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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

1. Introduction

Vegetable oils are becoming a promising alternative to diesel fuel because they are renewable in nature and can be produced locally and environmental friendly as well. They have practically no sulfur 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 byproduct (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 mono-esters and glycerin [8]. Transesterification process consists

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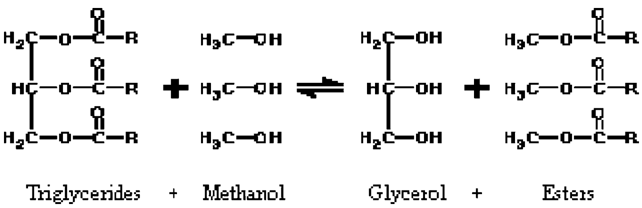
of a sequence of three consecutive reversible reactions. That is, conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. The glycerides are converted into glycerol and yielding one ester molecule in each step. The properties of these esters are comparable to that of diesel. The overall transesterification reaction can be represented by the following reaction scheme.



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, glycerin 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 catalyzed 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. 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

Table 1
Properties of rubber seed oil in comparison with the other oils

Property	Rubber seed oil	Sunflower oil	Rapeseed oil	Cotton seed oil	Soybean oil
Fatty acid composition (%)					
(i) Palmitic acid $C_{16:0}$	10.2	6.8	3.49	11.67	11.75
(ii) Stearic acid $C_{18:0}$	8.7	3.26	0.85	0.89	3.15
(iii) Oleic acid $C_{18:1}$	24.6	16.93	64.4	13.27	23.26
(iv) Linoleic acid $C_{18:2}$	39.6	73.73	22.3	57.51	55.53
(v) Linolenic acid $C_{18:3}$	16.3	0	8.23	0	6.31
Specific gravity	0.91	0.918	0.914	0.912	0.92
Viscosity (mm^2/s) at 40 °C	66.2	58	39. 5	50	65
Flash point (°C)	198	220	280	210	230
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6	39.6
Acid value	34	0.15	1.14	0.11	0.2