Development and Characterization of Biodiesel from Non-edible Vegetable Oils of Indian Origin

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Abstract

Increased environmental awareness and depletion of fossil fuel resources are driving industry to develop alternative fuels that are environmentally more acceptable. Vegetable oils are potential alternative fuels. Vegetable oils in India are produced from numerous oil-seed crops. While all vegetable oils have high energy content, most require some processing to ensure safe usage in internal combustion engines. Most detrimental properties of oils are its high viscosity, low volatility and polyunsaturated character. The most widely used method is to convert vegetable oils into biodiesel. Biodiesel fuels are primary esters, which are produced by transesterifcation of vegetable oils. Several vegetable oil esters have been investigated so far in different parts of the world and found suitable to be used in diesel engines. In present investigation, methyl esters of some non-edible vegetable oils of Indian origin (castor, linseed and ricebran) are prepared and their properties have been evaluated. The effect of temperature on the viscosity of vegetable oils and their esters was studied. Viscosity of vegetable oils drastically decreases after transesterification. Flash point and specific gravity of neat ricebran and linseed oil and their esters were also evaluated in this investigation.

Introduction

Increased environmental concerns, tougher clean air standards, increasing prices and uncertainties concerning petroleum availability necessitate the search for a viable alternative fuel, which is more environment friendly, hence vegetable fuel studies have become prominent among various potential alternatives. The idea of using vegetable oils as fuel for diesel engine is not new. When Rudolf diesel first invented the diesel engine, he demonstrated it at the 1900 world exhibition in Paris, employing peanut oil and said "The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become in course of time as important as petroleum and the coal tar products of the present time" [1]. In the 1930's and 1940's, vegetable oils were used as diesel fuels from time to time, but usually only in emergency situations. Recently, because of increase in crude oil prices, limited resources of fossil fuels and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. Biodiesel is biodegradable, non-toxic and essentially free from sulphur. It is renewable and can be produced from agriculture & plant resources.

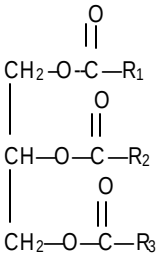
While short-term tests are positive, long-term usage of neat vegetable oils or their blends with diesel leads to various engine problems such as injector coking, ring sticking, injector deposits etc. [2,3]. High viscosity, low volatility and a tendency to polymerize within the cylinder are the root cause of many problems associated with direct usage of these oils as fuels [2]. The process of transesterification yields vegetable oil esters, which have shown promise as alternative diesel fuel as a result of improved viscosity & volatility characteristics. Several researchers investigate the different vegetable oil esters [3-7] and found esters comparable to diesel fuel. Muniyappa et. al., optimized the transesterification process for Soyabean oil, [3]. Freedman et. al. investigated the effect of various parameters on vegetable oil yield [4]. Several researchers transesterified the vegetable oils and found that properties are quite comparable to mineral diesel and performance and emission characteristics of CI engines using biodiesel in different proportion as a blend with mineral diesel improves [5-10]. Agarwal et.al. developed linseed oil methyl esters and found it comparable to diesel with improved emission characteristics compared to diesel [5,6]. Physical wear of various vital parts, injector coking, carbon deposits etc. were found to be substantially lower in case of 20% biodiesel fuelled engines [11].

The objective of this study is to investigate the effect of transesterifcation on the viscosity and other properties of non-edible vegetable oils of Indian origin and to evaluate the effect of temperature on the viscosity of neat vegetable oil and their methyl esters. Detailed results on the viscosity and other properties of oils and their esters are presented in this paper.

Composition of Vegetable Oils

Petroleum diesel fuel is a complex mixture of hydrocarbons with carbon atoms ranging between 12-18, whereas vegetable oils are mixture of organic compounds ranging from simple straight chain compound to complex structure of proteins and fat-soluble vitamins and are

commonly referred as triglycerides. Vegetable oils are usually triglycerides, generally with number of branched chains of different length, and have structural notation as shown.

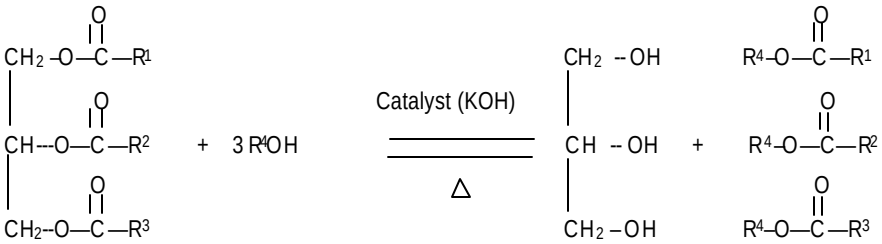


Where R^1, R^2, R^3 represent hydrocarbon (alkyl) groups of different carbon chain lengths.

The high viscosity of vegetable oils (30-200 cSt) as compared to diesel oil (3-4 cSt) at 40°C leads to unfavorable pumping and spray characteristics. The inefficient mixing of fuel with air contributes to incomplete combustion. The high flash point due to lower volatility characteristics results in increased carbon deposit formation, injector coking, lubricating oil dilution and degradation. Because of these problems, vegetable oils need to be modified to bring their combustion related properties closer to those of mineral diesel oil. The fuel modification is mainly aimed at reducing the viscosity and increasing the volatility. From previous studies, it is found that transesterification is the best way to modify the vegetable oil to be compatible as diesel engine fuel.

Transesterification

Chemically speaking, transesterification means taking a triglyceride molecule or a complex fatty acid and creating ester. It is a reversible reaction of fat or oil (triglyceride) with a primary alcohol to form esters and glycerol. Primary alcohols combine with the triglycerides to form glycerol & esters. The reaction is shown below. A catalyst is usually used to improve the reaction rate and ester yield. Since the reaction is reversible, excess alcohol is required to shift the equilibrium to the products side [12]. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and NaOH gets easily dissolved in it. This reaction can be catalyzed by alkalis, acids and enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide etc. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalysts in acid catalyzed reaction. Lipases can also be used as bio-catalysts. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially [4, 12].



(Triglyceride esters) Alcohol Glycerol Esters
Vegetable oil

Transesterification Reaction

For an alkali-catalyzed transesterification, the triglycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. Soap formation lowers the yield of esters and renders the separation of ester and glycerol difficult. The glycerol is then removed by gravity separation and remaining ester is mixed with hot water for separation of catalyst. Moisture can be removed using silica gel crystals [4-6,12]. Effect of different parameters like temperature, molar ratio of alcohol to oil, catalyst, reaction time have been investigated by several researchers and it was found that for base catalyzed transesterification at atmospheric pressure, 55-60°C temperature and 6:1 molar ratio of alcohol to oil, the yield is optimum [4,5,12].

Variables Affecting Transesterification

The most important variables affecting the yield of biodiesel from transesterification process are,

- ✓ Reaction temperature
- ✓ Molar ratio of alcohol to oil
- ✓ Catalyst
- ✓ Reaction time
- ✓ Presence of moisture and free fatty acids

The effect of reaction temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the reaction is conducted close to the boiling point of methanol (60°C to 70°C) at atmospheric pressure. The maximum yield of esters occurs at temperatures ranging from 55°C to 80°C at a molar ratio of 6:1 [4-6,12,13]. The effect of temperature on conversion of oils and fats into biodiesel has been studied by many of the researchers [4,6,12]. Freedman et al. studied the transesterification of refined soyabean oil with methanol (6:1), 1% NaOH catalyst, at three different temperatures 60°C, 45°C and 32°C. After 0.1 hour, ester yields were 94, 87, 64% for 60°C, 45°C and 32°C, respectively. After 1 hour, ester formation was identical for the 60°C and 45°C runs and only slightly lower for the 32°C run. It shows that temperature clearly influenced the reaction rate and yield of esters and transesterification can proceed satisfactorily at ambient temperatures, if given enough time, in the case of alkaline catalysts [4].

The effect of molar ratio

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3 mols of alcohol per mol of triglyceride to yield 3 mols of fatty esters and 1 mol of glycerol. To shift the transesterification reaction to the right, it is necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture. The second option is preferred, wherever feasible, since in this way, the reaction can be driven towards completion. When 100% excess methanol is used, the reaction rate is highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight [13]. Freedman et. al. studied the effect of molar ratio (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cottonseed oils behaved similarly and achieved highest conversions (93-98%) at a 6:1 molar ratio. Ratios greater than 6:1 do not increase yield much, however it interferes with separation of glycerol [4].

The effect of catalyst

Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed. However if a glyceride has a higher free fatty acid content and more water, acid-catalyzed transesterification is suitable. Sodium methoxide is found to be more effective than sodium hydroxide [4]. Sodium alkoxides are among the most efficient catalysts used for this purpose, although NaOH, due to its low cost, has attracted wide usage in large-scale transesterification. Partly due to faster esterification and partly because alkaline catalysts are less corrosive to industrial equipment than acidic catalysts, most commercial transesterification processes are conducted with alkaline catalysts. The alkaline catalyst concentration in the range of 0.5 to 1% by weight yields 94 to 99% conversion of vegetable oil into esters. Further, increase in catalyst concentration does not increase the conversion and it adds to extra costs because it is necessary to remove it from the reaction medium at the end of the reaction [4,13].

The effect of reaction time

The conversion rate increases with reaction time. Freedman et. al. transesterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60°C temperature. An approximate yield of 80% was observed after 1 minute for soybean and sunflower oils. After 1 hour, the conversions were almost the same for all four test oils (93-98%) [4]. Ma et al. studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef tallow. From one to five minute, the reaction proceeded very fast. The apparent yield of beef tallow methyl esters surged from 1 to 38% [12].

The effect of moisture and free fatty acids

Starting materials used for alkali-catalyzed transesterification of triglycerides must meet certain specifications. The triglyceride should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value is greater than 1, more NaOH is required to neutralize the free fatty acids. Water causes soap formation, which consumes the catalyst and reduces catalyst efficiency. The resulting soap causes an increase in viscosity, formation of gels and makes the separation of glycerol difficult. Freedman et al., stated that ester yields were significantly reduced if the reactants did not meet these requirements. Sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, which diminished their effectiveness [4]. The effects of free fatty acids and water on transesterification of beef tallow with methanol were investigated by Ma et. al. The results showed that the water content of beef tallow should be kept below 0.06% w/w and free fatty acid content of beef tallow should be kept below 0.5%, w/w in order to get the best conversion. Water content was a more critical variable in the transesterification process than were free fatty acids [12].

Experimental Matrix

Non-edible vegetable oils such as ricebran, castor, and linseed were obtained from the local market. These oils are converted into their methyl esters through base-catalyzed transesterifiation process. Methyl alcohol of 99.5% purity (Merck) having density of 0.791-0.792 kg/l and Potassium hydroxide(KOH) is used as catalyst for this process. Transesterification is performed for 1 hour at 55°C at atmospheric pressure. General molecular structure of castor, linseed and ricebran oils are given in table 1.

Table 1: Chemical Composition of Vegetable Oils

Vegetable Oil	16:0**	18:0	18:1	18:2	18:3	20:0	24:0
Ricebran	18.8	2.4	43.1	33.2	0.6	0.7	-
Linseed	5.0	2.0	20.0	18.0	55.0	-	-
Castor*	1.1	3.1	4.9	1.3	-	-	-

*Castor oil contains 89.6% of ricinoloic acid.
** The first digit is the carbon chain length and the second digit is the number of double bonds in the molecule (a:b means a is the number of carbon atoms in the chain and b shows number of double bonds).

The molecular weight of rice bran, castor and linseed is calculated on the basis of above chemical composition and it is 827.4, 889.7 and 835.8 respectively. For esterification in laboratory 1 liter of each oil was heated upto 65°C in round bottom flask and stirred vigorously. 5 grams of KOH was dissolved in methyl alcohol in 6:1 molar ratio in a separate vessel and was poured into round bottom flask, while stirring the mixture continuously. The mixture was stirred and maintained at 55°C for 1 hour and then allowed to settle under gravity for 24 hour. Bottom layer of Glycerol was removed and separated ester is mixed with hot water and allowed to settle under gravity for 24 hour. The catalyst gets dissolved in water, which is separated. The esters so prepared and neat vegetable oil and mineral diesel was tested for viscosity at different temperatures between 40°C and 100°C on Setavis kinemetic viscometer as per ASTM standards D445 and Flash point are evaluated experimentally as per standard test method ASTM D93.

Biodiesel Characterization

Several tests were conducted to characterize biodiesel in relation to diesel oil in order to evaluate various properties like viscosity, specific gravity and flash point. The results are shown in figures 1-7. The process of transesterification brings down specific gravity of the vegetable oils as shown in figure 1. The biodiesel so developed is completely miscible with mineral diesel oil.

The flash points of the samples were evaluated using closed cup pensky marten's apparatus. The results of flash point are shown in figure 2. The flash point of ricebran and linseed oil gets lowered after the transesterification of these oils (figure 2), but it was still higher than mineral diesel. Thus, biodiesel is found to be safe fuel in handling compared to diesel.

The experiments to evaluate the viscosity for various vegetable oil samples and biodiesel samples were conducted using Setavis Kinematic Viscometer. The viscosities were evaluated at various temperatures for all the samples. Vegetable oils have higher viscosity compared to diesel oil. Viscosity decreases drastically by converting these oils into their esters.

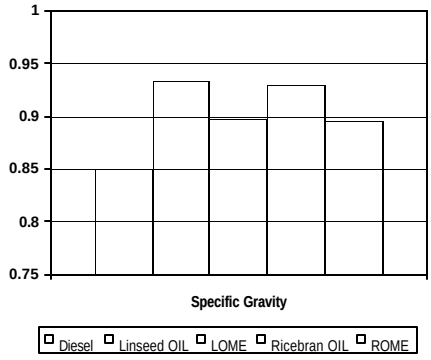


Figure 1: Specific Gravity for Different Oils and Esters

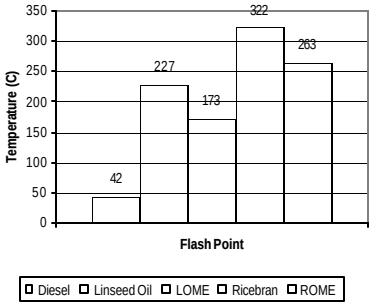


Figure 2: Flash Point (°C) for Different Oils and Esters

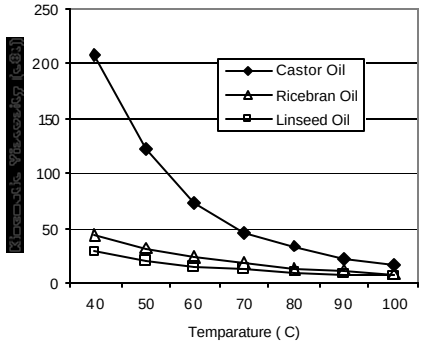


Figure 3: Viscosity V/s Temperature for Linseed, Ricebran, Castor oil

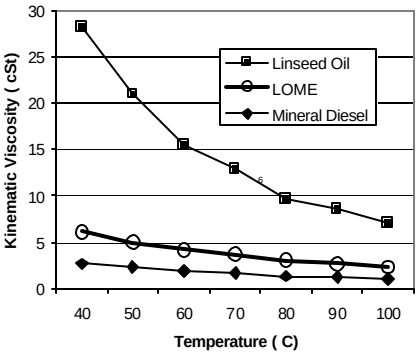


Figure 4: Viscosity Vs Temperature for Linseed oil, LOME and Diesel

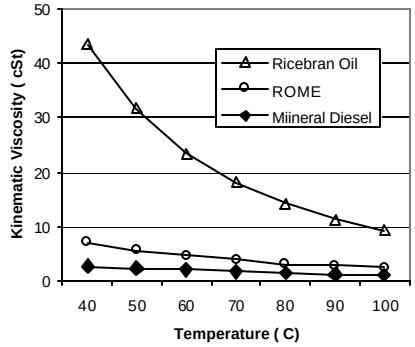


Figure 5: Viscosity Vs Temperature for Ricebran oil, ROME and Diesel

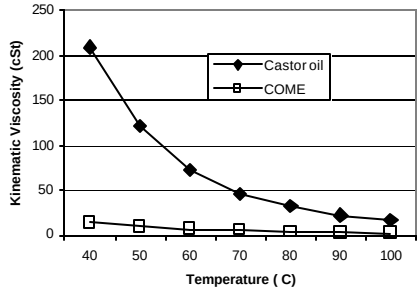


Figure 6: Viscosity Vs Temperature for Castor oil, COME

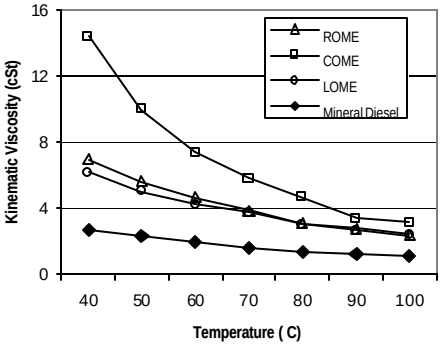


Figure 7: Viscosity Vs Temperature for ROME, LOME, COME and Diesel

The viscosity of linseed, ricebran and castor oil at 40°C is very high ranging between 28 cSt to 210 cSt, (figure 3), as compared to mineral diesel, which is having viscosity of 2.64 cSt at 40°C. High viscosity makes these oils unsuitable for direct use in CI engines. By converting these oils into their methyl esters, the viscosity reduces drastically and comes down in the range of 6-14 cSt (figure 4-7). It is also observed that the viscosity of castor oil and its methyl ester decreases more rapidly than other oils (figure 3,7). Viscosity of castor oil at 40°C reduces almost 15 times by transesterification (figure 6), so it can be used by blending it in small quantity with mineral diesel oil.

Conclusions

The transesterification of non-edible vegetable oil of Indian origin such as linseed oil, ricebran oil and castor oil is carried out and the possibility of using them in Compression Ignition engine is explored by bringing their relevant properties closer to mineral diesel oil. The major hurdles in their usage are high viscosity and low volatility. The problems of high viscosity in the use of vegetable oils as fuel for CI engine can be solved by transesterifying them to primary esters. The viscosity of methyl esters so formed is found to be quite low and was comparable to diesel oil. Flash point of esters reduces but still higher than mineral diesel, which makes them safer fuel in handling. Density (specific gravity) of vegetable oil also reduces after transesterification. Biodiesel is completely miscible with mineral diesel and can be blended in any proportion to mineral diesel oil.

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