

Technical Aspects of Biodiesel and its Oxidation Stability

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Abstract : Biodiesel is a clean burning alternative renewable fuel made from natural renewable sources. It is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, which conform to ASTM specifications for use in diesel engines. Biodiesel present a very promising alternative fuel to diesel oil and properties of this oil offer the advantage of immediate substitution in existing diesel engines with little or no modifications at all. But one of the major technical problems associated with the biodiesel is its susceptibility to oxidation, which can cause the fuel to become acidic and to form insoluble gums and sediments that can plug fuel filters. This is due to the unsaturated fatty acid chains and the presence of the double bond in the molecule, which produce a high level of reactivity with the oxygen, especially when it placed in contact with air. The oxidation of fatty acid chains is a complex process that proceeds by a variety of mechanisms. The various other factors influence the oxidation process of biodiesel includes light, temperature, extraneous materials, peroxides, size of the surface area between biodiesel and air. One of the methods of improving biodiesel oxidative stability includes the deliberate addition of antioxidants or modification of the fatty ester profile. This article discusses the technical aspects of biodiesel and its oxidation stability.

Keywords: Alternative fuel, biodiesel, engine performance, oxidation

Introduction

There is a limited reserve of the fossil fuels and the world has already faced the energy crisis of seventies concerning uncertainties in their supply. Also the fossil fuels are currently the dominant global source of CO₂ emissions and their combustion is posing stronger threat to clean environment. Hence, during recent years high activities can be observed in the field of alternative fuels, due to supply of petroleum fuels strongly depends on a small number of oil exporting countries and increase in the price of the crude oil.

In the year 2004 – 2005, India imported 75 % of crude oil from other countries to meet the energy requirements. The demand for diesel and gasoline increased drastically in the year 2008 - 2009. It has been estimated that the demand for diesel will be 66.90 Mt for the year 2011-2012. Hence, government of India has taken necessary steps to fulfill future diesel and gasoline demand and to meet the stringent emission norms. Biodiesel and alcohol are being considered to be supplementary fuels to the petroleum fuels in India¹.

For diesel engines, vegetable oils are the renewable alternative fuels. The concept of using vegetable oil as a fuel is nothing new. Dr. Rudolf Diesel first developed the diesel engine in 1895 with the full intention of running it on a variety of fuels, including vegetable oil. Diesel

demonstrated his engine at the World Exhibition in Paris in 1900 using peanut oil as fuel. Since Diesel's time, the design of the diesel engine has been modified so it can run on the cheapest fuel available: petroleum "diesel" fuel. However, despite the technical feasibility, vegetable oils as fuel could not get acceptance, as they were more expensive than petroleum fuels. This led to the retardation in scientific efforts to investigate the further acceptability of vegetable oils as fuel. Later, due to numerous factors as stated earlier, created renewed interest of researchers in vegetable oil as substitute fuel for diesel engines.

In view of the potential properties of the vegetable oils, a large number of investigations have been carried out internationally in the area of vegetable oils as fuel. Some of the vegetable oils from farm and forest origin have been identified. Jamieson listed over 350 oil bearing crops². Few researchers examined the fatty acid profiles of seed oils of 75 plant species having 30 % or more fixed oil in their seed. They reported that the fatty acid methyl esters of oils of 26 species were found most suitable for use as biodiesel and they meet the major specification of biodiesel standards of USA, Germany and Europe³.

Composition of Vegetable Oils

Vegetal oil, also known as triglycerides, is a mixture of fatty acid triesters of glycerol. In the triglycerides alkyl chains of vegetable oil, predominate the palmitic, oleic and linoleic fatty acids.

Various vegetable oils are distinguished by their fatty acid compositions. Myristic (14:0) palmitic (16:0), stearic (18:0), arachidic (20:0), Behenic (22:0), linoceric (24:0), Oleic (18:1), Erucic (22:1), Linoleic(18:2) and linoleinic (18:3) are commonly present fatty acids in vegetable oils in varying percentages. Fatty acids fully saturated with hydrogen have no double bonds⁴. Fully saturated triglycerides are solid at room temperature and thus as such can not be used as fuel. Triglyceride molecules have molecular weights between 800 and 900 and are thus nearly four times larger than typical diesel (C₁₆H₃₄) fuel. Due to higher molecular weights, vegetable oils have low volatility and because of their unsaturation, vegetable oils are inherently more reactive than diesel fuels. As a result, they are much more susceptible to oxidation and thermal polymerization reactions.

Properties of Vegetable oils and their blends

Fuel properties of vegetable oils have been studied by many researchers. Compared to the diesel, the vegetable oils have a acceptable cetane number (35 – 45), acceptable calorific value (88 – 94 % of diesel), low sulphur content (<0.02%), high viscosity, high carbon residue, high flash (220-280°C), cloud (17-18°C) and pour points (-6 to -12°C), and contains gumming impurities. The major problem with the direct use of vegetable oils as fuel into compression ignition (CI)

engines is their higher viscosity. It interferes the fuel injection and atomization and contributes to incomplete combustion, nozzle clogging, excessive engine deposits, ring sticking, contamination of lubricating oil etc. The problem of higher viscosity of vegetable oils can be overcome to a greater extend by various techniques, such as heating, dilution, emulsification and esterfication etc.

Biodiesel

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, which conform to ASTM D6751 specifications for use in diesel engines. Fuel-grade biodiesel must be produced to strict industry specifications in order to ensure proper performance. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend.

Biodiesel is produced by transesterification which is a process of using either ethanol or methanol, in the presence of a catalyst, such as potassium hydroxide, to chemically break the molecule of an oil or fat into an ester and glycerol. This process is a reaction of the oil with an alcohol to remove the glycerin, which is a by-product of biodiesel production. Figure 1 shows the transesterification reaction. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order.

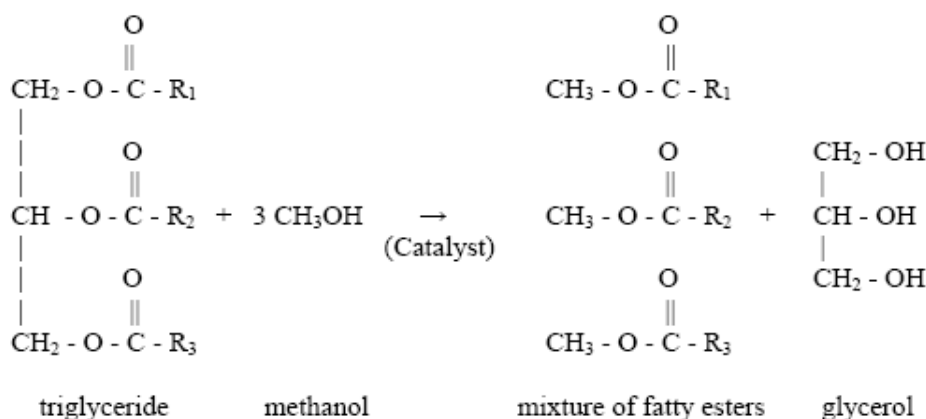


Fig.1 Transesterification Reaction

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts, among which alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective⁵. If the oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable. The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Methanolysis of beef tallow was studied with catalysts NaOH and NaOMe. Comparing the two catalysts, NaOH was significantly better than NaOMe⁶. Also without catalyst, biodiesel can be produced from vegetable oil using supercritical methanol transesterification reaction. Also this supercritical methanol process requires the shorter reaction time and simpler purification procedure because of the unused catalyst^{7,8}. It was also observed from the literature that the transesterification is faster when catalyzed by alkali. Economic feasibility study shows that the biodiesel obtained from non-edible oils is cheaper than that from edible oils⁹.

Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, there are large amounts of low cost oils and fats that could be converted into biodiesel^{10,11,12,13,14}. The problems with processing these low cost oils and fats are that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using alkaline catalyst. Therefore, two-step esterification process is required for these feed stocks. Initially the FFA of these can be converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction¹⁵.

Biodiesel Standards

Table 1 compares the ASTM fuel standards of diesel and biodiesel. From the analysis, we can observe that the biodiesel properties are close to the diesel.

Table 1. ASTM standard for diesel and biodiesel

Property	ASTM D975 (Diesel)	ASTM D6751 B100 (Biodiesel)
Flash point D93	325 K min	403 K
Water and sediment	0.05 max % vol	0.05 max % vol
Kinematic viscosity at 313 K	1.3 – 4.1 mm ² /s	1.9-6.00 mm ² /sec
Sulfated ash	-	0.02 max %wt
Ash	0.01 max %wt	-
Sulfur	0.05 max %wt	-
Sulfur	-	0.05 max %wt
Copper strip	No.3 max	No.3 max

corrosion		
Cetane number	40 min	47 min
Aromaticity	35 max % vol	-
Carbon residue	-	0.05 max % mass
Carbon residue	0.35 max % mass	-

Effect of Biodiesel on engine performance

It was observed from the literature¹⁰⁻¹⁸ that the use of biodiesel in diesel engine results in a slight reduction in brake power and a slight increase in fuel consumption. However, the lubricant properties of the biodiesel are better than diesel, which can help to increase the engine life. Also the exhaust emission of the biodiesel is lower than the neat diesel operation due to the presence of oxygen in the molecular structure of the biodiesel. Moreover, the biodiesel fuel is environment friendly, because biodiesel does not produce SOx and also there is no increase in CO₂ emission at global level.

Biodiesel Oxidation

Biodiesel has the same fatty acid profile as the parent oil or fat. Due to the fact that many vegetable oils possess a significant amount of fatty acids with double bonds, oxidative stability is of concern, especially when storing biodiesel over an extended period of time. The storage problem is exacerbated by storage conditions which may include exposure to air and/or light, temperatures above ambient, as well as presence of extraneous materials (contaminants) with catalytic effect on oxidation. Fuel instability, both oxidative and thermal, can give rise to sediment and gum formation and fuel darkening. These product characteristics can cause filter plugging, injector fouling, depositions in the engine combustion chamber, and malfunctions in various components of the fuel system¹⁹.

Oxidation mechanisms

The oxidation of fatty acid chains is a complex process that proceeds by a variety of mechanisms. The oxidation of the biodiesel is due to the unsaturated fatty acid chains and the presence of the double bond in the molecule, which produce a high level of reactivity with the oxygen, especially when it placed in contact with air or water. The primary oxidation products of double bonds are allylic hydroperoxides. In these species, the original double bond(s) may have shifted or undergone cis/trans isomerization. Hydroperoxides are unstable and easily form a variety of secondary oxidation products. Reactions of hydroperoxides include rearrangement to products of similar molecular weight, fission to give shorter-chain compounds (aldehydes and acids) and

dimerization to give higher molecular weight materials. The oxygen molecule, O₂, with which the olefinic fatty acid chains react, exists in two forms. The common ground state of oxygen is the triplet form 3O₂, which is a diradical, UO–OU. The other oxygen form is the excited singlet form 1O₂, which is more reactive than the triplet form by 22.5 kcal/mol. The amounts and nature of the hydroperoxides formed by these two forms of oxygen vary.

Abderrahim *et al*²⁰ studied the long storage stability of biodiesel prepared from different vegetable oils: high oleic sunflower oil, high and low erucic Brassica carinata oil respectively and used frying oil. His results showed that the acid value, density and viscosity increased, while iodine value decreased with increasing storage time. Juhun *et al*²¹. work shows that the initial structure alone does not dictate the reactivity of diesel soot and rather the initial oxygen groups have a strong influence on the oxidation rate. Their results shows that the diesel soot derived from neat biodiesel is far more reactive during oxidation than soot from neat diesel fuel. The biodiesel soot undergoes a unique oxidation process leading to capsule-type oxidation and eventual formation of graphene ribbon structures.

McCormick *et al.*²² examined the factors impacting the stability of biodiesel samples collected as part of a 2004 nationwide fuel quality survey in the United States. For the samples examined, they noticed that the polyunsaturated content (or oxidizability) has the largest impact on both increasing insoluble formation and reducing induction time. However, the formation of insolubles is also measurably decreased by increasing relative antioxidant content and increased by increasing total glycerin content. Philippe *et al.*²³ studied the kinetic of oxidation of rapeseed oil methyl ester (RME) in a jet-stirred reactor. Based on their experimental results, n-hexadecane is proposed to represent RME in the computations. The chemical kinetic reaction mechanism consisted of 225 species and 1841 reversible reactions. Their kinetic modeling gives a good description of the experimental results.

Oxidation stability standards

Since oxidative stability affects fuel quality, this issue has been addressed in some standards and plans exist to include specifications in other standards. Specifications related to oxidative stability have been included in the European biodiesel standard EN 14214 and are intended for the American standard ASTM D6751.

Conclusion

It was observed from the reported literature that the most of the transesterification studies have been done on edible oils like rapeseed, soybean, sunflower, canola etc. by using methanol and sodium / potassium hydroxide as catalyst. There are very few studies reported on non-edible oils. In addition, it is observed that the base

catalysts are more effective than acid catalysts and enzymes. The use of heterogeneous catalysts is a new area in the development of suitable catalysts in the transesterification of high free fatty acid oil. From the literature review, it is observed that the biodiesel properties are close to the diesel and satisfies fuel standards of many countries. It was reported that the combustion characteristics of biodiesel are similar as diesel and the engine power output with biodiesel was found to be equivalent to that of diesel. Moreover, the use of biodiesel in diesel engine results in drastic reduction engine emissions. The oxidation of biodiesel during storage period may be reduced by the use of antioxidants. From this review, we conclude that the biodiesel is a better alternative renewable fuel for the diesel.

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