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Production of Bio-diesel (Methyl Ester) from Simarouba Glauca Oil

Mishra S.R.*[1], Mohanty M.K.[2], Das S.P.[3] and Pattanaik A.K.[4]
[1]Department of Chemistry, C. V. Raman College of Engineering, Bhubaneswar, Odisha, INDIA
[2]Department of Farm Implement Design Unit, College of Agricultural Engineering and Technology, Bhubaneswar, Odisha, INDIA
[3]P.G. Dept. of Chemistry, Ravenshaw University, Cuttack, Odisha, INDIA
[4]P.G. Dept. of Chemistry, Khallikote (A) College, Berhampur, Odisha, INDIA

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Abstract

In developed countries, most of biodiesel is produced from the refined oil like soybean and canola etc. produced from farmers' field using methanol and alkaline catalyst. But a large amount of tree borne oils and fats are available for biodiesel production in developing and under develop countries. Simarouba glauca oil is one of these oils. This paper deals with the transesterification of Simarouba glauca oil by means of methanol in presence of Potassium hydroxide catalyst at less than 65^{0}C. The viscosity of biodiesel is nearer to that of the diesel. The biodiesel is characterized by TLC and the important properties of biodiesel such as density, flash point, cloud point, pour point, carbon residue and ash content are found out and compared with that of diesel. The studies encourage the production of biodiesel from unrefined Simarouba glauca oil as viable alternative to the diesel fuel.

Keywords: Simarouba glauca oil, biodiesel, transesterification, simarouba oil methyl ester

Introduction

Simarouba belongs to the family Simaroubaceae Quasia. It had also been known as paradise tree, Laxmi taru, Acetuno, a multipurpose tree that can grow well under a wide range of hostile ecological condition. Its origin is native to North America, now found in different regions of India. It was a medium sized tree generally attains a height about 20 m and trunk diameter approximately 50 – 80 cm and life about 70 years. It could grow under a wide range of agro climatic conditions like warm, humid and tropical regions. Its cultivation depends upon rainfall distribution (around 400 mm), water holding capacity of the soil and sub-soil moisture. It was suited for temperature range 10 – 40 ^{0}C, pH of the soil should be 5.5 – 8. It produces bright green leaves 20-50cm length, yellow flowers and oval elongated purple colored fleshy fruits[1].

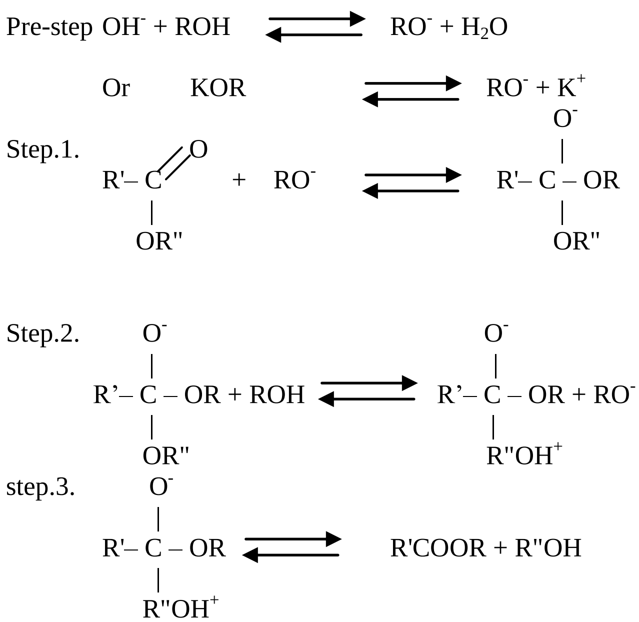
Its seeds contain about 40 % kernel and kernels content 55 -65% oil. The amount of oil would be 1000 – 2000 kg/ha/year for a plant spacing of 5m x5m. It was used for industrial purposes in the manufacture of soaps, detergents and lubricants etc. The oil cake being rich in nitrogen (7.7 to 8.1%), phosphorus (1.07%) and potash (1.24%) could be used as valuable organic manure [2].

Simarouba was a rich source of fat having melting point of about 29^{0}C. The major green energy components and their sources from Simarouba were biodiesel from seeds, ethanol from fruit pulps, biogas from fruit pulp, oil cake, leaf litter and thermal power from leaf litters, shell, unwanted branches etc.

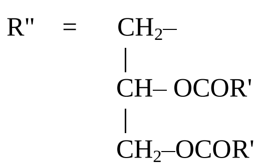
Unlike fossil fuels, biodiesel is a renewable source of energy, because it comes from biological sources like plants and animals which can be replenished by farming. On the other hand, fossil fuels come from underground deposits of hydrocarbons which cannot be renewed. Biofuels have become a matter of global importance because of the need for an alternative energy at a cheaper price and with less pollution[3]. Biodiesel was a domestic, renewable fuel for diesel engine comprised of mono-alkyl esters of long chain fatty acids derived from natural oils/ vegetable oils/animal fats designated as B100 and which meets the specification of ASTM D6751 or BIS IS15607:05. It was obtained by the transesterification of renewable materials composed of C_{14} – C_{20} fatty acids triglycerides with short chain alcohol such as methanol or ethanol under the presence of catalyst, usually a base like NaOH or KOH. Instead of using alcohol and catalyst separately, alkoxides such as CH_3ONa or CH_3OK were used to reduce tendency to from water. Biodiesel was often referred to as fatty acid methyl esters (FAME) when methanol was used. The Glycerol was produced as a by-product which has commercial value[4].

The transesterification reaction formally requires a molar ratio of alcohol to oil of 3:1 but in practice a molar ratio of 6:1 needs to be applied for the reaction to proceed properly to high yield. The transesterification usually requires about 1hour at normal pressure with the reaction temperature 60 – 65^{0}C (for methanol)[5].

Biodiesel Transesterification Reactions: Transesterification process consists of a sequence of three consecutive reversible reactions i.e. conversion of triglycerides to diglycerides followed by diglycerides to monoglycerides. The glycerides were converted into glycerol and one ester molecule at each step. The mechanism was represented in equations as follows[6].

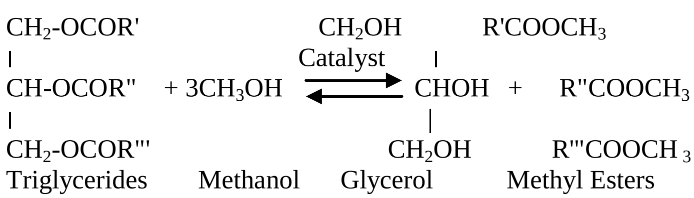


Where



R' = Carbon chain of fatty acid, R = Alkyl group of alcohol

The methanolysis transesterification reaction is represented in equation 1.



If the oil contains more than 5% free fatty acids (FFA), then a two step transesterification is applicable to convert the high FFA oils to its mono esters[7]. The first step, the acid catalyzed esterification reduces the free fatty acid content of the oil. The second step, alkaline transesterification process converts the products of the first step to its mono-esters and glycerol.

Material and Methods

Experimental Procedure for production of Biodiesel: The objective of this study was to develop a process for producing biodiesel from Simarouba glauca oil. The process consists of mainly transesterification i.e. after removing the impurities; the oil was transesterified into its mono esters using alkaline catalyst.

Simarouba seeds were collected from different part of Odisha, India and decorticated manually. The extraction of oil from Simarouba kernel was done by using mechanical expeller and solvent extraction by soxhlet apparatus using n-hexane as solvent. The yields were given in table-1.

Calculation of acid value: It was the amount of KOH required in milligrams to neutralize the free fatty acid present in one gram of oil expressed as acid value.

$$\text{Acid value} = \frac{\text{Volume of N/10 KOH in ml runs down}}{\text{Weight of the oil sample in gram}} \times 5.6$$

$$= 5.34$$

Generally free fatty acid value in the half of the acid value. Hence percentage of FFA of Simarouba glauca oil is 2.67. Potassium hydroxide flakes (Merck), methanol (99.8% pure, HIMEDIA) were used for the transesterification experiment. Gas chromatographic method was used to determine the fatty acid composition of the oil.

Process of Alkaline Transesterification: The apparatus was a 1Liter glass reactor (shown in figure-1) equipped with a digital rpm controller with mechanical stirrer, a water condenser and funnel, and surrounded by a heating mantle controlled by a temperature controller device. A digital temperature indicator had been used to measure the reaction temperature.

Reaction process: 750ml Simarouba oil was taken in the reactor. The anhydrous KOH and CH_3OH solution or pottasium methoxide (prepared recently) were added to the closed reaction vessel. The important parameter is stirring speeds and temperature which play a vital role in transestrification process[8]. The mixture was heated to the required reaction temperature of 60-65^{0}C by the temperature controller for about 2 hours with stirring speed of 600 rpm.

Samples of 10 ml were taken from the reaction mixture at regular intervals, typically 10 min, neutralized, and analyzed by gas chromatography. When the conversion of the oil was quantitative, as determined by the GC, the heating mantle was switched off. The mixture was then allowed to cool in the reactor and was neutralized with the stoichiometric amount of concentrated hydrochloric acid, appearing as two distinct phases after switching off the stirrer. These two phases were decanted using the bottom outlet of the reactor. The excess methanol in both phases was evaporated at vacuum. Biodiesel without further purification was a clear, light green liquid. The final Biodiesel layer required washing with tap water in order to remove the excess catalyst and the methanol. The final product after washing was heated to remove the moisture.

It had been observed that the best yield was obtained with a catalytic condition of 1% KOH. For higher value of catalytic concentration the value was lower. It had been found that when the oil contains large amount of free fatty acid the addition of KOH compensates the acidity and avoids catalytic deactivation. Whereas for refined oil with FFA less than 1 % the addition of excess alkaline catalyst results in the formation of an emulsion which increases the viscosity and leads to the formation of gels[10].

Analyses: The transesterification reaction was monitored by using thin layer chromatography shown in figure-2 to check the completion of the reaction.

Results and Discussions

The percentage composition of fatty acids present in Simarouba oil was determined by gas chromatographic analysis (Chemito CERES 800 plus G.C) and is represented in table-2. Simarouba glauca oil consists of 96.11% pure triglyceride esters. The physicochemical properties of Simarouba glauca oil were determined and compared with other oils and the results are presented in table-3. The fuel properties of Simarouba Oil Methyl Esters (SOME) are determined as per BIS, shown in table-4 and also compared with Karanja Oil Methyl Ester (KOME), Corn Oil Methyl Ester (COME) and Rapeseed Oil Methyl Ester (ROME).

Viscosity: Among the general parameters for biodiesel the viscosity controls the characteristics of the injection from the diesel injector because high viscosity leads to unfavorable pumping; inefficient mixing of fuel with air contributes to incomplete combustion which results in increased carbon deposit formation[15].

The kinematic viscosity of crude Simarouba oil was found to be 34 centistokes and it is reduced to 4.68 centistokes after transesterification. A graph is plotted between kinematic viscosity vs temperature and is given in figure-3. The kinematic viscosity decreases with increase in temperature.

Density: The comparison of densities of crude oil, SOME and diesel were given in figure-4. The higher densities of Simarouba oil and SOME as compared to diesel may be attributed to the higher molecular weights and triglyceride molecules present.

Flash Point: It was the lowest temperature at which the oil gives off enough vapors that ignite for a moment, when a tiny flame is brought near it. Flash point of crude Simarouba oil and SOME were determined 225^0C, 165^0C respectively and is compared with diesel in figure-5. The flash point of bio diesel was higher than the diesel, which was safe for transport.

The above listed properties from the experimental results indicate that SOME was the best suited as per BIS norms for using as bio diesel.

Table – 1
Percentage yield of oil from Simarouba Kernel

Extraction Method	Yield in %
Mechanical Expeller	15
Soxhlet Apparatus	55 – 60

Table – 2
The Fatty acid composition of Simarouba oil determined by Gas Chromatography in which the total number of Carbon and number of double bond is mentioned by first and second subscripts

Fatty acid	Percentage (%)
Stearic Acid ($C_{18:0}$)	27.3
Oleic Acid ($C_{18:1}$)	54.6
Palmitic Acid ($C_{16:0}$)	12.3
Linoleic Acid ($C_{18:2}$)	2.3
Arachidic Acid ($C_{20:2}$)	1.2
Erucic Acid ($C_{22:2}$)	0.4
Linolenic Acid ($C_{24:0}$)	0.2
Heptadecanoic Acid ($C_{17:2}$)	0.1

Table – 3
The physicochemical properties of Simarouba glauca oil (As per BIS method) with the comparisons of other oils

Chemical properties	Value				
	Simarouba Oil	Karanja Oil[9]	Corn Oil[12]	Beef Tallow Oil [6]	NeemOil[13]
Acid Value (mg KOH/gm)	5.34	5.06	0.23	-	-
Saponification value (mg KOH/gm)	176	187	-	193.202	189
Iodine value (gm/100gm)	83.4	86.5	125.4	35 – 48	99

Table – 4
The fuel properties of Simarouba Oil Methyl Esters (SOME) as determined as per BIS method with the comparisons of other oils of methyl esters

Property	Experimental Values				Test Method	BIS specification
	SOME	KOME[9]	COME[12]	ROME[14]		
Kinematic Viscosity at 40^0C in CSt	4.68	5.431	4.14	4.76	IS 1448 P: 25	2.5 – 6.0
Density at 15^0C Kg/m^3	865	889	865	885	IS 1448 P: 16	860-900
Flash Point ^{0}C	165	116	-	156	IS 1448 P: 20	≤ 120
Cloud Point ^{0}C	19	22	-5	-2	IS 1448 P: 10	-
Pour Point ^{0}C	14.2	15.8	-6	-7	IS 1448 P: 10	-
Carbon Residue % w/w	0.10	0.08	-	-	IS 1448 P: 8	≤ 0.05
Ash content % w/w	0.005	0.003	-	0.015	IS 1448 P: 4	≤ 0.02

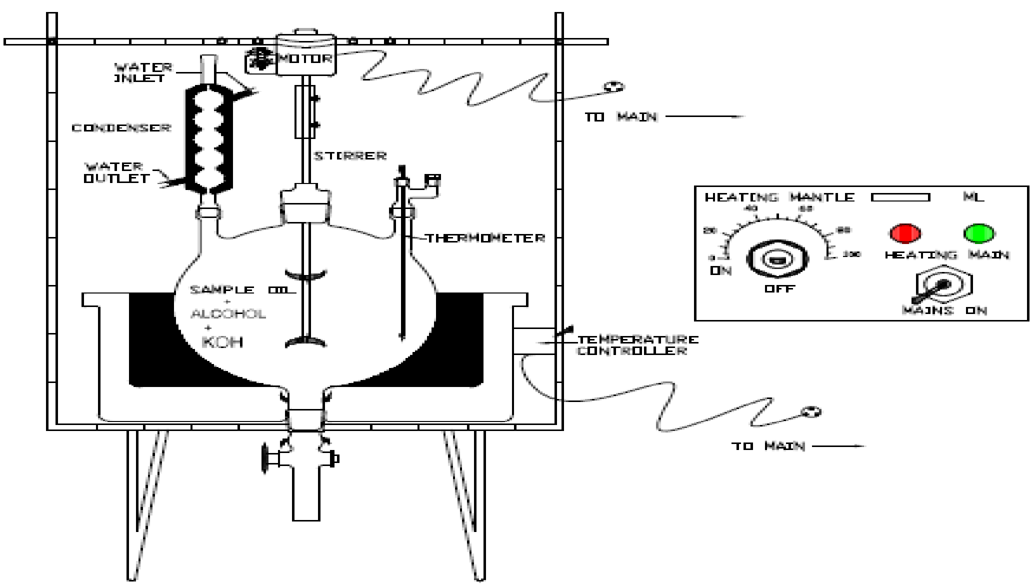


Figure-1
Transestrifeactor (Schematic diagram)

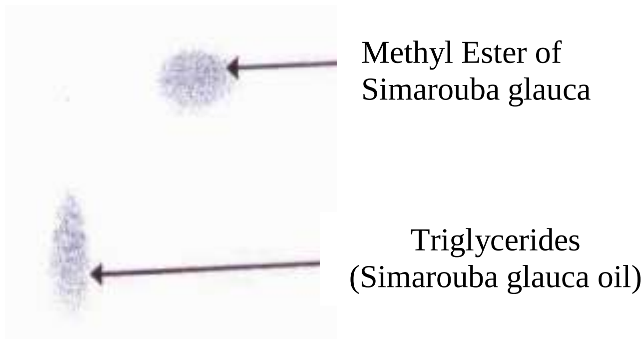


Figure-2
Thin Layer Chromatographic analysis. Triglycerides (Simarouba glauca oil) and Methyl Esters of Simarouba glauca

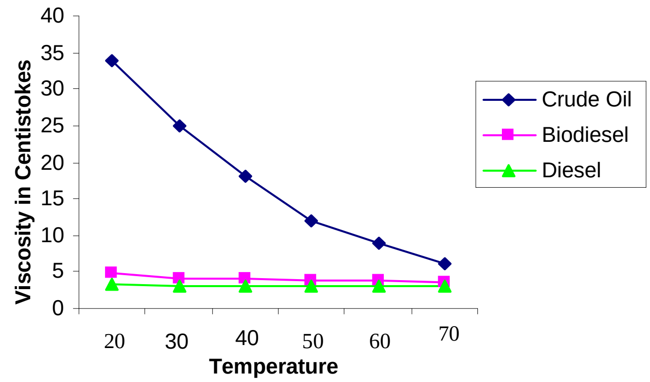


Figure-3
Kinematic Viscosity verses Temperature

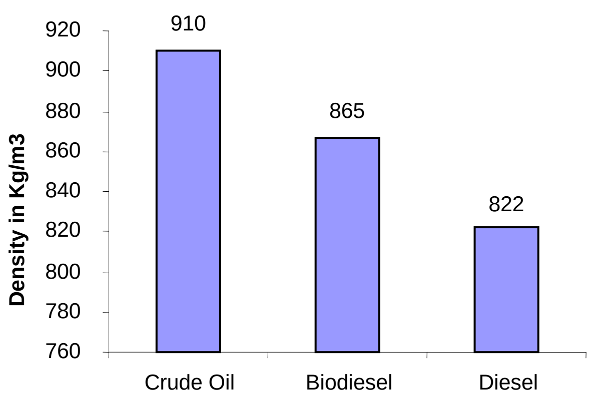


Figure-4
Comparison of densities of Crude Oil, SOME and Diesel

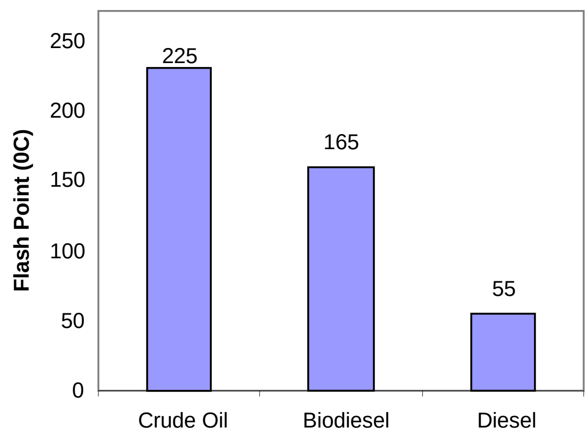


Figure-5
Flash point of crude Simarouba glauca oil, SOME and Diesel

Conclusion

Biodiesel has become more attractive to replace the petroleum fuels. As per reputed literature, most of the transestrification studies have been done on edible oils like rapeseed, soybean, and sunflower etc by using NaOH or KOH catalyst. The tree borne oil like Simarouba glauca is the most potential species to produce biodiesel in India which could offer opportunity the generation of rural employment. The process is based on the alkaline catalyzed transesterification and can be further improved to get high yield and good fuel quality Biodiesel.

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