n*-Butanol

Fig. 1. Effect of different alcohols (1-methanol, 2-ethanol, 3-propanol, 4butanol) on the production of biodiesel from waste cooking oils Methanol is a low molecular weight solvent thus simpler chemical structure of methanol is a probable reason for quicker, transesterification. On the contrary, butanol has complex chemical structure; therefore it is more difficult for transesterification to occur. The use of methanol as alkyl donor make purification easier, as the emulsion formed would easily breakdown. However reaction mixture formed is more stable in ethanolysis. This makes the manufacture, separation and purification of biodiesel difficult¹⁷. This result elucidate why the biodiesel yield from methanolysis was higher than ethanolysis in this study. All the biodiesel samples were also analyzed by ATR-FTIR spectroscopy.

Effect of temperature on transesterification of waste oils: The effect of temperature (30-60°C) on the transesterification of waste cooking oil was investigated. The fatty acid methyl ester contents were found to be directly proportional to the temperature up to 50 °C. Fig. 2 showed that increase in temperature led to the increase in fatty acid methyl ester contents. Further temperature increase declined the biodiesel production. As demonstrated by result in Fig. 2, maximum production of biodiesel was obtained with waste soybean oil at 50 °C. The reduction in yield of biodiesel above 50 °C can be attributed to the fact that higher than 50 °C accelerates the side saponification reaction of triglycerides. Temperature higher than 50 °C also affect the sensitivity of Lipase enzyme ultimately lead to the decrease in biodiesel yield¹⁸. Similarly, lower yield of biodiesel was obtained at 30 and 40 °C, because reaction remained incomplete at non-optimal temperature for lipase activity¹⁹. Moreover, rise in temperature causes the viscosity of oils to decrease and increased in the solubility of oil in methanol is responsible for enhanced biodiesel yield²⁰.



Soybean Sunflower Canola



Effect of reaction time on transesterification of oils: Reaction time is also factor that can affect the fatty acid methyl ester contents. To study the effect of reaction time transesterification reaction of waste cooking oil was carried out for 2, 4, 6 and 8 h. Reaction time of 2 h was found to be optimum for lipase-mediated biodiesel production for all the three waste oils (Fig. 3). The maximum production of the biodiesel was again obtained with soybean waste oil at 2 h reaction time. Further increase in the time period decreased the yield of biodiesel. The longer the reaction time, the more hydrolysis

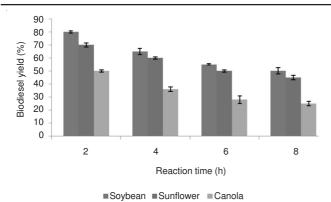
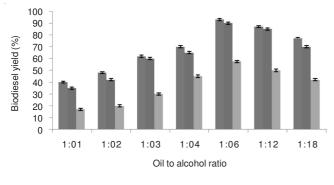


Fig. 3. Effect of stirring time on the production of biodiesel from waste cooking oils (1-Soybean; 2-Sunflower; 3-Canola).

of ester (reverse reaction of transesterification) occurs. It produces free fatty acid (FFA) and these free fatty acid result in the soap formation²¹, thus reducing yield of biodiesel. Hence, it can be concluded that the reaction time is also an important factor of product yield and increase in the reaction time lessen the product yield.

Effect of different oil to methanol ratio on the on the transesterification of oils: According to the stoichiometric equation of transesterification, 3 mol of alcohol would react with 1 mol of triglyceride to give 3 mol of fatty acid ester and 1 mol of glycerin¹⁹. But due to the variations in triglyceride (TAG) contents of waste cooking oils, the oil: alcohol ratio is need to optimize accordingly. For that reason, different waste cooking oil to alcohol ratios *i.e.* 1:1, 1:2, 1:3 1:4, 1:8, 1:12, 1:18, were examined (Fig. 4). The highest biodiesel yields (93, 90 and 57.5 %) for the soybean, sunflower and canola oil, respectively were obtained at 1:6 oil to methanol ratio.



Soybean Sunflower Canola

Fig. 4. Effect of oil to methanol ratio on the biodiesel production from waste cooking oils (1-Soybean; 2-Sunflower; 3-Canola).

Molar ratio higher than the stoichiometric value resulted in a greater reverse ester conversion²². Consequently, the reaction remained incomplete at the molar ratio less than 1:6. Moreover, increase of molar ratio requires longer time for the separation stage and raise process cost. Transestrification occur stepwise, triglycerides are primarily changed to diglycerides, then to monoglycerides and lastly to glycerol⁹. Reverse transestrification takes place in the presence of excess methanol, however formed monoglyceride increases the solubility of glycerol in produced biodiesel and thus leads to glycerolysis reaction²³. Saka and Kusdiana²⁴ reported maximum biodiesel production with a molar ratio of 1:42 of the rapeseed oil to methanol. However, any such molar ratio would raise the cost due to high use of solvent. Thus, it can be inferred that the present study suggests a more economical operation for biodiesel production.

FTIR analysis of all biodiesel samples obtained through transesterification of waste soybean, sunflower and canola oils at optimized conditions were also performed (Fig. 5). Biodiesel production was observed highest in waste soybean oil. FTIR is simple, more reproducible and accurate method for oil and biodiesel quantification. In mid-IR region, fatty acid methyl ester has several significant peaks with a strong infrared absorption around 1735-1750 cm⁻¹ due to the ester carbonyl bond peak of biodiesel²⁵. FTIR analysis of biodiesel samples of waste soybean, sunflower and canola oil at optimized conditions was also performed in present work (Fig. 5). The highest absorbance in this region was observed for the biodiesel samples obtained by transesterification of soybean waste oil and minimum values were revealed in the case of canola and these results are corresponding to the oil yield results.

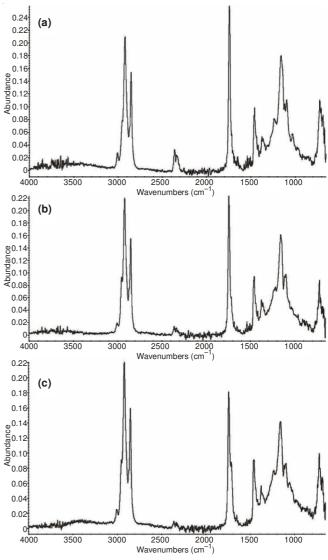


Fig. 5. FTIR analysis of fatty acid methyl ester produced by transesterification of soybean (a), sunflower (b) and canola (c)

Conclusion

It is concluded by the present study that optimal conditions of soybean, sunflower and canola waste cooking oil were 1:6 oil-to-methanol ratio, at 500 C reaction temperature, alcohol type methanol and reaction time 2 h. The biodiesel production potential of waste cooking oils on the basis of %yield was found to be in order of soybean> sunflower > canola *i.e.* 93, 90 and 57.5 %, respectively under optimized conditions. The study provided evidence that waste cooking oil might be employed as a potential source of biodiesel. Further research work is needed to study the effectiveness of such fuels in diesel engines.

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