

Study and analysis of bio-diesel different properties and their assessment routes

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Abstract

Environmental concerns and limited amount of petroleum resources have caused interests in the development of alternative fuels for internal combustion (IC) Engines. As an alternative, biodegradable, renewable and sulphur free biodiesel is receiving increasing attention. Biodiesel is known as the mono-alkyl-esters of long chain fatty acids derived from renewable feedstock, such as, vegetable oils or animal's fats, for use in compression ignition engines. present study focuses on Study and analysis of biodiesel blends different properties and estimation routes. Biodiesel was made by the well-known transesterification process. Different properties, their impact and preparation methodologies have investigated in this study. The outcome of present research will help both practitioner and researchers of bio diesel.

Keywords: Bio-diesel, properties, preparation routes, renewable.

1. Introduction.

Biodiesel is the name of a clean burning alternative fuel produced from domestic, renewable resources. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression ignition (diesel) engines upto 20% with no major modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulphur and aromatics. Biodiesel is a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM (American Society for Testing & Materials) D 6751. The major components of vegetable oils and animal fats are triacylglycerols (TAG; often also called triglycerides). Chemically, TAG are esters of fatty acids with glycerol (1,2,3-propanetriol; glycerol is often also called glycerine) [1]. The TAG of vegetable oils and animal fats typically contain several different fatty acids. Thus, different fatty acids can be attached to one glycerol backbone. The fatty acids profile is probably the most important parameter influencing the corresponding properties of a vegetable oil or animal fat. To obtain biodiesel, the vegetable oil or animal fat is subjected to a chemical reaction termed transesterification. In that reaction, the vegetable oil or animal fat is reacted in the presence of a catalyst (usually a base) with an alcohol (usually methanol) to give the corresponding alkyl esters (or for methanol, the methyl esters) of the FA mixture that is found in the parent vegetable oil or animal fat. Figure 1 depicts the transesterification reaction. Biodiesel can be produced from a great variety of feedstock. These feedstocks include most common vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut) and animal fats (usually tallow) as well as waste oils (e.g., used frying oils) [2]. The choice of feedstock depends largely on geography. Depending on the origin and quality of the feedstock, changes to the production process may be necessary.

Biodiesel is miscible with petro diesel in all ratios. In many countries, this has led to the use of blends of biodiesel with petro diesel instead of neat biodiesel. It is important to note that these blends with petro diesel are not biodiesel. Blends with petro diesel are denoted by acronyms such as B20, which indicates a blend of 20% biodiesel with petro diesel [3].

2. Biodiesel production: Transesterification

To obtain biodiesel, the vegetable oil or animal fat is subjected to a chemical reaction termed as transesterification. In this reaction, the vegetable oil or animal fat is reacted in the presence of a catalyst (usually a base like KOH) with an alcohol (usually methanol CH_3OH) to give the corresponding alkyl esters (or for methanol, the methyl esters) of the FA (fatty acid) mixture that is found in the parent vegetable oil or animal fat. Preparation care must be taken to monitor the amount of water and free fatty acids in the incoming vegetable oil. If the free fatty acid level or water level is too high it may cause problems with soap formation (saponification) and the separation of the glycerine by-product downstream. Catalyst is dissolved in the alcohol using a standard agitator or mixer [4]. The alcohol/catalyst mix is then charged into a closed reaction vessel and the vegetable oil is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix is kept just above the boiling point of the alcohol (around $70\text{ }^\circ\text{C}$, $158\text{ }^\circ\text{F}$) to speed up the reaction though some systems recommend the reaction take place anywhere from room temperature to $55\text{ }^\circ\text{C}$ ($131\text{ }^\circ\text{F}$) for safety reasons. Recommended reaction time varies from 1 to 8 hours; under normal conditions the reaction rate will double with every $10\text{ }^\circ\text{C}$ increase in reaction temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. The glycerine phase is much denser than biodiesel phase and the two can be gravity separated with glycerine simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster. Once the glycerine and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation [5]. In other systems, the alcohol is removed and the mixture neutralized before the glycerine and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream. The glycerine by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerine (water and alcohol are removed later, chiefly using evaporation, to produce 80-88% pure glycerine). Once separated from the glycerine, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage. [6]

3. Pyrolysis: cracking

Thermal cracking or pyrolysis is the process that causes the break of the molecules by heating at high temperatures that is, by the heating of the substance in the absence of air or oxygen in temperatures superior to $450\text{ }^\circ\text{C}$, forming a mixture of chemical compounds with properties very similar to those of petro diesel. In some situations, that process is supported by a catalyst for the break of the chemical connections, in order to generate smaller molecules. Fats can be pyrolysis for the production of smaller chain compounds. The pyrolysis of fats has been investigated for more than 100 years, especially in countries with small oil reserves. Typical catalysts to be used in the pyrolysis are the silicon oxide SiO_2 and aluminium oxide Al_2O_3 [7]. The

equipment for pyrolysis or thermal cracking is expensive. However, the products are chemically similar to diesel oil. The removal of the oxygen of the process reduces the benefits of an oxygenated fuel, reducing its environmental benefits and usually producing a fuel closer to gasoline than diesel. By the international nomenclature, the fuel produced by thermal cracking is not considered biodiesel, in spite of being a biofuel similar to the diesel oil. Cracking has great applicability in places that need smaller production volume and with smaller availability of qualified work. The catalytic or thermal cracking produces a mixture of condensed hydrocarbons with output of around 80% in an organic phase. There is an aqueous phase, around 5% to 10% and the remaining are gases [8]. Cracking has as strong point the absence of formation of aromatic compounds, of great pollutant potential. The history of biodiesel starts in the mid 1800's. In those days the process of transesterification was used to separate glycerine from oil. Glycerine was a useful product in then (and is still useful today) being widely used in the cosmetic, food and explosives industries. When Rudolf Diesel demonstrated his diesel engine at the Paris Show in 1900, he ran it on straight peanut oil – not even biodiesel. By the early 1900's petroleum fuels were plentiful and cheap. Increasingly more sophisticated fuel injection systems were designed to run these fossil fuel derived oils. Over the years this has meant that vehicles have evolved to run thinner fossil diesels rather than thicker vegetable oils. In the 2000's when crude prices started rising again and with a new world awareness on pollution and global warming, bio fuels again become popular. Government subsidy of bio fuel industries became common, especially in the first world. This has given industry the economic security needed to invest in bio fuels [9]. It is interesting to note that the history of biodiesel has shown that countries who have government support and subsidy for their bio fuels industry have large scale commercial production (the US, EU) while countries who do not have such subsidies do not.

5. Biodiesel: Properties

Viscosity, which is a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another, affects the atomization of a fuel upon injection into the combustion chamber and thereby, ultimately, the formation of engine deposits. The higher the viscosity, the greater the tendency of the fuel to cause such problems. The viscosity of transesterified oil, i.e., biodiesel, is about an order of magnitude lower than that of the parent oil. The kinematic viscosity of B10, B15, B20 blends and cotton seed methyl ester were found as 2.19, 2.38, 2.28 and 3.6 centistokes at 40°C [10]. Cotton seed methyl ester had the kinematic viscosity 7.692 percent less than that of diesel. High viscosity is the major fuel property explaining why neat vegetable oils have largely been abandoned as an alternative diesel fuel (DF). Kinematic viscosity (ν), which is related to dynamic viscosity (η) by density as a factor, is included as a specification in biodiesel standards. It can be determined by standards such as ASTM D445 or ISO 3104. Fatty acid methyl esters are Newtonian fluids at temperatures above 5°C [11]. The viscosity of petro diesel fuel is lower than that of biodiesel, which is also reflected in the kinematic viscosity limits (all at 40°C) of petro diesel standards, which are 1.9–4.1 mm²/s for DF2 (1.3–2.4 mm²/s for DF1) in the ASTM petro diesel standard D975 and 2.0–4.5 mm²/s [11]. The difference in viscosity between the parent oil and the alkyl ester derivatives can be used to monitor biodiesel production. Viscosity increases with chain length (number of carbon atoms) and with increasing degree of saturation. This holds also for the alcohol moiety because the viscosity of ethyl esters is slightly higher than that of methyl esters. Factors such as double-bond configuration influence viscosity (cis double bond configuration giving a

lower viscosity than trans), whereas double-bond position affects viscosity less. Branching in the ester moiety, however, has little or no influence on viscosity. Redwood viscometer apparatus is used for determining the viscosity of oil expressed as a time of flow in seconds through specified hole made in a metallic piece.

6. Measuring routes for different performance parameters

Redwood viscometer

The Redwood Apparatus measures viscosity in empirical units and not in absolute units such as Centistokes. It is possible to convert Redwood viscometer readings to absolute units, for which the specification issued by the institute of petroleum London, may be consulted. The method is primarily applicable for viscosity determination of oil which flows in a Newtonian manner that is if it possesses a linear relationship between shearing stress and rate of shear under the test conditions.

Mode of operation

The flow time measurements for petroleum products should be made at the following temperatures.

21°C, 37.8°C, 40°C, 60°C, 93°C, 121°C, 149°C, 204°C

For fuel oils the minimum temperature is 40°C

For flux oils the temperature of test be 93°C

The apparatus Redwood viscometer will correctly indicate the viscosity flow time if it stands between 3 seconds to 2000 seconds.

Sampling

For determinations at temperatures of 93°C or lower, of the time sample, without stirring, in a loosely stoppered container filled as completely, as possible for a hour at 100°C by immersions in a suitable liquid bath maintained at the temperature, e.g. a boiling bath. Then adjust the temperature of which is slightly below the test temperature carry out subsequent hearing by using a source of heat not higher than 121°C or higher do not heat temperature [12]. When a series of viscosities is to be determined at several temperatures being and before those at the lower temperatures. Determine the viscosity within 1 hour of the sample reaching the desired temperatures.

Preparation route

- Clean the oil cup with a suitable solvent, e.g. carbon tetrachloride and then dry it thoroughly using soft tissue paper or some similar material which will not leave any fluff. Clean the jet hole by any line thread.
- Set up the viscometer, using the circular spirit level to ensure that is level. Fill the bath with water for determinations at 93°C and below, and for higher temperatures, with oil having a suitably low viscosity at the test temperature for determination about 93°C fill the bath to a level not less than 10mm, below the rim of the oil cup at the test temperature.
- Viscometer bath was to a few degrees above the desired test temperature. Sample was poured into the oil cup through a filter of metal gauge. Temperature of the bath was adjusted until the sample in the cup is maintained at the test temperature stirring the contents of the bath and cup during this procedure preferably using continuous stirring for the bath. Sample was stirred during the preliminary period e.g. by means of the ball valve, closing the bottoms of the jet by suitable means, but did not stir the sample during the actual determination. When the temperature of the sample has become suite steady at the desired value, liquid level

was adjusted by allowing the sample to flow out until the surface of the sample touches, the filling point. Oil cup and curved slot was placed in the vocer. Clean, dry, stand 50ml was placed from the bottom of the jet [13]. Stop the time recorder at the instant the sample reaches the graduation mark of the flask and the final reading of the coil cup thermometer was noted.

- Any determination of the temperature of the sample in the oil cup varies during the run by more than 0.1°C for temperatures of 60°C or below by more than 0.3°C or by more than 8.5°C at 121°C was rejected.



Fig 1: Redwood viscometer for the measurement of Kinematic viscosity

Cloud Point

The temperature, expressed to the nearest degree Centigrade at which a cloud or haze appears when the oil is cooled under prescribed conditions is known as the cloud point.

Pour Point

The lowest temperature, expressed as a multiple of 3°C at which the oil is observed to flow when cooled and examined under prescribed conditions. The blends B10, B15, B20 have higher cloud and pour point as compare to diesel. The cloud and pour point of cotton seed methyl ester was also higher as compared of diesel respectively. The results indicated that the blend B10 was observed the cloud point nearly to that of diesel.

Cloud Point Pour Point: setup

The method of cloud point is intended for use only on oils, which are transparent in layers 40mm in thickness and have cloud point below 40°C . The method for pour point is intended for use on any petroleum oil. In the determination of the cloud point, the sample was cooled under prescribed conditions and was inspected at intervals of one degree centigrade until a cloud or haze appears. In the determination of the pour point, the sample cooled under prescribed conditions and was inspected at intervals of 3°C until it will no longer move when the place of surface was held vertical for 65 seconds, the pour point was then taken as 3°C above the temperature of cessation of flow [14]

Cold Refrigeration Bath

The refrigeration bath can be operated from above room temperature to below minus 30°C . Kept the sample to be tested in glass jar, fit the rubber cork and keep vertically in the jacket provided. The test temperature was below 0°C or upto -30°C . The jacket was filled around glass jar with a little quantity of ethyl alcohol for proper contact of cooling media. Thermocouple pin (thermocouple bulb) was fitted in rubber cork upto centre of glass

jar. Main switch was put on; red neon lamp indicates its operation. The cooling was occurred within 30 to 40 minutes after start of refrigeration system.

Cloud Point Procedure

Sample was bringing to temperature of at least 15°C above the approximate cloud point and then pour it into the jar to a height of the 51 to 57 mm close the jar with the cork so that the thermometer bulb rests on the centre of the bottom of the jar. Jar was inserted into the jacket. Bath temperature was maintained at minus 1°C to 2°C. At each thermometer reading of the one degree centigrade, jar was removed from the jacket quickly but without disturbing the oil. Material was inspected for cloud, and jar was replaced. This complete operation was not taken more than 3 seconds. If the sample does not show cloud when it has been cooled 10°C places the jar in another bath maintained at a temperature of minus 15°C to 18°C. If the sample does not show a cloud when it has been cooled to minus 7°C place the jar and jacket in another bath maintained at a temperature of minus 32°C to minus 35°C [15]. When as inspection of the sample first reveals and distinct cloudiness or haze at the bottom of the jar, record the reading of the thermometer as the cloud point.



Fig 2: Cloud and pour point setup

The sample was poured, heated in a water bath into the jar to a height of 51 to 57mm. Jar was closed with the cork carrying thermometer no.1 so that the thermometer bulb was immersed vertically in the sample with the beginning of the capillary 3mm below the surface. Sample was heated without stirring to a temperature of 46°C in a bath maintained at a temperature not higher than 48°C. The sample was cooled to 32°C in air or in water bath at approximately 25°C. If a pour point below minus 35°C is expected, the sample was cooled in air or in water bath to 16°C and replaced the thermometer no.1 by thermometer no.2, fit the gasket on to the jar 25mm from the bottom and insert the jar into the jacket. When the sample has cooled to allow the formation of wax crystals, great care was not to disturb the mass of sample not to permit the thermometer to shift in the sample, any disturbance of the spongy network of crystals will lead to false results. Bath temperature was maintained at temperature of minus 1°C to plus 2°C. Jacket and jar was supported in a vertical position in the bath beginning at a temperature 12°C above the expected pour point at each thermometer reading which is a multiple of 3°C, jar was removed from the jacket carefully, and tilt it just enough to see whether the oil will move and replace it [16]. This complete operation was not taken more than 3 seconds, if the oil has not ceased to flow when it has been cooled to 9°C, place the jar in another bath maintained at a temperature of minus 32°C to minus 35°C. If the pour point is very low, maintained additional bathes with successively lower temperature differentials of about 18°C transfer in the jar and jacket when the temperature of the sample

reaches a point 27°C above the temperature of the new bath. As soon as the sample ceases to flow when the jar is tilted hold the jar in horizontal position for exactly 5 second. If the sample shows any movements replace the jar in the jacket and cool down the sample another 6°C . If the oil shows no movement during the 5 seconds record the reading of the thermometer.

Flash Point

The temperature at which a material gives so much vapour that this vapour when mixed with air, forms a ignitable mixture and gives a momentary flash on application of a small pilot flame. The blends B10, B15, B20 have higher flash and fire point as compare to diesel. The flash and fire point of cotton seed methyl ester was found higher than that of diesel respectively. The results indicated that the blend B15 was observed the flash and fire point 16.66 percent higher than that of diesel.

Pensky-Martens Flash Point: Setup

The sample is heated in a test cup at a slow and constant rate with continual stirring. A small test flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is taken as the lowest temperature at which the application of the test flame causes the vapour above the sample to ignite momentarily. Biodiesel containing dissolved or free water may be dehydrated with calcium chloride or by filtering through a suitable filter paper or a loose plug of dry absorbent cotton. Warming the biodiesel is permitted, but it shall not be heated for prolonged periods or above a temperature of 16°C below its expected flash point. Thorough clean and dry all parts of the cup and its accessories before starting the test, being sure to remove any solvent which has been used to clean the apparatus. Support the tester on a level, steady table. Fill the cup with the sample to be tested to the level indicated by the filling mark. Place the lid on the cup and set the latter in the stove. Take care that the locating devices are properly engaged. Insert the thermometer [17]. Light the test flame and adjust it to 4.0mm in diameter. Supply host at such a rate that the temperature recorded by the thermometer increases not less than 5°C nor more than 6°C per minute. Turn the stirrer 90 to 120 rev/min stirring in a downward direction. If the biodiesel is known to have a flash point of 105°C or below, apply the test flame when the temperature of the biodiesel is a whole number not higher than 17°C below the flash point, and thereafter at each degree rise of temperature. Apply the test flame by operating the mechanism on the cover which controls the shutter and test flame burner so that the flame is lowered into the vapour space of the cup in 0.5 seconds, left in its lowered position for one second and quickly raised to its high position. Do not stir the biodiesel while applying the test flame. If the biodiesel is known to have a flash point above 105°C apply the test flame in the manner prescribed in above paragraph at each temperature, that is, a multiple of 3°C , beginning at a whole number temperature reading not higher than 17°C below the flash point. Record as the flash point the temperature read on the thermometer at the time and test flame application causes a distinct flash in the interior of the cup. Do not confuse the true flash point with the bluish halo that sometimes surrounds the test flame at applications preceding the one that cause the actual flash.



Fig 3: Pensky Martin Flash Point

Calorific value of combustion

The heat of combustion or calorific value of a fuel is an important measure since it is the heat produced by the fuel within the engine that enables the engine to do the useful work. The gross heat of combustion of fuel samples was determined with the help of a wisdom scientific works make isothermal bomb calorimeter. A fuel sample of 1 ml was burnt in the bomb of calorimeter in the presence of pure oxygen. The sample was ignited electrically. As the heat was produced, the rise in temperature was measured [18]. The water equivalent (effective heat capacity of the calorimeter) was also determined using pure and dry benzoic acid as test fuel. Each sample was replicated three times.

The gross heat of combustion of the fuel samples was calculated using the equation given below. The calorific value of diesel, cotton seed methyl ester and blend B10 were found as 43,000, 40,000 and 40,300 KJ/Kg respectively. The calorific value of blend B10 is decreased by 6.27% than that of diesel whereas the calorific value of cotton seed methyl ester is decreased by 6.97% than that of diesel. The result shows that the calorific value of B10 blend is lower than diesel fuel.

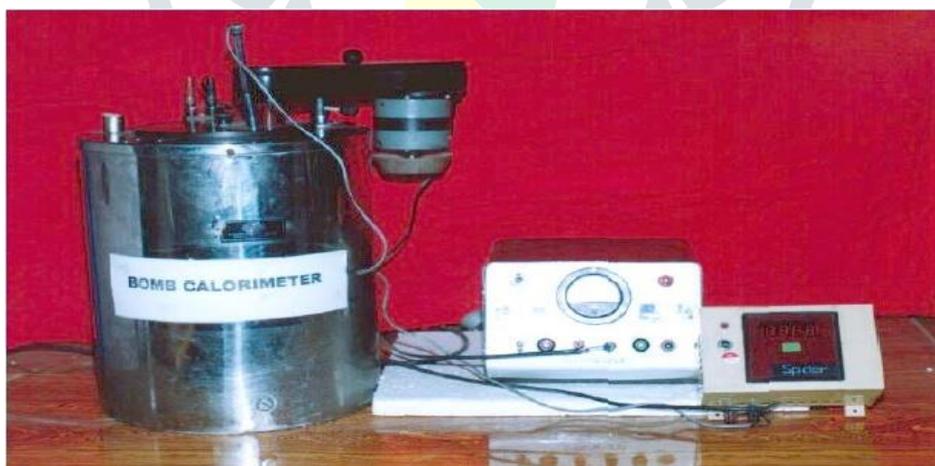


Fig 3: Isothermal bomb calorimeter

Ash Content

Ash in a fuel can result from oil, water soluble material compounds or extraneous solids, such as dirt and rust. The ash content of diesel, cottonseed oil and cottonseed oil ester were measured as per the standard ASTM D482-IP 4 of institute of petroleum, USA [19]. An electric muffle furnace of wiswo make was used in the experiment. In order to measure to ash content, sample was taken in a silica dish. The dish was first weighted empty and then with the fuel sample. The sample weight was obtained from the difference between the initial

and final weight of the dish. The sample was then placed in the muffle furnace and heated at $775\pm 25^{\circ}\text{C}$ for two hours. Each sample was replicated three times. The ash content was obtained using the equation given below



Fig5: Muffle furnace for of ash content

Carbon Residue

Carbon residue was determined for different fuels by using a carbon residue apparatus. The measurement was made in accordance with the ASTM D189-IP 13 of institute of petroleum, London [20]. The procedure determines the amount of carbon residue left after evaporation and pyrolysis of an oil. It is intended to provide some indication of relative coke forming properties. In this method, 10 g weight to the nearest 5 mg of each fuel sample was weighed free of moisture and other suspended matter into an iron crucible of the apparatus. The crucible was then placed in the centre of skid more crucible of the apparatus and the sand was levelled in the large sheet iron crucible and then the skid more crucible was set on it in the exact centre of the iron crucible. Thereafter, the covers were applied to both skid more and iron crucible loosening the latter fitting to allow free exit to the vapours as it formed. The fuel sample was then heated with a high strong flame from gas burner for 20 min. When the smoke appeared on the chimney, immediately the burner was moved or tilted so that the gas flame plays on the sides of the crucible for the purpose of igniting the vapours. After that the ignited vapour was burnt uniformly with the flame above the chimney for another period of time. When the vapour ceased to burn and no further smoke was observed, the burner was adjusted and the heat was held as at the beginning to make the bottom and the lower part of the sheet iron crucible, a cherry red for about 15 min. Thereafter, the burner was removed and allowed to cool until no smoke appeared. The cover of skid more was then removed with a tong and it was cooled and weighed [21]. The ester of cotton seed and their blends were found to have carbon residue content lower than that of diesel which is better for engine performance and it also prevents carbon deposition inside the combustion chamber. The blend B20 has lowest carbon residue content as compare to B10 and B15.



Fig 6: Carbon Residue (Rams Bottom)

7. Biodiesel: Necessities

Environmental viewpoint

In 2000, biodiesel became the only alternative fuel in the country to have successfully completed the EPA-required Tier I and Tier II health effects testing under the Clean Air Act [22]. These independent tests conclusively demonstrated biodiesel's significant reduction of virtually all regulated emissions, and showed biodiesel does not pose a threat to human health.

Biodiesel contains virtually no sulphur or aromatics, and use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matter. Study showed that the production and use of biodiesel, compared to petroleum diesel, resulted in a 78.5% reduction in carbon dioxide emissions [23]. Moreover, biodiesel has a positive energy balance. For every unit of energy needed to produce a gallon of biodiesel, at least 4.5 units of energy are gained.

Energy Security view point

With agricultural commodity prices approaching record lows, and petroleum prices approaching record highs, it is clear that more can be done to utilize domestic surpluses of vegetable oils while enhancing our energy security [24]. Because biodiesel can be manufactured using existing industrial production capacity, and used with conventional equipment, it provides substantial opportunity for immediately addressing our energy security issues.

8. Conclusions

The kinematic viscosity of vegetable oils is about an order of magnitude greater than that of conventional, petroleum-derived diesel fuel. High viscosity causes poor atomization of the fuel in the engine's combustion chambers and ultimately results in operational problems, such as engine deposits. Since the renewal of interest during the late 1970s in vegetable oil derived fuels, four possible solutions to the problem of high viscosity have been investigated: transesterification, pyrolysis, dilution with conventional petroleum-derived diesel fuel, and micro emulsification. The high viscosity of vegetable oils as a major cause of poor fuel atomization resulting in operational problems such as engine deposits was recognized early. Although engine modifications such as higher injection pressure were considered, reduction of the high viscosity of vegetable oils usually was achieved by heating the vegetable oil fuel. Pyrolysis, cracking, or other methods of decomposition of vegetable

oils to yield fuels of varying nature is an approach that accounts for a significant amount in past. From societal prospective, biodiesel can provide a better future as it eco-friendly in nature.

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