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POLANGA OIL BASED BIO-DIESEL (POBD): A CLEAN BURNING LIQUID FUEL FOR INDIAN RAILWAYS APPLICATION.

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Abstract- To minimize the air pollution impact on the environment specially in Indian Railways(IR) premises, IR has decided to run its locomotives as well as road vehicles on non-edible oils based Fatty acid of methyl ester (FAME) fuels and its blend with HSD oil. In the present paper, bio-diesel was prepared by triple stage trans-esterification process from the non-edible Polanga oil (Callophyllum Anophyllum) collected from Diesel shed Kharagpur (South Eastern Railway) .The prepared bio-diesel and its blends with HSD oil were characterized by its physical and fuel properties such as density,viscosity,flash point, pour point, cloud point and water content etc. From the obtained results, the best yield percentage was obtained using oil/methanol ratio (v/v) of 10.5:1, potassium hydroxide as catalyst 0.85%(w/v), reaction duration of 120 minutes with a stirring speed of 450rpm.The yield percentage of Polanga oil bio-diesel(POBD) was 87% under optimum conditions. From the results as obtained, it was clear that the produced bio-diesel (POBD) fuel was within the recommended standards of Bio-diesel as per IS:15607/2005 and its properties were also comparable with the high speed diesel (HSD)as per IS:1460/2005, presently used in Indian Railways.

Keywords: Bio-diesel,Indian Railways(IR), HSD oil, transesterification and optimization.

1. INTRODUCTION

Energy is an essential input for economic growth, social development, human welfare and improving the quality of life. Since their exploration, the fossil fuels continued as the major conventional energy source. With increasing trend of modernization and industrialization, the world energy demand is also growing at a faster rate. Apart from their indigenous production, majority of developing countries import crude oil to cope up with their increasing energy demand. Thus, a major chunk of their hard earned export earnings is spent for purchase of petroleum products. India is also a net energy importer and almost 80% of the country's export earnings are directly spent for purchase of petroleum products. There had been sharp increase in the consumption pattern of petroleum products in India. The transport (Rails as well as roads) as well as the agriculture sectors are the major users of diesel fuel.

Now a days fossil fuel becomes the matter of global concern due to its over exploitation and the same times, deteriorating the environmental conditions. IR (Indian Railways) has one of the largest and busiest rail networks in the world, transporting over 18 million passengers and more than 2 million tonnes of freight daily[1]. Indian Railways has already taken a lots of sustainable initiatives to protect the environment from further deterioration by using bio-diesel made from different non-edible oils to meet its requirement Compared to petroleum diesel. Bio-diesel has lower emission of pollutants, biodegradable and better lubricity.[2,3].Bio-diesel has a higher cetane number than diesel fuel,no aromatics, no sulphur and contains 10-11% more oxygen by weight.[4]. Hence a considerable work has been done by Indian Railways at Research Design and Standards Organization (RDSO) and IRIMEE to assess the suitability of Bio-diesel for the India Railways application as an alternative to power the Diesel locomotives as well as road vehicles.[5].Hence, the use polanga (calophyllum and anophyllum), a non-edible oil should be given higher priority over the other oils as bio-diesel feedstock.

The objective of the paper is both to develop self-sufficiency energy source that is non-polluting, environment friendly and cost effective. The properties of biodiesel were very similar to those of existing diesel (HSD oils IS: 1460/2005) and it can be blended in various proportion to the diesel to achieve the target fixed up by IR upto 20%(twenty percentage) blend with HSD oil by 2030 [6].

2. EXPERIMENT AND RESULT

Depending on the climate and soil condition different nations are looking into different vegetable oils for diesel fuel substitute.In India, being a tropical country, 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 of low in cost was desirable. In the present paper, non-edible polanga (Calophyllum inophyllum) oil was collected from Diesel shed Kharagpur (SER) to find out suitable three stage transesterification production process to convert it into biodiesel . To achieve maximum yield

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polanga bio-diesel,the optimum conditions were studies.The results of product yield (POBD),of all the experimental data are summarized from table no-1 to 5.

2.1 Biodiesel production and process optimization

Zero-catalysed transesterification (Removal of organic matter and gum):

The first stage removes the organic matters and other impurities present in the samples of polanga oil using reagent. The presence of impurities creates problems in the yield and in phase separation between the glycerine and esters. This necessitates the pretreatment of procured vegetable oils in the first stage. This is a zero-catalysed transesterification in which mixture of raw vegetable oil, methanol, ortho-phosphoric acid and toluene was stirred at a constant speed and temperature for 0.5 hours to 4.0 hours. 1 litre of oil was mixed with 350 ml of methanol, 5 ml of toluene and 5 ml of ortho-phosphoric acid as a reagent. Toluene helps in dissolving the organic matter with methanol and separating it from the neat oil along with impurities. Different methanol to oil ratio in % volume basis (6% to 40%) and reaction times (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 hours) were used to investigate for the optimization and their influence on the acid value of raw vegetable oils. The mixture was stirred in air tight reaction flask for 2 hours at 66oC. The heating set up should be just above the boiling point of the alcohol (66oC) to accomplish the reaction. The speed of the stirrer was kept the same for all test runs at 450 rpm. The reactions were carried out with continuous stirring. The product from the first stage was allowed to settle and complete phase separation was visualized. The upper layer which consisted of methanol-water fractions, organic matter, gum, toluene and other impurities were separated from the lower layer. The acid value of the lower layer, which was raw material for the second stage.

2.2 Acid-catalysed transesterification:

Anhydrous sulphuric acid (98.4%) was used as catalyst in the acid-catalysed transesterification. The product of the first stage was mixed with various proportions of anhydrous sulphuric acid starting from 0.1% (v/v) along with methanol in volume basis and stirred at a temperature of 55oC with reaction
time of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 hours. The stirring speed was maintained at 300 rpm for all the experiments.

2.3 Alkaline-catalysed transesterification:

The product of the second stage (pure triglyerides) was transesterified to monoesters of fatty acids (biodiesel) using alkali catalyst KOH in the third stage. The second stage product i.e. pure triglycerides having less than 4% FFA, was used in the third stage. 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 110oC 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.The complete process for bio-diesel production is shown in Figure-1 and all the optimized results are produced in table no 1 to 3.

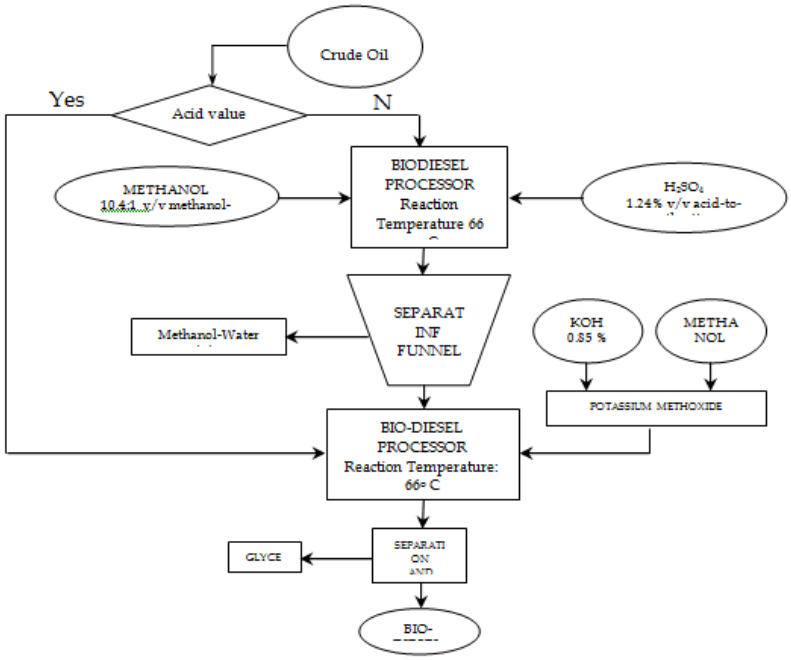

Figure 1. Schematic process for Bio-diesel Production.

1st stage (zero- catalyzed transestrrification)

S.No.	Parameters	Polanga oil
1.	Feedstock oil (litre)	1
2.	Methanol (ml/litre of oil)	350
3.	Toluene (ml/litre of oil	5
4.	Ortho phosphoric acid (ml/litre of oil	5
5.	Reaction duration (minutes)	120
6.	Reaction temperature (oC)	66
7.	Stirring speed (RPM)	450
8.	Settling time (minutes)	120
9.	FFA (%)	14.5

Table no-1

2nd stage (acid - catalyzed transestrrification)

S.No.	Parameters	Polanga oil
1.	Methanol (ml/litre of oil)	75
2.	Sulphuric acid (ml/litre of oil	6.5
3.	Reaction temperature (oC)	55
4.	Reaction duration (minutes)	240
5.	Stirring speed (RPM)	300
6.	Settling time (minutes)	120
7.	FFA (%)	2.1

Table no-2

3rd stage (acid - catalyzed transestrrification)

S.No.	Parameters	Polanga oil
1.	Oil to Methanol ratio (v/v)	10.5:1
2.	% KOH (w/v)	0.85
3	Reaction temperature (oC)	66
4	Reaction duration (minutes)	120
5.	Yield %	87

Table no-3

3. RESULTS AND DISCUSSION

3.1 Effect of methanol amount on methyl esters yield:

The quantity of alcohol added to feedstock 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 maximum conversion efficiency is achieved very close to the volumetric ratio of oil to methanol was 10.5:1 for polanga oil . With further increase in volumetric ratio, no significant improvement in the conversion efficiency was observed.

3.2 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. The maximum conversion efficiency during base catalysed transesterification was achieved at 0.85 % of KOH respectively for polanga 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.

3.3 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 550 rpm is sufficient to accelerate the reaction for optimal condition. It has also been observed that the ester yield increases with increase in reaction duration. Results obtained from the present experiments with polanga oil revealed that about 120 minutes of reaction duration is

suitable for the completion of the base catalysed transesterification reaction. Thus, reaction duration of about 120 minutes is sufficient for the completion of the reaction.

3.4 Effect of reaction temperature:

The effect of temperature on transesterification for the four types of oil was studied. The optimum temperature was found to be 66oC.

Properties comparison of diesel and Polanga oil bio-diesel.

S.No.	Fuel	Density (kg/m3 at 25oC	Viscosity (cSt) at 40oC	Calorific value (MJ/kg)	Flash point (oC)	Pour point (oC)	Cloud point (oC)
1.	Diesel	840	2.87	44.0	76	3.1	6.5
2..	PB100	869	3.99	41.3	111	3.6	10.8
3.	PB20	852	43.1	2.98	86	3.0	7.8
4.	PB40	854	42.8	3.30	91	3.2	8.5
5.	PB60	860	42.3	3.61	96	3.4	10.6
6.	PB80	862	41.9	3.72	111	3.6	10.8

Table no-4

3.6 Fourier Transform Infrared Spectroscopy (FTIR) analysis of Polanga oil Bio-diesel

FTIR of HSD oil and bio-diesel are furnished in Figure 2 to 3 and the comparative features are tabulated in Table 5. The FTIR spectrum was run in Shimadzu IR Prestige 21 instrument in a range of 4000 – 400 cm-1 wave number.

FTIR of Polanga Biodiesels and HSD oil

Material	Wave number (cm-1)	Remark
HSD oil	2926-2725	=C-Hstr (aromatic)
	1598, 1458	Aromatic C = Cstr
	1375	C – Hdef
	1303, 1163	Aromatic C – Cstr
	1031 – 727	C-Hbending
Polanga biodiesel	3462.22	H-bonded O-H group
(POBD)	3005.10	=C-Hstr
	2925.01,2852.72	C-Hstr of –CH3 or –CH2-
	1743.65	-C= O str (Carbonyl)
	1627.92,1587.42	C = Cstr Asymmetric str
	1359.82, 1462.04	C-Hbending
	1170.79,1244.08	C – O str (ester)
	879.54,848.68,723.31	C-Hbending

Table no-5

Analyzing the spectrum of HSD oil it was found that the aromatic =C-Hstr is quite prominent in the range of 2926 to 2725 cm-1 showing the presence of aromatic hydrocarbons. The HSD oil shows all other characteristic peaks related to the presence of various saturated and unsaturated hydrocarbons.

However, in comparison to biodiesel obtained from polanga , a sharp peak was found at 1743.65 cm-1 showing the carbonyl structure vibration. This may be of ester, acid chlorides or acid anhydrides which absorb energy between wave number 1770 to 1725 cm-1. Additional spectral region 1170.79 to 1244.08 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 the polanga oil. In fact biodiesels contain alkyl ester which facilated in controlling the viscosity of the medium. Other prominent peaks of C=Cstr vibration, C-Ostr vibration, C-H bending vibration etc are also present in the FTIR study.

Weaker peaks at 3462.22 cm-1, 3782.41 cm1 and 1018 cm-1 are characteristic peak of hydroxyl group of primary alcohol which shows the presence of trace amount of CH3OH which was used during the transesterification.

The absence of free O-Hstr frequency at 3600 cm-1 or hydrogen bond O-H frequency at 3300 cm-1 shows that the sample POBD was free from any free fatty acid. Though, sulphuric acid was used to remove the FFA, absence of peaks between 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, 2349 cm1 shows the absence of any absorbed water and CO2 molecules in the sample.

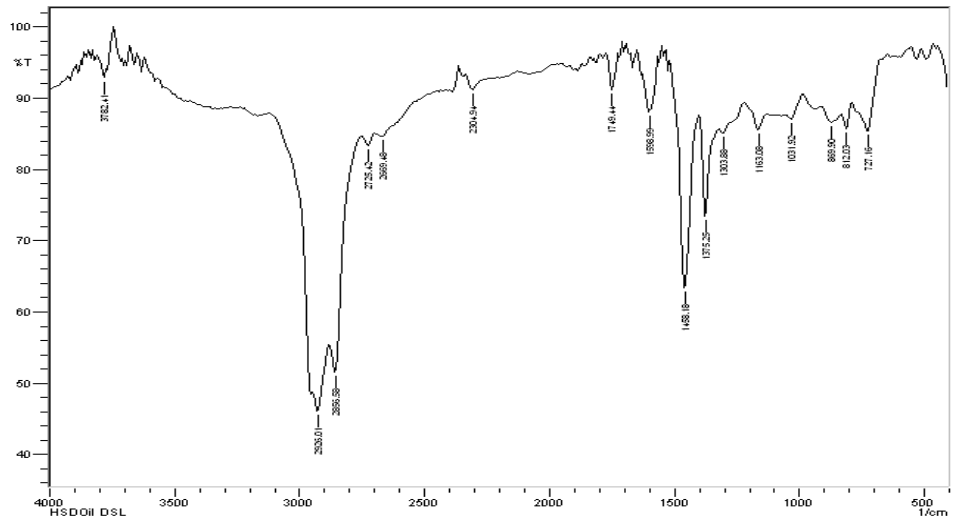

Figure 2: FTIR Spectra of (HSD Oil) Diesel

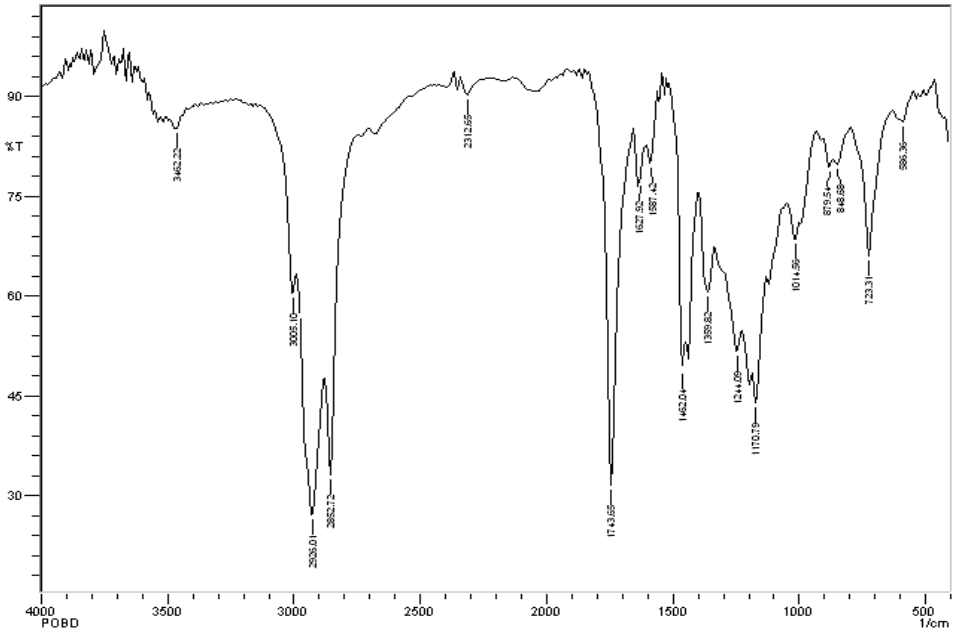

Figure 3: FTIR Spectra of (POBD) Polanga Bio-diesel.

4. CONCLUSION

Following conclusions are drown based on the experimental results obtained through the triple stage transesterification of polanga oil bio-diesel and compare its properties to the HSD oil used in IR.

Polanga based bio-diesel appears to be an attractive option for the substitute of HSD oil used in Indian Railways.

It has been observed that biodiesel production from feedstocks with high FFAs (Free Fatty Acids > 4%) 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 triple stage transesterification for polanga oil are developed to convert the high FFA oils to its esters. .

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 10.5:1 of alcohol favours the completion of alkaline catalyzed transesterification process in 120 minutes for the formation of polanga oil methyl ester (PB100) which is sufficient to give 87% yield of ester respectively.

The density and viscosity of vegetable oil gets drastically reduced after esterification. The density and viscosity of biodiesel were very close to petroleum diesel oil.

The flash point of biodiesel is greater than that of diesel and calorific value is slightly lower than that diesel. Hence due to lower calorific value, the specific fuel consumption may be slightly increased.

6. 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.
7. The FTIR analysis of diesel oil confirmed the presence of aromatic hydrocarbons, various saturated and unsaturated hydrocarbons. The analysis of the spectrum of biodiesel provided supporting evidence of esters. The analysis also confirmed the complete esterification of polanga oil.
All these tests for characterization of bio-diesel demonstrated that the properties of polanga bio-diesel are in close agreement with the diesel making it a potential candidate for the Indian railways as well as for other sector application .

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