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Production of Biodiesel from Waste used Cooking Oil using two Different Alkaline Catalysts

Rajagopal. K[1], Johnson.J[2], Selwin Rajadurai.J[3]

[1]Department of Physics, Government College of Engineering., Tirunelveli,Tamil Nadu,India.
[2]Department of Physics, Research scholar,M.S.University, Tirunelveli, Tamil Nadu,India.
[3]Department of Mechanical Engineering, Government College of Engineering.,Tirunelveli,Tamil Nadu,India.

Abstract: Biodiesel has been produced from used waste cooking oil by transesterification process using methanol with two different alkaline catalyst such as NaOH and KOH in order to measure the effect of catalyst on the biodiesel yield and on physical and thermodynamical parameters. Some of the physical and thermodynamical properties like density, viscosity, flashpoint and calorific values of the biodiesel have been experimentally measured and reported. These values are within the ASTM and Indian standards indicating the applicability of this biodiesel as an alternative source in diesel engines.
Key words: Biodiesel, waste cooking oil, Potassium Hydroxide, Sodium Hydroxide.

Introduction:

Most of the developing countries including India spends huge foreign exchanges on import of crude oil (189.24 MT of crude oil in the year2013-2014)[1] to meet the industrial demand every year. However the petroleum reserves are depleting very fast and forcing researchers to identify alternative fuel sources. The usage of some percentage of biodiesel blended with petroleum diesel vastly saves the exchequer on import constrains in developing nations like India. For example recent statistics[2] shows that blending 5% biodiesel with petroleum diesel can save up to 4000 crore of Indian rupees. Work on production of biodiesel has gaining momentum in recent years since biodiesel is a nontoxic, biodegradable, renewable fuel that can be produced from both edible ,non edible oils, animal fats and used waste oils.. Though in terms of sulphur content, lubricity, cetane number, flashpoint, aromatic content and biodegradability factor biodiesel has an edge over petro diesel, it has certain disadvantages in terms of higher viscosity, pour point, lower calorific value, volatility and oxidation stability. However CO_2 emission from biodiesel operated vehicles contribute less to the atmosphere in comparison to diesel operate vehicles, thereby there is a possibility of reduction in green house gases. A recent report estimates a reduction of CO_2 gases by 3.2 Kg in the atmosphere for every 1 Kg usage of biodiesel instead of petro diesel[3-6]. In developed countries biodiesel is produced from edible sources such as peanut, arn, palm, sunflower oils etc while in developing countries including India every attempt is made to produce biodiesel from non edible sources such as karanja, Jatropha, rubber seed, neem etc[7]. We have also produced biodiesel from two non edible seeds such as karuvel and salicornia[8,9].Some authors have produced biodiesel from used waste cooking oils[10,11].India uses over fifteen million tons of edible oil for consumption as per recent statistics and even if 10% of this quantity is thrown as waste it comes around 1.5 million tons[12]. Generally most of the waste used cooking oil is disposed off in the land mass or water bodies that may lead to increase in pollution levels. Alternatively if the unused waste cooking oil is looked as a biodiesel source, there is possibility of huge saving of foreign exchanges. This paper highlights the production of biodiesel from the waste used cooking oil collected from our college hostels by two different alkaline catalyzed transesterification process.

Preparation of waste cooking Oil:

The waste used cooking oil has been collected from GCE College hostels and filtered by filter paper couple of times to remove impurities present in the oil. The filtered clean cooking oil has been then used for the experiment.

Chemicals and reagents:

The chemicals and reagents (sodium hydroxide (NaOH) ,Potassium hydroxide (KOH) in pellet form, anhydrous Na_2So_4 and Methanol)have been used in this study are of AR grade with purity >99% procured from Highmedia laboratories Pvt. Ltd., India. These chemicals have been used without any further purification.

Experimental setup to produce biodiesel:

The reactor used for experiments is a 5000 ml five-necked round-bottomed flask placed over the heating mantle. The central neck has been connected to a stirrer. The stirrer rod is attached to a motor on the top and a propeller at the bottom. The stirrer rod is passed in to the reactor through a tightly packed hole in the rubber cork placed on the central neck to make sure that the reactor is airtight. The stirrer is driven by an electric motor equipped with a speed regulator. The purpose of the stirrer is to mix the reactants thoroughly. The second neck is equipped with a reflux condenser (for preventing the methanol from escaping out of the reactor). Third neck is used for thermo-well. A platinum RTD temperature sensor (PT-100) has been placed in the thermo-well for temperature measurement inside the reactor. The sensor has been connected to a digital temperature indicator and a Proportional integral derivative (PID) controller to control temperature of reaction mixture. Fourth neck is used for loading the reactants in to the reactor while the fifth neck is closed with air tight Rubber cap.

Production of biodiesel by transesterification:

The type of transesterification process is determined by the Free Fatty Acid content(FFA) present in the oil which is related ,by its acid number. The acid number of any oil has been defined in terms of the number of milligrams of KOH required to neutralize the free acids present in 1 gm of oil. If the Free Fatty Acid number is less than 2% then single step transesterification process is followed using alkali catalyst only. However, if the Free Fatty Acid content is greater than 2 %, then two steps transesterification process have to be followed in steps using acid and alkali catalyst respectively. In the present investigation, the FFA content of waste cooking oil has been found to be 0.9848%, and hence single step transesterification process as discussed in the succeeding section has been followed.

Fig 1.Biodiesel production plant

This paper deals with the production of biodiesels from the waste cooking palm oil using two different alkaline catalysts namely potassium hydroxide & sodium hydroxide to see the effect of these catalyst on the biodiesel yield and their effect on physico chemical parameter values.

Transesterification also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except that an alcohol is used instead of water[13]. This has been widely used to reduce the viscosity of the triglycerides. The transesterification is represented as

RCOOR’	+	R’’OH	↔	R’COOR’’	+	ROH
Ester		Alcohol		Ester		Alcohol

If methanol is used in this process then it is called methanolysis. Methanolysis of triglycerides is represented as

CH_2COOR_1				CH_2OH		R_1COOCH_3
+						
$CHCOOR_2$	+	$3CH_3OH$	CATALYST	CHOH	+	R_2COOCH_3
+			NaOH / KOH			
CH_2COOR_3				CH_2OH		R_3COOCH_3
Parent oil		Methanol		Glycerin		Methyl ester

2000 ml. of waste cooking palm oil free from water and contaminants has been taken in the biodiesel round bottomed flask. The base catalyzed trans-esterification reaction has been carried out with methanol to oil ratio as 1:4v/v. Sodium hydroxide (NaOH) has been used as catalyst at 1% w/v of oil. The oil, preheated to 60^{o}C in a heating mantle for about 5 - 10 min, has been used in order to achieve the maximum yield. Initially sodium hydroxide (NaOH) has been added to the preheated oil. The reactant mixture has been stirred continuously at the rate of 600 rpm and the temperature of the reactants has been maintained at 60^{o}C. The system has been maintained airtight to prevent the loss of alcohol. Reaction has been carried out for 1 hour.

These optimum values have been found by comparing the yield of methyl esters from several reaction ratio’s. After the attainment of preestablished time, the mixture has been carefully transferred to a separating funnel and allowed to stand overnight. The lower layer (glycerol, methanol and most of the catalysts) has been suitably drained out. The upper layer that consists of methyl esters, some methanol and traces of the catalyst has been washed with warm doubly distilled deionised water (70°c) in order to remove the impurities like uncreated methanol, uncreated oil and catalyst. The methyl ester has been finally heated to 110°c then dried with anhydrous Na_2So_4 to get rid of any water [14].

Fig 2. Settling flask

Fig 3. Water Washing

The whole experiment has been repeated with KOH as the catalyst and the biodiesel yield in both the cases has been calculated using the equation.

$$\text{Biodiesel Yield} = \frac{\text{Mass of biodiesel produced } x \text{ 100}}{\text{Mass of waste cooking oil used}}$$

Our experimental investigation proves that ,the yield of the biodiesel has been much higher (95 %) in the case of NaOH catalyst than the KOH catalyst case (85 %).

Measurement of Physical and thermodynamical properties of the biodiesel produced using standard instruments:

Density:

Density is defined as the weight of a unit volume of the fuel is an important property of the biodiesel. Fuel injection equipment that operates on volume metering system is sensitive to density of the fuel. In case of biodiesel, slightly higher mass of fuel has to be injected compared to petroleum diesel due to its higher density [15].

The densities (ρ) of biodiesels have been measured using a single stem pycnometer (pyrex glass) of bulb capacity of 12×10^{-3} dm^3 having a graduated stem with 5×10^{-7} dm^3 division. All density measurements have been performed in triplicate with the pycnometer[16]. The weighing has been done by using a high precision AND electronic balance (model HR 300, Japan) with a precision of $\pm$0.1mg. The reproducibility of density measurements is $\pm$ 2.8×10^{-4} $g\cdot cm^{-3}$. The pycnometer with test solution has been allowed to stand for about 30 minutes in the thermostatic water bath so as to minimize thermal fluctuations. The temperatures of the solutions have been maintained to an uncertainty of ±0.01 K in an electronically controlled thermostatic water bath (Eurotherm, INSIN Private Ltd, Chennai). The density values of the samples have been measured at 15^0C to compare with Indian standards and are reported in Table-1. The experimentally measured density values of the biodiesel samples are within Indian Standards thereby indicates that the biodiesel produced from waste cooking oil can be used in diesel engines without any modifications with appropriate blend with petrodiesel.

Viscosity:

Viscosity is the measure of internal friction of the fuel to its flow. Viscosity of the fuel influences the fuel injection process and atomization of the fuel[15]. Biodiesel generally has higher viscosity than petroleum diesel. Furthermore, viscosity is very sensitive to engine performance and in cases where the values are higher than the petro diesel then it leads to poor atomization of the fuel, incomplete combustion, chocking of the injectors and ring carbonization[17,18].Thus blending of biodiesel with petrodiesel is favoured to be used as fuel in Diesel engines without any modifications.

Viscosity of the biodiesel samples has been measured with suspended level Ubbelohde viscometer [19] with a flow time of 186 s for distilled water at 303.15 K. The flow time has been measured by a digital stop watch capable of registering time accurate to $\pm$ 0.01 s. An average of three sets of flow times for each solution is taken for the purpose of the calculation of viscosity. The overall experimental reproducibility is estimated to be within ± 2×10^{-3} m.Pa.s. The viscometer filled with test solution has been allowed to stand for about 30 minutes in the thermostatic water bath so as to minimize thermal fluctuations. The temperatures of the solutions have been maintained to an uncertainty of ±0.01 K in an electronically controlled thermostatic water bath (Eurotherm, INSIN Private Ltd, Chennai). The viscosities of the biodiesel samples have been measured at 40^0C to compare with Indian Standards and are reported in Table.1.It is clear that the experimentally measured viscosity values of the biodiesel samples are within Indian Standard thereby approves the applicability of these fuels in Diesel engines.

Flash Point:

Heat of combustion is an important engine parameter that measures the energy content in a fuel. Flash point is a measure of the temperature to which a fuel must be heated such that a mixture of the vapour and air above the fuel can be ignited. The petro diesel have high flashpoint (54^0C minimum; 71^0C being typical values. The flash point of neat biodiesel is typically greater than 93^0C[20]. As the biodiesel shows higher flash point comparing to petro diesel, it is considered as nonhazardous fuel.

The flash point of the biodiesel produced from the waste cooking oil has been measured by Cleveland open cup apparatus. The sample has been poured in to a cup in the Cleveland open cup apparatus up to the marking present in the cup. The sample in the cup has been heated using an electric heater and the temperature of the sample has been measured using a thermometer capable of measuring temperature up to 300^o C with a resolution of ±2^0C. At fixed interval of temperature rise a small gap is opened on the lid and a flame is projected over the gap. At the flash point temperature, a flash appeared over the gap on the lid. The experiments have been repeated thrice and the average values of the flash point of the samples are reported in Table- 1 along with Indian Standard recommended. The experimentally measured Flash Point values satisfies the recommended Indian Standards.

Calorific value:

Calorific value is another fuel property which measure the energy content in a fuel viz it has a direct correlation with the efficiency of the fuel. Calorific value of the biodiesel produced from waste cooking oil has been measured using the bomb calorimeter. Initially the calorimeter constant has been determined using benzoic acid as fuel. Then 1 gram of biodiesel fuel has been filled in a small cup inside the bomb. Oxygen at sufficient pressure has filled inside the bomb using a pressure regulator. The bomb has been placed inside a vessel containing 2 liters of water. Then the biodiesel has been made to burn inside the bomb using a spark created by electrical short circuit. The temperature rise of the water surrounding the bomb has been measured using a digital thermometer. The calorific value of the biodiesel fuel has been determined using the temperature rise of the water and calorimeter constant and are given in Table 1.The calorific values of the biodiesel are lower than that of petro diesel because of their oxygen content [21].The presence of oxygen in the biodiesel may help for complete combustion of fuel in diesel engine when used a blend with petrodiesel.

Table-1: Physical & Thermodynamical parameters of biodiesel produced from waste cooking oil with NaOH / KOH as catalyst

Properties	Unit	Biodiesel using NaOH	Biodiesel using KOH	Standards	
				IS15607:2005	ASTM
Density (15^0C)	kg/m^3	876.2	876.4	860-900	860-900 D4052
Viscosity (40 ^{0}C)	mm^2/s	4.591	4.654	2.5-6.0	1.9-6.0 D6751
Flash point	^{0}C	176	177	120^0C min	130^0C min D6751
Calorific value	kJ/kg	36212.86	36044.88	NA	

Conclusion:

- Biodiesel has been produced from waste cooking oil, using two different base catalyst to see the effect of catalyst on the biodiesel yield. Our experiment proves that the biodiesel production with NaOH catalyst gave maximum yield (95 %).
- The physical and thermo dynamical parameters such as density, viscosity, flash point and calorific value have been determined experimentally. These values also depends on the type of catalyst used in the transesterification process.
- The biodiesel produced from waste cooking oil has physical and thermo dynamical parameters which are within Indian and ASTM Standards indicating the applicability of this fuel in diesel engines.

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