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ASIAN JOURNAL OF SCIENCE AND TECHNOLOGY

ISSN: 0976-3376

Asian Journal of Science and Technology
Vol. 11, Issue, 03, pp.10831-10834, March, 2020

RESEARCH ARTICLE

WASTE COOKING OIL AS A VIABLE SOURCE OF BIODIESEL IN METROPOLITAN CITIES

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ARTICLE INFO

Article History:
Received 15th December, 2019
Received in revised form
29th January, 2020
Accepted 17th February, 2020
Published online 28th March, 2020

Key words:
Biodiesel, Waste Cooking Oil, Transesterification.

ABSTRACT

The development of a country is directly linked with its natural resources of energy. The fossil fuels are getting depleted and the environmental issues have energized the development of alternative energy sources. Biodiesel from non-edible oils play an important role in this aspect. Waste cooking oil is one of the alternative sources of biodiesel. The metropolitan cities like Bangalore have large number of restaurants and produce over 20,000 L of waste cooking oil every day. Biodiesel production has been carried out adopting a two stage process, involving acid esterification and alkali catalyzed transesterification. Transesterification was carried out using 1:6 oil to methanol molar ratio at 60 °C for 60 minutes. The density and viscosity of waste cooking oil reduced from 917.41 Kg/m^3 to 879.10 Kg/m^3 and 43.5 mm^2/s to 4.99 mm^2/s respectively by transesterification process. There was improvement in calorific value of oil from 32.5 MJ/kg to 34.2 MJ/kg of biodiesel.

Citation: ***Sushma, U S., Lokesh, H.B., Rajesh Kumar, K., Bheema Raju, V.*****, 2020.** "Waste cooking oil as a viable source of biodiesel in metropolitan cities", *Asian Journal of Science and Technology*, 11, (03), 10831-10834.

INTRODUCTION

The need for energy is increasing continuously, because of increase in industrialization and urbanisation. The basic sources of energy are petroleum, natural gas, coal, hydro, and nuclear. India is the third largest importer of crude oil after United States and China and continues to rely on imports considerably. In 2015, India imported 278 billion liters of crude oil. More than 72 % of the fuel requirement for transport sector is met out by diesel. Further, it is estimated that the average demand for transport fuels will rise from an estimated 134 billion liters in 2015 to 225 billion liters in 2026 (Aradhey, 2016). Biofuels are viewed as a means to provide a higher degree of national energy security in an environmentally friendly, cost-effective and sustainable manner. Biodiesel produced from vegetable oils or animal fat by transesterification process appears to become an alternative to diesel. When biodiesel is produced from refined edible oils, the cost of feedstock contributes to more than 70 % of the total cost of biodiesel.

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In India non- edible oils such as honge (*Pongamia pinnata*), neem (*Azadirachta indica*), mahua (*Madhuca indica*), jatropha (*Jatropha curcas*) and rubber (*Hevea brasiliensis*) are well known for biodiesel production (Kumar, 2015). The waste cooking oil may also be one of the resources for biodiesel production. The oil (lipids) is an integral part of frying. In frying, oil is heated in the presence of air and light at temperatures of 160-200 °C for a long period of time. For economical reasons, the same oil/fat is used many times or continuously. Generally, in public restaurants, frying is conducted in the same oil for several days; however, in household frying, fat is exchanged after several weeks. Physical changes observed in vegetable oil after frying are (i) an increase in the viscosity (ii) an increase in the specific heat, (iii) a change in the surface tension, (iv) a change in color, and (v) an increase in the tendency of fat to foam (Kulkarni, 2006). The studies conducted on frying oil suggest that, during frying basically three types of reactions occur: thermolytic, oxidative, and hydrolytic (Nawar, 1984; Mittelbach, 1999). As a combined result of all these chemical reactions, many undesirable compounds are formed during frying. Waste oil has many disposal problems like water and soil pollution, human health concern and disturbance to the aquatic ecosystem (Carlinia, 2014; Gopal, 2014).

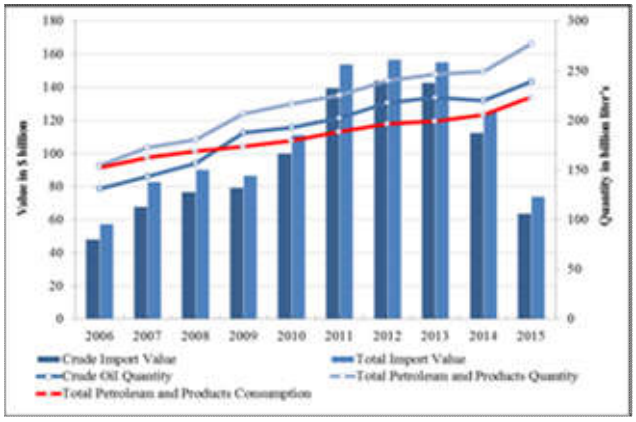

Table 1. Properties of waste cooking oil

Properties	Values
Acid value (mg KOH/g)	8.12
FFA (%)	4.6
Saponification value (mg KOH/g)	168
Iodine value (g I_2/100g)	67
Viscosity (mm^2/s)	43.5
Density ($kg/m^{3)}$	917.41
Calorific value (MJ/kg)	32.5

Biodiesel production from waste cooking oil may be one of the solutions for these problems.

MATERIALS AND METHODS

The waste cooking oil (WCO) was procured from Hot Chips stores at Yalahanka, Bengaluru. The WCO was filtered, heated to 110 °C to remove the moisture and used for biodiesel production.

Biochemical analysis of WCO: The acid value, saponification value and iodine value of the oil were carried out as per standard methods (Jayaraman, 1981). The density (Pycnometer), viscosity (Cannon- Fenske viscometer) and calorific value (Bomb calorimeter) of the oil were determined.

Biodiesel production from WCO: A two stage acid-base process was used for the production of biodiesel using H_2SO_4 as acid catalyst for pretreatment (acid esterification) and NaOH as base catalyst for transesterification process with methanol. In acid esterification stage, 5 % (w/w) of H_2SO_4 based on free fatty acid (FFA) content and 40:1 methanol to FFA molar ratio were added to the oil (Kumar, 2015; Kumar, 2013). The pretreatment reaction was carried out at 60 °C for 1 h in a 2 L round bottom flask fitted with a reflux condenser, a temperature sensor and a sampling port with constant stirring on a magnetic stirrer and PID temperature controller. The reaction mixture was then subjected for settling in a separating funnel for 1 hour. The upper layer rich in water, methanol and acid fraction was discarded and the lower layer was taken for transesterification reaction in the second stage. The acid value of the treated oil was determined by acid-base titration.

The amount of NaOH required for neutralization of FFA in the pretreated oil was determined by titration. The NaOH required for neutralization of FFA in addition to 3.5 g/L NaOH catalyst for the reaction was dissolved in methanol (1: 6 oil to methanol molar ratio) to form sodium methoxide (CH_3ONa) (Kumar, 2015; Kumar, 2013).

The transesterification process was carried out at 60 °C for 60 mins. Then the reaction mixture was subjected for settling in a separating funnel to form upper biodiesel layer and lower glycerin layer. The glycerin was separated and the biodiesel thus produced was washed twice with water, acidified with 0.1 % acetic acid and two washes with hot water. Finally, the biodiesel was dried by heating at 110 °C to remove the moisture, cooled, filtered and then subjected for further analysis.

Quality analysis of WCO biodiesel: The biodiesel properties were measured as per the American Society for Testing and Materials (ASTM) methods as follows: kinematic viscosity (ASTM D445), flash point (ASTM D93), copper strip corrosion test (ASTM D130), cloud and pour point (ASTM D2500 and ASTM D97), and water and sediments (ASTM D 2709). The oxidation stability was tested as per EN14112 test method. The acid value, iodine value, density and calorific value were determined by standard methods.

RESULTS AND DISCUSSION

Large quantities of waste cooking oils and animal fats are available throughout the world, especially in the developed countries. Management of such oils and fats pose a significant challenge because of their disposal problems and possible contamination of the water and land resources. Even though some of this waste cooking oil is used for soap production, a major part of it is discharged into the environment. In India 217.09 lakh tons of edible oil is used for consumption out of which 127.31 lakh tons comes from import in 2015. Since India is dependent on imports for the edible oil, use of edible oil for fuel purpose is forbidden. Metropolitan cities like Bangalore are the prime centers for education, industrialization etc. There are more than 8800 restaurants and numerous hot chips and snacks centers which produce fried oil (https://www.zomato.com/bangalore). One of the estimates says that, approximately 92 lakh tons of waste cooking oil is produced in a year in India (Annanymous, 2015).

The properties of WCO can change depending on the frying conditions, such as temperature and cooking time. The cooking process causes the vegetable oil, triglyceride to break-down to form, diglycerides, monoglycerides, and free fatty acids (FFAs) (Haigh et al., 2014). The amount of heat and water in the frying increases the hydrolysis of triglycerides, therefore it causes a growth of the free fatty acids in the WCO. (Carlinia, 2014; Kawentar, 2013). Moreover, because of oxidation and polymerization reactions, there is an increase in the viscosity and the saponification number of the WCO when compared with the original oil. During the transesterification reaction, the presence of water in the WCO samples often leads to hydrolysis, whereas high FFA content and high saponification number can lead to saponification reactions. Both hydrolysis and saponification reactions cause low biodiesel yield and high catalyst consumption (Carlinia et al., 2014)

Biochemical properties of WCO: The properties of the WCO used for the study is given in the Table 1. The oil was dark brown in color and found to contain moisture that inhibits biodiesel production. There was 6-8% water content which is removed by heating at 110 °C in open container. The acid value of the oil was 8.12 mg KOH/g oil i.e., 4.6% free fatty

Table 2. Properties of WCO biodiesel and comparison with pongamia, jatropha biodiesel

Properties	WCO	Pongamia[1]	Jatropha[1]	ASTM D6751	BIS (ISO 15607)
Density (kg/m^3)	879.10	884-886	878-880	--	860-900
Kinematic viscosity (mm^2/s)@40 °C	4.99	5.4 -5.6	4.8-4.9	1.9-6.0	2.5-6.0
Copper strip test	1a	1a	1a	3	Class1
Cloud point (°C)	6	15	3	--	--
Pour point (°C)	4	12	-1	--	--
Flash point (°C)	162	162	158	130 Min	120 Min
Acid value (mg KOH/g)	0.34	0.36	0.32	0.5 Max	0.5 Max
Iodine value (g I_2/100g)	69.3	71.3	76.7	--	120 Max
Water and sediments (%)	Nil	Nil	Nil	0.05 Max	0.05 Max
Sulphated ash (%)	0.008	0.005	0.004	0.02	0.02 Max
Oxidation stability (h)	1.5	--	--	--	6.0 Min
Calorific value (MJ/kg)	34.2	36	35.6	--	--

[1]Kumar et al. 2013

acid in oil. Hence the FFA was reduced by acid esterification process prior to transesterification

Properties of WCO biodiesel: The properties of biodiesel produced from waste cooking oil are given in the Table II. The properties of WCO biodiesel were on par with other biodiesel produced from non-edible oils.

Density: The density of wco biodiesel was 879.10 kg/m^3. Biodiesel density is usually higher than that of fossil diesel fuel, with specific values depending on fatty acid composition. It was also observed that the density of oil reduced from 917.41 kg/m^3 to 879.1 kg/m^3 by transesterification process.

Kinematic viscosity: Kinematic viscosity affects lubrication in the injector and fuel atomization (Knothe, 2001). The viscosity of WCO biodiesel sample was 4.99 mm^2/s, which was in the range specified by ASTM (1.9-6.0 mm^2/s) and BIS (2.5-6.0 mm^2/s) standards. It was also noted that there was a substantial decrease in kinematic viscosity from 43.5 mm^2/s to 4.99 mm^2/s by transesterification process.

Copper strip corrosion: The copper strip corrosion test indicates the potential compatibility problems with the fuel system components made of copper alloys such as brass and bronze. This is also one of the measures of presence of mineral acids in the biodiesel sample that cause the corrosion of the engine parts. The copper strip corrosion test was No. 1a which indicated that the inorganic acids are within the limits (No.3) in the biodiesel.

Cloud point and pour point: The cloud point is a test used to characterize the low temperature operability of biodiesel. It defines the temperature at which a cloud or haze appears in the biodiesel under prescribed test conditions. The cloud point of biodiesel is generally higher than petroleum diesel. The cloud point of WCO biodiesel sample was 6 °C. The lowest temperature at which movement of biodiesel is observed is known as pour point. The pour point of biodiesel was 4 °C.

Flash point: The flash point temperatures are required for proper safety and handling of fuels. The flash point varies inversely with the fuel's volatility. The flash point of 162 °C was recorded for WCO biodiesel. The flash points for biodiesel specified by ASTM and BIS are 130 and 120 °C respectively. The flash point of biodiesel must meet criteria for ensuring that the biodiesel does not contain traces of methanol (Gerpen, 2004).

Acid value: The acid value, a measure of free fatty acids in WCO biodiesel was 0.34 mg KOH/g. In the present study, the acid value of biodiesel sample was within the specifications provided by ASTM and BIS. The free fatty acids can lead to corrosion and may be an indication of water in the fuel (Gerpen, 2004). However, the acid number changes due to the normal oxidation process over time.

Iodine value: The iodine value indicates the total number of double bonds (i.e., level of saturation) in a mixture of molecules. It helps to indicate the oxidation stability and provide information about the fuel's tendency to form sludge, affect lubricant quality and may cause corrosion. Higher iodine value represents lower oxidation stability, also the presence of poly unsaturated fatty acids that may polymerize at high temperature and form sludge and affect the performance of the engine (Fan, 2009; Drapcho, 2008). The iodine value for WCO biodiesel was 69.3 gI_2/100g. The iodine value of the biodiesel is purely dependent on the source from which biodiesel was produced.

Water and sediment: Biodiesel should be clear in appearance and free of water and sediment. The presence of these materials generally indicates poor fuel handling practices. However, the water and sediments in the current study were below 0.05 %. Water and sediment can shorten filter life or plug fuel filters, which can lead to engine fuel starvation. In addition, water can also promote fuel oxidation and microbial growth.

Sulphated ash: The sulphated ash content in WCO biodiesels was 0.008 % which was well within the specification given by ASTM/BIS (0.02 % max.). Sulphated ash is a measure of the amount of metals contained in the fuel. Ash forming materials may be present in three forms: abrasive solids, soluble metallic soaps and residual biodiesel catalysts. Abrasive solids and biodiesel catalyst materials result in wearing of fuel system and internal engine components exposed to fuel after injection. The metallic soaps can contribute to deposits in the fuel system and all ash forming compounds can contribute to the accumulation of materials on diesel particulate filters, requiring continuous filter maintenance.

Oxidation stability: Biodiesel fuels are unstable due to natural oxidation process. The oxidation stabilities of WCO biodiesels was 1.5 h. The oxidation process involves a free radical chain reaction that continues until the reactive molecular links or available oxygen is depleted. The peroxides (hydro peroxides) are reactive oxidizing agents formed during the initial steps of

fuel oxidation (18). Subsequent steps in the oxidation process produce acids, gums, polymers, and other insolubles. The test method utilized predicts the amount of time that fuel can be stored before the production of acids indicating that the fuel is becoming unstable. The biodiesel failed in oxidation stability test, the reason being biodiesel obtained from the oil are easily attacked by the enzymes and degrade easily whereas petroleum fuels exhibit extremely long storage stability periods. It is reported that the oxidative stability decrease with increase in poly-unsaturated fatty acids such as linoleic acid and linolenic acid esters (Giwa, 2010). However, the oxidative stability of the fuel could be enhanced by adding antioxidants.

Calorific value: The calorific value of WCO (32.5 MJ/kg was increased to 34.2 MJ/kg by transesterification process. The variation in fatty acid composition of different oils used for biodiesel might be a reason for variation in calorific value of biodiesel produced from different oil samples.

Conclusion

The waste cooking oil obtained from hotels, hot chips or any food industry could be converted into biodiesel. There was 90% recovery of biodiesel. Biodiesel from waste cooking oil in metropolitan cities may be an alternative for waste disposal as well as the oil could be made use of for the power generation for the hotel industry. This helps in development of clean cities in India.

Acknowledgement

The authors acknowledge the support from International center for research in agro-forestry, Department of Science and Technology, New Delhi.

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