



Received on 03 February, 2011; received in revised form 10 March, 2011; accepted 20 April, 2011

METHYL ESTER PRODUCTION FROM *SCHLICHERA OLEOSA*

Mallela Gandhi*¹, N. Ramu² and S. Bakkiya Raj³

Department of Mechanical Engineering¹, Department of Physics², Department of Biotechnology³,
Vel Tech High Tech, Dr. Rangarajan, Dr. Sakunthala Engineering College, Chennai, Tamil Nadu,
India

ABSTRACT

Keywords:

Schlichera oleosa seeds oil,
Esterification,
Transesterification,
Schlichera oleosa Methyl Ester

Correspondence to Author:

Mallela Gandhi

Department of Mechanical
Engineering, Vel Tech High Tech, Dr.
Rangarajan, Dr. Sakunthala
Engineering College, Chennai, Tamil
Nadu, India

Biodiesel is produced from vegetable oils (edible & non edibles) and animal fats. The methyl ester of vegetable oils, known as biodiesel are becoming increasingly popular because of their low environmental impact and potential as a green alternative fuel for diesel engine and they would not require significant modification of existing engine hardware. At present, biodiesel is commercially produced from the refined edible vegetable oils such as *Schlichera oleosa* seeds oil, etc. by alkaline-catalyzed esterification process. This process is not suitable for production of biodiesel from many unrefined non-edible vegetable oils because of their high free acid value. Hence, a two-step esterification method is developed to produce biodiesel from high FFA vegetable oils. The biodiesel production method consists of acid-catalyzed (H_2SO_4) pretreatment followed by an alkaline-catalyzed (KOH) transesterification. Methyl ester of *Schlichera oleosa* is derived through esterification and transesterification process.

INTRODUCTION: The diesel engines dominate the field of commercial transportation and agricultural machinery due to its ease of operation and higher fuel efficiency. The consumption of diesel oil is several times higher than that of petrol. Due to the shortage of petroleum products and its increasing cost, efforts are on to develop alternative fuels especially, to the diesel oil for fully or partial replacement. It has been found that the vegetable oils are promising fuels because their properties are similar to that of diesel and are produced easily and renewably from the crops. Vegetable oils have comparable energy density, cetane number, heat of vaporization and Stoichiometric air-fuel ratio with that of the diesel fuel.

None other than Rudolph Diesel, the father of diesel engine, demonstrated the first use of vegetable oil in compression ignition engine. He used peanut oil as fuel for his experimental engine. Viscosity of vegetable oils is several times higher than that of diesel. Viscosity of liquid fuels affects the flow properties of the fuel, such as spray atomization, consequent vaporization, and air-fuel mixing in the combustion chamber. Higher viscosity of oils had an adverse effect on the combustion in the existing diesel engines.

In recent years^{1,2}, systematic efforts were under taken by many researchers to determine the suitability of vegetable oil and its derivatives as fuel or additives to the diesel. Blending, emulsification, thermal cracking and transesterification are the commonly adoptable methods to use the vegetable oil as fuel in diesel engines. Recent years, biodiesel have received significant attention both as a possible renewable alternative fuel and as an additive to the existing petroleum-based fuels. Biodiesel exhibits several merits when compared to that of the existing petroleum fuels. Many researchers have shown that particulate matter, unburned hydrocarbons, carbon monoxide, and sulfur levels are significantly less in the exhaust gas while using biodiesel as fuel. However, an increase in the levels of oxides of nitrogen is reported with biodiesel.

Presently, considerable research has been undertaken to understand the performance characteristics of biodiesel-fueled engine as well as the biodiesel production technology.

Biodiesel is a chemically modified alternative fuel for use in diesel engines⁴, derived from vegetable oils and animal fats. Biodiesel is produced commercially by the Transesterification of vegetable oils with alcohol. Methanol or ethanol is the commonly used alcohols for this process. The direct use of alcohols as fuel causes corrosion of various parts in the engine. The transesterification process solves this problem. The carbon cycle of vegetable oils consists of release and absorption of carbon dioxide. Thus, the accumulation of carbon dioxide in atmosphere reduces. This was an exploratory investigation to determine the effect of fuel on the engine performance characteristics and infrastructure needed to use this fuel. This testing proved that the biodiesel could easily be used as a feasible alternative fuel.

The experimental results of various researchers support^{5,6} the use of biodiesel as available alternative to the diesel oil for use in the internal combustion engines. It is also important to note that most of the experiments conducted on biodiesel are mainly obtained from refined edible type oils only. The price of refined oils such as sunflower, soybean oil and palm oil are high as compared to that of diesel. This increases the overall production cost of the biodiesel as well. Biodiesel production from refined oils would not be viable as well as economical for the developing countries like India.

Hence, it is better to use the non-edible type of oils for biodiesel production. In India, non-edible type oil yielding trees such as mahua, sal, linseed, castor, karanji, neem, rubber, jatropha, kusum and cashew are available in large number. The production and utilization of these oils are low at present, because of their limited end usage. Utilization of these oils/ biodiesel as fuels in internal combustion engines is not

only reducing the petroleum usage, but also improves the rural economy. Efforts are made here to produce biodiesel from typical unrefined oil (*Schlichera oleosa* seed oil) and to use it as the fuel in diesel engines.

Characterization of *Schlichera oliosa* seeds oil: In the present investigation^{7,8}, the *Schlichera oliosa* seed oil, a non-edible type vegetable oil is chosen as a potential alternative for producing biodiesel and use as fuel in compression ignition engines. The estimated availability of *Schlichera oleosa* seed is about 25, 000 oil potential per tones per annum. In the past *Schlichera Oliosa* seed oil was exported from India to Germany. This market has now fallen away. Current (1979) production in India is 4000-5000 tons. *Schlichera Oliosa* seed kernels (0.45 lacks of tones of seed) contain 40.3% of yellowish brown colored oil. The one or two almost round seeds some 1.5cm in diameter and weighing between 0.5 and 1.0g.

The weight of 1000 seeds is 500-700 g. *Schlichera oleosa* evergreen trees with the height up to 30 m and the girth up to 3 m. The leaves are paripinnate, 20-40 cm long. The leaflets are 2 to 4 pairs, elliptic or elliptic-oblong, coriaceous, margins entire and apex rounded. The flowers are minute, yellowish green; male or bisexual, fascicled in spike like axillary racemes 7.5 to 12.5 cm long. The fruits are berry, globose or ovoid, and hard skinned. The seeds are brown, irregularly elliptic, slightly compressed, oily, enclosed in a succulent aril.

S. oleosa is widely in the sub-Himalayan region, Chattishgarh, throughout central and southern India, Burma, Ceylon, Java and Timor. The oil obtained from its seeds is called *Schlichera oleosa* seed oil or Macassar oil which is traditionally used for the cure of itch, acne, burns, other skin troubles, rheumatism (external massage), hair dressing and promoting hair growth. In Thailand, *S. oleosa* named Ta-Khro is found in the Northern, North-eastern, South-eastern, Southwestern and Central region. It is used in the wood industry. The wood is suitable for fuel wood and

charcoal, the bark is used as dye and the young leaves are eaten as vegetable. In this study, Ta-Khro seeds were blended and macerated with hexane. The oil was then separated and hexane was evaporated *in vacuo*. The fatty acid composition was investigated by GC/MS after methylation (fig. 1).

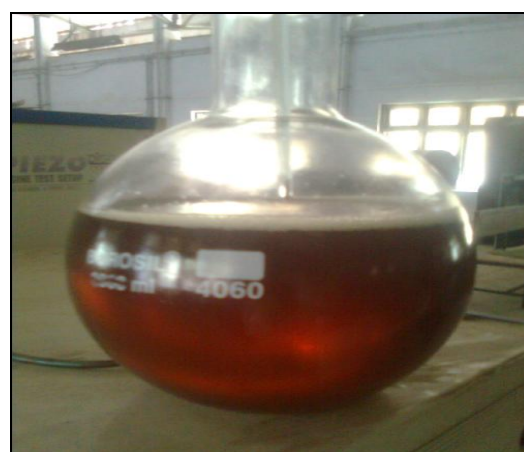
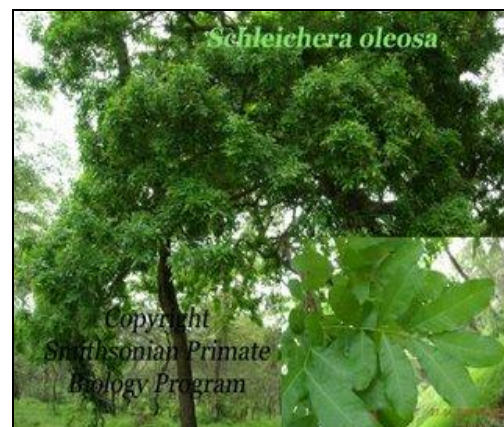


FIG. 1: SCHLEICHERA OLEOSA TREE, SEEDS AND OIL

Fatty acid profile showed 16 components. Linolelaidic acid, the *trans* form of linoleic acid, was found as dominant fatty acid (49.7%). The next below were eicosenoic acid or gondoic acid (29.5%), palmitic acid (7.6%), linoleic acid (5.6%) and oleic acid (2.8%). oleic acid was previously well-known as major fatty acid in *Schlichera oleosa* oil. However Basu's study showed the different result which reported 50% linoleic acid. This study revealed the *trans* fatty acid in *Schlichera oleosa* seed oil.

FFA composition in *Schleichera oleosa* seeds oil: C14:0 Myristic acid (0.01%), C16:0 Palmitic acid (7.59%), C16:1 n-7 Palmitoleic acid (1.80%), C18:1 n-9 *Cis* Oleic acid (2.83%), C18:2 n-6 *Trans* ,Linolelaidic acid (49.69%), C18:2 n-6 *Cis* Linoleic acid (5.56%), C18:3 n-3 *alpha*-Linolenic acid (0.26%), C20:1 n-9 Eicosenoic acid (29.54%), C20:2 n-6 Eicosadienoic acid (0.24%), C21:0 Heneicosanoic acid (0.04%), C22:0 Behenic acid (1.14%), C22:1 Erucic acid (1.22%), C24:0 Lignoceric Acid (0.03%), C22:6 Docosahexaenoic acid (0.02%).

***Schleichera oleosa* Methyl Ester Conversion Processes:**

Methodology: The objective of this study is to develop a technique for producing biodiesel from a low-cost feedstock like crude *Schlichera oleosa* seed oil. The esterification process consists of the following two stages.

Acid-Esterification: The acid-catalyzed pretreatment process reduces the high FFA content of the crude oil to about 2% FFA.

Alkaline-Transesterification: The products of first step are transesterified using alkaline catalyst. The important parameters affecting the esterification process such as alcohol to vegetable oil molar ratio, catalyst amount, and reaction temperature and reaction duration are analyzed.

Esterification Procedure: Esterification is done as a pretreatment step to the transesterification procedure

when the FFA content is higher than 2%. In practice, it is a bit more complicated to implement than transesterification. A by product of the process is water, which impedes the reaction. The Molecular weight of *Schlichera oleosa* seed oil is 840 grams. As there is more FFA in the oil, more methanol percentage wise must be added to compensate for the water. To overcome this, industrial producers use counter current reactors that enable a continuous flow of high FFA oil in and water out.

A round bottom flask of 1500 cm³ is used as laboratory scale reactor for the present analysis. The *Schlichera oleosa* seed oil in the flask was heated on a hot plate having magnetic stirrer arrangement. The mixture was stirred at the same speed for all test runs. The temperature maintained for the whole esterification process is between 55-60°C and maintained 2 hr. Alcohol to vegetable oil molar ratio is one of the important factors that affect the conversion efficiency of the process. For the Stoichiometric transesterification, 3 mol of alcohol are required for each mole of the oil.

However, in practice, the molar ratio should be higher than this theoretical ratio in order to drive the reaction towards early completion. Sulphuric acid is used as catalyst in the acid-catalyzed pretreatment. Experimentally it is optimized that 5ml per liter by volume of the sulphuric acid (H₂SO₄) a molar ratio of 6:1 (ratio of methanol and oil) gave the maximum conversion efficiency. After the reaction is completed, the products are allowed to separate into two layers. The water and glycerol very low density is coming upper layer and lower layer is ester oil, this is called as pretreatment oil as shown **fig. 3**. This process is called as esterification processes.

Transesterification Processes: Bio-diesel is produced by transesterification which is a process of using either ethanol or methanol, in the presence of a catalyst, such as potassium hydroxide or NaOH, to chemically break the molecule of an oil or fat into an ester and

glycerol. This process is a reaction of the oil with an alcohol to remove the glycerine, which is a by product of bio-diesel production. **Figure 2** shows the transesterification reaction.

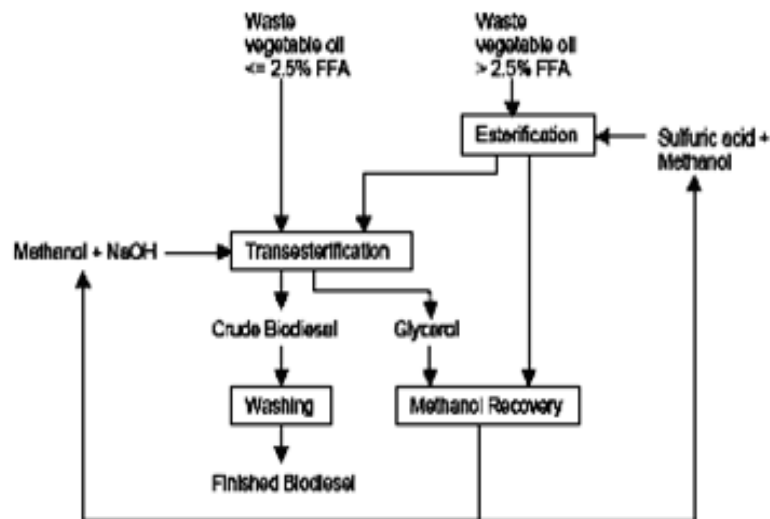


FIG. 2: BLOCK DIAGRAM FOR TRANSESTERIFICATION PROCESSES AND ESTRIFICATION PROCESSES

The reactor for producing biodiesel from *Schlichera oleosa* oil is a small batch type reactor. The first we are taken pretreatment oil temperature is 50-55°C. The products of the first stage pretreatment oil are used as the input of the alkaline Transesterification process. A molar ratio of 6:1 and 10grms by weight of potassium hydroxide (KOH) is found to give the maximum ester yield. The reaction time is maintains 2hr at 60°C. After the reaction is completed, the products are allowed to separate into two layers. The lower layer contains impurities and glycerol. This top layer (ester) is separated and purified using distilled water. Hot

distilled water (20% by volume) is sprayed over the ester and stirred gently and allowed to settle in the separating funnel. The lower layer is discarded and upper layer (purified biodiesel) is separated.

Transesterification of the oil produces methyl esters (biodiesel) and glycerol. The methyl ester layer is a light yellow liquid that is on top or bottom of the glycerol layer, which is dark brown in color. The mixtures may be kept overnight and allowed to separate by gravity. Otherwise, the methyl ester is separated from the glycerol and washed with water and acetic acid until the washing water is neutral. The methyl ester is then dried by heating. Materials and energy flows for the transesterification of *Schlichera oleosa* seed oil into biodiesel are shown in **Fig. 3**.

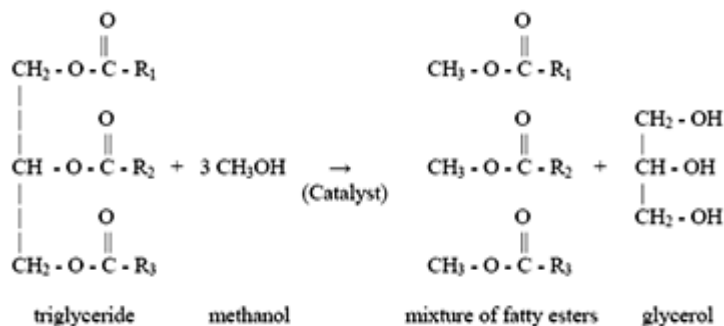


FIG. 3: TRANSESTERIFICATION PROCESSES THROUGH THE SOME





(a) SOME 100% (b) SOME 20% (c) SOME 40% (d) SOME 60% (e) SOME 80%

FIG. 4: SOME BLENDING FUELS

RESULTS: The important properties of *Schlichera oleosa* Methyl Esters are found out and compared with

TABLE 1: SOME BLENDING FUEL PROPERTIES

Fuel SOME	Viscosity @40°C (cSt)	Density@ 40°C (Kg/m ³)	Flash point (°C)	Fire point (°C)	Calorific Values (kj/kg)
100	14.2	850	150	157	41,650
80	12.03	840	109	117	41,720
60	9.73	830	88	93	41,790
40	8.00	820	85	89	41,860
20	3.33	809	80	84	41,930
Oil	40.36	860	225	231	38,140

The viscosity was substantially reduced from a value of 41 to 14 cSt. The calorific value of methyl ester is lower than that of diesel because of its oxygen content. The flash point of the ester is higher than that of diesel. A different percentage of biodiesel addition with diesel can definitely improve the flash point of the resultant mixture. Hence, this fuel is safer to store and transport compared to that of pure diesel.

DISCUSSIONS AND CONCLUSIONS: The unrefined *Schlichera oleosa* seed oil is chosen as a potential non-edible vegetable oil for the production of biodiesel. Alkaline-catalyzed esterification process could not produce biodiesel from high FFA oils like the *Schlichera oleosa* seed oil. Successful efforts are made here for the production of biodiesel from unrefined *Schlichera oleosa* seed oil. The two-step esterification process converts the crude high FFA *Schlichera oleosa* methyl ester to a suitable form of fuel for diesel engines. Viscosity and density of methyl esters of *Schlichera oleosa* methyl ester are found to be close to that of diesel. The flash point of biodiesel is higher than that of diesel. Lower concentration of esters in biodiesel

diesel (Table 1). It can be seen that the properties of *Schlichera oleosa* oil methyl esters are quite comparable to that of other blending *Schlichera oleosa* methyl esters.

The result shows that, transesterification improved the important fuel properties of the oil like specific gravity; viscosity; flash point and acid value. The comparison shows that the methyl ester has relatively closer fuel properties to diesel than that of original unrefined *Schlichera oleosa* seed oil.

blends can be used as the performance improver. The important properties of biodiesel produced from *Schlichera oleosa* methyl ester are quite close to that of diesel. Hence the methyl esters of *Schlichera oleosa* methyl ester can be a prospective fuel or performance improving additive in compression ignition engines. Use of the biodiesel as partial diesel substitute can boost the farm economy, reduce uncertainty of fuel availability and make farmers more self-reliant. Also, this help in controlling air pollution to a great extent.

REFERENCES:

1. Tat, M. E. and J. H. Van Gerpen, "Biodiesel Blend Detection Using a Fuel Composition Sensor", ASAE Paper No. 01-6052, presented at the American Society of Agricultural Engineers 2001 Annual meeting, Sacramento, Calif., July 2001.
2. Canakci, M. and J. Van Gerpen, "A Pilot Plant to Produce Biodiesel from High Free Fatty Acid Feedstocks", ASAE Transactions 46(4) 2003 pp. 945-954. This paper was also published as SAE Paper No. 01-6049, 2001.
3. Chanida Palanuvej and Niran Vipunngeun Fatty acid constituents of *Schleichera Oleosa* (lour) oken. Seeds oil, College of Public Health Sciences, Chulalongkorn University, Bangkok 10330.
4. S. Ramadhas, C. Muraleedharan, S. Jayaraj, Performance and emission evaluation of a diesel engine fueled with methyl

- esters of rubber seed oil, *Renewable Energy* 30 (2005) 1789–1800.
5. J. Van Gerpen, B. Shanks, and R. Pruszko, "Biodiesel Production Technology" National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393, 303-275-3000.
 6. Canakci, M. and J. Van Gerpen, "The Performance and Emissions of a Diesel Engine Fuelled with Biodiesel from Yellow Grease and Soybean Oil", ASAE Paper No. 01-6050, 2001
 7. Canakci, M. and J. Van Gerpen, "Biodiesel Production from Oils and Fats with High Free Fatty Acids", *Transactions of the American Society of Agricultural Engineers*, V. 44, No. 6, 2001, pp. 1429-1436.
 8. Mikolajczak C.R. Smith, J. R. Cyanolipids of Kusum (*Schleichera trijuga*) Seed Oil Northern Regional Research Laboratory ARS, USDA.
