Biodiesel production from high FFA rubber seed oil


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ABSTRACT
Currently, most of the biodiesel is produced from the refined/edible type oils using methanol and an alkaline catalyst. However, large amount of non-edible type oils and fats are available. The difficulty with alkaline-esterification of these oils is that they often contain large amounts of free fatty acids (FFA). These free fatty acids quickly react with the alkaline catalyst to produce soaps that inhibit the separation of the ester and glycerin. A two-step transesterification process is developed to convert the high FFA oils to its mono-esters. The first step, acid catalyzed esterification reduces the FFA content of the oil to less than 2%. The second step, alkaline catalyzed transesterification process converts the products of the first step to its mono-esters and glycerol. The major factors affect the conversion efficiency of the process such as molar ratio, amount of catalyst, reaction temperature and reaction duration is analyzed. The two-step esterification procedure converts rubber seed oil to its methyl esters. The viscosity of biodiesel oil is nearer to that of diesel and the calorific value is about 14% less than that of diesel. The important properties of biodiesel such as specific gravity, flash point, cloud point and pour point are found out and compared with that of diesel. This study supports the production of biodiesel from unrefined rubber seed oil as a viable alternative to the diesel fuel.

KEYWORDS: Rubber seed oil, Biodiesel, Esterification

INTRODUCTION
Vegetable oils are becoming a promising alternative to diesel fuel because they are renewable in nature and can be produced locally and environmentally friendly as well. They have practically no sulphur content, offer no storage difficulty, and they have excellent lubrication properties. Moreover, vegetable oils yielding trees absorb more carbon dioxide from the atmosphere during their photosynthesis than they add to the atmosphere on burning. Hence, they essentially help to alleviate the increasing carbon dioxide content in the atmosphere. The substitution of diesel oil by renewable fuels produced within the country generates higher foreign exchange savings, even for the major oil exporting countries. Therefore, developing countries can use this kind of project not only to solve their ecological problems but also to improve their economy. In view of the several advantages vegetable oils has potential to replace petroleum-based fuels in the long run. In the recent years, systematic efforts have been made by several researchers [1–6] to use the various vegetable oils as fuel in compression ignition engines. The calorific value of vegetable oil is comparable to that of diesel. However, their use in direct injection diesel engines is restricted by some unfavorable physical properties, particularly their viscosity. The viscosity of vegetable oil is about ten times higher than that of diesel. Therefore, the vegetable oil cause poor fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats resulting in serious engine fouling. This necessitates the reduction in viscosity of the vegetable oils for use as fuel in CI engines. The commonly employed methods to reduce the viscosity of vegetable oils are blending with diesel, emulsification, pyrolysis, cracking and transesterification[7]. Among these, transesterification of vegetable oils

appears to be more suitable because the by product (glycerol) has commercial value. Transesterification (alcoholysis) is the chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters. The long and branched chain triglyceride molecules are transformed to monoesters and glycerin[8]. Transesterification process consists of a sequence of three consecutive reversible reactions. That is, conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. The glycerides are converted into glycerol and yielding one ester molecule in each step. The properties of these esters are comparable to that of diesel. The overall transesterification reaction can be represented by the following reaction scheme.

![Reaction Scheme](image)

Stoichiometrically, three moles of alcohol are required for each mole of triglyceride, but in practice a higher molar ratio is employed in order to displace the equilibrium for getting greater ester production. Though esters are the desired products of the transesterification reactions, glycerine recovery also is important due to its numerous applications in different industrial processes. Commonly used short chain alcohols are methanol, ethanol, propanol and butanol. The yield of esterification is independent of the type of alcohol used. Therefore, the eventual selection of one of these three alcohols will be based on cost and performance considerations. The methanol is used commercially because of its low price. Alkaline hydroxides are the most effective transesterification catalysts as compared to acid catalysts. Potassium hydroxide and sodium hydroxide are the commonly used alkaline catalysts. Alkaline catalysed transesterification of vegetable oils is possible only if the acid value of oil is less than 4. Higher percentage of FFA in the oil reduces the yield of the esterification process. A wide variety of high FFA oils are available in large quantities. But these are unsuitable for human consumption. These are mainly used for making low-cost soap. It is difficult to transesterify these high FFA vegetable oils using the commercially available alkaline catalyst process. Esterification of the low cost high FFA oils would substantially reduce the production cost of biodiesel. The purpose of the present study is to develop a method for esterification of high FFA vegetable oils. Rubber seed oil, typical non-edible high FFA oil is considered as a potential feedstock for biodiesel production in this study.

2. Experimental Work:

2.1 Characterization of rubber seed oil:

The annual rubber seed production potential in India is about 150 kg per hectare. Rubber seed kernels (50–60% of seed) contain 40–50% of brown color oil. The estimated availability of rubber seeds in India is about 30,000 tons per annum, which can yield rubber seed oil to the tune of about 5000 tons. Rubber trees yield 3-seeded ellipsoidal capsule, each carpel with one seed. Rubber seeds are ellipsoidal, variable in size, 2.5–3 cm long, mottled brown, lustrous, weighing 2–4 g each. Capsules are spread over the ground. These are collected and kernels are separated by breaking the capsules. These kernels are dried to remove the moisture. The kernels are crushed in the crushers and the oil is filtered. At present rubber seed oil does not find any major applications and hence even the natural production of seeds itself remain underutilized. The filtered oil is used as feedstock for the biodiesel production in this study. The fatty acid composition and the important properties of rubber seed oil in comparison with other oils is given in Table 1 [8–12]. It consists of 18.9% saturation comprising of palmitic and stearic acids and 80.5% unsaturation comprising mainly of oleic, linoleic and linolenic acids. Saturation fatty acid methyl esters increase the cloud point, cetane number and improve stability whereas more polyunsaturates reduce the cloud point and cetane number and stability. The type and percentage of fatty acids contained in vegetable oil depends on the plant species and on the growth conditions of the plant. Though vegetable oils are of very low volatility in nature, it quickly produces volatile combustible compounds upon heating. The free fatty acid content of unrefined rubber seed oil was about 17%, i.e. acid value of 34. The yield of esterification process decreases considerably if FFA value is greater than 2%. Canakci and Van Gerpan[1,13] found that transesterification would not occur if FFA content in the oil were about 3%. It has been found that the alkaline catalyzed transesterification process is not suitable to produce esters from unrefined oils. In order to reduce the acid value (i.e. for reducing FFA), the oil is to be refined. Refining of vegetable oils increases the overall production cost of the biodiesel. Acid esterification is a typical method of producing biodiesel from high FFA oil [1]. But it requires more methanol and is time consuming also. Development of any method to produce the biodiesel from high FFA oils is significant. Hence, the efforts are made to esterify a typical high FFA type of oil, i.e. rubber seed oil in this study.
Table 1: Properties of rubber seed oil in comparison with the other oils

<table>
<thead>
<tr>
<th>Property</th>
<th>Rubber seed oil</th>
<th>Sunflower oil</th>
<th>Rapeseed oil</th>
<th>Cotton seed oil</th>
<th>Soybean oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acid composition (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(i) Palmitic acid C16:0</td>
<td>10.26, 83, 4911.67</td>
<td>11.75</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(ii) Stearic acid C18:0</td>
<td>8.7, 3.260, 85, 0.89, 3.15</td>
<td>0.85, 3.26</td>
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<tr>
<td>(iii) Oleic acid C18:1</td>
<td>24.616, 93, 64.4, 13.27, 23.26</td>
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<td></td>
</tr>
<tr>
<td>(iv) Linoleic acid C18:2</td>
<td>9.6, 73, 7322.3, 57.5155, 53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(v) Linolenic acid C18:3</td>
<td>16.3, 08.23, 06.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Specific gravity</td>
<td>0.910, 0.918</td>
<td>0.918, 0.914, 0.912</td>
<td>0.912, 0.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity (mm²/s) at 40°C</td>
<td>66.2, 58</td>
<td>39.5, 5065</td>
<td>50, 65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>198, 220</td>
<td>280, 210, 230</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calorific value (MJ/kg)</td>
<td>37.5, 39.5, 37.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid value</td>
<td>340.15, 1.14</td>
<td>0.110, 2</td>
<td></td>
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</tr>
</tbody>
</table>

2.2. Esterification procedure:

2.2.1. Methodology:

The objective of this study is to develop a process for producing biodiesel from a low-cost feedstock like crude rubber seed oil. The process consists of two steps namely, acid esterification and alkaline esterification.

(a) Acid esterification: The first step reduces the FFA value of crude rubber seed oil to about 2% using a catalyst.

(b) Alkaline esterification: After removing the impurities of the product of the first step, it is transesterified to mono-esters of fatty acids using an alkaline catalyst. The parameters affecting the process such as alcohol to oil molar ratio, catalyst amount, reaction temperature, and duration are analyzed.

2.2.2. Esterification setup:

A round bottom flask is used as laboratory scale reactor for these experimental purposes. A hot plate with a magnetic stirrer arrangement is used for heating the mixture in the flask. The mixture is stirred at the same speed for all test runs. The temperature range of 40–50 °C is maintained during this experiment. Four trial runs are carried out for each combination of reactants and process conditions. The average of the results is presented in Figs. 1–4.

Fig. 1: Effect of molar ratio on conversion efficiency (step 1).

sulphuric acid and impurities moves to the top surface and is removed. The lower layer is separated for further processing (alkaline esterification).

2.3. Acid esterification:

One litre of crude rubber seed oil requires 200 ml of methanol for the acid esterification process. The rubber seed oil is poured into the flask and heated to about 50 °C. The methanol is added with the preheated rubber seed oil and stirred for a few minutes. 0.5% of sulphuric acid is also added with the mixture. Heating and stirring is continued for 20–30 min at atmospheric pressure. On completion of this reaction, the product is poured into a separating funnel for separating the excess alcohol. The excess alcohol, with sulphuric acid and impurities moves to the top surface and is removed. The lower layer is separated for further processing (alkaline esterification).

2.3.1. Effect of alcohol to oil molar ratio:

The molar ratio of alcohol to vegetable oil is one of the important factors that affect the conversion efficiency as well as production cost of biodiesel. The conversion efficiency is defined as the yield of the process represented in terms of percentage. Molar ratio is the ratio of number of moles of alcohol to number of moles of glycerides in the oil.
Theoretically, transesterification reaction requires three moles of alcohol for each mole of oil. However, in practice, the molar ratio should be higher than that of stoichiometric ratio in order to drive the reaction towards completion. That is, 96 g of methanol is required for 910 g of rubber seed oil. Canakci and Van Gerpan [1,13] advocate the use of large excess quantities of methanol (15:1–35:1) while using the sulphuric acid as catalyst. The conversion efficiency of first step in relation with molar ratio obtained during the present study is shown in Fig. 1. The maximum conversion efficiency is achieved very close to the molar ratio of 6:1. With further increase in molar ratio there is only little improvement in the conversion efficiency. The first step reduces the viscosity of the oil. Also, it has been found that the reduction in viscosity increases with increase in molar ratio.

2.3.2. Effect of acid catalyst amount:

The amount of acid catalyst used in the process also affects the conversion efficiency of the process. The catalyst amount is varied in the range of 0.25–2% for five different values (0.25, 0.5, 1, 1.5 and 2% of sulphuric acid). These percentages are volume fractions of the oil supplied for this reaction. The effect of the catalyst amount on the conversion efficiency is shown in Fig. 2. The acid-catalyst process stains the maximum conversion efficiency at 0.5% of sulphuric acid. Also, it is noted during the present experiments, that excess addition of sulphuric acid, darken the color of the product. Lower amount of sulphuric acid addition affects the yield of the second step.

2.3.3. Effect of reaction temperature:

At room temperature the conversion efficiency is noted to be very low (about 10% only) even after 2 h of stirring. With increase in temperature the conversion takes place at a faster rate. The optimum temperature for this reaction is found to be in the range of 45–58°C. At higher reaction temperatures, there is a chance of loss of methanol and increase in darkness of the product. High reaction temperature increase the production cost of biodiesel also.

![Fig. 2: Effect of acid catalyst amount on conversion efficiency.](image)

2.4. Alkaline esterification:

Alkaline catalyzed esterification process uses the experimental setup of acid catalyzed pretreatment process. The products of first step are preheated to the required reaction temperature of 45–58°C in the flask. Meanwhile, 5 gm of NaOH is dissolved in 300 ml methanol and is poured into the flask. The mixture is heated and stirred for 30 min. The reaction is stopped, and the products are allowed to separate into two layers. The lower layer, which contained impurities and glycerol, is drawn off. The ester remains in the upper layer. Methyl esters are washed to remove the entrained impurities and glycerol. Hot distilled water (10% by volume) is sprayed over the surface of the ester and stirred gently. Lower layer is discarded and yellow color layer (known as biodiesel) is separated.

2.4.1. Effect of methanol to oil molar ratio:

The amount of methanol required for esterification is analyzed in terms of the molar ratio. Stoichiometrically, the methanol/triglyceride molar ratio required is 3:1. But, in practice this is not sufficient to complete the reaction. Higher molar ratio is required to drive the reaction to completion at a faster rate. It is observed that lower molar ratios requires longer reaction period. The effect of molar ratio on conversion efficiency is shown in Fig. 3. It has been seen that yield of the process increases with increase in molar ratio. The maximum ester yield is obtained for the molar ratio of 9:1. With further increase in molar ratio the conversion efficiency more or less remains the same. The excess methanol moves over the ester layer. Excess methanol in the ester decreases the flash point of the biodiesel. The excess methanol can be removed by washing.
2.4.2. Effect of alkaline catalyst amount:

The alkaline catalyst, sodium hydroxide concentration in the range of 0.3–1% (weight of NaOH/weight of oil) is used in the present experimental analysis. The effect of catalyst amount on conversion efficiency is shown in Fig. 4. The maximum conversion efficiency is achieved at 0.5% of NaOH. Addition of excess amount of catalyst, gave rise to the formation of an emulsion, which increased the viscosity and led to the formation of gels. Esterification does not take place for insufficient amount of NaOH addition.

2.4.3. Effect of reaction temperature:

The maximum yield of ester is obtained at the temperatures of 45℃–58℃. The decrease in yield is observed when the reaction temperature goes above 50℃. However, other researchers [3,4] achieved better results at temperatures above 50℃ and up to 70℃ while using refined linseed oil and brassica carinata oil, respectively. The reaction temperatures greater than 60℃ should be avoided, in the case of rubber seed oil, because they tend to accelerate saponification of the glycerides by the alkaline catalyst before completion of the alcoholysis.

2.5. Properties of methyl esters of rubber seed oil:

The fuel properties of rubber seed oil methyl ester in comparison with those of other esters is shown in Table 2 [5,7–9,14–16]. The experimental procedures adopted for the fuel property analysis are also given in Table 2. Most of the fuel properties of rubber seed oil methyl ester are quite comparable to those of other esters and...
diesel. The chromatographic analysis supports that the biodiesel contains large amount of C18. The C, H, O composition of rubber seed oil methyl esters are 76.85, 11.82 and 11.32%, respectively. The present results obtained show that, the transesterification process improved the fuel properties of the oil with respect to specific gravity, viscosity, flash point and acid value. The comparison of these properties with diesel shows that the methyl ester has a relatively closer fuel property values to that of diesel (than that of oil). The viscosity of biodiesel is closer to that of diesel. Hence, no hardware modifications are required for handling this fuel (biodiesel) in the existing engine. The calorific values of methyl esters are lower than that of diesel because of their oxygen content. The presence of oxygen in the biodiesel helps for complete combustion of fuel in the engine. The flash point of rubber seed oil is lowered by transesterification but it is still higher than that of diesel. A small percentage addition of biodiesel with diesel increases the flash point of diesel. Hence, it is safer to store biodiesel– diesel blends as compared to diesel alone. The properties of biodiesel are compared with ASTM biodiesel standards The tested properties of methyl esters of rubber seed oil are found to be in reasonable agreement with ASTM 6751.

Conclusion:
The production of fuel-quality biodiesel from low-cost, high FFA feed stocks is investigated in the present study. It is found that the feedstocks with high FFAs could not be transesterified with the commercially available alkaline catalyst transesterification process. The reason is alkaline catalysts react with the FFAs to form soap that prevents the separation of the glycerin and ester. A two-step transesterification process is developed to convert the high FFA oils to its esters. The first step (acid catalyzed transesterification) reduces the FFA content of the oil to less than 2%. The alkaline catalyst transesterification process converts the products of the first step to its mono-esters and glycerol. The effects of alcohol to oil molar ratio, catalyst amount, reaction temperature and reaction duration are analyzed in each step. Excess addition of sulphuric acid darkens the product. It has been also found that the conversion efficiency is strongly affected by molar ratio of alcohol to oil. The molar ratio of 6:1 favors the completion of alkaline catalyzed esterification process with in half an hour. The maximum ester conversion is achieved at the reaction temperature of 45G5 8C. The viscosity of biodiesel is nearer to that diesel. The flash point of biodiesel (about 130 8C) is greater than that of diesel and the calorific value is slightly lower than that of diesel. This two-step esterification method reduces the overall production cost of the biodiesel, as it uses low cost unrefined non-edible oils. The present analysis reveals that biodiesel from unrefined rubber seed oil is quite suitable as an alternative to diesel. However, further research and development on additional fuel property measures, long-term run and wear analysis of biodiesel-fueled engine is also necessary.

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