Biodiesel Production from Sal (Shorea Robusta) Seed Oil

H.S. Pali[1] , N. Kumar[2]

[1,2] *Centre for Advanced Studies and Research in Automotive Engineering, Delhi Technological University, Delhi-110042, India.*

*harvirpali@gmail.com

Abstract— **Biodiesel from renewable sources like vegetable oils, animal fats etc. are significantly evaluated as an alternative to fossil fuels. In this context, the present work deals with an underutilized vegetable oil known as "Shorea robusta" or Sal seed oil" as a potential feedstock for biodiesel production which can considerably increase the feedstock availability. The production potential of sal seed oil is a gigantic 1.5 million tons a year and the geo-climatic penetration of the plant is sub-continental with special presence in Odisha, Chhattisgarh and Madhya Pradesh. In the present work, pressure filtered Sal seed oil was transesterified sal seed methyl ester (Biodiesel) with 1:9 oil to methanol molar ratio, 0.5% by weight of catalyst (potassium hydroxide), 65°C reaction temperature and 450 rpm agitation speed leading to an ester yield of 96.8%. The results of physico-chemical properties indicated that kinematic viscosity (5.8 cSt), density (0.884 gm/cc), heating values (40.28 MJ/kg) of the Sal oil methyl ester (SOME) was well within the ASTM/EN standard limits. Oxidation stability was more than 06 hours in the biodiesel rancimat. The fatty acid profiles of SOME showed richness of saturated fatty acids like Pentadecanoic acid and Mysteric acid.**

Keywords— **Alternative fuel, biodiesel, diesel engine, sal seed oil, transesterification etc.**

I. INTRODUCTION

After the market based reforms in the year 1991, the resurgent Indian economy exhibited impressive growth. The rapid growth in the economy was coupled with improved infrastructure, mobility and industrial activity. The same may be evident from the exponential increase of automobile fleet in India from 0.3 million units in 1953 to 142 million units in 2011 with an annual growth rate of 9.9% between the years 2001-2011[1]. The rising prosperity and improving living standards resulted in higher energy demands. A significant part of this energy in India is obtained from crude oil derived products like petrol and diesel used in internal combustion engines. With no substantial diversification in energy supply, India continued to be dependent on imported crude oil to fuel its economy as it lacked oil reserves. While it's domestic crude oil production stood stagnant at less than 1000 barrels per day (BPD) in the period 2001-11, its crude oil imports increased stupendously from 2200 BPD to 3400 BPD in the same duration resulting in huge trade deficit and humongous amount of forex outflow to fund the imports [2]. Apart from this, the depletion in fossil fuel reserves, rising green house gas (GHG) emissions due to fossil fuel burning and the resultant environmental degradation as well as global warming are another area of major concern. According to the International Energy Outlook of 2011, which was published by the U.S. Energy Information Administration, the global usage of liquid fuels will increase from 85.7 million barrels per day in 2008 to 112.2 million barrels per day in 2035. In addition, the transport sector will account for 82% of the total increase in liquid fuel use, with the remaining growth attributed to the industrial sector [2]. With this projection India will be importing 100% of its total crude oil requirement by 2035 [2].

The most popular petroleum fuels in India are gasoline and diesel used as motor fuels in spark ignition and compression ignition engines respectively. Amongst them, diesel engines have proven their utility in the transportation and power sectors due to their higher efficiency and ruggedness and hence play a pivotal role in rural as well as urban Indian economy [3]. With respect to usage, diesel engines are largely favored across a wide spectrum of activities like automotive application, small and decentralized power generation, prime mover for farm and agricultural machineries, small scale industrial prime mover and so on. The same may be evident from the Ministry of petroleum, Government of India data that shows that the consumption of diesel in the year 2012 was 4.5 times higher than motor gasoline in the same period [4].Therefore, even a partial substitution of mineral diesel by any renewable and carbon neutral alternative fuel can have significant positive effect on economy and environment in terms of reduction in carbon footprints and dependence on imported crude oil.

In the light of the above discussion, it may be stated that renewable, sustainable, efficient and cost effective alternative fuel to mineral diesel with reduced carbon footprints are one of the critical needs of the hour [5,6]. In this context, bio-origin liquid fuels like vegetable oil, animal fats etc. are long considered as suitable greener alternative to diesel. However, higher viscosity and density of crude bio-origin oils create operational problems in engines like poor fuel atomization and vaporization, injector chocking, lubricating oil dilution, increased carbon deposit, reduced efficiency etc. Therefore, vegetable oils are not recommended for direct diesel engine application. However, there are several methods like dilution, pyrolysis, transesterification and engine hardware modification etc. in which vegetable oil can be used in diesel engines. Amongst them, transesterification has been established as the best method to use vegetable oils in diesel engines. In the process of transesterification, the triglycerides of the bio-origin oils are converted in to fatty acid alkyl esters and glycerol by reacting with alcohol in presence of a suitable catalyst. Those fatty acid alkyl esters that conform to ASTM D6751 [7] or EN 14214 [8] standards are termed as biodiesel. Biodiesel is considered as a better fuel than mineral diesel on many grounds. Superior lubricity, renewable background, lack of sulfur and aromatic compounds, superior flash point and biodegradability along with reduction in regulated exhaust emissions are some of the improved characteristics of biodiesel compared to the conventional mineral diesel [9,10].

In the last decade, rising food inflation worldwide was partly attributed to the diversion of food crops for biodiesel production in many developed western countries. This phenomenon of food verses oil was critically debated in a global scale. In this context, developing countries like India cannot afford food crops or edible oils for biodiesel production especially when there is a billion plus mouths to be fed. Therefore, Indian Government decided to choose non-edible energy crops growing at drought or barren lands as the feedstock for biodiesel production. Jatropha curcas was selected as the most suitable tree born oil seed for the flagship program "National Biodiesel Mission" launched by Indian Government in 2009. However, the mission to accomplish 20% blending by 2012 was not realized on account of a number of reasons out of which lack of sufficient feedstock was cited as a major bottleneck. In the light of the above discussion, it may be stated that other potential sources of biodiesel must be explored relentlessly so that Government's biofuel policy will be supported and the feedstock base can be enlarged sufficiently to address the ever rising demand of fuels. In this context, the present research deals with the potential of biodiesel production from a still untapped non-edible oil source known as "Shorea robusta" or "sal seed oil". This is primarily a forest product with a sub-continental presence. However, it has a dominant penetration in states like Odisha, Chhatishgarah, Madhya Pradesh, east Maharashtra etc. The annual estimated production of sal seeds is around 1.5 million tonnes and the sal seed oil or fat production is around 0.18 million tonnes a year [11,12]. In the present investigation, sal seed oil is to be transesterified to produce sal oil methyl ester (SOME) and various physico-chemical properties to be evaluated and compared the corresponding ASTM/EN standards.

II. MATERIALS AND METHODS

A. SAL SEED PLANT

Shorea robusta is a large, deciduous tree up to 50 m in height. Under normal conditions the tree attains a height of 18-32 m and girth of 1.5-2 m. Bole is clean, straight and cylindrical but often bears epicormic branches. Crown is spreading and spherical. Bark is dark brown and thick, with longitudinal fissures deep in poles, becoming shallow in mature trees; provides effective protection against fire. The tree develops a long taproot at a very young age [13]. Fig.1 shows flowers and seeds of sal.

B. EXTRACTION OF NEAT SAL SEED OIL

As sal seed is a forest product, the direct access to the procurement was difficult. Therefore, the extracted sal seed oil which was in butter form was procured from some of the outlets of Odisha Forest Development Corporation in Bhubaneswar. At room temperature the oil remains in butter form. Fig.2 shows the sal seed oil butter procured for the present investigation and the oil.

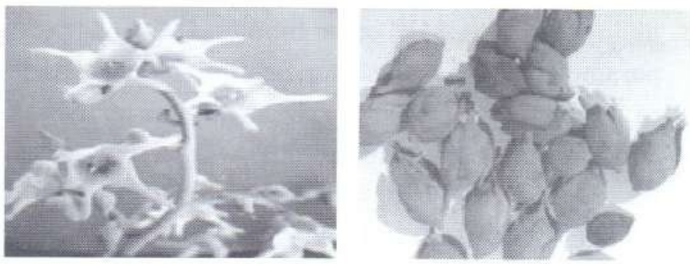

Fig. 1 Example of an unacceptable low-resolution image

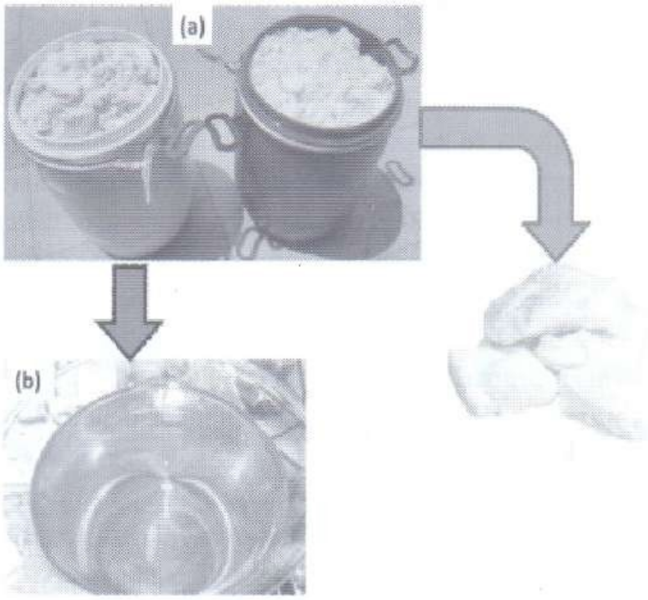

Fig. 2 (a) – Sal seed oil butter at room temperature, (b) – sal seed oil after heating.

C. TRANSESTERIFICATION FOR PRODUCTION OF SAL SEED OIL METHYL ESTER

Biodiesel is normally produced by the transesterification process in which the triglyceride of the vegetable oil is converted in to fatty acid alkyl esters and glycerol in presence of a catalyst. The most commonly used alcohol is methanol to produce methyl esters. It is generally referred as fatty acid methyl esters (FAME) [14]. The general scheme of the transesterification reaction for FAME is presented in equation (1.1), where R is a mixture of fatty acid chains [15].

$$\begin{array}{llcll} CH_2-O-CO-R_1 & & & CH_2-OH & R_1-COOCH_3 \\ | & & \text{Catalyst} & | & \\ CH-O-CO-R_2+3CH_3OH & & \leftrightarrow & CH-OH+R_2-COOCH_3 & \\ | & & & | & \\ CH_2-O-CO-R_3 & & & CH_2-OH & R_3-COOCH_3 \\ \text{Triglyceride} & \text{methanol} & & \text{Glycerol} & \text{methylester} \end{array} \quad (1.1)$$

The free fatty acid contents of the sal seed oil was as low as 0.42% leading to a simple and one stage transesterification process to produce sal seed oil methyl ester (SOME) or sal biodiesel. Various process parameters for the transesterification stage were 1:9 oil to methanol molar ratio, 65°C reaction temperature, 450 rpm agitation speed, 0.5% by weight of the catalyst (potassium hydroxide) and a reaction time of 60 minutes. The ester yield was more than 96%. Fig.3 shows the SOME after water washing.

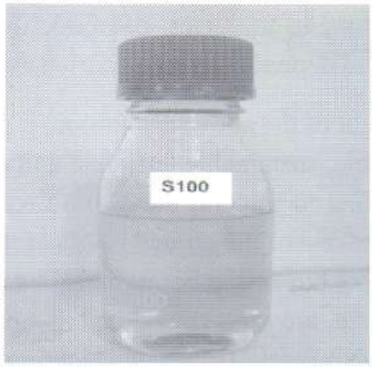

Fig. 3: – Sal seed oil methyl ester (S100)

D. PHYSICO-CHEMICAL CHARACTERIZATION

Various physico-chemical and fuel properties like density, viscosity, calorific value, cold flow properties, oxidations stability, fatty acid profiles etc. of the final SOME was determined in the laboratory. Apart from neat SOME, 5%, 10%, 15% and 20% blends of SOME in diesel named as S5, S10, S15 and S20 was also subjected to physico-chemical characterization. Fig.4 shows various test fuels for characterization. The respective equipments used for the tests were of standard quality with errors and repeatability within the permissible limits. Table 1 shows various equipments, their manufacturers and measurement standards.

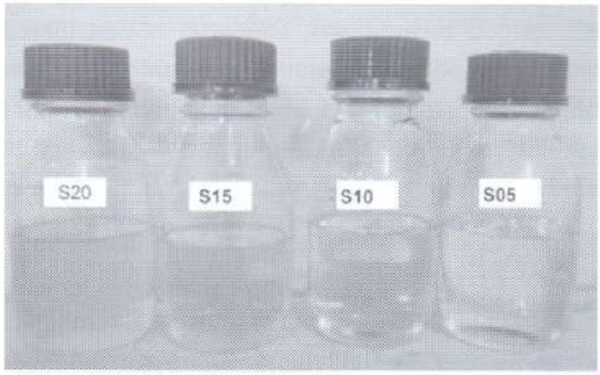

Fig. 4. SOME Blend

III. RESULTS AND DISCUSSION

As discussed earlier, the production of sal seed oil methyl ester was carried out in a single stage transesterification process. In this context, a series of initial transesterification processes are carried out and a suitable range for individual process parameters like reaction time, temperature, catalyst concentration etc. were determined corresponding to the optimum conditions. Based on the experiments and some references of earlier research work, the test matrix for transesterification stage was prepared as shown in table 2.

It may be evident that 0.25% by weight of catalyst and 60 minutes time produced the maximum ester yield of 98%. For simplicity, reaction temperature was fixed at 65°C, molar ratio was 1:9 and agitation speed was 450 rpm same for all the experiments.

A sample of fatty acid methyl ester produced form any feedstock can be termed as a biodiesel when it complies to the established international standards. Therefore, chracterisation and standardization of methyl ester samples produced in the transesterification is an integral part of biodiesel quality control. In this context, the sample of SOME produced was subjected to a comprehensive physicochmeical and fuel characterisation and the results were compared with the correpsonding ASTM/EN standards as mentioned in table 3. Moreover, the variation of significant properties like density, viscosity and heating value with increasing volume fraction of SOME in diesel was also shown in tertms of bar chat in Fig. 5. This is very much significant in terms of diesel engine application. The SOME vlume frcation was limited within 20% as per the Government of India's biofuel policy that envisages a 20% blending of alternative fuels in diesel.

TABLE I
Equipments, manufacturers and standards

S. No	Property	Equipment	Manufacturer	ASTMD6751	ASTMD6751 LIMITS
1	Kinematic viscosity	Petrotest viscometer	Anton Parr, UK	D445	1.9-6 cSt
3	Oxidative stability	873 Rancimat	Metrohm, Switzerland	D675/EN14112	3/6 hours
4	Density	U tube density meter	Anton Parr, UK	D1298/ISO12185	0.86-0.9g/cc
5	CFPP	Automatic NTL 450	Normalab, France	D6371	Not specified
6	Calorific value	Parr 6100 Bomb calorimeter	IKA, UK	Not specified	Not specified

It may be observed that a marginal reduction in density was realized after neat Sal oil was transesterified to produce SOME. Although, SOME showed 5.5% higher density than mineral diesel, but it was still well within the ISO 12185 standard limit of 0.86-0.89 g/cc. Mean while, viscosity of the neat oil was reduced drastically from 157 cSt to nearly 5.8 cSt after transesterification. Although the viscosity of the final

SOME sample was still higher than mineral diesel by a factor of 2, but it suitably conformed to ASTMD6751 standard. The heating value shown by the SOME sample was very much comparable to mineral diesel. The oxidation stability of the SOME was commendable and conformed to both D675 and EN14112 standards on account of higher composition of saturated fatty acids.

TABLE II
Test matrix for transesterification

Experiment No.	Catalyst concentration (% by original oil mass)	Reaction time (minutes)	Ester yield (%)
1	1.3	90	94
2	1.3	100	94.7
3	1.3	110	95.2
4	1.4	90	96
5	0.5	60	96.8
6	1.4	110	96.4
7	1.5	90	95.2
8	1.5	100	96.3
9	1.5	110	96.9

Table III
Various physico-chemical properties of sal seed oil, SOME and diesel

Sl No	Properties	Sal oil	SOME	Diesel
1	Density at 15°C (g/cc)	0.899	0.884	0.8239
2	Viscosity at 40°C (cSt)	157	5.88	2.956
3	Calorific value (MJ/Kg)	39.78	40.28	45.49
4	Oxidation stability (hours)	--	> 6	--

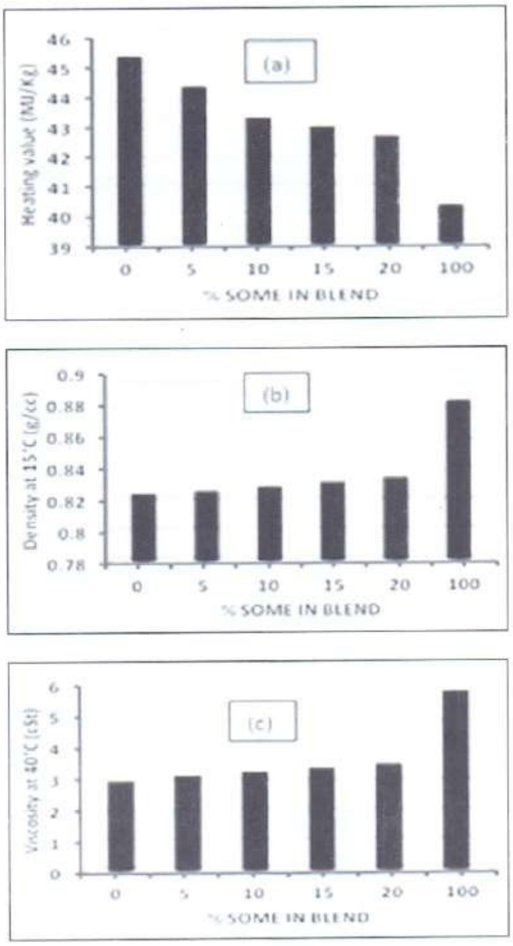

Fig. 5: (a) Variation of heating value with % blend,
(b) Variation of density % blend,
(c) Variation of viscosity with % blend

Fig. 5 shows the variation of heating value, density and viscosity with % blend. It may be observed that up to 20% blend of SOME in diesel, no significant variation in key properties was observed. Rather, the dissolved oxygen content and superior cetane rating of the SOME is supposed lead towards better combustion and enhanced efficiency. However, the viscosity of the neat SOME is very close to the upper ASTM limits.

The detailed fatty acid profile of the SOME sample was determined using high precision gas chromatography equipment. The fatty acid profile in terms f peaks is shown in Fig.6 and detailed composition is provided in the table 7.

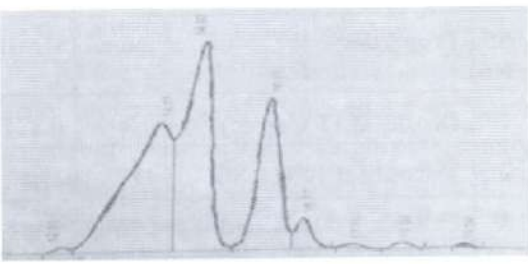

Fig. 6: Fatty acid profile of SOME in terms of peaks.

TABLE IV
Fatty acid composition of SOME

Fatty Acid	Lipid number	Weight (g/mol)	(% wt)
Lauric acid	C12:0	200.317	0.58
Mysteric acid	C14:0	228.38	37.23
Pentadecanoic acid	C15:0	242.39	36.03
Palmitic acid	C16:0	256.42	21.69
Palmitoleic acid	C16:1	192.17	3.26
Cis-10-heptadecanoic acid	C17:1	270.45	0.43
Oleic acid	C18:1	282.47	0.59
Linoleic acid	C18:2	280.45	0.15
Saturated			95.53
Unsaturated			4.43
Total			99.96

It may be easily referred from the table 7 that SOME contains nearly 95.53% saturated fatty acids and only 4.43% unsaturated fatty acids in its composition. Due to this the oil bears the form of butter at room temperature. It may be easily stated that the cold flow properties of SOME are also will be inferior. Although the cold flow properties were not evaluated in the present investigation, but the same may be studied and additives should be added to improve the cold flow properties in future studies. However, presence of saturated fat increases the storage stability of the oil manifold. The same was evident from the oxidation stability test that showed significantly low amount of peroxide formation in the biodiesel rancimat for more than 6 hours confirming to the EN standards.

IV. CONCLUSIONS

Biodiesel has enormous prospects in India as far as energy security and environmental aspects are concerned. However, the challenges to materialize the 20% blending target is also very much intriguing. In this context, exploration of new and underutilized non-edible seed oils is of paramount significance. The initiative taken in the present research work to explore sal or Shorea Robust as a biodiesel feedstock is a small step in the right direction. Biodiesel production from the sal seed oil was carried out in the present study by a transesterification process and then a comprehensive physico-chemical characterization was carried out.

- The results indicated that 0.25% by mass of catalyst (potassium hydroxide), 65°C temperature and 60 minutes time with the same 450 rpm agitation speed. The oil to methanol molar ratio was fixed at 1:9 for both the stages.

- The results of physico-chemical properties were very much encouraging with all the parameters highly accommodating with the corresponding ASTM/EN/ISO standards. The results indicated that kinematic viscosity was 5.8 cSt, density was 0.884 gm/cc and heating values was 40.28 MJ/kg.

- The fatty acid profiles of the Sal seed oil methyl ester showed the richness of Pentadecanoic acid and Mysteric acid. Besides, the saturated fatty acids account for nearly 95.53% and unsaturated fatty acids were nearly 4.43% as indicated by the gas chromatography apparatus.

- The oxidation stability of SOME was more than 6 hours conforming to the stringent EN14112 standard. The cold flow plugging point of SOME was found to be 5°C as compared to -9°C exhibited by the neat diesel.

Therefore, it may be concluded that use of Sal seed oil as a feedstock for biodiesel production is feasible and practicable in Indian conditions. Concrete efforts need to be made by all the stake holders to commercialize sal biodiesel as an alternative fuel.

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Harveer Singh Pali is a graduate from MJP Rohilkhand, Bareilly and did his Master of Technology from UPTU, Lucknow in Mechanical Engineering. Currently he is working as a Research scholar in Mechanical Engineering Department at Delhi Technological University, Delhi under the guidance of Dr. Naveen Kumar. His interest includes biofuels, renewable energy, and diesel engines.

Naveen Kumar is currently a Professor of Mechanical Engineering at Delhi Technological University (Formerly Delhi College of Engineering) and has over 22 years of experience in the industry, teaching, and research. His research interests include the development of various bio-fuels and their utilization in decentralized power systems. Dr. Kumar has extensively traveled abroad and has interacted with various universities and industries in both developed and developing countries. He has executed many sponsored research projects funded by both Government and Industry. He has to his credit large number of research papers/articles.