ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology
Vol. 2, Issue 5, May 2015

Optimization of Production and Quality Assessment of Biodiesel from Karanja Vegetable Oil

Satya Deo Ram[1], Jai Prakash[2], S.K Dhiman[3], Arvind Lal[4] , Arbind Kumar[5]

Principal In-charge, Govt. Women's Polytechnic, Bokaro[1],

Faculty, Department of Mechanical Engineering, RTCIT Ormanji, Ranchi[2]

Faculty, Department of Mechanical Engineering, Birla Institute of Technology, Mesra, Ranchi[3,5]

Indian Railways Institute of Mechanical and Electrical Engineering, Jamalpur[4]

Abstract: Production of Biodiesel and optimization of transesterification process variables affecting biodiesel production is worthy of continued study because of its environmentally beneficial attributes and its renewable nature. Optimization of process variables will maximize biodiesel yield with effective reduction in production costs. The process variables affecting the yield and characteristics of biodiesel produced from Karanja (Pongamia Pinnata) vegetable oil were studied, the achieved results were analyzed and a set of recommendations proposed. From the obtained results, the best yield percentage was obtained using oil/methanol ratio (v/v) of 10:1, potassium hydroxide as catalyst 0.9% (w/v), reaction temperature of 66^0 C and reaction duration of 105minutes at stirring speed of 450 rpm. The yield percentage of biodiesel obtained was 91% under optimum conditions. From the results it was clear that the produced biodiesel fuel was within the recommended standards of biodiesel fuel.

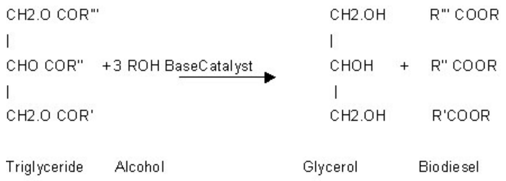
Keywords*:* Biodiesel, vegetable oil, transesterification, optimization and quality assessment.

INTRODUCTION

Energy is the prime mover of the development process. It is the most important resource needed to propel a country on the path of economic, industrial and social development. Consumption of fossil fuels has increased to a greater extent and the use of these energy resources is seen as having major environmental impact. Energy diversification is seen as an insurance policy against geopolitical risks and government insecurity about fossil fuel costs and fuel safety. Biodiesel production is worthy of continued study and optimization of production variables because of its environmentally beneficial attributes and its renewable nature [1]. A major constraint towards widespread commercialization is the high price of biodiesel. The immediate solution to address higher price hurdle is to research and develop methods to minimize the cost of biodiesel. A reduced cost option is to produce biodiesel from low cost fats and vegetable oils. Another option for cost reduction is to reduce the cost of processing vegetable oil through optimizing the process variables that affect the yield and purity of biodiesel. This study is intended to consider aspects related to the feasibility of the production of biodiesel from locally available karanja vegetable oil in an attempt to reduce the cost of biodiesel. The process variables affecting the yield and characteristics of biodiesel from karanja oil were studied and obtained results were analyzed and a set of recommendations was proposed. Biodiesel refers to a diesel equivalent, processed fuel which is derived from biological sources. It is defined by the World Customs Organization (WCO) as a mixture of mono-alkyl esters of long chain (C_{16}–C_{18}) fatty acids derived from vegetable oil or animal fat, which is a domestic renewable fuel for Compression-Ignition (C.I) Engines and meets the specifications of ASTM D6751. Despite being vegetable oil energetically favorable, direct use of straight vegetable oils as fuels in C.I engines is problematic. Due to very high viscosity and low volatility, straight vegetable oils do not burn completely and forms deposits of acrolein (a highly toxic substance formed through thermal decomposition of glycerol) that clogs the fuel injector of C.I engines and results in complete seizure of the engine.

Biodiesel Production

Several production methodologies have been reported. These include blending of oils, microemulsion, pyrolysis and transesterification. Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis. This process has been widely used to reduce the viscosity of vegetable oils (triglycerides). The transesterification reaction is represented by the general equation.



DOI 10.17148/IARJSET.2015.2502

Where R', R'' and R''' are different types of fatty acid chains associated with the oil.

If methanol is used in the above reaction it is termed as methanolysis. Triglycerides are readily transesterified in the presence of a catalyst at atmospheric pressure and at a temperature of approximately 60 to 70^{o}C with an excess of methanol. The mixture at the end of reaction is allowed to settle. The lower glycerol layer is drawn off, while the upper methyl ester layer is washed to remove entrained glycerol and is then processed further for removal of excess methanol and moisture. The process for biodiesel production is shown in Figure 1.

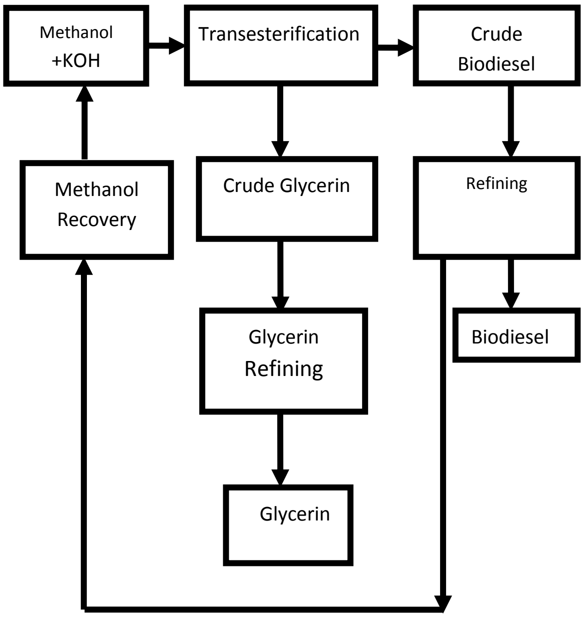


Fig. 1: Schematic Process for biodiesel production

Transesterification involves stripping the glycerine from the fatty acids with a catalyst (potassium hydroxide or sodium hydroxide) and replacing it with anhydrous alcohol that is usually methanol. The resulting raw product is then centrifuged and washed with water to cleanse it of impurities. This yields methyl or ethyl ester (biodiesel) and small amount valuable by-product glycerol, used in making soaps, cosmetics and numerous other products [2].

The three basic methods of ester production from vegetable oil or fats are the base catalyzed esterification, the acid catalyzed esterification and enzymatic catalysis. The most commonly used method among these is the base catalyzed transesterification technique as it is the most economical process [3]. The transesterification reaction is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of catalyst considerably accelerates the adjustment of the equilibrium [4]. The stoichiometric reaction requires 1 mole of a triglyceride and 3 moles of alcohol. However, an excess of alcohol is used to increase the yield of alkyl esters and to allow its phase separation from glycerol to be formed [5]. Through optimizing process variables that affect the yield and the purity of biodiesel, optimal transesterification conditions that produce maximum biodiesel yield could be determined. The extent of transesterification and side reactions depends upon the type of feedstock, catalyst formulation, catalyst concentration, oil to alcohol ratio, reaction temperature and reaction duration. Free fatty acid and moisture content in the feedstock oil plays a crucial role in the production of biodiesel. To complete the alkali catalyzed reaction, a free fatty acid (FFA) value lower than 3% is needed [6]. Before starting the transesterification process, free fatty acids must be reduced to below 3% with a base catalyst or preprocessed with acid esterification to esters [7]. The vegetable oils used in transesterification should be substantially anhydrous. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. Soap formation reduces catalyst efficiency, causes an increase in viscosity and leads to gel formation and hence makes the separation of glycerol difficult. Since prices of edible oils are higher than non-edible oil, karanja vegetable oil which is non-edible oil and locally available in the region of Jharkhand have been chosen and investigated.

Process Variables affecting Biodiesel Production

Use of methanol was dominated in most of the literature reviewed therefore in the present study, methyl rather than ethyl ester production have been modeled. This is because of the fact that methyl esters are predominant commercial products. Also, methanol is considerably cheaper than ethanol and the recovery of unreacted alcohol is much easier. Among the most commonly used alkaline catalysts in the biodiesel industry are the potassium hydroxide (KOH). Methanolysis with 0.9% wt. of KOH catalyst resulted in successful conversion giving the best result. It was observed that the product volume steadily increased from 0.5% w/v concentration of the catalyst until it reached its peak at 0.9% w/v of catalyst concentration. Thereafter a decrease was witnessed. One of the most important variables affecting the yield of ester is the ratio of oil to methanol. For maximum conversion to ester, the optimum ratio of oil/methanol (v/v) obtained was 10:1. The temperature had no detectable effect on the ultimate conversion to ester. However, higher temperatures decrease the time required to reach maximum conversion. For this reason the reaction temperature was kept at 66^{0} C. Since transesterification reaction can only occur in the interfacial region between the liquids and also due to the fact that fats and methanol are not totally miscible, transesterification is a relatively slow process. As a result, a vigorous mixing is required to increase the area of contact between the two immiscible phases. Optimum mixing speed was found to be 450 rpm for maximum conversion.

EXPERIMENTATION

Biodiesel, the name popularly given to fatty acid alkyl esters, has become an attractive option for the replacement of petro-diesel because of their desirable qualities. The question of course, is if biodiesel has so many advantages, why should its use have to be legislated for at all? The primary reason for this is the cost. It was only during the very peaks of the oil spike of 2008 that biodiesel was able to approach the cost of biodiesel. Of this cost, about 60-85% comes from the feedstock. The issue of alternative feedstock is thus of great concern.

Biodiesel has an interesting characteristic that is its fuel properties depend on the feedstock. This is because of the fact that biodiesel is not a pure substance but is a mixture of alkyl esters that result from the transesterification reaction between the triglyceride and an alkyl alcohol. The most commonly used alcohol is methanol due to its low cost and the resulting esters are called fatty acid methyl esters (FAMEs). The reaction is represented stoichiometrically as shown in Fig. 2. Since they determine the average molecular weight and reactivity of the mixture, the fuel properties of biodiesel depend on the nature and relative quantity of the alkyl groups attached to the glycerin molecule; R_1, R_2 and R_3. This is commonly called the fatty acid profile of the triglyceride. The structure of each fatty acid has an impact on the fuel properties. The most frequently cited parameters are the average chain length and the degree of unsaturation of the fatty acid.

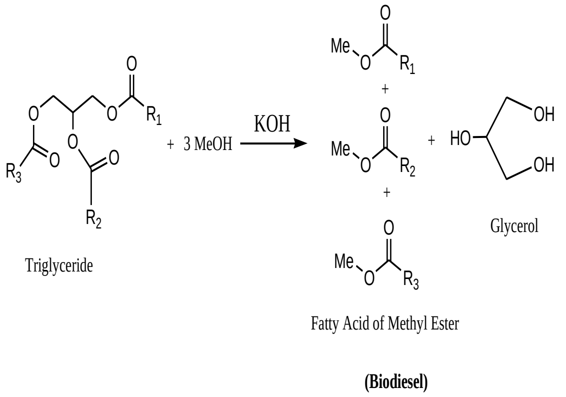


Fig. 2: Stochiometric representation of transesterification reaction.

By extrapolation from the behavior of pure FAMEs and from literature review a general statement may be made that the cetane number, heat of combustion, viscosity and the oxidative stability increases as the chain length increase and decrease as the number of double bonds increase on the other hand lubricity decreases as the chain length increases and decreases as the number of double bonds increases. These fuel properties all interact in a complex manner to give the final observable effect on engine performance and emissions.

Depending on the climate and soil conditions, different nations are looking into different vegetable oils for diesel fuel substitute. Worldwide, the feedstock for biodiesel production in greatest supply are soybean oil, palm oil, sunflower oil, rapeseed oil, coconut oil, etc. which are edible in Indian context. Since edible oil demand is higher than its domestic production, it is not desirable to divert these oils for production of biodiesel in India. Being a tropical country, India is rich in forest resources having a wide range of trees, which yield a significant quantity of oil seeds. Thus, development of biodiesel from locally available non edible oil seeds which are low in cost is a more rational basis. In the present study, investigation have been undertaken to find out suitable production process for biodiesel derived from non-edible karanja oil (Pongamia pinnata). The physico-chemical properties of raw karanja oil procured from local market is shown in Table1:

Physico-chemical Properties of Karanja oil

Sp. Gravity (15 deg C)	0.910-0.940
Flash Point (deg C)	205^oC
Cetane Index	56.2
Sulphur %	0.02
FFA %	2.53

Initially, experiments were conducted in the laboratory set up as shown in Fig. 3. The biodiesel reactor consists of heating mantle, reaction glass flask and mechanical stirrer. The working capacity of the reaction flask was 1 liter. It consisted of three necks one for stirrer, other for condenser and inlet for reactants as well as for the thermocouple to observe the reaction temperature. The important variables that influence transesterification conversion were oil temperature, reaction temperature, reaction duration, ratio of oil to methanol, catalyst type and concentration and mixing intensity. The variable parameters were optimized in the test set up of 1 liter capacity reactor and the optimized parameters were used for production of larger quantity of biodiesel in a 5 liter capacity per batch as shown in Fig. 3.

Fig.3: Biodiesel Reactor of 5 Liter capacity per batch.

The triglyeride was transesterified to monoesters of fatty acids (biodiesel) using alkali catalyst KOH. When the reaction was complete, the products were allowed to settle in two layers. The lower layer contained the impurities and glycerol. The top ester layer was separated and purified using warm distilled water. After washing, the final product was heated to 110^0 C for 15 minutes in the oven to remove water and was stored in air tight jar for further use.

This resulted in a clear light liquid with density and viscosity close to petro-diesel. Flow chart for biodiesel production from karanja oil is shown in Fig.4.

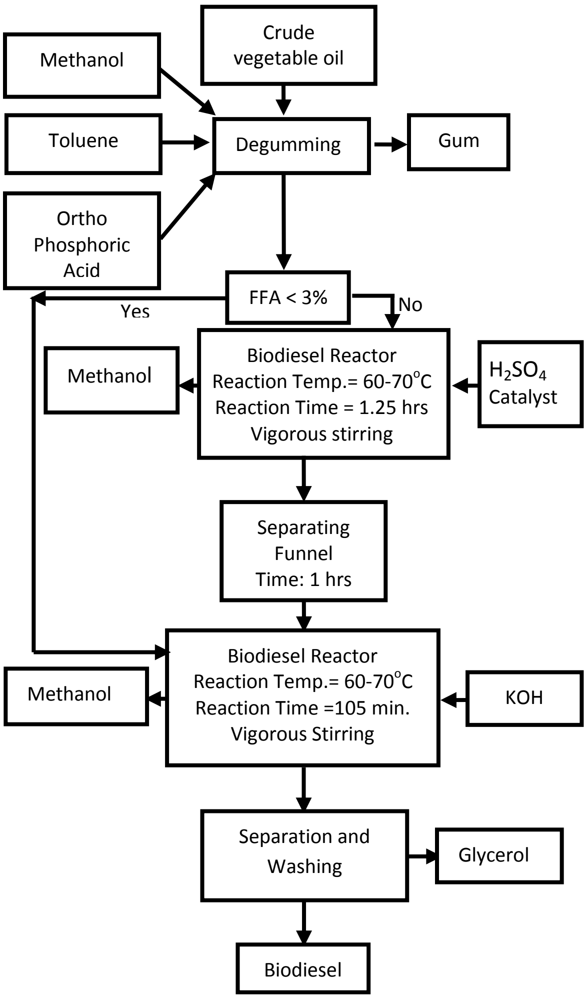


Fig. 4: Flow chart for biodiesel production

RESULTS AND DISCUSSION

To achieve maximum yield of biodiesel using karanja vegetable oil, the optimum conditions were studied. The results of product yield of all experimental yields are summarized in Table 2.

Table 2: Optimized parameters for biodiesel production

S.No.	Parameters	Karanj oil
1.	Oil to Methanol ratio (v/v)	10:1
2.	% KOH (w/v)	0.9
3	Reaction temperature (^{o}C)	66
4	Reaction duration (minutes)	105
5.	Yield %	91

(i) Effect of methanol amount on methyl esters yield

The quantity of methanol added to karanja oil is one of the important factors that affects conversion efficiency as well as production of cost of biodiesel. The conversion efficiency is defined as the yield of the process represented in terms of percentage. The amount of methanol required for base catalysed transesterification is analysed in terms of volumetric ratio. Stoichiometrically, the methanol to triglyceride molar ratio is 3:1. But in practice, this is not sufficient to complete the reaction. Higher amount of methanol is required to drive the reaction to completion at faster rate. It is observed that lower amount of methanol requires longer reaction period. The conversion efficiency of base catalysed transesterification obtained during present study is shown in Fig. 5. The maximum conversion efficiency was achieved very close to oil to methanol ratio (v/v) of 10:1 for karanja oil. With further increase in volumetric ratio, no significant improvement in the conversion efficiency was observed.

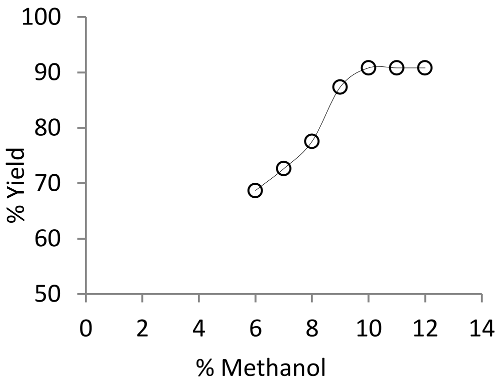


Fig. 5: Effect of Methanol Quantity on yield during base catalysed transesterification

(ii) Effect of catalyst on methyl esters yield

The catalyst accelerates the transesterification reaction. Potassium hydroxide was used as catalyst in the present experimental analysis. Potassium hydroxide in the range of 0.5 to 1.5% (weight of KOH/volume of oil) was investigated to study the catalyst amount on the conversion efficiency as shown in Fig. 6. The maximum conversion efficiency during base catalysed transesterification was achieved at 0.9 % of KOH for karanja oil. In the course of tests, it was observed that addition of excess amount of catalyst, gave rise to the formation of emulsion, which increased the viscosity and led to the formation of gel.

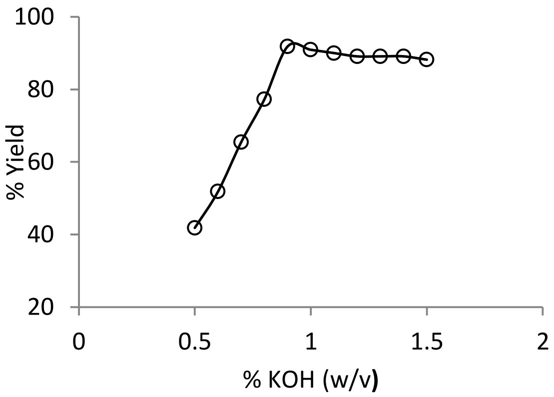


Fig. 6: Effect of catalyst on yield during base catalysed transesterification

(iii) Effect of reaction duration on methyl esters yield

In order to achieve an effective interaction between the catalyst and the oil during transesterification, it is essential that they must be stirred well at constant rate. It has been observed that a mixing intensity of 450 rpm was sufficient to accelerate the reaction for optimal condition. It has also been observed from Fig. 7 that the ester yield increases with increase in reaction duration. Results obtained from the present experiments with karanja oil revealed that about 105 minutes of reaction duration is suitable for the completion of the base catalyzed transesterification reaction.

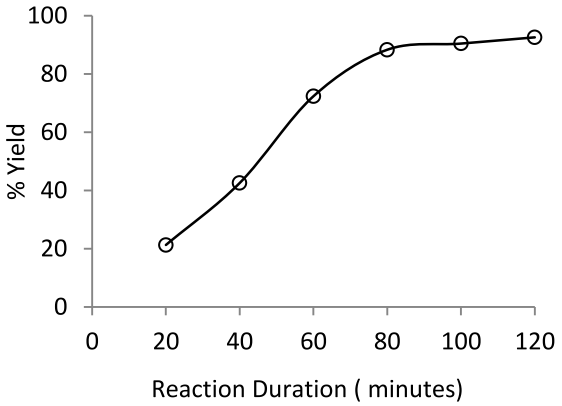


Fig. 7: Effect of reaction duration on yield during base catalysed transesterification

(iv) Effect of reaction temperature

The effect of temperature on transesterification of karanja oil was studied and the optimum temperature was found to be 66°C.

(v) Properties comparison of Diesel and Karanja Biodiesel

S.No.	Fuel	Density (kg/m^3) at 25^0C	Viscosity (cSt) at 40^0C	Calorific value (MJ/kg)	Flash point (^{0}C)	Pour point (^{0}C)	Cloud point (^{0}C)	% carbon residue (%Wt)
1.	Diesel	840	2.87	44.0	76	3.1	6.5	0.3
2.	Biodiesel	883	4.37	42.1	163	5.1	14.6	0.25

(vi) Differential Scanning Calorimetric studies of Karanja Biodiesel

The DSC study of karanja biodiesel is furnished in Fig.8. It shows a small inflection at -44°C amounting to 0.3398 mW/mg of energy which can be attributed to small segmental motion of the hydrocarbon long chain molecules. A sharp of endotherm is noted at 0.1°C which can be attributed to the vibrational motion of the molecule. Further endotherms were noted within a range are 20 – 45°C and are attributed to the vibrational and rotational motion of the molecule.

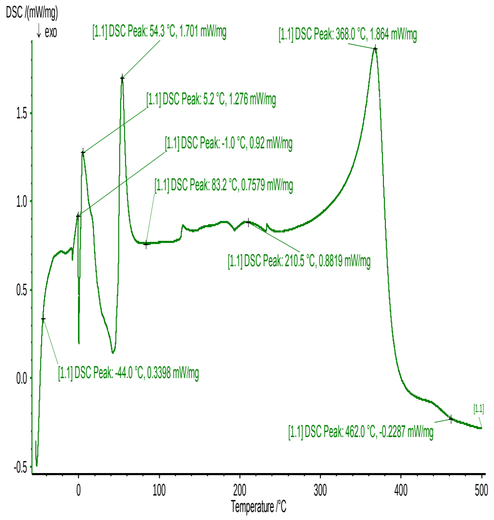


Fig.8. DSC Study of Karanja Biodiesel

With increase in temperature, at 54.3°C, the graph shows a sharp exotherm which can be attributed to the starting of breaking of long chain molecules. With further increase in temperature, oxidation stage reaches with absorption of energy.

FTIR of Karanja biodiesel and the comparative features are tabulated in Table 4. The FTIR spectrum was run in Shimadzu IR Prestige 21 instrument in a range of 4000 – 400 cm^{-1} wave number.

(vii) Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR of Karanja biodiesel are tabulated in Table 3. The FTIR spectrum was run in
Shimadzu IR Prestige 21 instrument in a range of 4000 – 400 cm^{-1} wave number.

Table 3: FTIR of Karanja Biodiesel

Material	Wave number (cm^{-1})	Remark
Karanja Biodiesel	3782.41	O-H_{str} (non-bonded)
	3464.15	H-bonded O-H group
	3005.10	=C-H_{str}
	2926.01,2854.65	-C-H_{str} of –CH_3 or –CH_2-
	1743.65	-C= O str (Carbonyl)
	1647.21,1600.92	C = C_{str} Asymmetric str
	1359.82,1460.11	C-$H_{bending}$
	1168.86, 1246.02	C – $O_{str(ester)}$

In the biodiesel obtained from karanja oil, a sharp peak was found at 1743.65 cm^{-1} showing the carbonyl structure vibration. This may be of ester, acid chlorides or acid

DOI 10.17148/IARJSET.2015.2502

anhydrides which absorb energy between wave number 1770 to 1725 cm^{-1}. Additional spectral region 1168.86 to 1246.02 cm^{-1} however, provides the supporting evidence of esters, as only esters show a strong C-O-C or C-O-R stretching peak at 1200 cm^{-1}. This shows the complete esterification of karanja oil. In fact biodiesels contain alkyl ester which facilated in controlling the viscosity of the medium. Other prominent peaks of C=C$_{str}$ vibration, C-O$_{str}$ vibration, C-H bending vibration etc are also present in the FTIR study.

Weaker peaks at 3464.15 cm^{-1}, 3782.41 cm^{1} and 1018 cm^{-1} are characteristic peak of hydroxyl group of primary alcohol which shows the presence of trace amount of CH_3OH which was used during the transesterification.

The absence of free O-H$_{str}$ frequency at 3600 cm^{-1} or hydrogen bond O-H frequency at 3300 cm^{-1} show that the sample KOBD is free from any free fatty acid. Though, sulphuric acid was used to remove the FFA, absence of peaks in the region 1080 to 1130 cm^{-1} shows the complete removal of sulphate group from the sample. Likewise absence of frequencies at 3657 cm^{-1}, 1595 cm^{-1}, 3756 cm^{-1} and at 667 cm^{-1}, shows absence of any absorbed water and CO_2 molecules in the sample.

CONCLUSION

As a developing economy, India faces dual challenge of pursuing economic growth and environmental protection. In order to promote economic development and environmental protection, it is imperative for the country to consider new paradigms for domestic energy production and consumption, thus incorporating the exploitation of its renewable energy resources. Based on the exhaustive experimental investigations with special reference to transesterification process, the following conclusions are drawn:

1. Biodiesel is an attractive option for the replacement of petro-diesel because of their desirable properties. It can be produced from locally available vegetable oils through a chemical reaction known as tranesterification.

2. Transesterification is a low cost process which brings about a change in the molecular structure of the vegetable oil molecules, thus bringing down the levels of viscosity, density and unsaturation of vegetable oil.

3. It has been observed that biodiesel production from feedstocks with high FFAs (Free Fatty Acids > 3%) is extremely difficult using alkaline catalyzed transesterification process. This is because the alkaline catalysts react with FFAs to form soap that prevents separation of glycerin and ester. Thus a two step esterification for karanja are developed to convert the high FFA oils to its esters.

4. The effects of alcohol to oil volume, catalyst amount and reaction duration are analyzed in each step of the process. Excess addition of sulphuric acid darkens the product. It has been observed that the conversion efficiency is strongly affected by the amount of alcohol. The volumetric ratio of 10:1 of alcohol favours the completion of alkaline catalyzed transesterification process in 105 minutes for the formation of karanja oil methyl ester (KB$_{100}$) which is sufficient to give 91% yield of ester.

5. The density and viscosity of karanja oil gets drastically reduced after esterification and are very close to petroleum diesel oil.

6. The flash point of biodiesel is greater than that of diesel and calorific value is slightly lower than that diesel.

7. Transesterification method reduces the overall production cost of biodiesel as it uses cheap, unrefined non-edible vegetable oil.

8. The addition of biodiesel to diesel fuel changes the physico-chemical properties of the blends. With the increase of biodiesel concentration in diesel-biodiesel blends, the kinematic viscosity, cetane number, flash point and fire point of the blends increase.

9. Differential Scanning Calorimetry studies provided the structural information and material properties of biodiesel. The DSC curves helped in analyzing the kinetics of oxidation process of the alkyl esters obtained from karanja oil.

10. The FTIR analysis of biodiesel provided supporting evidence of esters. The analysis also confirmed the complete esterification of karanja oil.

All these tests for characterization of biodiesel demonstrated that the properties of biodiesel are in close agreement with the diesel making it a potential candidate for the application in compression ignition engines.

REFERENCES

[1] Refaat, A.A, Attia, N.K, Sibak,, H. Aazid, Sheltawy, El and Eldiwani, G.I. 2008. Production Optimization of Biodiesel from Waste Vegetable Oil. Int.J. Environ.Sc. Tech, 5(1), 75-82.
[2] Cheng, S.F, Choo, Y.M, Chuah, C.H. 2004. Kinetics study on transesterification of palm oil. J. oil Palm Res., 16(2), 19-29.
[3] Dorado, M.P., Ballesteros, E, de Ameida, J.A, Krause, R. 2002. Transesterification of Karanja oil by solid basic catalysts. Am. Soc. Agr. Biol. Eng.,45(3), 525-529.
[4] El Mashad, H.M, Zhand, R, Roberto, J. 2006. Biodiesel production from fish oil. American Society of Agricultural Engineers Annual Meeting, 066144.
[5] Ma, F, Hanna, M.A. 1999. Biodiesel production: A Review. Bioresource Tech., 70 (1), 1-15.
[6] Meka, P.K, Tripathi,V, Singh, R.P. 2007. Synthesis of Biodiesel fuel from Safflower oil using various rection parameters. J. Oleo Sci. 56 (1), 9-12.
[7] Singh, A.K., Fernando, S. 2006. Catalysed fast – transesterification of Soyabean oil using ultrasonication. ASAE Annual Meeting, 066220.

DOI 10.17148/IARJSET.2015.2502