ALTERNATE FUEL DEVELOPMENT FROM HIGH ACID VALUE TAMANU SEED OIL METHYL ESTER

T.Prabahar[1]

[1] *Lecturer, Department of Mechanical Engineering (R&A/C), Valivalam Desikar Polytechnic College(Government Aided), Nagapattinam, Tamilnadu, India.*

ABSTRACT

Ever since the world witnessed the oil crisis, there has been unprecedented stock piling of oil taking place by the developed countries. The world is confronted with the twin crisis of fossil fuel depletion and environmental degradation. The indiscriminate extraction and consumption of fossil fuel has led to the reduction of petroleum reserves. The most feasible way to meet the growing demand is by utilizing alternative fuels. This is the right time to search for liquid fuels as an alternative to diesel. Therefore it is important to explore the feasibility of substitutions of diesel with an alternative fuel, which can be produced within the country on a massive scale for commercial utilization. Alternative fuels should be easily available, environment friendly and techno economically competitive.

Bio-diesel obtained from vegetable oils are being considered as a promising option. Vegetable oils, being renewable, are widely available from a variety of sources and have low sulphur contents close to zero, and hence cause less environmental damage than diesel. For this purpose, new energy crops which may not be used for edible purposes are identified. In this paper, an attempt has been made to identify a new non-edible Tamanu seed oil which can be used as bio-diesel. Being a non-edible oil category, Tamanu seed oil will not arise food versus fuel conflict. The well known Triple stage Transesterification process is used for bio-diesel preparation. The properties of Tamanu oil is tested in the laboratory and compared with diesel and other vegetable oils of its same category.

The test reports says that the bio-diesel extracted from Tamanu seed oil will be one of the definite solutions for petroleum diesel. The density and viscosity of the Tamanu Oil Methyl Ester (TOME) was found to be close to the petroleum diesel oil. All the tests for characterization of bio-diesel demonstrated that almost all the important properties of bio-diesel are in very close agreement with the diesel oil making it a potential fuel for the application in compression ignition engines for complete replacement of diesel fuel.

Keyword : - *Biodiesel, Alternate fuel, Tamanu oil, Blending, Transesterification, Extraction.*

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1. INTRODUCTION

Energy is an essential input for economic growth, social development, human welfare and for improving the quality of life. Since their exploration, the fossil fuels continued as the major convectional energy source. With increasing trends of modernization and industrialization, the world energy demand is also growing in a faster rate. Besides the fuel crisis, the other problem of concern is the degradation of environment due to fossil fuel combustion. Thus it is essential that low emission alternate fuels must be developed for use in diesel engines. Vegetable oil is one of the main sources. In the recent years, serious efforts have been made by several researchers to use different vegetable oils as fuel in existing diesel engines. The research and development activities in several countries on this subject have been mostly on edible oils. In India, biodiesel produced from non-edible oil seeds like jatropha, pungamia, cotton seed etc. are given first preference. The present paper is an attempt to review the possibilities of using tamanu oil as biodiesel by studying the process available, fuel properties and economical analysis of tamanu oil production. Some literature shows that tamanu oil has been used as lamp oil in the ancient times. Thus the emphasis of the present work is to experimentally evaluate the possibilities of using tamanu oil which is developed from one of the easily available non-edible oil seed in India.

1.1 Alternative diesel fuels

Alternative fuels should be easily available, environment friendly and techno economically competitive. One of such fuel is triglycerides and their derivatives. Vegetable oils, being renewable, are widely available from a variety of sources and have low sulphur contents close to zero, and hence cause less environmental damage (lower green house effect) than diesel.

1.2 Utilization of vegetable oil as diesel fuel

It has been found that, these neat vegetable oils can be used as diesel fuels in conventional diesel engines, but this leads to a number of problems related to the type and grade of oil and local climatic conditions. The injection, atomization and combustion characteristics of vegetable oils in diesel engines are significantly different from those of diesel. The high viscosity of vegetable oil interferes with injection process and leads to poor fuel atomization. The inefficient mixing of oil with air contributes to incomplete combustion, leading to heavy smoke emission, and the high flash point attributes to lower volatility characteristics. These disadvantages, coupled with the reactivity of unsaturated vegetable oils, do not allow the engine to operate trouble free for longer period of time. These problems can be solved, if the vegetable oils are chemically modified to biodiesel, which is similar in characteristics to diesel.

2. BIODIESEL

The biodiesel is a methyl ester of fatty acids made from vegetable oils and animal fat. The biodiesel may be classified as edible and non-edible oil. “Rudolf Diesel” demonstrated his first diesel engine at the world exhibition at Paris in the year 1900 by using peanut oil as fuel. The major sources of biodiesel are soya bean oil, rice bran oil, palm oil, pungamia oil, cotton seed oil, jatropha oil, tamanu oil etc. The main reason for selection of non-edible oil are, there is no demand, inexpensive, renewable, more availability and not for food.

2.1 Advantages of biodiesel as diesel fuel

The advantages of biodiesel as diesel fuel are liquid nature portability, ready availability, higher combustion efficiency, low sulphur and aromatic content, higher cetane number and higher biodegradability. Main advantage of biodiesel is its domestic origin, reducing the dependency on imported petroleum, high flash point, inherent lubricity and no engine modification is needed.

3. INTRODUCTION TO TAMANU OIL

Tamanu tree, having the Botanical name Calophyllum Inophyllum, is generally called as Alexandrian Laurel in English.

3.1 Plant description

The tamanu tree often grows in coastal regions as well as nearby lowland forests. Tamanu tree is 2-3 meter high, and has a thick trunk cover with a rough, black and cracked bark. It has elliptical, shiny tough leaves. Its flowers, arranged in clusters, are spherical drupes. The grey, ligneous and rather soft nut contains a pale yellow kernel, which is odourless when fresh. Tamanu kernels have very high oil content (75 %). A greenish yellow oil is obtained by cold pressing of these kernels.

3.2. Raw tamanu oil processing

The oil extracted from these nuts is called tamanu oil. The nuts are cracked and the kernels are extracted. The seeds need to be Sun-dried on rocks for 1-2 months leaving it for oil formation. Kernels turn from creamy white to brown during the process. During the Sun-drying, kernels loss weight from a mean 7 gm of fresh kernels to about 4.5 gm of dry and oil-rich ones. These kernels have longer shelf life. Any moldy nuts should be discarded. The oil is then extracted by cold pressing and filtration.

3.3. Characterization of tamanu oil

The unrefined but filtered tamanu oil is dark green in colour and is used as feed stock for biodiesel production in this study. The fatty acid composition and the important properties of tamanu oil in comparison with other non-edible oils are given.

Table–1 Properties of tamanu seed oil in comparison with other non-edible oils:

Property of the oils	Tamanu (Calophyllum Inophyllum)	Cotton (Gossypium Herbaceum)	Karanja (Pongamia Pinnata)	Jatropha (Jatropha Curcus)
Fatty acid composition: Palmitic acid (%)	0	11.67	11.65	16.0
Stearic acid (%)	0	0.89	7.5	6.5
Oleic acid (%)	41.6	13.27	51.59	43.5
Linoleic acid (%)	24.3	57.51	16.46	34.4
Linolenic acid (%)	0	0	2.65	0.8
Acid value (mg KOH /gm)	44	0.11	5.06	3.8

Tamanu oil contains 24.96% saturated acids (palmitcs and stearic) and 72.65% unsaturated acids (oleic, linoleic and lenolenic). Saturation fatty acid alkyl esters increase the cloud point, cetane number and stability. The free fatty acid (FFA) content of unrefined filtered tamanu oil was found to be 22%. i.e. acid value of 44 mg KOH/gm. Its free fatty acid content was determined by a standard titrimetry method.

The yield of esterification process and quality of biodiesel decreases considerably if acid value is greater than 4 mg KOH/gm. i.e. free fatty acid content is 2%. Therefore, development of any method to produce biodiesel from high acid value oil is significant. Hence, the efforts are made to esterify a typical high free fatty acid type of oil, i.e. Tamanu seed oil in this study.

4. EXPERIMENTAL SYSTEM DEVELOPMENT FOR BIODIESEL FORMULATION

4.1. Methodology

Experiments were conducted in a laboratory set up which consists of heating mantle, reaction flask which is made of glass and mechanical stirrer. The working capacity of reaction flask is 3 liter. It consists of three necks. One for stirrer, and the others for condenser and inlet of reactant as well as for placing the thermometer to observe the reaction temperature. The flask has a stopcock at the bottom for collection of the final product. The progress of the reaction was observed by measuring the acid value.

In course of the test, it was observed that the appropriate quality of biodiesel could be produced from tamanu seed oil in following three stages so that the physio-chemical properties were close to those of petro-diesel.

4.1.1. Zero catalyzed transesterification

The first stage removes the organic matters and other impurities present in the unrefined filtered tamanu oil using toluene as reagent.

4.1.2. Acid catalyzed transesterification

The intermediate stage reduces the acid value of the oil about 4 mg KOH/gm corresponding to a FFA level of 2% by using H_2so_4 as catalyst.

4.1.3. Alkaline catalyzed transesterification

The product of the intermediate stage (pure triglyceride) is transesterified to mono-esters of fatty acids (biodiesel) by using NaoH as alkali catalyst.

4.2. Process of biodiesel production

4.2.1. Tranaesterification process

Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. This process has been widely used to reduce viscosity of triglycerides.

Fig– 1 Biodiesel production setup

4.2.2. Chemistry of transesterification reaction

The overall transesterification reaction is given by three consecutive and reversible equations as below:

$$\text{Triglyceride} + \text{ROH} \xrightleftharpoons{\text{catalyst}} \text{Diglyceride} + R^{1}\,\text{COOR}$$

$$\text{Diglyceride} + \text{ROH} \xrightleftharpoons{\text{catalyst}} \text{Monoglyceride} + R^{11}\,\text{COOR}$$

$$\text{Monoglyceride} + \text{ROH} \xrightleftharpoons{\text{catalyst}} \text{Glycerol} + R^{111}\,\text{COOR}$$

The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule per mole of glyceride at each step.

The overall chemical reaction of the transesterification process is:

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CH2OCOR'''                              CH2OH       R'''COOR
     |                                  Catalyst      |
CH2OCOR''   +   3 ROH     ------>       CH2OH   +   R''COOR
     |                                                |
CH2OCOR'                                CH2OH       R'COOR

Triglyceride      Alcohol               Glycerol     Biodiesel
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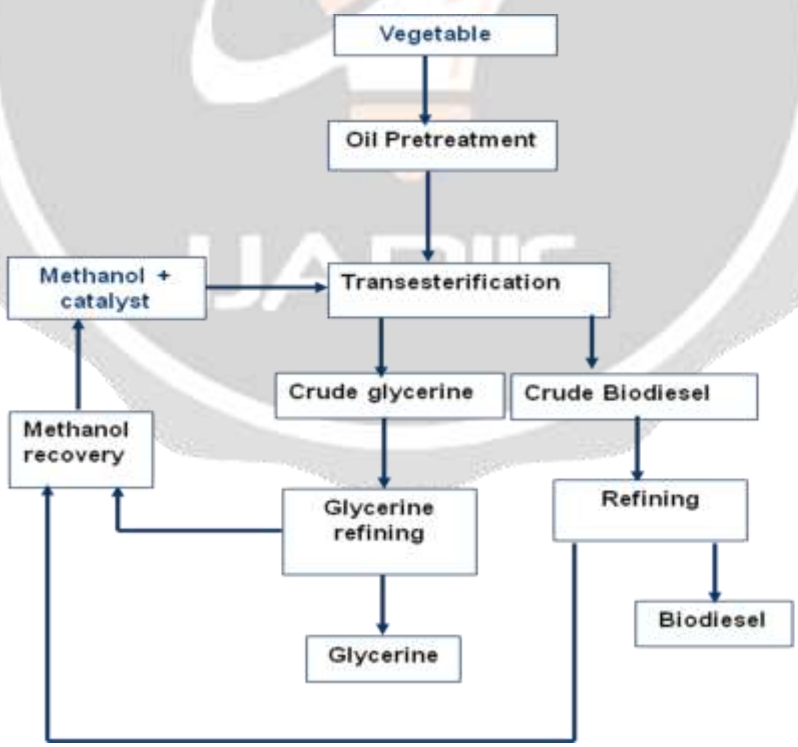
Where, R^1, R^{11}, R^{111} are long-chain hydrocarbons which may be the same or different with R= - CH_3 / C_2H_5

5.BIODIESEL PRODUCTION PROCEDURE



The raw tamanu oil was extracted by mechanical expeller in which small traces of organic matter, water and other impurities were present. These materials were creating problems in yield and in the phase separation between the glycerin and esters. This necessitates the pretreatment of tamanu oil in the first stage.

One liter of tamanu oil was mixed with 350 ml of methyl alcohol and 5 ml of toluene as a reagent. Toluene helps in dissolving the organic matter with methanol and separating it from the neat oil along with other impurities. Different methanol to oil ratio (0.15, 0.20, 0.25, 0.30 and 0.35) and reaction times (0.5 h, 0.10 h, 0.15 h, 0.20 h) were used to investigate for the optimization and their influence on the acid value of crude tamanu oil. The mixture was stirred in the air closed reaction flask for 2 hours at 65^0C. The heating set up should be just above the boiling point of the alcohol i.e 65^0C to accomplish the reaction. The speed of the stirrer was kept same for all test runs. i.e 450 rpm. The product from the first stage was allowed to settle for 1 hour and complete phase separation was visualized. The upper layer which consisted of methanol-water fraction, organic matter toluene and other impurities was separated from the lower layer. The acid value of the required lower layer is determined and found to be 18 mg KOH / gm corresponding to FFA of 9%.

Anhydrous sulphuric acid (98.4%) was used as catalyst in the acid catalyzed transesterification. Experimentally it was optimized that 0.65% by volume of the H_2SO_4 acid and a molar ratio of 6:1 gave the maximum conversion efficiency of free fatty acid value of the product of the second stage below 4 mg KOH / gm. the duration of the reaction was 4 hour.

The product of second step having FFA less than 2% was used as the raw material for the final stage. A molar ratio of 9:1 and the 1.5% by weight of sodium hydroxide was found to give the maximum ester yield for reaction duration of 4 hour.

After the reaction was completed the products were allowed to separate in two layers. The lower layer is separated and purified by using warm water. After washing, the final product was heated up to 70^oC for 15 min. under vacuum condition and stored for further use. This resulted in a clear amber-light yellow liquid with a viscosity similar to petro-diesel.

Table-2 Properties of biodiesel from different oils:

Vegetable oil methyl esters (Biodiesel)	Kinematic viscosity (mm^2/s)	Cetane Number	Calorific value (MJ/kg)	Pour point (^{0}C)	Flash point (^{0}C)	Density (kg/l)
Peanut	**4.9**	**54**	**33.6**	**-**	**176**	**0.883**
Soya bean	**4.5**	**45**	**33.5**	**-7**	**178**	**0.885**
Palm	**5.7**	**62**	**33.5**	**-**	**164**	**0.875**
Sunflower	**4.6**	**49**	**33.5**	**-**	**183**	**0.860**
Diesel	**3.06**	**50**	**43.8**	**-16**	**76**	**0.855**
20% Biodiesel	**3.2**	**51**	**43.2**	**-16**	**128**	**0.859**

Table-3: Properties of tamanu oil methyl ester in comparison with diesel and blends:

Fuel blends	Viscosity (cSt)	Calorific value (MJ/kg)	Flash point (^0C)	Cloud point (^0C)	Pour point (^0C)
HSD	**2.87**	**44.22**	**76**	**6.5**	**-3**
B20	**2.98**	**43.85**	**86**	**7.8**	**2.8**
B40	**3.30**	**42.65**	**91**	**8.5**	**2.8**
B60	**3.61**	**40.98**	**96**	**10.6**	**3.2**
B80	**3.72**	**39.23**	**111**	**10.8**	**3.6**
B100	**4.92**	**38.66**	**140**	**13.2**	**4.3**

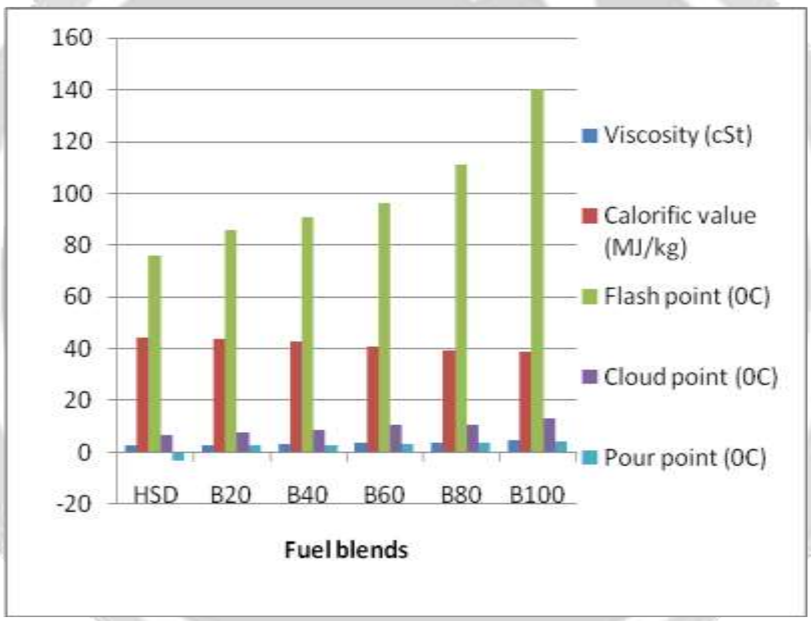


Chart -1 Properties of tamanu oil methyl ester

The physio-chemical properties of the tamanu oil, neat petro-diesel, neat biodiesel (B 100) and its blend of 20% at each step were evaluated as per the ASTM standard methods and the results are in accordance with ASTM. The fuel properties of tamanu oil methyl ester and its different blends with diesel are shown in Table-3. It is observed that the chemical characteristics of the tamanu oil methyl ester were found to be in the close range of engine requirement.

5.1. Economics of biodiesel utilization

The major obstacle to produce biodiesel is higher cost than petroleum diesel. The actual cost will depend also on economics of scale in manufacturing and the political decision to promote biodiesel in the country. The cost factor may also be considered taking in the view of increased rural employment opportunities, indigenous energy sufficiency and savings of foreign exchange. There would also be employment generation in storage, oil extraction etc. The glycerin and cake would be valuable products, which further reduces the cost of biodiesel. Oil cake can be used as a raw material for production of biogas which would be a leverage to start many types of industries. Reduction of tax on biodiesel by government is one of the effective ways to bring down the cost.

6. CONCLUSION

The density and viscosity of the tamanu oil methyl ester (TOME) obtained after triple stage transesterification was found to be close to the petroleum diesel oil. The flash point of all the blends of TOME was higher than that of diesel oil. Particularly, the 100% biodiesel also demonstrated comparatively higher flash point than petroleum diesel oil and was in safe range for storage. All the tests for characterization of biodiesel demonstrated that almost all the important properties of biodiesel are in very close agreement with the diesel oil making it a potential fuel for the application in compression ignition engines as a complete replacement for diesel fuel.

7. REFERENCES

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