ISSN : 0974 - 7435 Volume 9 Issue 5

BioTechnology
An Indian Journal

FULL PAPER

BTAIJ, 9(5), 2014 [177-180]

Winterization of Jatropha biodiesel

N.Vedaraman[1]*, Sudharsan Srinivasan[2], P.C.Seshasai[2], K.C.Velappan[1]
[1]Chemical Engineering Division, Central Leather Research Institute, Adayar, Chennai-600020 (INDIA)
[2]IVth year Chemical Engineering, School of Chemical and Biotechnology, SASTRA University, Thanjavur, (INDIA)
E-mail : nvedaraman@yahoo.co.in

ABSTRACT

The Fuel from vegetable oil, which can be considered as a good alternate for diesel is made by a common process called tranesterification. It is the process used for the production of Biodiesel which consists of fatty acid methyl esters (FAME) from the triglycerides. In base catalyzed tranesterification process the raw oil should be of good quality and the oil should not have free fatty acid (FFA) and moisture content more than 0.5%. In many cases, large quantity of oils contains higher moisture content and FFA and to transesterify these oils acid catalyzed tranesterification process is preferred which is not sensitive to higher FFA and moisture. One problem with biodiesel is poor low temperature stability. During winter the Northern, Western and Eastern part of India experience temperature from 15°C to 2°C whereas in Southern part the temperature is relatively high with a minimum temperature of 20°C. Due to the low temperature the saturated fatty acid alkyl esters in the biodiesel bound to crystallize and cause problems in Compression Ignition engine (Diesel engine) when 100% biodiesel is used as fuel. Jatropha is renewable non-edible oil and not expensive compared to other oils like Coconut, Sunflower, Palm, Neem, Rice bran. The aim is to produce vegetable oil based fuel (Biodiesel) using high FFA Jatropha oil by acid catalyzed tranesterification process using methanol with sulfuric acid as catalyst. The reaction is carried out at 65° C – 70° C for 14 hours. The biodiesel obtained is washed with hot distilled water and dried in oven at 105° C. Winterization of biodiesel is then carried out at different temperature from 35° C – 0° C for a period of 12 hours and solid fractions are filtered and weighed to find its usability at different cold temperatures.

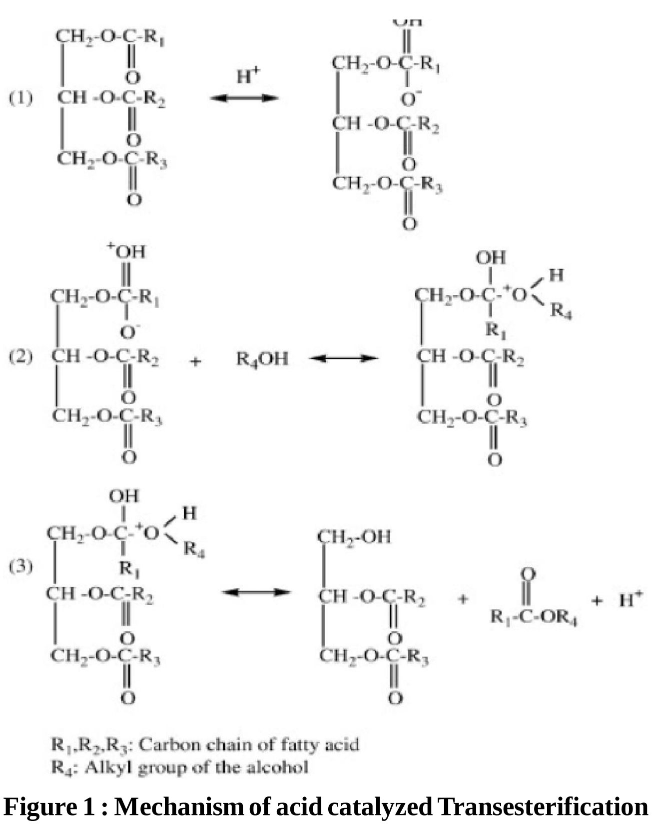
KEYWORDS

Acid catalyzed tranesterification;
Biodiesel;
Jatropha oil;
Winterization.

INTRODUCTION

Energy plays a very important role in our day to day lives. The energy sources on earth is broadly classified into three categories. They are renewable energy, non-renewable energy, and nuclear energy. Due to population explosion and raising demands for fuel consumption, people started overexploiting the fossil fuels which in turn depleted the non-renewable energy source. So, there is only limited amount of non-renewable source of energy for human consumption. This has brought oil crisis which increased the price of fuels such as petrol, diesel, LPG etc. If this situation prevails then the entire earth might run out of petroleum by 2050. To overcome this problem Bio-refinery came into the picture to replace Petroleum-refinery. Hence, Bio-diesel can be considered as an alternate fuel to run vehicles. The major advantage of using Bio-diesel is because of its less emission of CO_2 and other pollutants when compared to the fossil fuel. Practically biodiesel is considered to be an effective blending material to diesel for use in compression ignition (CI) engines than for direct use[1] and it does not cause problem to the CI engine since it has got the similar properties as conventional diesel.

Biodiesel can be prepared by tranesterification with alcohols such as methanol, ethanol, propanol or other alcohols using acid, alkali, or enzyme as catalyst. The process of transesterification was performed in the presence of methanol. This process was used to minimize the viscous nature of the vegetable oil and thereby improving the physical properties of bio-fuel to enhance



R1,R2,R3: Carbon chain of fatty acid
R4: Alkyl group of the alcohol

Figure 1 : Mechanism of acid catalyzed Transesterification reaction

the engine's performance. In this process the tri-glycerides reacts with alcohol to get Fatty acid Methyl Ester (FAME) and glycerol as shown in Figure1.

One major disadvantage of biodiesel is its performance under low temperatures[2]. Depending upon the nature of oil, the biodiesel produced may cause problems during winter due to crystallization. Crystallization occurs in Biodiesel at a high temperature due to the presence of saturated FAME which have higher melting point. Winterization is the process of studying the performance of bio-diesel under cold conditions, where the bio-diesel is subjected to different cold temperatures and the crystals which were formed are filtered out. Each type of biodiesel has a varying content of saturated FAME. Various methods are employed to improve cold flow properties[3]. Additives such as anti-gel are used to prevent the formation of wax in the crystals. There are heated fuel filters available that can run off vehicle battery[10]. Biodiesel can also be made from branched chain alcohols (isopropyl) reducing crystallization (consequently its crystallization temperature) because crystallization occurs due to the presence of uniformity, which can be reduced in this process[4].

Jatropha curcas belongs to the Euphorbiaceae family. It can grow well in countries like Africa, India, South East Asia and China. When Jatropha is planted, it will mature in 3 months and will continue producing seeds and flowers for more than 40 years. Jatropha can withstand high temperature and heavy rainfall. A single Jatropha seed can produce 40% of oil.

Different oils have different crystallization onset temperature. Since bio-diesel is liable to crystallization of its high melting saturated esters at cool operating temperature, removal of saturated esters by winterization was assessed as a means of reducing the crystallization onset temperature of biodiesel[5]

The southern region of India such as Tamilnadu, even in winter the temperature never goes below 10°C. So the biodiesel seldom undergoes crystallization. But as we move towards northern regions such as Delhi, in winter the temperature goes much below 10°C, where winterization plays a major role. The important criteria to design a winterization process are the temperature of crystallization of bio-diesel and the rate of cooling of oil[6]. These parameters play an important role in separating the fats as distinct crystals and facilitating their filtration from oil. Winterization is the process of exposing the oils at various lower temperatures such as

30, 25, 20, 15, 10 and 5°C and the amount of crystals formed are recorded. The winterized biodiesel can be then used effectively at low temperature. Bio-diesel was subjected to winterization at different temperatures and the quantity of solid fraction was found in mass %. GC (Gas Chromatography) analysis was done to analyze the composition of fatty acid in the Jatropha bio-diesel.

EXPERIMENTAL PROCEDURE

Materials

Jatropha Oil was purchased and used without refining. Methanol, Sodium Hydroxide, Sulfuric Acid, Sodium Chloride and Calcium Chloride were analytical grade purchased from S.D fine Chemicals, India.

Equipments

REMI Heating Mantle with Magnetic Stirrer, Chilling Unit–Sub Zero Cooling Instruments, Liebig Condenser and Two necked round bottom Flask were the major equipments used for this study.

Process

Unrefined Jatropha oil was transesterified with acid catalysis using 0.5 % concentrated sulfuric acid by weight with respect to oil and 30 % by weight of methanol along with un-refined oils at a temperature range of 65-70°C maintained over a period of 13-14 hours [7,8]. Once the reaction is over the contents were allowed to settle for 3 hours in a separating funnel. Top Product (biodiesel) from the reactor is subjected to hot water wash to remove excess methanol and catalyst from biodiesel. The product yield was calculated on mass basis as (Wt. of Biodiesel/ Wt. of Oil) x 100.

Fuel properties

Various fuel properties were measured as per the standard procedures, and the results are given in TABLE 1. GC analysis was done using an AGILENT 6850 Series GC System. HP-1, Column – DB-23 fused silica Column - 202 × 200 × 105 mm (HWD), Detector – Flame Ionization Detector, Split 1:50 and N_2 Flow – 1 ml/min. Temperature programming was done as follows – 160°C for 3 minutes at 6°C/min, 180°C for 2 minutes at 5°C/minutes and 230°C for 11 minutes at 4°C/ minute. The area % gave the corresponding quantity of Fatty Acid present in the biodiesel. The GC results are given in TABLE 2.

Winterization

Winterization[9] is a process of exposing the biodiesel at various lower temperatures and recording the amount of crystals formed. Based on these values percentage solid (%solid) and liquid (%liquid) is determined.. The main purpose is to separate the saturated methyl esters at its specific solidifying temperature and reduce the overall crystallization onset temperature. This will help in using bio-diesel at low temperature without clogging its filter parts by its crystals. The experiment was carried out on all the different biodiesel at samples at 20°C, 15°C, 10°C, 5°C and 0°C correspondingly for a minimum period of 12 hours. It was done using a refrigerator. Samples were weighed and poured into flasks and kept inside the chilling unit. The temperature was set and the samples left for 12 hours. After that the samples were transferred to similar flask using a filter paper and funnel. The filter paper and the crystals separated out with it were weighed and the liquid separated out was also weighed.

RESULTS AND DISCUSSION

As commercial jatropha oil contains free fatty acid and moisture, initial experiments with alkali catalyst didn't yield biodiesel hence sulfuric acid was used as acid catalyst. Theoretically for every mole of oil 3 moles of methanol was required for transesterification process. In this case the quantity of methanol which was present in excess was used to shift the equilibrium towards forward

TABLE 1 : Fuel properties of Jatropha Biodiesel

Biodiesel	DENSITY (KG/M^3)	VISCOSITY (CST) AT 40°C	FLASH POINT (°C)	FIRE POINT (°C)	CLOUD POINT (°C)	POUR POINT (°C)
Jatropha	886	5.8	171	175	+3	-6

TABLE 2 : Chemical composition of Jatropha oil methyl ester by GC analysis

Biodiesel	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0
Jatropha	0.18	13.30	7.10	41.80	35.80	0.34	0.27

direction for the formation of products. Although the excess methanol was washed with water along with alkali in commercial scale, the excess methanol has to be recovered by distillation. For every 100 g of oil, 30 g of methanol is sufficient for obtaining good yield. As the boiling point of methanol is 64.7°C, so the reaction was conducted at temperature is in the range of 65-70°C for the easy formation of biodiesel. The sulphuric acid catalyst used was 0.5% on the weight of oil for good yield.

Biodiesel yield obtained as high as 95 %. Biodiesel properties are given in TABLE 1. The viscosity of raw oil was 44 cSt whereas for biodiesel was 5.8 cSt. It shows that transesterification reduces the viscosity of oil to almost one seventh to one eighth of its original value. Flash point and fire point was within the range of 170°C – 175°C.

Gas chromatography

The percentage of Fatty Acid Methyl Ester in each biodiesel is shown in TABLE 2. Jatropha oil methyl ester is rich in C18:1, C18:2 fatty acids.

Winterization results are tabulated in TABLE 3. During winterization, up to 20°C there is no haziness or crystal formation. However, a further cooling to 15 and 10°C the solid formation was about 2%. A further cooling to 8°C the amount of solids separated was 4%. A further cooling to 5 and 0°C leads to significant loss of fuel.

CONCLUSION

Biodiesel was produced from jatropha oil by acid transesterification process. The yield by transesterification was 95 %. Different fuel properties were measured for the biodiesel and they are within the standard specifications.

TABLE 3 : Amount of liquid fraction in winterized Jatropha biodiesel at different temperatures

TEMPERATURE °C	20	15	10	8	5	0
AMOUNT OF LIQUID FRACTION COLLECTED (%)	100	99.5	98.0	96	81.3	77.5

The Gas Chromatography analysis shows that jatropha oil is rich in C18:1, C18:2 fatty acids. Winterization studies was conducted for the biodiesel at 20°C, 15°C, 10°C, 5°C and 0°C and was found that during winterization up to 20°C there is no haziness or crystal formation however, a further cooling to 15°C and 10°C the solid formation was about 2%. A further cooling to 8°C the amount of solids separated was 4%. Based on this study it can be concluded that by winterizing of jatropha, biodiesel can be used up to a temperature of 10°C with a minimal removal of solid fraction amounting to 2 %. Jatropha has a huge potential in the field of biodiesel production because of the fact that it is non-edible oil and also has reasonable cold flow properties hence can be exploited to the fullest.

REFERENCE

[1] R.L.McCormick, T.L.Alleman, J.A.Waynick, S.R.Westbrook, S.Porter; Stability of Biodiesel and Biodiesel Blends, National Renewable Energy Laboratory, NREL/TP-540-39721, 1-25 **(2006)**.

[2] Inmok Lee, Lawrence A.Johnson, Earl G.Hammond; Reducing the Crystallization Temperature of Biodiesel by Winterizing Methyl Soyate, JAOCS, **73(5)**,.631-636 **(1995)**.

[3] T.L.Ooi, C.M.Teoh, S.K.Yeong, S.Mamot, Salmiah; Enhancement of cold stability of palm oil methyl esters, Journal of Oil Palm Research, **17**, 6-10 **(2005)**.

[4] Inmok Lee, Lawrence A.Johnson, Earl G.Hammond; Use of Branched-Chain Esters to Reduce the Crystallization Temperature of Biodiesel, JAOCS, **72(10)**, 1155-1160 **(1995)**.

[5] Pushpinder S.Puri;Winterization of oils and fats, Journal of the American Oil Chemists society, **57**, A932, December 01 **(1980)**.

[6] Inmok Lee; Reducing the crystallization temperature of biodiesel by winterizing methyl soyate.

[7] Laurean'o'Canoira, Ramón Alcántara, Ma JesúsGarcía-Martínez, Jesús Carrasco; Biodiesel from Jojoba oil-wax: Transesterification with methanol and properties as a fuel, Biomass and Bioenergy, **30(1)**, 76–81 **(2006)**.

[8] Jon Van Gerpen; Biodiesel processing and production, Fuel Processing Technology, **86**, 1097–1107 **(2005)**.

[9] Ángel Pérez, Abraham Casas, Carmen María Fernández, María Jesús Ramos, Lourdes Rodríguez;Winterization of peanut biodiesel to improve the cold flow properties. Bioresource Technology, **101(19)**, 7375-7381, October **(2010)**.

[10] www.marquemotors.com