

Bio-fuels as Alternative fuels for Internal Combustion Engines

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Abstract- The petroleum based fuels used for Internal Combustion Engines steadily achieving a steep pricing demand because of the Industrialization of the world. These petroleum based fuels are obtained from limited resources. These limited resources are highly concentrated in certain region of the world. So, countries not having these resources are facing energy/foreign exchange crises mainly due to the import of crude petroleum. Hence, it is necessary to look for alternative fuels which can be produced from resources available locally with in the country such as alcohol, biodiesel, vegetable oil etc. The present paper attempts to review critically on the aspects of production, characterization and the status of vegetable oil and biodiesel. This paper also reviews the experimental research work carried out on these fuels in various countries. The world resources of primary energy and the raw materials are limited. According to an estimate the reserves will last for 218 years for coal, 41 years for oil, and 63 years for natural gas. The global population of motor vehicles on the roads today is ½ a billion which is more than 10 times higher than what was in 1950.

Index Terms- Bio-Diesel production, Emulsions, transesterification, properties of biodiesel and Emission.

I. INTRODUCTION

The term bio-fuel is used to refer to solid, liquid and gasses fuels predominantly produced from bio mass. Biomass can be converted into liquid and gasses fuels through them mechanical and biological routes. Bio fuels are non polluting, locally available, accessible, sustainable and reliable and obtained from renewable sources. A variety of fuels can be produced from biomass which includes ethanol, methanol, biodiesel, hydrogen methane and Fischer- Tropsch diesel. Bio fuels are broadly classified as primary and secondary bio fuels. The secondary biofuels are further classified as first generation, second generation and third generation biofuels. The Primary biofuels are used in an unprocessed form primarily for heating, cooking and electricity production. The fuel wood, wood chips, pellets, animal waste, forest and crop residue and land fill gas come under the category of primary biofuels. The examples for first generation secondary bio fuels are bio ethanol and bio diesel. Biodiesel is obtained by transesterification of plant oils such as palm, coconut, jatropha, used cooking oil, sunflower oil, rape seed oil and soyabeans oil. Bio ethanol is obtained by fermentation of starch or sugars. Wheat, brley, corn, and potato come under starch. The sugar cane, sugar beet comes under

sugars. Bio diesel from algae, bio ethanol from algae and see weeds, hydrogen from green algae and microbes are the examples of third generation biofuels. Bio ethanol or butanol by enzymatic hydrolysis, methanol, Fischer-Tropsch gasoline and diesel, mixed alcohol, dimethyl ether and green diesel by thermo chemical process and bio-methane by anaerobic digestion come under second generation secondary bio fuels.

II. BIODIESEL PRODUCTIONS

History

Producing biodiesel from the vegetable oils is not a new process. Scientists E. Duffy and J. Patrick performed it as early as 1853. Rudolph Diesel designed the original diesel engine to run on vegetable oil. Rudolph Diesel the inventor of the engine that bears his name, experimented with fuels ranging from powdered coal to peanut oil, and used peanut oil to fuel one of his engines at the paris Exposition of 1900. Because of the high temperature created, the engine was able to run a variety of vegetable oils including hemp ad peanut oil. At the 1911 world's Fair in Paris, Dr. R. Diesel ran his engine on peanut oil and declared "the diesel engine can be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it". One of the first uses of transesterified vegetable oil was powering heavy-duty vehicles in South Africa before World War II.

The use of vegetable oils as alternative renewable fuel competing with petroleum was proposed in the beginning of 1980s. The advantages of vegetable oils as diesel fuel are: liquid nature-portability, ready availability, renewability, higher heat content, lower sulfur content, lower aromatic content and biodegradability.

Production process of biodiesel:

Biodiesel is commonly produced by the transesterification of the vegetable oil or animal fat feedstock.

2.1 Stage of Biodiesel production: Single Phase

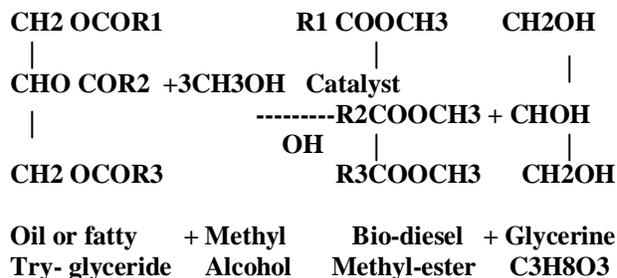
- Filtration of the oil to remove the suspended impurities.
- Heating the oil to about 65^o c under controlled agitation with a stirrer using 200-350 RPM.
- Based on the quantum of free fatty acid available in the oil decide, the amount of Methyl alcohol and alkali (NaOH & KOH) to be added to the oil.

- Add the Methoxide and continue the heating maintaining the temperature between 65⁰c to 70⁰c agitating using a stirrer at 500 rpm
- Give a process time of 45 to 60 minutes. Collect a small quantity of the mixture in a small beaker and check up the completion of the reaction. Clear separation of two layers, ie Biodiesel at the top and Glycerine etc. at the bottom, indicating the completion of the process.
- Transfer the above mixture in to a settling vessel and allow to cool and settle for 2 to 3 hours. The biodiesel on the top and the Glycerine, un-reacted oil and other impurities at the bottom.
- Collect the Glycerine portion by decanting.
- The top portion which is Bio-Diesel will be alkaline, wash with distilled or de-mineralized water number of times to get the Bio-diesel to neutral stage, ie., about 7pH
- The washing will be containing soap solution which can be used for cleaning purpose.
- The Bio-diesel which contain some quantity of water can be dried in an air-oven at 110⁰c-120⁰c.

2.2 Two phase process

- Take known quantity of oil (Previously filtered up to 53 microns thickness sieve)
- Add 1.5 ml of concentrated sulphuric acid and 80ml of Methanol per litre of oil.
- Heat and stir at 50⁰/1400 rpm for 2 hours.
- Settle over night.
- Prepare sodium methoxide or Potassium solution ie. 8-12 gms NaoH or 12 to 17 gms , KOH in 120-130 ml methanol per litre of oil.
- Add 50% volume of methoxide solution heat the content to 60⁰c for neutralization.
- Add remaining 50% volume of Methoxide at about 60⁰ c stir at about 60⁰ c stir at 500 rpm and 1 hour process time.
- Phase separation is noticed and transfers the content to settling vessel.
- Settle for three hours.
- Drain the bottom layer containing Glycerine etc.
- Top layer is bio-diesel and is alkaline in nature. Wash it with water, using air-pump, bubbling slowly.
- After 4 to 5 washes Bio-diesel will became neutral.
- Measure the quantity of Biodiesel and arrive the yield. In case of pungam oil yield is around 85%.
- Heat the Bio-diesel at 110⁰ c for removal of water if any present. After heating Bio-diesel is clear. Settle for some time and use.

Reaction showing the production of Bio-diesel



III. PROPOSED EXPERIMENTAL RESEARCH WORK

The manufacturing of Bio-diesel has been tried with the following oils.

1. Corn oil
2. Canola oil
3. Mauha oil
4. Cotton seed oil

3.1 General Assessment:

The quality of Bio-diesel can be generally assessed by Miscibility test with a) water b) Methanol. When equal quantity of Bio diesel and water are mixed together in a test tube there will be a distinct two layers, the top being Bio-Diesel and bottom water. Any impurities and unreacted raw oil will form another layer. Similarly when Bio-diesel is mixed with Methanol, the pure Bio-diesel get dissolved in Methanol and any impurities will be seen as a separate layer.

3.2 Regular Quality test:

The following tests are generally carried out in the laboratory to assess the quality of the Bio-diesel. Mostly these requirements are covered under different specifications and the methods of the test under IS-1448-1960.

- i) Density ii) Acid number iii) Water content
 vi) Flash point v) Kinetic Viscosity vi) Ester content vii) Cetane number viii) Distillation test ix) Total sulphur x) Carbon Residue

Glycerine content:

Glycerine is the by-product during the manufacture of Bio-diesel. It is not properly filtered, glycerine may be present along with the glycerine.

Processing of Bio-Diesel through Transesterification

Process description and Equipment required for Lab Grade Trans-Esterfication in the laboratory for trainee industries for tiny industries and lab attached to engineering Colleges and Technical Institutions.

- Mantle for heating the oil operated by electric power
- Three way Neck Flask capacity to hold 2 liters of oil and the flask should be round bottom.
- Stirrer operated by small motor fixed to the stand so that it can be inserted into the flask to run smoothly inside the flask in the center of the round bottom flask
- Two glass plastic or glass beakers.

- One liter capacity plastic beakers and ½ liter beakers numbering two.
- One Dharma meter showing the temperature upto 100⁰C to 200⁰C.
- One separator to drain the layers of oil Methanol and Glycerol fixed to the stand.
- Water cooling system made of glass with rubber tube connected to the flask at one and other and connected by over head tank small plastic drum.
- Other items such as plastic spoons litmus paper and filter papers extra as per the requirement.
- Glass type water cooling condenser fitter to three ways round bottom flask on the other end.
- R.P.M. (Revolution per minute) Regulator box with socket plugs and two plugs to insert for electric supply required.
- Stand required semi circular to keep the mantle for heating.
- Small funnel type test tube with 10 ml crude oil capacity to immerse the Dharma meter.
- Office table to install the equipment.

3.3 Raw Material Required

Solvent: Methanol or Ethanol

Catalyst: Sodium Hydroxide / potassium Hydroxide / Sodium Methoxide (**Preferably Sodium Methoxide can be used**)

Oil: Required quantity of oil one or two liters crude pure oil or refined oil preferably refund oil shall give pure Trans-Esterfication without any soap content.

Process to convert oil by Trans-esterfication using Methanol or Ethanol.

- Take required quantity of oil say one or two liters of pure crude or refined oil and we have to pre-heat upto 20⁰C to 30⁰C and cool it down naturally do not use eyes or any other method and cool it to room temperature.
- Take the pre-heated oil after cooling down pour into the glass flask.
- Now take 250ml of Methanol mix it with oil of 10 to 20ml of oil and pour it in the round bottom flask and stir it with stirrer for about 10 to 15 minutes. Take a plastic beaker and pour 150ml of Methanol into the beaker and now take the catalyst of 30gms and vigoursly mix it with and by plastic spoon. The Methanol contained in the beaker, if necessary you can with filter paper.
- Pour the mixture of methanol and catalyst into the flask containing oil and stir it well up to room temperature that mixes well with the oil.
- Now slowly raise the temperature of the oil mixture and stir it well till the required temperature is obtain and reaction take place and we can observed that the mixture of the oil changes to orange brown colour so that we can understand that reaction has taken place and cool it down automatically by natural method to the room temperature.

- When we observe with dharma meter that it has cool down up to the room temperature pour the reacted oil mixture into a separator which is fixed to the stand.
- Now wait and observe the separator and you will notice that three layers are formed in the separator. The first layer on the upper portion is methyl ester (bio-diesel) and the middle layer is Methanol which is recovered after the process. The reaction takes only the required quantity of Methanol in the remaining which is the separator is only a recovered Methanol which can re-used for next processing if required.
- The third layer which is semi sold state is glycerol which is white or creamy colour.
- Now put a beaker under the nose of the separator and open the knob of the separator till the third layer is passed into the beaker and immediately close the knob.
- Now put another beaker under the nose of beaker and open the knob till second layer is drained into the beaker and immediately close the knob.
- Take another beaker under the nose and drain the eastern of the upper layer into the beaker which is methyl ester transferred into Bio-Diesel if require it has to be given a watery wash. To remove any impurities inside the easter. By heating to 20⁰C to 30⁰C the water will be evaporate and pure bio-diesel is obtained which can be used purely or adding 20% to 30% with mineral diesel as a blend.

The properties and characteristics of biodiesel are follows according to the ASTM standard.

Table 1. ASTM D-6751 Standards for bio-diesel

Flash point	130 ⁰ C min (150 ⁰ C average)
Water and sediment	0.050% by vol., max
Kinematic viscosity at 40 ⁰ c	1.9-6.0 mm ² /s
Ramsbottom Carbon residue, % mass	0.10
Sulfated ash	0.020% by mass, max.
Sulfur	0.05% by mass, max.
Copper strip corrosion	No. 3 max
Cetane	47 min.
Carbon residue	0.050% by mass max.
Acid number-mg KOH/g	0.80 max
Free glycerin	0.020% mass
Total glycerine (free glycerine and unconvertedglycerides combined)	0.240% by mass, max.
Phosphorus content	0.001 max. % mass
Distillation	90% @ 360 ⁰ C

IV. BENEFITS AND DRAWBACKS OF BIODIESEL

4.1 Benefits:

- The higher cetane number of biodiesel compared to petro-diesel indicates potential for higher engine performance.

- Reduced vehicle emissions
- Reduced engine wear because of the fuel's excellent lubricity ability to lubricate the engine and fuel systems.
- Increased safety in storage and transport because the fuel is nontoxic and biodegradable.
- Reduced dependence on foreign oil suppliers and associated price fluctuations.
- Biodiesel molecules are simple hydrocarbon chains, containing no sulphur or aromatic substances, associated with fossil fuels.
- Reduction of greenhouse gases at least 3.3 kg CO₂-equivalent per kg of biodiesel.

4.2 Draw backs:

- The need in order engines to replace rubber fuel hoses and gaskets with synthetics because of biodiesel's tendency to deteriorate rubber.
- Possible concerns with engine warranties.
- Limited commercial availability of fuel if we are not going to process it our self.

Ethanol is also an attractive alternative fuel because it is a renewable bio-based resource and it is oxygenated, thereby providing the potential to reduce particulate emissions in compression ignition engines. Ethanol can be produced through fermentation of sugar derived from corn or cellulosic biomass. About 90% of ethanol produced from corn. Although essentially no ethanol is currently produced from cellulose, research and development is under way to develop and improve the technology required to produce ethanol from cellulosic biomass. Because of the limited supply of corn, ethanol produced from corn cannot meet a large enough fraction of the transportation fuel demand.

Ethanol is one of the possible fuels for diesel replacement in compression Ignition (CI) engines. The applications of ethanol as a supplementary CI engine fuel may reduce environmental pollution, strengthen agricultural economy, create job opportunities, reduce diesel fuel replacements, and thus contribute in converting a major commercial energy source. Ethanol was first suggested as an automotive fuel in USA in the 1930s, but was widely used only after 1970.

Alcohol is made from renewable resources like biomass from locally grown crop and even waste products such as waste paper, grass and tree trimmings etc. alcohol is an alternative transportation fuel since it has properties, which would allow its use in existing engines with minor hardware modifications.

Alcohols have higher octane number than gasoline. A fuel with a higher octane number can endure higher compression ratios before engine starts knocking, thus giving engine ability to driver more power efficiently and economically. Alcohol burns cleaner than regular gasoline and produced lesser carbon monoxide, HC and Oxides of Nitrogen [25, 27,28]. Alcohol has higher heat of vaporization; therefore, it reduces the peak temperature inside the combustion chamber leading to lower NOx emissions and increased engine power. However, the aldehyde emissions go up significantly. Aldehydes play an important role in formation of photochemical smog.

Methanol (CH₃OH) is a simple compound. It does not contain sulfur or complex organic compounds. Methanol gives higher engine efficiency and is less flammable than gasoline but the range of the methanol-fueled vehicle is as much as half less because of lower density and calorific value, so larger fuel tank is required. The cost of methanol is higher than gasoline. Methanol is toxic, and has corrosive characteristics, emits ozone creative for maldehyde. Methanol poses an environmental hazard in case of spill, as it is totally miscible with water. Ethanol is similar to methanol, but it is considerably cleaner, less toxic and less corrosive. It gives greater engine efficiency. Ethanol is grain alcohol, and can be produced from agricultural crops e.g. sugar cane, corn etc. ethanol is more expensive to produce, has lower range, poses cold starting problems and requires large harvest of these crops. Higher energy input is required in ethanol production compared to other energy crops and it leads to environmental degradation problems such as soil degradation.

The physical properties of alcohols in comparison to CNG, DME and petroleum fuels are given in table 2.

Alcohol fuels, ethanol and methanol and ethanol have similar physical properties and emission characteristics as that of petroleum fuels (table 2). Alcohol's production is cheaper, simple and eco-friendly. This way, alcohol would be a lot cheaper than gasoline fuel. Alcohol can be produced locally, cutting down on fuel transportation costs. Alcohol can be used directly in an engine or it can be blended with gasoline or diesel fuels. Alcohol fuels can be successfully used as IC engine fuels either directly or by preparing biodiesel. Transesterification process utilizes methanol or ethanol and vegetable oils as the process inputs. This route of utilizing alcohol as a diesel engine fuel is definitely a superior route as the toxic emissions (aldehydes) are drastically reduced. The problem of corrosion of various engine parts utilizing alcohol as fuel is also solved by way of transesterification

Table2. Comparison of various properties of primary alcohols with gasoline and diesel

Property	Methane	Methanol	Dimethyle ether	Ethanol	Gasoline	diesel
Formula	CH ₄	CH ₃ OH	CH ₃ OCH ₃	CH ₃ CH ₂ OH	C ₇ H ₁₆	C ₁₄ H ₃₀
Molecular weight (g/mol)	16.04	32.04	46.07	46.07	100.2	198.4
Density (g/m ³)	0.00072 ^a	0.792	0.661 ^b	0.785	0.737	0.856
Normal boiling point 30 ⁰ c	-162	64	-24.9	78	38-204	125-400
LHV (kj/g)	47.79	19.99	28.62	26.87	43.47	41.66
Energy (Mj/kg)	51.76	22.36	30.75	29.4	47.46	46.94
Carbon content (wt %)	74	37.5	52.2	52.2	85.5	87
Sulfur content (ppm)	~7-25	0	0	0	~200	~250

^a Values per cm³ of vapor at standard temperature and pressure.

^b Density at p=1 atm and T = -25^oC

V. DISCUSSIONS

5.1 The biodiesel production in general consists of the following steps:

Mixing of methanol and catalyst

The catalyst is typically sodium hydroxide (caustic soda). Dry caustic is dissolved in methanol by simple mixing. Care must be exercised to ensure the dry caustic (typically pellets or flakes) does not take too much water in storage. Water has also an adverse impact on downstream processing)

5.2 Reaction:

The methanol / catalyst mix is then charged into a reactor, either continuously or batch, and the oil is added. The reaction mix is kept at approximately 150 degrees F for between 1 and 8 hours vigorous agitation. Excess methanol is normally utilized to ensure total conversion of the fat / oil to esters. The catalyst will first react with any free fatty acids in the oil to form soap. There must be enough additional catalyst to catalyze the reaction, as well as to react with the free fatty acids.

5.3 Methanol removal:

In some systems, the excess methanol is removed at this stage via a simple flash process or distillation. In other systems, the methanol is removed after the glycerin and ester have been separated. In either case, the methanol is recovered and reused using conventional equipment. Care must be taken to ensure no water accumulates in the recovered methanol stream.

5.4 Separation:

Once the reaction is complete and the methanol has been removed, two major products exist: glycerine and methyl esters. Due to the density difference between glycerine (10 pounds / gal) and methyl esters (7.35 pounds / gal) the two are allowed to gravity separate and glycerine is simply drawn off the bottom. In some cases a centrifuge is used to separate.

5.5 Glycerine neutralization:

The resultant glycerine contains unused catalyst and soaps which are neutralized with an acid (usually hydrochloric or phosphoric) to form salts and sent to storage as crude glycerine. In some cases (for example, if potassium hydroxide is used as a catalyst rather than sodium hydroxide and phosphoric acid is used as the quench acid), the salt is recovered for fertilizer. In most cases the former is used as catalyst. The glycerine is typically 80-88% pure and ready to be sold as crude glycerol.

5.6 Methyl ester washes:

One separate from the glyceride, the methyl esters are washed gently with warm water to remove residual catalyst or soaps, dried and sent to storage. It is typically 98% ester and ready to be sold as fuel. In some cases, the esters are distilled under vacuum to achieve even higher purity.

5.7 Removal of the free fatty acids

Removal of the free fatty acid from the raw oil can be accomplished by caustic washing, steam stripping, or liquid extraction.

The free fatty acid removed must be used in some manner, usually burned for fuel, sold on the open market as a feed ingredient, or used as a feedstock for acid esterification.

5.8 Transesterification

The most common derivatives of agricultural oil for fuels are methyl esters. These are formed by transesterification of the oil with methanol in the presence of a catalyst. Sodium hydroxide is the most common catalyst.

5.9 Equation:

100kg of oil + 24 kg of methanol + 2.5 kg of NaOH -----
100kg of biodiesel + 26 kg of glycerine.

VI. CONCLUSIONS

Biodiesel made through a chemical process called transesterification whereby the glycerin is separated from the fat or vegetable oil. The process leaves behind two products- methyl esters (the chemical name for biodiesel) and glycerin (a valuable product usually sold to be used in soap and other product) Biodiesel can be process from any type of vegetable oils and animal fat. Food grade vegetable oils such as soyabean, canola, palm oil, sunflower oil and peanut can be used to produce biodiesel. Biodiesel can also be processed from animal fats such as lard, tallow, chicken fat, fish oils and used cooking oils from restaurants. The direct use of vegetable oils in fuel engine is problematic due to high viscosity and low volatility; they do not burn completely and form deposits in the fuel injectors of diesel engines. So, biodiesels produced from vegetable oils appear to be a potential alternative source to petro-diesel. Biodiesel reduces nearly all form of air pollutions. Most importantly, biodiesel reduces air toxics and cancer-causing compounds. Biodiesel is made from cooking oil and alcohol, so if spill it on the ground, it will quickly degrade into natural organic residues. Biodiesel is very new and it is catching slowly, because it is expensive. Make sure that the biodiesel used meets ASTM Standard there are no water, sediment or thick viscous layers on the bottom. Biodiesel can be store about the same length of time as diesel fuel. However storage longer than six month is not recommended.

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