

A REVIEW ON INVESTIGATION OF BIODIESEL PROPERTIES

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Abstract-Due to the increasing awareness of the depletion of fossil fuel resources and environmental issues, biodiesel became more and more attractive in the recent years. Biodiesel production is a promising and important field of research because the relevance it gains from the rising petroleum price and its environmental advantages.

The general method to produce biodiesel is transesterification of non-edible oil, edible oil and waste cooking oils with methanol in the presence of either base or strong acid catalysts. Transesterification reaction is quite sensitive to various parameters. An ideal transesterification reaction differs on the basis of variables such as fatty acid composition and the free fatty acid content of the oil. Other variables include reaction temperature, ratio of alcohol to vegetable oil, catalyst, mixing intensity, purity of reactants. This paper reviews the processing of transesterification and well explained procedure to calculate and measure the various biodiesel properties. The different biodiesel properties are free fatty acid value, density, viscosity, flash point and fire point, cloud point and pour point, carbon residue content and ash residue content.

Keywords: Biodiesel, viscosity, FFA content, calorific value, carbon residue content

1. INTRODUCTION

The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials [3]. As the demand for vegetable oils for food has increased tremendously in recent years, it is impossible to justify the use of these oils for fuel use purposes such as biodiesel production. Moreover, these oils could be more expensive to use as fuel [2, 3] compares the cost of biodiesel production based on the materials used. It can be seen that amongst the four materials such as palm oil, jatropha oil, soya bean oil and waste cooking oil, waste cooking oil can be seen as the cheapest and most economical raw material for biodiesel production [1]. Used cooking oil has sufficient potential to fuel the compression ignition engines. The kinematic viscosity of used cooking oil (UCO) is about 10 times greater, and its density is about 10% higher than that of mineral diesel. These properties play vital role in the combustion; therefore these must be modified prior to the use of UCO in the engine. Many techniques have been developed to reduce the kinematic viscosity and specific gravity of vegetable oils, which include pyrolysis, emulsification and transesterification. Among these techniques, transesterification is the hot favorite [2].

Biodiesel has promising lubricating properties and cetane ratings compared to low sulfur diesel fuels. Depending on the engine, this might include high pressure injection pumps, pump injectors (also called unit injectors) and fuel injectors [4]. The calorific value of biodiesel is about 37.27 MJ/kg. This is 9% lower than regular Number 2 petro diesel. Variations in biodiesel energy density are more dependent on the feedstock used than the production process [6]. Still these variations are less than for petro diesel. It has been claimed biodiesel gives better lubricity and more complete combustion thus increasing the engine energy output and partially compensating for the higher energy density of petro diesel [4, 5].

The color of biodiesel ranges from golden to dark brown, depending on the production method. It is slightly miscible with water, has a high boiling point and low vapor pressure [7]. The flash point of biodiesel (>130 °C, >266 °F) is significantly higher than that of petroleum diesel (64 °C, 147 °F) or gasoline (-45 °C, -52 °F). Biodiesel has a density of ~ 0.88 g/cm³, [12] higher than petro diesel (~ 0.85 g/cm³). Biodiesel contains virtually no sulfur, and it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel to aid with lubrication, as the sulfur compounds in petro diesel provide much of the lubricity [12].

2. NEED FOR BIODIESEL

Due to the increase in price of petroleum and environmental concern about pollution coming from automobile emission, biodiesel is an emerging as a developing area of high concern [9]. The world is confronted with the twin crises of fossil fuel depletion and environmental degradation. Alternative fuels, promise to harmonize sustainable development, energy conversion, management, efficiency and environmental preservation. Vegetable oil is a promising alternative to petroleum products [11]. The economic feasibility of biodiesel depends on the price of crude petroleum and the cost of transporting diesel over long distances to remote areas.

3. PRODUCTION OF BIODIESEL

There are different processes which can be applied to synthesize biodiesel such as direct use and blending, micro emulsion process, thermal cracking process and the most conventional way is transesterification process. This is because of the fact that this method is relatively easy, carried out at normal conditions, and gives the best conversion efficiency and quality of the converted fuel [2].

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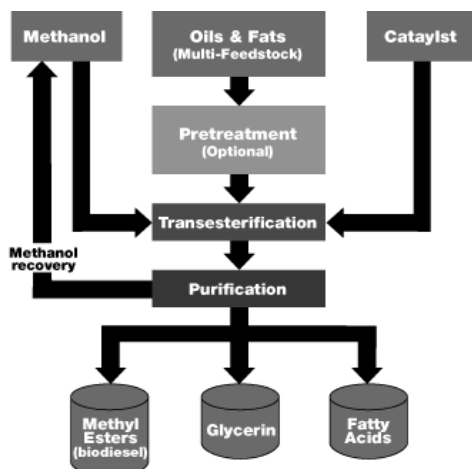


Fig: 3.1 Flow chart of Transesterification process [2]

4. BIODIESEL PROPERTIES

The equipments which were used to determine the fuel properties of biodiesel were determined according to the relevant specifications from the biodiesel standards ASTM D6751. Most of these parameters comply with the limits prescribed in the ASTM D6751 [12]. The characteristic fuel properties of biodiesel were determined in accordance with standards of Bureau of Indian Standards, New Delhi and the Institute of Petroleum, London.

Properties	Method used
Kinematic Viscosity	IS: 1448[P: 25]:1976
Flash point and fire point	IS: 1448[P: 32]:1992
Cloud point and pour point	IS: 1448[P: 10]:1970
Ash Content (%)	ASTM D482
Carbon residue content (%)	ASTM D189
Calorific value (KJ/Kg)	IS: 1448[P: 6]:1984
FFA content (%)	Titration with 0.1N NaOH

Properties of the biodiesel were determined on different apparatus. Table 4.2 shows the list of the apparatus on which properties were tested.

Properties	Apparatus used
Density	Weighing balance
Kinematic viscosity	Redwood Viscometer
Flash point and fire point	Flash and fire point apparatus
Ash content	Muffle furnace
Cloud point and pour point	Cloud and pour point apparatus
Carbon residues	Carbon residue apparatus
Calorific value	Bomb calorimeter

4.1 Procedure for calculating the FFA Value:-

As FFA can cause saponification therefore it is important to know the FFA content (<0.2) within an oil batch and it is necessary to take steps to reduce the content for success in the transesterification process. FFA content can be acquired from the use of a titration [9].

The method for FFA estimation is described below [9]:

1. Take 50 ml spirit in a conical flask with the addition of the indicator phenolphthalein
2. 10 ml of base oil is added to the conical flask
3. Heat contents until first bubbling occurs (approx 70°C)
4. Phenolphthalein will indicate end of reaction as a red/pink colour when NaOH is used as titrate (0.1N)
5. When quantities are know the FFA content can be calculated.

Weight of sample = Volume × density

$(28.2 \times V \times N) / (\text{weight of sample})$

Where V = volume of NaOH consumed in the titration and N = Normality of NaOH

4.2 Procedure for calculating the viscosity:-

Viscosity can be defined as the resistance to flow of liquid due the internal friction between the liquid and surface. It plays an important role in the performance of an engine fuel system operating through a wide range of temperature [11].

A Redwood viscometer was used for measurement of kinematic viscosity of selected fuel samples. The instrument measures the time of gravity flow in seconds of a fixed volume of the fluid (50 ml) through specified orifice made in a agate piece as per IS:1448 [P:25] 1976. The apparatus could be used for flow time between 30 to 2000 seconds. The fuel was filled in a cup fitted with agate jet at the bottom up to a specified level indicated in a cup. The cup was surrounded by water jacket having an immersion heater [11]. The heater was heated to 38⁰C by regulating the rate of heating using a voltage regulator of the instrument. A simple metallic ball was used to open and close the agate jet. A standard 50 ml volumetric glass was kept below the agate jet to collect a falling fuel samples. Each test was replicated thrice. Kinematic viscosity in centistokes was then calculated from time units by using the relationships:-

$$V_k = 0.26 t - 179/t \quad (1)$$

When $34 < t < 100$ and

$$V_k = 0.24 t - 50/t \quad (2)$$

When $t > 100$

V_k = Kinematic viscosity in centistokes, cSt

t = Time for flow of 50 ml sample,



Fig: 4.1 Redwood viscometer [18]

4.3 Density

Bio-diesel is slightly heavier than conventional diesel fuel (specific gravity 0.88 compared to 0.84 for diesel fuel). This allows use of splash blending by adding bio-diesel on top of diesel fuel for making bio-diesel blends. Bio-diesel should always be blended at top of diesel fuel [12]. If bio-diesel is first put at the bottom and then diesel fuel is added, it will not mix.

4.4 Flash And Fire Point

The temperature, at which material gives so many vapors, when mixed with air, forms an ignitable mixture and gives a momentary flash on application of a small pilot flame [10]. Flash point can indicate the possible presence of highly volatile and flammable material in relatively non volatile material. The flash and fire point of the fuel samples was determined as per IS: 1448 [P: 32]: 1992. A Pensky Martin Flash Point (closed) apparatus as shown in fig 4.2 was used for measuring the flash and fire point of the fuel samples [7].

The procedure to calculate the Flash point is given below:-

1. The sample was filled in the test cup up to the specified level and heated by heating the air bath with the help of a heater.
2. The fuel sample was stirred at a slow constant rate. The sample was heated in such a way that rate of temperature rise was approximately 5⁰C per min.
3. The temperature was measured with the help of a thermometer of -10 to 400⁰C range.
4. At every 1⁰C temperature rise, flame was introduced for a moment with the help of a shutter.
5. The temperature at which a flash appeared in the form of sound and light was recorded as flash point.
6. The fire point was recorded as the temperature at which fuel vapor catches fire and stays for minimum of five seconds.



Fig 4.2: Pensky Marten apparatus used for measurement of flash and fire point [18]

4.5 Cloud And Pour Point

The Cloud and Pour point is the measure which indicates that the fuel is sufficiently fluid to be pumped or transferred [11]. Hence it holds significance to engines operating in cold climate. The cloud and pour point of fuel samples were determined as per IS: 1448 [P: 10]: 1970 using the cloud and pour point apparatus as shown in fig 4.3.

The procedure of calculate the cloud point is given below:-

1. The apparatus mainly consists of 12 cm high glass tubes of 3 cm diameter.
2. These tubes are enclosed in an air jacket, which is filled with a freezing mixture of crushed ice and sodium chloride crystals.
3. The glass tube containing fuel sample is taken out from the jacket at every 1°C interval as the temperature falls, and is inspected for cloud formation.
4. The point at which a haze was first seen at the bottom of the sample was taken as the cloud point.

The apparatus and the procedure for the pour point were same as for cloud point only the sample was pre-heated to 48°C and then cooled to 35°C in air before it was filled in the glass tube. Thereafter, the cooled samples were placed in the apparatus and withdrawn from the cooling bath at 1°C interval for checking its flow ability. The pour point was taken to be the temperature 1°C above the temperature at which no motion of fuel was observed for five seconds on tilting the tube to a horizontal position [7].



Fig 4.3: Cloud and pour point apparatus [18]

4.6 Ash Content

Ash in a fuel can result from oil, water soluble material compounds or extraneous solids, such as dirt and rust [22]. The ash content of diesel, cotton seed and mustard oil were measured as per the standard **ASTM D482-IP 4** of Institute of Petroleum, USA. An electric muffle furnace of was used in the experiment as shown in fig 4.4. The procedure for calculate the value of Ash content is given below:-

1. First, sample was taken in a silica dish.
2. The dish was first weighed empty and then with the fuel sample (14-15 gm).
3. The sample weight was obtained from the difference between the initial and final weight of the dish.
4. The sample was then placed in the muffle furnace and heated at 500°C for 20 minutes. The ash content was obtained using the equation given below:-

$$A_C = \frac{(\text{Wt. of dish after exp.} - \text{Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

Where, A_C = Ash content, percent



Fig 4.4: Muffle Furnace [18]

4.7 Carbon Residue

Carbon residue was determined for different fuels by using a carbon residue apparatus. The measurement was made in accordance with the ASTM D189-IP 13 of Institute of Petroleum, London [18]. This procedure determines the amount of carbon residue left after evaporation and pyrolysis of an oil. It is intended to provide some indication of relative coke forming properties.

The procedure for calculate the value of Ash content is given below [7]:-

1. First, the bulb was weighed empty and then with the fuel sample (4-5 gm).
2. Add 4-5 gm fuel in a bulb and weighed gain.
- 3 The sample weight was obtained from the difference between the initial and final weight of the bulb.
4. The sample was then placed in the carbon residue measurement content and heated at 500⁰C for 20 minutes. The carbon residue content was obtained using the equation given below:-

$$C_r = \frac{WC}{W_s} \times 100$$

Where,

C_r = Carbon residue, %, W_c = Weight of carbon residue, g, W_s = Weight of the sample, g



Fig 4.5: Carbon Residue Content Apparatus [18]

4.8 Calorific Value

The heat of combustion or calorific value of a fuel is an important measure since it is the heat produced by the fuel within the engine that enables the engine to do the useful work [22]. The gross heat of combustion of fuel samples was determined as per IS: 1448 [P: 6]: 1984 with the help of a Widson Scientific Works make Isothermal Bomb Calorimeter (Fig.4.6). A fuel

sample of 1 ml was burnt in the bomb of calorimeter in the presence of pure oxygen. The sample was ignited electrically. As the heat was produced, the rise in temperature was measured [9]. The water equivalent (effective heat capacity of the calorimeter) was also determined using pure and dry benzoic acid as test fuel [18].

The gross heat of combustion of the fuel samples was calculated using the equation given below:

$$H_C = \frac{W_C \times \Delta T}{M_S}$$

Where,

H_C = Heat of combustion of the fuel sample, Cal/g

W_C = Water equivalent of the calorimeter, Cal/ $^{\circ}$ C

ΔT = Rise in Temperature, $^{\circ}$ C and M_S = Mass of sample burnt, g



Fig 4.6: Bomb Calorimeter used for measurement of Calorific value [18]

5. CONCLUSION

Biodiesel has attracted wide attention in the world due to its renewability, biodegradability, non toxicity and environmentally friendly benefits. When the biodiesel was prepared from oil by the transesterification process, generally two properties were checked. These properties were FFA Value (Free Fatty Acid) and Viscosity. The FFA content of the raw oil will determine the quantity of biodiesel as the final product. A very low content of FFA (<0.2) can give a full 100% yield. With extremely low viscosities may not provide sufficient lubrication for the pumps and Injector plungers. Higher viscosity is also not desirable as too viscous fuel increases pumping losses in injector pump and injectors, which reduces injection pressure resulting in poor atomization. Saturated esters, which have higher cloud and pour point than unsaturated ones, have a marked influence on qualifying cold properties. At temperatures approaching the beginning of crystal formation, the viscosity rapidly increases, and the viscosity of the blends changes between biodiesel and the diesel fuels depending on their ratio This review paper highlights the procedure to measure the various biodiesel properties .The values of biodiesel properties and their blends should be in range and properly checked before use in C.I. engines.

6. REFERENCES

- [1] Mustafa Balat , Havva Balat “A critical review of bio-diesel as a vehicular fuel” Energy Conversion and Management 49, Page 2727–2741, 24 March 2008.
- [2] Alemayehu Gashaw, Tewodros Getachew and AbileTeshita, “A Review on Biodiesel Production as Alternative Fuel”, journal of forest products and industries, 2015, 4(2), 80-85 ISSN:2325–4513, ISSN 2325 – 453X.
- [3] Gerhard Knothe, Jon Van Gerpen, Jürgen Krahl “The Biodiesel Handbook” AOCS Press Champaign, Illinois, 2005.
- [4] <https://en.wikipedia.org/wiki/Biodiesel>
- [5] Report of the committee on development of bio-fuel, Planning Commission India, 16 April 2003.
- [6] Fangrui Maa, Milford A. Hannab, “Biodiesel production: a review” Bioresource Technology 70, Page 1-15, 2 February 1999.
- [7] Satishchandra Shamrao Ragit, “Process standardization, characterization and experimental investigation on the performance of biodiesel fuelled C.I.Engine”, PhD. Thesis, Department of mechanical engineering, Thapar university, Patiala, 2011.
- [8] Gerhard Knothe “Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters” Fuel Processing Technology 86, Page 1059– 1070, 2005.
- [9] Varun Singla, “Study of performance and emission characteristics of different blends of biodiesel prepared from waste cottonseed oil”, M.E. Thesis, Department of mechanical engineering, Thapar university, Patiala, 2012.
- [10] S.S. Ragit, S.K. Mohapatra, K. Kundu, Prashant Gill, “Optimization of neem methyl ester from transesterification process and fuel characterization as a diesel substitute”, Biomass and Bioenergy, 35 (2011) 1138-1144.
- [11] Vaneet, “Comparative analysis of performance and emission characteristics of C.I. engine fuelled with three different blends of biodiesel derived from waste mustard oil”, M.E. Thesis, Department of mechanical engineering, Thapar university, Patiala, 2012.

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- [12] Sandeep Singh, S.K. Mohapatra, Sumeet Sharma and K. Kundu, "Characteristics of biodiesel derived from waste cotton seed oil and waste mustard oil", International Conference on Advancements and Futuristic Trends in Mechanical and Materials Engineering (October 3-6, 2013), vol.2, Punjab Technical University Jalandhar.
- [13] P.K. Gupta, Rakesh Kumar, B.S. Panesar, and V.K. Thapar "Parametric Studies on Bio-diesel prepared from soybean Oil" Agricultural Engineering International: the CIGR Ejournal. Manuscript EE06 007, Vol. IX, April 2007.
- [14] A.P. Sathiyagnanam, and C.G. Saravanan, "Experimental Studies on the Combustion Characteristics and Performance of A Direct Injection Engine Fueled with Biodiesel/Diesel Blends", vol III, 2011.
- [15] Y. Zhang, M.A. Dube, D.D. McLean, M. Kates, "Biodiesel production from waste cooking oil, Process design and technological assessment", Bioresource Technology, 89 (2003) 1–16.
- [16] Ayhan Demirbas, "The Progress and recent trends in biodiesel fuels", Energy Conversion and Management, 50 (2009) 14–34.
- [17] Osmano Souza Valente, Vanya Marcia Duarte Pasa, Carlos Rodrigues Pereira Belchior, Jose Ricardo Sodre, Physical-chemical properties of waste cooking oil biodiesel and castor oil biodiesel blends Fuel 90 (2011) 1700–1702.
- [18] Sandeep Singh, "Study of various methods of biodiesel production and their properties" M.E. Thesis, Department of mechanical engineering, Thapar University, Patiala, 2012.
- [19] A.V. Krishna Reddy et al., Experimental determination of Brake thermal Efficiency and brake specific fuel Consumption Of diesel engine fuelled with biodiesel, A.V. Krishna Reddy et al. / International Journal of Engineering and Technology.
- [20] Experimental studies on a diesel engine using cotton seed as fuel, M. Pugazhvadivu and G. Sankaranarayanan.
- [21] Mohit Vasudeva, "Comparative study of engine performance and exhaust emission characteristics of a 4-stroke compression ignition engine operated with various blends of biodiesel extracted from crude rice bran oil and rice bran oil", M.E. Thesis, Department of mechanical engineering, Thapar university, Patiala, 2012.
- [22] S. Naga Sarada, M. Shailaja, A.V. Sita Rama Raju, Optimization of injection pressure for a compression ignition engine with cotton seed oil as an alternate fuel International Journal of Engineering, Science and Technology Vol. 2, No. 6, 2010, pp. 142-149.
- [23] R. Anand, G. R. Kannan, K. Rajasekhar Reddy and S. Velmathi, The performance and emissions of a variable CR diesel engine fuelled with bio-diesel from CSO ARPN Journal of Engineering and Applied Sciences Vol. 4, No. 9, November 2009.