Biodiesel from multi-used Waste Cooking Oil: Basic Transesterification

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Abstract—This current study focuses on the attributes of biodiesel extruded from waste cooking oil that was obtained from confectionery shop where multiple times it was re-used. This altered all unsaturated to approximately saturated fatty acids which are hazardous to human health and cause various diseases, perhaps due to the presence of free radicals. Basic transesterification method has been employed for oil to useful product conversion (Biodiesel) in presence of catalyst (Potassium hydroxide) and alcohol (methanol) to convert triacylglycerol to fatty acid. The process leading to biodiesel production by basic transesterification is 100% pure and clear and may be efficiently used in mixed form in different ratio with petrodiesel. The biodiesel obtained showed Specific gravity and acid value within the range of American society for Testing and Materials standards. However, some parameters such as FFA value and cetane value were slightly lower than compared to ASTM standard and parameters such as pH value was higher than the ASTM standard, which is also seen in case of biodiesel obtained from plant lipid/animal fats

Introduction

Due to regular enhance the use and demand of fuels result in decrease of fossil fuel reserves day by day. On the other side, increase the use of fossil fuels lead to environment damage, global warming, climate change, depletion of non-renewable fuels and energy security. Environmental issues e.g. global warming and change in climate have to be resolved with immediate action and this urgency resulted in development and production of renewable and degradable fuels.

Biodiesel is a mixture of fatty acids and methyl group which results in formation of fatty acid methyl ester (FAME); derived from the plant and animal fats. The fatty acid composition has huge impact on the properties and consequently on the performance of biodiesel thereof [1]. Unsaturated ethyl or methyl esters of fatty acids are produce by transesterification of triaclyglycerols using basic or alcoholic method, known as biodiesel [2]. Use of biodiesel has been increasing rapidly as an alternative source of energy[3]

Biodiesel is similar to petroleum diesel and beside this it has few other useful properties like non-toxic nature, renewability and sustainability. Chain length, level of unsaturation, cetane number, melting point, oxidative stability and heat of combustion are other important analyzed properties of biodiesel. Apart from these, it has low sulfate emissions and provides financial opportunities for provincial producers.[4] Biodiesel produced from edible plant oil are known as 1st generation biodiesel, that type of biodiesel utilized oil or fats from pea-nuts [5]. Biodiesel produced from inedible plant oils are said to be 2nd generation biodiesel for example, jatropha oil, jojoba oil and squander oils and multi-used edible oil which is unhealthy and waste oil. Biodiesel produced from oleaginous micro-organisms like microalgae etc are called 3 generation biodiesel. Single cell oils (SCO) are produced by oleaginous unicellular microorganisms by utilizing various waste materials as sources of carbon and nutrition [6]. In this study biodiesel is made from multi-used vegetable oil due to its change in saturation level, i.e., from unsaturated to approximately saturated and lead to various health issues, as it cannot be use for cooking purpose. Hence we can use this to make biodiesel by basic transesterification method. This biodiesel can be used directly without any modifications. To achieve high performance, low-temperature operability and oxidative stability, biodiesel should contain low concentrations of both long-chain saturated FAMEs and polyunsaturated FAMEs [7]. The two main features influencing the properties of biodiesel are; distribution of size and the degree of unsaturation in the fatty acid structures. So, this study emphasized on quantification of unsaturated and saturated fatty acids and also studying the physical and chemical properties of the resultant biodiesel including pH, specific gravity, water content, ash content, free fatty acid number, iodine value, refractive index and cetane number of produced biodiesel.

Material and methods

Chemicals and reagent: methanol, potassium hydroxide (KOH), phenolphthalein, potassium iodide, Sodium thiosulphate, iodine, starch, sodium hydroxide.

Apparatus used: conical flask, measuring cylinder, beakers, burette, glass rod, hot plate.

Conversion of waste oil to biodiesel: The basic transesterification was done by using potassium hydroxide as a reagent for the production of biodiesel from multi-used cooking oils. About 20 ml of oil was taken in a flask and heated on a heating plate upto 70°C. A mixture of 5 ml methanol and 1 g of potassium hydroxide was prepared separately. This prepared mixture was poured when the oil had been heated to proper temperature. Some white fumes were observed during the addition of methanol and KOH mixture in the oil flask. The flask was shaken and then kept untouched for layer separation. Different layers can be seen in the flask after Sometime. As a result, 2 separate layer formed, upper layer was of unsoluble crude biodiesel and lower layer was soluble gylcerol; isolate the biodiesel and purified by water, impurities get soluble in water and biodiesel float upon water. This biodiesel can be used as fuel.

Gas chromatography-mass spectrographic analysis(GC-MS)

GCMS analyzed the fatty acid methyl ester on a Shimadzu GCMS—QP 2010 Plus (Shimadzu, Japan) fitted with a SP –2560 capillary column (100 m×0.25 mm i.d).on a Shimadzu GCMS—QP 2010 Plus (Shimadzu, Japan) fitted with a SP–2560 capillary column (100 m×0.25 mm i.d).The individual peaks were identified Gas chromatography mass spectrographic analysis(GCMS)

Physical properties: All physical properties like smell, color and physical state of oil sample and biodiesel can be known by sensory evaluation.

Specific gravity:- it express the density of biodiesel with water at $15^{\circ}C$

Chemical properties:

pH: pH is determine by using ph analyzer.

Ash content: gravimetrically determined the ash content by using muffle furnace at 550 °C.

Free fatty acid and acid number:

AOCS method are used to determine the free fatty acid content. Prepared a mixture solution of 1g fuel sample with 95% ethanol & 2 ml phenolphthalein indicator; neutralize the ethanol by titrating the solution with Sodium Hydroxide(NaOH) until pink color appeared. The pink color was persist for at least 30 second.

Calculation: Free fatty acid (%) = ml of alkali × N × 28.2/w,

Acid number (mg KOH/g) = $1.99 \times FFA$ (%).

Iodine value: AOAC Official method was used to determine iodine value, take 2 flask, put 1g biodiesel in 1 flask and other was without oil as control were taken; 25ml Wij sol. and 25ml chloroform were taken in both flask and place in dark for a hour at room temperature. Afterwards 20ml KI solution and 150ml distilled water were added to each; sodium thiosulphate was used to titrate the solution until the color change from yellow to pale thereafter 1-2ml starch solution was added and continue the titration until the blue color of solution disappear.

Calculation: Iodine value = $(B - S) \times N \times 12.7/w$

where B is the titer value of blank (ml), S is the titer value of sample (ml); N is the normality of hypo; w is the weight of oil taken(g)

Refractive index: Abbe's refractometer used to measured refractive index by placing 2–3 drops of the sample on the prism surface.

Cetane number: It indicates the ignition properties of biodiesel, it is inverse function of a fuel's ignition delay. saponification value and iodine value are used to calculate the cetane value. The cetane number was calculated using the following equation

Cetane number:- 46.3 + 5458/SN - $0.225 \times I$

where S is saponification number, I is Iodine value.

Results and discussion

Multi-used vegetable oil was used for the convesion of biodiesel by basic transesterification, 20ml waste oil was transesterified to approximately 11ml biodiesel which was equal to 55% conversion rate (w/w).

Physical properties

State: Waste vegetable oil was viscous liquid with brownish color but after transesterification it changes from brownish-viscous liquid to yellow.

Specific gravity: Specific gravity shows relative density of liquid to water. In this study, specific gravity was found to be 0.858g/ml.

Properties	ASTM standards	Basic (studied) Transesterifi cation	Crude salmon oil (Dave et	Jatropha curcus oil(Sarker 2016)
Physical state		Liquid	al. 2014) Clear liquid	Liquid
Color		Pale yellow	Orange	-
Specific gravity	0.87-0.90 g/cm3	0.857 g/cm3	0.921 g/cm3	-
pН	7	7.5	6.8	7.8

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Iodine value	<120	22.01 I ₂ /100g	116.79gI ₂ /	94 gI ₂ /100
	$I_2/100g$		100g	g
Free fatty	<2.5%	0.65%	1.23%	-
Acid				
Acid value	< 0.8	1.30	2.441	-
(mg KOH/g)				
Refractive	1447-1.48	1.480	1.47	-
index				
Cetane	>47	39	49.39	38
number				

Chemical properties

pH: pH of obtained biodiesel sample recorded as 7.5 which is near to ASTM standards and ph of waste oil was 7; which is neutral.

Free fatty acids (FFA): The free fatty acid value for biodiesel was found to be 0.65% which is less than ASTM standards. Quality of fats and oils indicated by concentration of free fatty acids.

Acid number: Acid value of obtained FAMEs was recorded 1.30 mg NaOH/g which is slightly more than ASTM standards.

Refractive index: Refractive index for biodiesel was recorded as 1.480 which was nearly equals to the ASTM standards.

Iodine value: Iodine value was found to be 22.01 $I_2/100g$; which is less than ASTM standards; it indicates the amount of unsaturated fatty acid of FAMEs which show easy drying capacity of biodiesel.

Cetane value: It indicates the ignition properties of biodiesel, it is inverse function of a fuel's ignition delay; the obtained cetane value was recorded as 39; which is less than ASTM standards.



Figure 1. saturated fatty acid composition



Figure 2. Unsaturated fatty acid composition

GC-MS analysis data of biodiesel produced from waste cooking oil has been compiled and major FAMEs have been represented in the bar diagram (Fig 1&2). We observed that unsaturated fatty acids, mostly 9-octadecenoic acid, were present in large amount as compared to saturated fatty acids.



Figure 3. Waste oil to biodiesel conversion

The aim of this study was to know the properties of biodiesel produced from waste cooking oil. FAMEs was analyzed by GC-MS for detection of various components. Transesterified waste oil were used to find the physical and chemical parameters and also compared with biodiesel from salmon oil, jatropha oil & ASTM standards. In this study, it was noted that cetane number was within range i.e 39, which should be 47 but studied value was equal to jatropha oil. Refractive index was nearly equal to ASTM standards and Crude salmon oil which was 1.480 in our study. Iodine value should be <120 $I_2/100g$ according to ASTM standards and in our study is was noted as 22.01 I₂/100g which is lower and in jatropha oil it was 94 gI 2 /100 g. Free fatty Acid content was recorded as 0.65% which was lower than ASTM standards <2.5% and Crude salmon oil 1.23%. Acid value should be <0.8 mg KOH/g according to ASTM standards and in study it was 1.30 mg NaOH/g which is more than ASTM standards but less than Crude salmon oil 2.441 mg KOH/g. Higher acid values cause problem due to corrosion and clogging of engine. Specific gravity in our study was 0.857 g/cm3 and almost equal to ASTM standards but lower than Crude salmon oil. pH of biodiesel from waste oil was 7.5 which was more than ASTM

standards as well as crude salmon oil but slightly lesser than jatropha oil. Low pH affect the catalyst during reaction. pH of biodiesel is a major factor for all types of transesterification. The comparative study of biodiesel properties including specific gravity, pH, acid value, iodine value, free fatty acid, refractive index (Table) indicated that the biodiesel obtained from waste cooking oil is a suitable fuel and further removal of the water would enhance its fuel properties.

Conclusion

In this study, biodiesel produced from multi-used waste cooking oil was used to characterize its physical and chemical properties. FAME profile analysis was done by GC-MS characterization method. Physico-chemical properties in this study showed that specific gravity and refractive index were within the range of ASTM standards. Iodine value, free fatty acid and cetane number were found to be lower than the ASTM standards. Some parameters of produced biodiesel such as pH, acid value were higher than ASTM standards. Minute modification during production of biodiesel might enhance fuel properties.

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Compliance with ethical standards:

Conflict of interest The authors declare that they have no conflict of interest.

Human studies and informed consent This article does not contain any studies with human participants or animals performed by any of the authors.

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