Synthesis and Characterization of Biodiesel from *Simarouba Oil* Using Hetrogeneous Catalyst

S K Senapati

Centurion University of Technology & Management, Odisha, India

B P Mishra and S K Biswal

Centurion University of Technology & Management, Odisha, India

dr.skbiswal@cutm.ac.in

Abstract-Biodiesel is fatty acid methyl ester of vegetable oils produced by transesterification reaction in presence of suitable acid or base catalysts. The production technology of biodiesel from various edible oils such as Palm oil, Sunflower oil, Soybean oil etc has already been commercially available by conventional base- catalyzed transesterification reaction, where as there is a large research gap in the use of non-conventional catalyst and non-edible oils for the production of biodiesel [9]. In this paper, an attempt has been taken to prepare the biodiesel from simarouba non-edible oil of high free fatty acid (FFA) content >2.0 by transesterification reaction with methanol in presence of calcium oxide (CaO) heterogeneous catalyst at optimum temperature 60C, for 4 hour reaction period at 600rpm stirring speed under reflux condition. The Simarouba oil methyl ester (SOME) characterized for various typical properties as per ASTM D6751 or BIS-IS15607:05 specifications. Then, the blend of SOME with ultra-low sulphur Diesel (ULSD) fuel prepared i.e. B5, B15, B20 and tested for changes in physic-chemical properties such as viscosity, low temperature performance, Lubricity etc.

1. INTRODUCTION

Simarouba Glauca, family of simaroubaceae commonly known as Paradise Tree or Laxmitaru tree, is a medium sized evergreen tree, which is receiving a great interest as a promising energy crop and medicinal plant for the future. Brought from the tropical forests of Central America in 1960's, Paradise Tree, Lakshmitaru is now well flourished in Orissa, Maharashtra, Karnataka, Tamilnadu, Kerala and also at introductory stage of plantation in other states like Gujarat, Rajasthan, Andhra Pradesh and West Bengal. All parts of the plant namely, seed, shell, fruit pulp, leaf, leaf litter, unwanted branches, stem, bark, and root generate products that are useful in the production of food, fuel, manure, timber, medicine etc. The tree is well suited for the all the geographical regions of India. It reclaims wastelands, arrests soil erosion, supports soil microbial life and increases ground water levels. The plant starts fruiting at the age of 5-6 years. An adult plant can yield 20-50 kg seeds and about 200 trees can be accommodated per hectare [1]. About 1-2 tons of oil can be produced from one hectare of wasteland under Simaruba plantation [1]. Its oil is comparable with that of palm oil with regard to the physico-chemical characteristics. It is also having toxins in seeds. *Simarouba glauca*seeds contain 55-65% oil [1], the oil contains palmitic (12%), stearic (28%), and oleic acid (58%), with a low level of linoleic acid (2%). The fatty acid composition of this oil quite similar to palm oil and jatrophacurcus oil. This oil contains more saturate fatty acid in comparison to jatropha, karanja oils and possesses good anti-oxidation properties [11].Mishra SR et.al [1] prepared biodiesel from simarouba oil by transesterification reaction in presence of KOH as catalyst with oil to methanol molar ratio 6:1 at reaction temperature 60-65 for 2 hours at 600 rpm stirring speed. The biodiesel prepared analysed for viscosity, pour point, carbon residue and ash content.Dhanesh D et.al prepared methyl ester by base catalytic transesterification reaction and evaluated the performance of simarouba oil biodiesel in engine at different doses.Ayahan et.al [2] prepared biodiesel from CaO in super critical condition of 1:41 molar ratio of oil to methanol at increased temperature with short reaction time of 6minutes in 3% CaO catalyst.

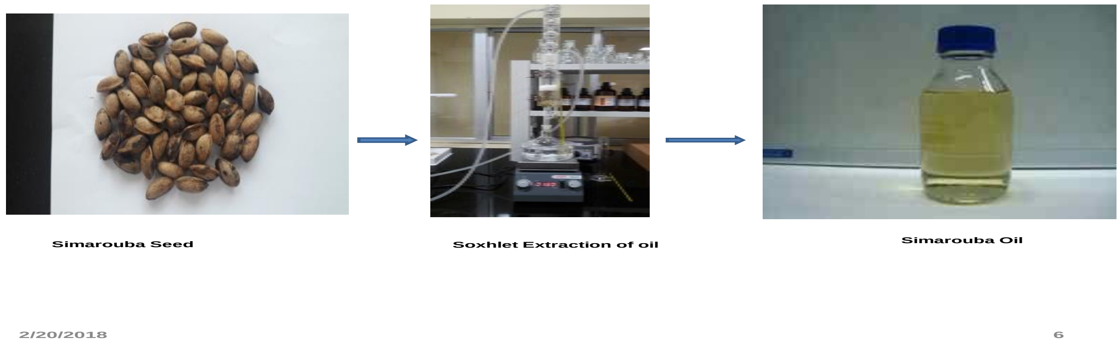
1.0 Material & Methods:

1.1 Extraction of Oil:

The simarouba tree carries fruits in the month of march-April and largely planted in the road side of capital region, Odisha. The fruits become dark black on ripen and fall down on ground. These fruits collected, washed with tap water to remove the pulp and sun dried. then the seeds removed from hard kernel and extracted the oil by soxhlet method by utilizing n-Hexane as solvent.The oil content found about 65% after removal of solvent and trace moisture followed by filtration. The raw oil tested as per standard ASTM, IS methods for suitable use in transesterification reaction. The free fatty acid content is slightly higher than the recommended doses of <2.0 mgKOH/g for transesterification reaction. However, the transesterification reaction in presence of CaO catalyst can be carried out in high FFA content oil without acid esterification reaction (10). Kinematic viscosity of extracted oil is 41.7cSt and acidity content is 4.5mg KOH/g.

1.2 Transesterification Reaction:

Trans-esterification of simarouba glauca oil was conducted in a 500ml Erlenmeyer l flask fitted with a water cooled condenser in a constant water bath maintained at 60-65°C on a heater cum magnetic stirrer equipment. Transesterification reaction with hetrogeneous catalyst (CaO) carried out in methanol to oil molar ratio of 12:1 at temperature 60-65C, stirring at 600rpm for 4hrs duration. Prior to transesterification reaction, the calcium oxide catalyst calcined at 900C for 4 hours and cooled in descicator with proper lid to avoid contact with carbon dioxide to form calcium carbonate and deactivate the catalytic activity. After transesterification reaction, the solid Cao catalyst separated by filtration and retained for further use. The filtrate settled for overnight for separation of glycerol and ester. The separated ester purified for analysis and further blending with ultra low diesel fuel for characterization. The ester content confirmed by ^{1}H NMR with 96.5% yield. The ultra low sulphur with <10ppm sulphur content collected from IOC Refinery for this study.



1.3 Blend with ultra-lowSulphur Diesel (ULSD) Fuel:

The methyl ester of simarouba oil (SOME) blended with ultra low sulphur diesel fuel (<10ppm sulphur) in the doses of 5%, 10%,15% & 20% and denoted as B5, B10, B15 & B20 respectively. All the blends tested as per ASTM, BIS standard test methods for Density, Viscosity, flash point, pour point, cold flow plugging point (CFPP), sulphur content and Lubricity. The results mentioned in Table-2.

Table 2: Properties of simarouba biodiesel and its blends

S.No.	Properties	Method	ULSD	B100	B5	B10	B15	B20
1	Density, kg/m^3	P16	838.3	870.5	839.3	840.6	841.3	843.6
2	Kin.Viscosity,cSt	P25	2.986	4.752	3.051	3.082	3.188	3.225
3	Flash Point,C	P20	54.0	164.0	55.5	56.0	57.0	60.0
4	Pour Point,C	P10	-9	15	-6	-3	0	3
4	CFPP,C	P110	-6	12	-5	0	6	9
5	Lubricity,wsd,µm	ISO12156	423	252	205	184	175	165

1.4 Lubricity test by HFRR

The high frequency reciprocating rig (HFRR) is used to evaluate the lubricity property of diesel fuel as per ISO 12156 method. The maximum wear scar dia (wsd) by HFRR for diesel fuel is 460 micron. Lower wear scar diameter (wsd) is an indication of better lubricity property of diesel fuel. Lubricity property of ultra low sulphur diesel fuel gets reduced due to reduction of sulphur content up to 10ppm or lower . However, the lubricity property of this diesel fuel gets improved by addition of 5% fatty acid methyl ester [4]. The HFRR test is a computer-controlled reciprocating friction and wears test system. The HFRR test consists of a ball that is placed on a flat surface. Sample is put into experimental place at 60C temperature. Steel ball is placed on a holder which is vertically tightly and then it is pressed on flat surface which is fixed horizontally with applying load. While contact surface is completely submerged into the fluid. The ball is then vibrated rapidly back and forth using a 1-mm stroke while a 200-g mass is applied for 75 minutes. The blends of biodiesel prepared above tested for lubricity performances in HFRR vis-à-vis ULSD fuel.

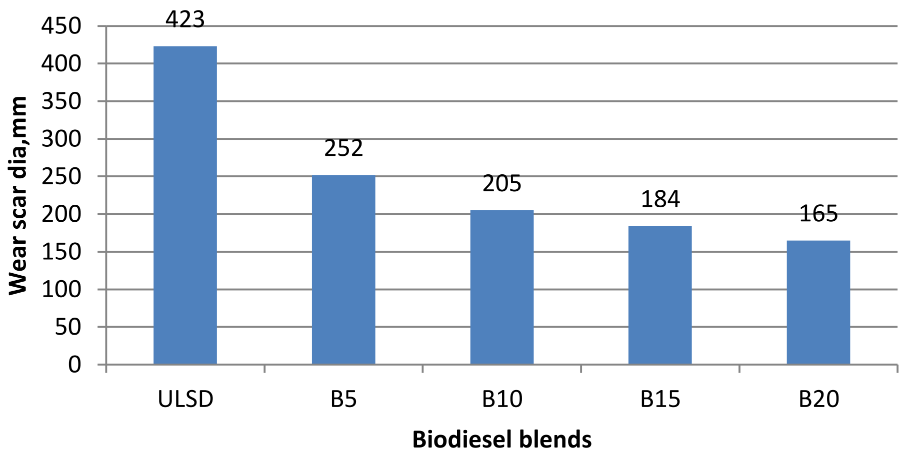
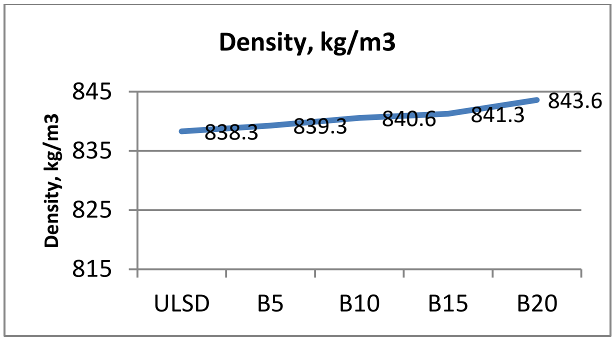


Fig-1: wear scar dia, mm of biodiesel blends by HFRR

2.0 RESULTS & DISCUSSIONS

The simarouba seeds contain about 65% oil as quantified by soxhlet extraction in almost 6 cycles running with n-Hexane as solvent. The raw oil characterized for Density, Viscosity, free fatty acid content, Saponification value for suitability in transesterification reaction by Calcium Oxide as heterogeneous base catalyst due to its advantages over homogeneous alkali catalyst on overcome of water washing for separation of soap and catalyst. The fatty acid profile of simarouba oil characterized by GC-MS, it contains about 40% saturate fatty acids include Palmitic (C16:0),12.5% and Stearic (C18:0), 26.5% and mono & poly unsaturated acids about 60% includes Oleic acid (C18:1) of 54.2% , linoleic acid (C18:2) of 3%. Due to more saturated fatty acid content in comparison to palm or Karanja oil, this oil possesses poor low temperature properties such as pour point and CFPP. The low temperature properties gets improve by dopping suitable pour point depressant additives. With about 100-200ppm doses, the pour point of blend B20 gets improved from 0 to -9 degree C. The viscosity of B100 is more than the ULSD and the blends of B5 to B20 increases viscosity to some extent, but within the limit of BIS diesel specification IS1460-2018. Density of B100 is higher than petro diesel and meets specification limit of IS16531-2016 and the blends density increases in linear, but within the specification limit.



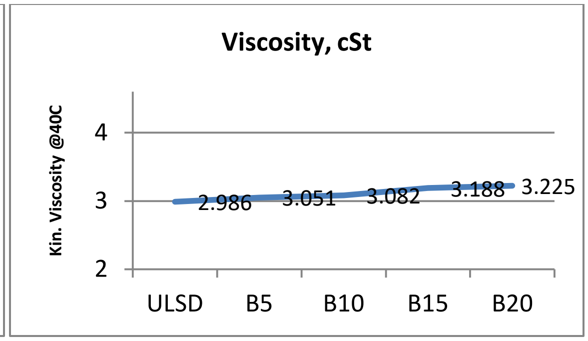


Fig 2: Density of blends

Fig 3: Kin Viscosity of blends

The lubricity is defined by the ability to reduce friction and wear on surfaces under load and relative motion. Generally, smaller wear scar signifies greater lubricity that ensures the effectiveness of interfacial lubricant fuel film on the separating action of these surfaces. This thin film is formed by adsorption of polar molecules of fuel on metal surfaces. Lubricity increases somewhat with chain length. However, the lubricity-enhancing effects of double bonds are greater than that of extended chain length. The simarouba oil contents about 40% saturated and about 60% unsaturated long chain fatty acids, those improve the lubricity properties as obtained HFRR test results. The lubricity value in terms of low wsd value gets reduced from B5 to B20 and it shows the better lubricity observed in methyl ester of simarouba oil blending with ultra-lowSulphur diesel fuel. The Sulphur content of methyl ester is 2ppm, which has no effect on the blends and remain bellow 10ppm of ULSD fuel.

2. CONCLUSIONS

Transesterification of simarouba oil was carried out by using calcium oxide as heterogeneous catalyst and effective conversion of methyl ester obtained in oil to methanol molar ratio 1:12 at 60C for 4 hours reaction period at 600rpm strirring speed. The use of heterogeneous rather than homogeneous catalysts for biodiesel synthesis has advantages of avoiding water washing and conserving water, eco-friendly, catalyst re-use and reduction of process cost. Preparation and utilization of calcium oxide obtained from the various waste materials has been investigated by researchers. The advantages of heterogeneous catalyst are re-cyclable, cost-effective and eco-friendly due to no water washing required. From this study, it has been observed that there is no deviation in properties as per standard specification biodiesel for the blends from B5 to B20. It is observed from this study, the simarouba oil is a potential source for the production of biodiesel by heterogeneous catalyst.

REFERENCES

[1]. Mishra S.R et.al. "Production of biodiesel (methyl ester) from simarouba oil, *Research Journal of Chemical Sciences*. vol.2(5), 66-71, May (2012).

[2]. AyihanDemirbas" Biodiesel from Sunflower oil in supercritical methanol with calcium oxide" energy coversion& management, Elsevier, vol48,3, March 2007.

[3]. Bobade S.N et.al. "Detail study on the properties of Pongamia pinnate (Karanja) for the production of Biofuel" *Research Journal of Chemical Sciences*. vol.2(7), 16-20, July (2012).

[4]. Gerhard Knothe et.al "Lubricity of Components of Biodiesel and Petrodiesel" – Energy & Fuels Vol.19, No-3, June 2005.

[5]. F.Yasar et.al, " Comparing the lubricity of different biodiesel fuels," – 6th International advanced Technologies symposium,Turkey

[6]. Meeta Sharma "A heterogeneous catalyst for transesterification of Argemone Mexicana oil" J Am Oil ChemSoc(2012), 89:1545-15555.

[7]. Gerhard Knothe et.al "Lubricity of Components of Biodiesel and Petrodiesel" – Energy & Fuels Vol.19, No-3, June 2005.

[8]. Indian Standard IS 16531:2016 – Biodiesel, Diesel Fuel Blend (B6 to B20) Specification.

[9]. Indian Standard IS-15607:2016 - Biodiesel (B100) Fatty Acid Methyl Esters (FAME) Specification.

[10]. ASTM D6751- "Standard specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels.

[11]. Joseph PV et.al, "Study of some non-edible vegetable oils of Indian origin for lubricant application"- Journal of Synthic Lubrication, vol-34,Aug2007

[12] AlokKumar Tiwari, AkhileshKumar, HifjurRaheman "Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: An optimized process" Biomass and BioenergyVolume 31, Issue 8, August 2007, Pages 569-575

[13] RakeshSarin, MeetaSharma, S.Sinharay, R.K.Malhotra "Jatropha–Palm biodiesel blends: An optimum mix for Asia" FuelVolume 86, Issues 10–11, July–August 2007, Pages 1365-1371

[14] M.M.GuiK.T.LeeS.Bhatia "Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock" EnergyVolume 33, Issue 11, November 2008, Pages 1646-1653