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A Study on Methanol and Biodiesel as Petro Fuel Alternatives.

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ABSTRACT

The usage of bio-fuels particularly ethanol, methanol and bio-diesel is not a new. They are the fuels when Ford invented his popular model T automobile, similarly the Rudolf Diesel's prototype engine was made to run on vegetable oil. When productions of petro fuels were commenced, they became fuels of people choice as they were cheaper and readily available. However in the recent fast the scarcity of fossil fuels, environmental concerns, and global warming made people to rethink about fuels obtained from biomass, particularly oxygenated fuels. It was found that liquid fuels obtained from biomass are less polluting, as their exhaust emissions do not contain harmful components. Methanol is found to be an excellent blending agent for gasoline and bio-diesel. Ethanol increase the octane rating of gasoline and biodiesel increase the octane rating of petro-diesel. Besides this these bio-components increases the life span of vehicles due to their better lubricating. Bio-fuels particularly ethanol and bio-diesels are fuels of future, because they are renewable, biodegradable and less polluting.

Keywords: Methanol, Bio-diesel, Iodine Value, Acid Value, Flash Point, Fire Point, Viscosity

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INTRODUCTION

Feedstock

In the early 1970s, methanol to gasoline process was developed by Mobil for producing gasoline, ready for use in vehicles. One such industrial facility was built at Motunuiin, New Zealand in the 1980s. In the 1990s, a large amount of methanol was used in the United States to produce the gasoline additive methyl tert-butyl ether (MTBE). In addition to direct use as a fuel, methanol (or less commonly, ethanol) is used as a component in the transesterification of triglycerides to yield biodiesel. Dimethyl ether (DME) also can be blended with liquefied petroleum gas (LPG) for home heating and cooking, and can be used as a diesel replacement for transportation fuel [1].

Transesterification

The alcohol reacts with the fatty acids to form the mono-alkyl ester (biodiesel) and crude glycerol. The reaction between the bio lipid (fat or oil) and the alcohol is a reversible reaction so excess alcohol must be added to ensure complete fuel conversion in vehicles. One of the potential drawbacks of using high concentrations of methanol (and other alcohols, such as ethanol) in fuel is the corrosivity to some metals particularly to aluminium. When it is produced from wood or other organic materials, the resulting organic methanol (bio alcohol) has been suggested as renewable alternative to petroleum-based hydrocarbons. Low levels of methanol can be used in existing vehicles. The advantage of methanol is that it could be adapted to present internal combustion engines with minimum modification in both engines and infrastructure to store and deliver liquid fuel [2].

Feedstock Pretreatment

Common feedstock used includes yellow grease (recycled), virgin vegetable oil and tallow. Recycled oil is processed to remove impurities from cooking, storage, and handling, such as dirt, charred food, and water. Degumming to remove phospholipids and other plant matter is common, though refinement processes vary. Regardless of the feedstock, water is removed as its presence during base-catalyzed transesterification causes the tri glycerides to hydrolyze, giving salts of the (soaps) instead of producing biodiesel [3].

Determination and Treatment of Free Fatty Acids

A sample of the cleaned feedstock oil is titrated with a standardized base solution in order to determine the concentration of carboxylic acids present in the vegetable oil sample. These acids are then either esterified into biodiesel, esterified into glycerides, or removed, typically through neutralization [4].

Reactions

In catalyzed transesterification lipids (fats and oils) reacts with alcohol (typically methanol or ethanol) to produce biodiesel and an impure co product, glycerol. If feedstock oil is used, acid-catalyzed esterification can be used to react fatty acids with alcohol for producing biodiesel. Other methods, such as fixed-bed reactors, supercritical reactors, and ultrasonic reactors, forgo or decrease the use of chemical catalysts [5].

Product Purification

Products of the reaction include not only biodiesel, but also byproducts, soap, glycerol, excess alcohol, and trace amounts of water. All of these byproducts must be removed to meet the standards, but the order of removal is process-dependent. The density of glycerol is greater than that of biodiesel, and this property difference is exploited to separate the bulk of the glycerol co product. Residual methanol is typically recovered by distillation and reused. Soaps can be removed or converted into acids [6].

Supercritical Process

An alternative, catalyst-free method for transesterification uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock, free fatty acids are converted to methyl esters instead of soap, so a wide variety of feed stocks can be used. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but energy costs of production are similar or less than catalytic production routes [7].

Ultra-and High-Shear In-line and Batch Reactors

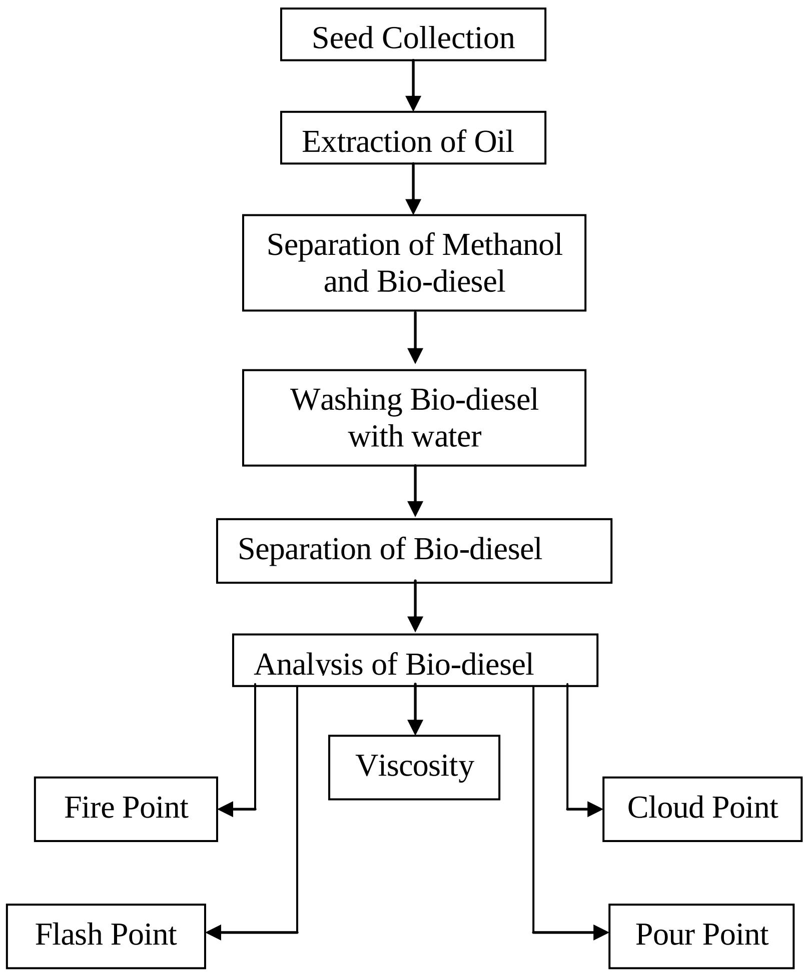
Ultra-and high shear in-line or batch reactors allow production of biodiesel continuously, semi-continuously, and in batch-mode. This drastically reduces production time and increases production volume. The reaction takes place in the high-energetic shear zone of the ultra-and high shear mixer by reducing the droplet size of the immiscible liquids such as oil or fats and methanol. Therefore, the smaller the droplet size the larger the surface area the faster the catalyst can react [8].

Ultrasonic Reactor Method

In the ultrasonic reactor method, the ultrasonic waves cause the reaction mixture to produce and collapse bubbles constantly. This activation simultaneously provides the mixing and heating required to carry out the transesterification process. Thus using an ultrasonic reactor for biodiesel production drastically reduces the reaction time, reaction temperatures, and energy input. Hence the process of transesterification can run inline rather than using the time consuming batch processing. Industrial scale ultrasonic devices allow for the industrial scale processing of several thousand barrels per day [9].

EXPERIMENTAL RESULTS

Major Steps in Experimental Work



Iodine value of oil [Hanus method]

Iodine value is defined as the number of parts by weight of iodine reacting with 100 parts by weight of oil or fat. The drying of oil is generally proportional to its iodine value. Iodine value indicates the degree of unsaturation of fatty acids present in the oil or fat. The determination of iodine value is of great importance in characterization of oil and also in finding the proposition of an adulterant in a sample of oil. In Hanus method of determination of the iodine value, a known weight of oil is dissolved in CCl_4 and treated with excess volume of iodine mono-bromide solution. The unused IBR is back titrated against std. $K_2S_2O_7$. About 0.52 to 1 gram of oil is weighed accurately and dissolved in 25 ml of IBr solution. The resulting mixture if is turbid is cleared by adding a small additions of a known value of $CC1_4$ this is moisturized with few drops of AGKI solution and then is inserted into the bottle. The bottle is kept aside for 40 to 60 min with occasional shaking. Then the reacted mixture is diluted with 200 ml of water followed by addition of 20 ml 10% aq. KI solution. The mixture is titrated with thio taken in the burette, by using starch as indicator added near the end point. A duplicate is also conducted and a blank titration is carried out without the oil using exactly the same quantity of CCl_4.

Let 'a' ml be the volume of thio required for excess iodine bromide solution and 'b' ml be the blank titrate value.

$$\text{Iodine value} = [(b-a) \times 127/1000] \times [100/w] \times \text{strength of thio}$$

Where 'w' is the weight of oil taken.

Table 1: Iodine Value

Vol. % of Bio-diesel	Pure Diesel	5% Blended	10% Blended	15% Blended	20% Blended	Pure Bio-Diesel
Iodine value	7.84	6.382	5.84	4.46	3.2	3.74

Figure 1: Iodine Value

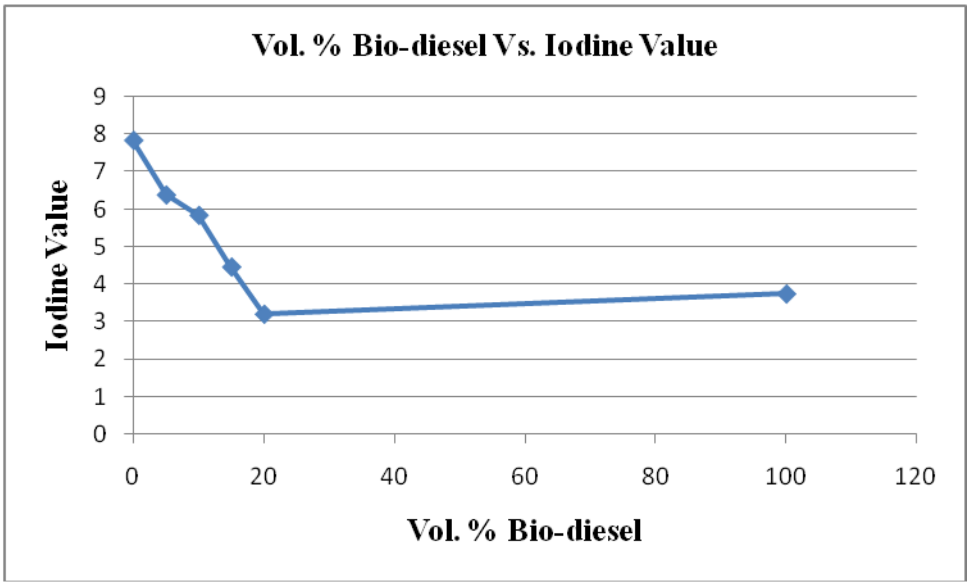


Table 1 and Figure 1 show the variation of iodine value with different proportions of blending.
Discussion: When petro diesel is blended with bio-diesel its iodine value is found to decrease. This shows the improved quality of petro-diesel.

Acid Value of Oil

Acid value of lubricating oil is defined as the number of milligrams of KOH required to neutralize the free acid present in 1 gram of the oil sample. In good lubricating oils, the acid value should be less than 0.1. Increase in acid value should be taken as an indicator of oxidation of oil, which may lead to gum and sludge formation beside corrosion. Weigh accurately about 5 grams of oil. Taken the oil sample into a 250 ml conical flask and add 50 ml of neutral alcohol. Heat the flask over a water bath for about 30 min. Cool the flask and the contents to room temperature and added a few drops of phenolphthalein indicator. Titrate with 0.1N KOH solution until a faint permanent pink color appears at the end point.

Acid value = No. of milligrams of 0.1N KOH used x 5.6

Where 5.6 represents the amount of KOH in milligrams presents per each ml of 0.1N KOH solution.

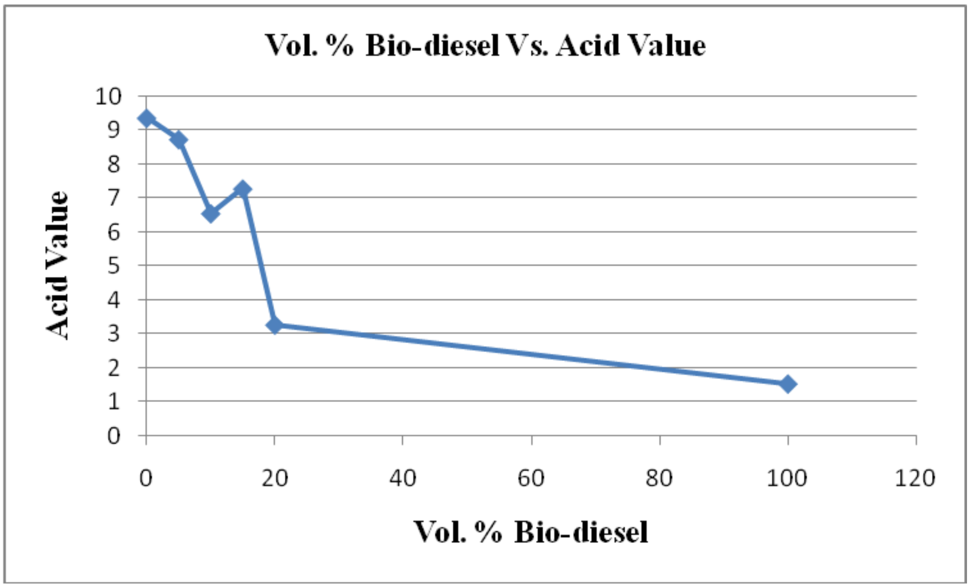
Acid value = (volume of 0.1N KOH used in the test /weight of oil) x 5.6

Table 2 and Figure 2 show the variation of acid value with different proportion of blending.

Table 2: Acid Value

Vol. % of Bio-diesel	Pure Diesel	5% Blended	10% Blended	15% Blended	20% Blended	Pure Bio-Diesel
Acid value	9.368	8.7376	6.553	7.281	3.27	1.52908

Figure 2: Acid Value



Flash Point

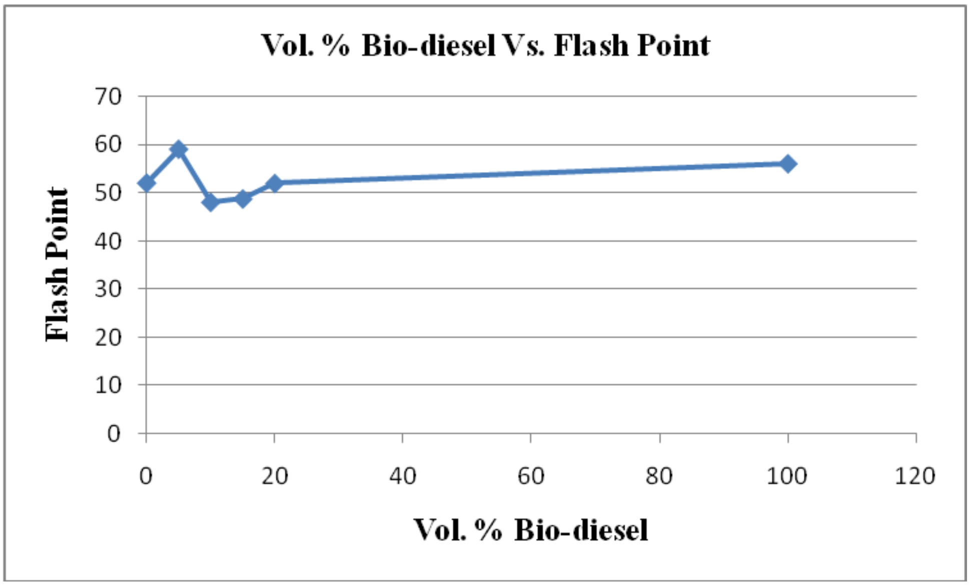
The flash point may be defined as the lowest temperature at which oil on vaporization gives sufficient quantity of vapors that will flash if brought into contact with flame. In case of lubricating oils, it is an index of the danger in using them for lubrication. Lubricants with high flash point are preferred so as to avoid any sort of explosion.

Table 3 and Figure 3 show the variation of flash point with different proportion of blending.

Table 3: Flash Point

Vol. % of Bio-diesel	Pure Diesel	5% Blended	10% Blended	15% Blended	20% Blended	Pure Bio-Diesel
Flash Point ^{0}C	52	59	48	48.7	51.9	56

Figure 3: Flash Point, ^{0}C



Fire Point

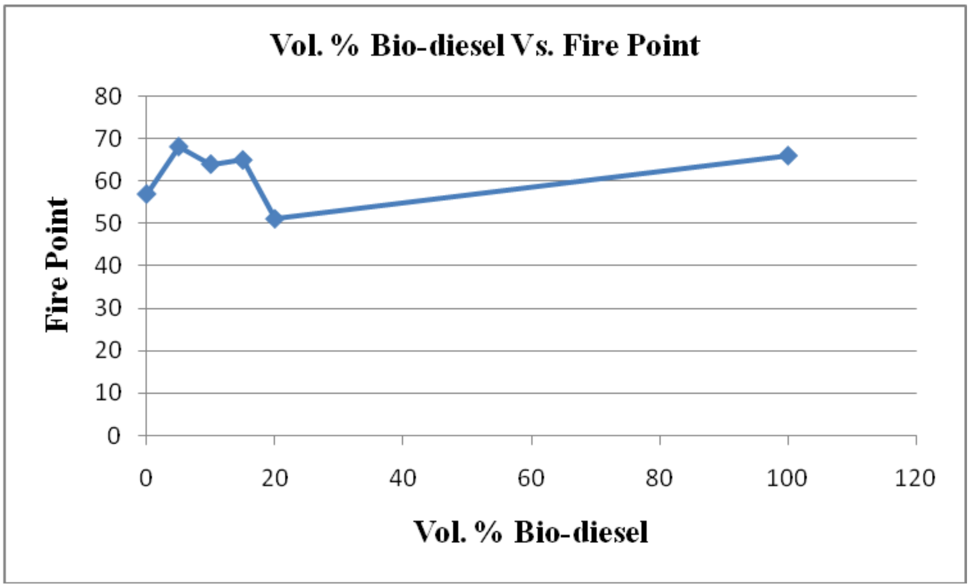
The fire point of oil is the lowest temperature at which it will give enough vapors, which on rising will begin to produce a continuous flame above the oil. The fire point of oil is determined in the same manner as the flash point. After the flash point has been obtained the oil is heated continuously at the rate of 4-5 ^{0}C per minute. At certain temperature the oil well ignites and continues to burn for a period of at least 5 seconds. The temperature at which such thing will happen is noted, that will give the fire point of the oil. Flash and fire point of different blends for diesel.

Table 4 and Figure 4 show the variation of fire point with different proportion of blending.

Table 4: Fire Point

Vol. % of Bio-diesel	Pure Diesel	5% Blended	10% Blended	15% Blended	20% Blended	Pure Bio-Diesel
Fire Point ^{0}C	57	68.1	64	65	51.2	66

Figure 4: Fire Point, ^{0}C



Discussion: Both flash and fire points are slightly increased when petro diesel is blended with 5%, 10%, 15% and 20% bio diesel. However the increase is very minimal, it is not consider as disadvantage. It can be also conclude that slight increase in flash points reduces the inflammability petro diesel.

Viscosity

Viscosity is the most important property, which is considered while selecting lubricant, for a particular application. It is a measure of internal resistance in the fluid.

Level the redwood viscometer apparatus with the help of spirit level. Fill the heating bath with the water up to a level just above the hoop gauge in the oil cup. Close the orifice and fix thermometer at an appropriate position at oil cup and heating bath. Record the temperature of the pure oil in the oil cup. Move the orifice and note down the time in seconds for effuse of 50 ml of oil through the orifice. Repeat the same for different blends of oil.

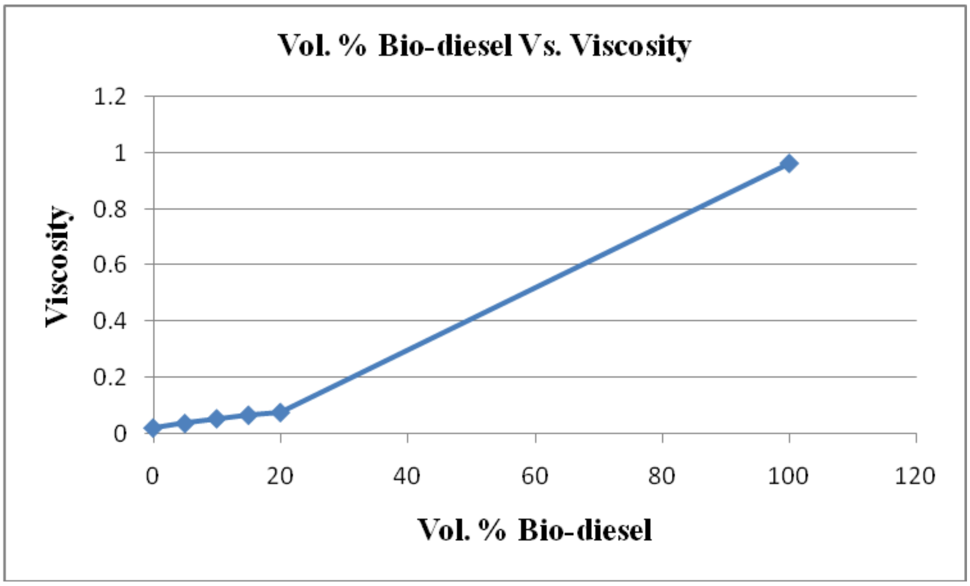
Kinematic viscosity = AT-(B/T) centistokes; A = 0.00247, B =0.05

Table 5 and Figure 5 show the variation of viscosity with different proportion of blending.

Table 5: Viscosity

Vol. % of Bio-diesel	Pure Diesel	5% Blended	10% Blended	15% Blended	20% Blended	Pure Bio-Diesel
Viscosity	0.021	0.037	0.054	0.0664	0.076	0.96

Figure 5: Viscosity, Centistokes



CONCLUSIONS

Replacing petroleum fuel with ethanol and biodiesel in the next four years, even in blended form would significantly reduce CO_2 emissions. This change would replace the exponential growth rate of CO_2 emissions with a linear one which continues to be problematic because it is still consistently increasing. Clearly, ethanol and biodiesel are environmentally responsible alternatives to petroleum-based gasoline and diesel, and are a good transitional option in what needs to be global effort in slowing greenhouse gas emissions and global warming.

Increasing worries over energy security in the face of growing demand, dwindling supplies of oil, and international conflicts and wars drove countries dependent on energy imports to look for alternative, homegrown sources. Interest in bio-fuels further intensified with the search for new opportunities for economic development, especially in agriculture.

This was particularly relevant in emerging economies such as India and China however, creating new jobs and a new industry are also attractive prospects in the developed world, where many established sectors such as agriculture and manufacturing are increasingly precarious. And, most recently, the growing awareness of the dangers of global climate change reinforced the challenge to find alternatives to fossil fuels as the dominant form of energy.

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