Mixing Stability of Biodiesel Blends

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Abstract

Nowadays, with the rise of energy consumption demands, high greenhouse emission and a need to find a new renewable energy and we have started to venture into biodiesel manufacturing where made from transesterification of triglyceride feedstock. This includes oil-bearing crops, animal fats, and algal lipids. Example of popular biodiesel that had been commercialised was, soybean from United States, rapeseed oil from Europe and palm oil in southeast Asia (Hoekman, Broch, Robbins, Ceniceros, & Natarajan, 2012). Biodiesel becomes a lot more popular for some of its properties such as, biodegradable, sustainable and also environmentally beneficial, thereby providing lower gas emission profile. Based on a research by (Ferella, Mazziotti Di Celso, De Michelis, Stanisci, & Vegliò, 2010) mentioned that jatropha curcas, rape plant and palm trees absorb greater amount of carbon-dioxide than that contributed to the atmosphere when used as fuel in diesel engines. It is also stated that biodiesel has similar physiochemical properties to that of diesel produced from crude oil and can be used directly to run existing diesel engines without major modifications or as a mixture with petroleum diesel and produces less harmful gas emission such as sulphur oxide. However, the direct use of vegetable oil as fuel in compression ignition engines is problematic due to their high viscosity (about 11-17 times greater than diesel fuel) and low volatility. They do not burn completely and form carbon deposits in the fuel injectors of diesel engines. Transesterification can further improve the vegetable oils viscosity by lowering their viscosity and enhancing their physiochemical properties.

Keywords: Biodiesel, Stability, B5, Iodine value, Viscosity

1.0 Introduction

Biodiesel is an alternative diesel fuel derived from the varied processes of vegetable oils, animal fats, or waste frying oils to give the corresponding fatty acid methyl esters [31, 44]. In the transport sector it can be used blended with fossil diesel fuel and in pure form. The major chemically bound oxygen component in the biodiesel fuel has the effect of reducing the pollutant concentration in exhaust gases due to better burning of the fuel in the engine [36]. It is also described as an alternative fuel which improves environmental conditions and contributes to gaining energy sustainability [35].

As biodiesel fuels are becoming commercialized and with its biodegradability, it is important to examine their properties as respect to transport, storage, or processing. Demirbas [32] has summarized the biodegradability data of petroleum and biofuels available in the literature and showed heavy fuel oil has low biodegradation of 11%, in 28 day laboratory studies while biodiesels have 77%–89% biodegraded, and diesel fuel was only 18% biodegraded.

Some studies have been conducted focusing on how biodiesel stimulated the degradation of petrol--diesel in varied environments. However, there are very few studies concentrated on biodiesel degradation under different storage temperatures and storage environments such as in a sealed or ambient environment, and in an environment with or without the presence of water moisture. Mittelbach and Gangl [41] studied the degree of physical and chemical deterioration of biodiesel produced from rapeseed and used frying oil under different storage conditions. They found there has severe effects when the fuel was exposed to daylight and air. But they found there were no significant differences between undistilled biodiesel made from fresh rapeseed oil and used frying oil. In their study, the viscosity and neutralization numbers rose during storage and did not reach the specified limits for over 150 days.

Zullaikah et al. [46] examine the effect of temperature, moisture and storage time on the accumulation of free fatty acid when they used a two-step acid-catalyzed process to produce the biodiesel from rice bran oil. Their results showed rice bran stored at room temperature showed that most triacylglyceride was hydrolyzed and free fatty acid (FFA) content was raised up to 76% in six months. Leung et al. [40] divided twelve biodiesel samples into 3 groups and stored at different temperatures and environments to monitor the regular interval over a period of 52 weeks. Their results showed that the biodiesel under test degraded less than 10% within 52 weeks for those samples stored at 4 and 20°C while nearly 40% degradation was found for those samples stored at 40°C.

Bouaid et al. [21] used four different vegetable oils: high oleic sunflower oil (HOSO), high and low erucic Brassica carinata oil (HEBO and LEBO) respectively and used frying oil (UFO) to produce biodiesel through the process of transesterification. These biodiesels were then used to determine the effects of long storage under different conditions on oxidation stability. Their samples were stored in white (exposed) and amber (not exposed) glass containers at room temperature for a 30-months study period. Their results showed that acid value, peroxide value, viscosity and insoluble impurities increased, while iodine value decreased with increasing storage time. They also found there has slight differences between biodiesel samples exposed and not exposed to daylight before a storage time of 12 months and after this period the differences were significant.

Karavalakis et al. [27] investigated the impact of various synthetic phenolic antioxidants on the oxidation stability of biodiesel blends with the employment of the modified Rancimat method. Their experimental results revealed Butylated hydroxytoluene (BHT) and butylated hydroxyanisol (BHA) showed the lowest effectiveness in neat biodiesel, whereas their use in biodiesel blends showed a greater stabilizing potential. Propyl gallate (PG) and pyrogallol (PA) additives showed the strongest effectiveness in both the neat biodiesel and the biodiesel blends. They conducted an ageing process-- a naturally ageing process of the biodiesel blends for a period of 10 weeks; samples were taken every 2 weeks to simulate the automotive biodiesel stored in the fuel tank of a vehicle. Their results showed a sharp decrease in fuel stability, significantly increased in acid value but limited effects in viscosity over time. The addition of antioxidants resulted in some increases in viscosity and acid value of the biodiesel blends.

In this study, one commercial biodiesel and three laboratory-produce biodiesels were used to verify the effect of storage temperature, type of storage container, storage time as well as the moisture content on the properties of the biodiesel. The major properties analyzed in this study include acid value, iodine value, viscosity, flash point, and heating value. The variation of the chemical species in the tested biodiesel were also analyzed and compared.

2.0 Literature Review

2.1 Phase separation of biodiesel

The phase separation phenomenon was determined by investigating the mixing stability of the diesel and ethanol blended fuel. The purposes are to rely on the ethanol blending ratio, contents of the additive (biodiesel fuel), and the condition of the test bottle cap ("open" or "closed").

In the study of the Mixing Stability and Fuel Properties of Diesel-Ethanol Blended Fuels, the 5% and 10% biodiesel fuel volumetric ratios were added to the diesel-ethanol blended fuel to prevent phase separation. Moreover, the effect of "closed" and "open" cap conditions on the phase separation was also investigated. An experiment was done and the results shows that the separation ratio increased as the ethanol blending rate increased. Therefore, it can be said that the separation ratio was determined by the ethanol blending ratio in both cases of 0% and 5% additive. In the case of 10% BD additive, the separation phenomenon occurred between 24 h and 48 h. From the results, it can be confirmed that the addition of biodiesel fuel affected the relaxation of the occurrence of the phase separation between diesel and ethanol fuels. Through the mixing stability experiment, it can be concluded that the diesel-ethanol blended fuels are sufficient stable fuels to use in a diesel engine if those fuels include some biodiesel fuel with storage under the closed condition.(1)

2.2 Biodiesel blends (B5 and Lower Blends)

The specification for conventional diesel fuel, ASTM D975, allows up to 5 volume % biodiesel to be blended into compliant diesel fuels. The biodiesel must meet D6751. The biodiesel blend must meet all the numeric requirements for diesel fuel properties specified in D975; none were changed or relaxed to accommodate biodiesel. ASTM Method D7371 Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method) must be used to determine the biodiesel blend percentage.

2.3.1 Oxidation Stability of Biodiesel

The major factor that influencing the properties of Biodiesel is the fatty acid profile of biodiesel that also corresponds to that of parent oil. It is because of significant amount of fatty acids with double bonds, oxidative stability has been found to be of significant concern when the biodiesel is stored over an extended period of time. So, this is the causes of why the oxidation stability becomes an important criterion for biodiesel fuel quality [2,3].

It is reported that stability of biodiesel is inferior to petro-diesel and therefore, the blending of biodiesel with petro-diesel will affect its fuel stability significantly [4]. The poor biodiesel stability is attributed to the presence of double bonds in the fatty acids that may ultimately lead to formation of gum and other oxidation byproducts. Almost all the biodiesels have significant amounts of esters of oleic, linoleic or linolenic acids. These esters undergo auto-oxidation with different rates depending upon the numbers and positions of the double bonds and result in the formation of a series of by-products like acids, esters, aldehydes, ketones, etc.

During oxidation process, the fatty acid methyl ester usually forms a radical next to the double bond. This radical quickly binds with the oxygen of the air, which is itself a biradical and forms peroxide radical (Figure 1). The rapid radical destruction cycle begins thereafter. This peroxide radical immediately creates a new radical from the fatty acid methyl ester, which in turn binds with oxygen of the air and in this way, the destructive radical auto-oxidation cycle starts. During this process, up to 100 new free radicals are created quickly from one single radical meaning thereby that decomposition occurs at an exponentially rapid rate resulting in the formation of a series of by-products [5]. These species so formed cause the fuel to eventually deteriorate. Finally, the oil spoils and become rancid very quickly. Oxidative rancidity begins with an initial chain reaction followed by propagation reaction that involves unstable peroxides and hydroperoxides followed by the termination reactions resulting in the formation of aldehydes, alcohols and carbonic acids (Figure 1).

Initiation:	$RH + I \longrightarrow R. + IH$
Propagation:	$R. + O2 \longrightarrow ROO.$
	$ROO. + RH \longrightarrow ROOH + R.$
Termination:	$R. + R. \longrightarrow R\text{-}R$
	$ROO. + ROO. \longrightarrow$ Stable Product (1)

2.3.2 Storage stability of biodiesel

Studies of the storage stability of biodiesel found that exposure to heat and air greatly accelerated degradation of biodiesel, but when stored at 20 °C in closed containers or stored after the addition of an antioxidant, the biodiesel remained stable. Further research on the stability of biodiesel for 180 days of storage showed that exposure to metals also increased the rate of degradation, and that exposure to higher temperatures in pro-oxidizing conditions accelerated loss of stability [6]. Bondioli et al. assessed the applicability of accelerated test methods designed for evaluating storage stability (ASTM International [ASTM] D4625) and oxidative stability (ASTM D2274) of petroleum diesel to biodiesel. In conjunction with measuring filterable and adherent insoluble product formation over 24 weeks of storage at 43 °C, they monitored production of acids, peroxides, aldehydes, and polymers, and increase in viscosity. [7].

Antioxidant additives were found to improve the storage stability of biodiesel. However, the effectiveness of these additives is influenced by the amount of double bonds, and thus the reactivity, of the biodiesel samples [8 and [9]. Although storage conditions strongly influence the stability of biodiesel, production and purification can play a large role in long-term stability.

Longer-term storage of biodiesel for low-use applications of diesel fuel, such as back-up generators, will require higher oxidation reserve than is necessary for typical use to ensure that the fuel remains stable. The ASTM specifications for B100 and biodiesel blends include guidance for stability monitoring when fuel is stored for greater than 6 months [10] and [11]. In the case of petroleum diesel fuel, guidance is offered for storage times greater than 12 months [12]. It is recommended that acid value and particulate matter be measured regularly to ensure the fuel has not degraded prior to use. The instability of biodiesel compared to petroleum diesel leads to many questions and concerns about storing fuel that may contain even low concentrations of biodiesel. This study seeks to determine if biodiesel blends can be stored for longer periods of time as long as three years and if so what the necessary fuel properties to ensure adequate oxidation reserve and thus stability during storage may be.

2.4 Stability Measurement

2.4.1 Viscosity

High viscosity is present inside vegetable oils and it causes a number of problems, such as low atomization, incomplete combustion, injector clogging and low oxidation stability due to polyunsaturated content [28]. To overcome these problems, transesterification of vegetable oil were carried out to obtained biodiesel with better qualities than those of diesel fuels. Such as, biodegradability, significant reduction of CO, SO, unburned hydrocarbons, volatile organic compounds and particulate matter emissions [24]. Biodiesel has become alternatives for diesel engines; it has much higher density and viscosity compared to diesel fuel. Viscosity is the most important transport properties of a fuel, influencing especially the injection system. At low temperatures, viscosity increases thus biodiesel and combinations of diesel fuel shows similar viscosity-temperature dependence [26].

2.4.2 Iodine Value

Biodiesels with high iodine value (IV) will tend to be less stable and more susceptible to oxidation due to their high degree of unsaturation [20]. A research by [21] stated that iodine value (IV) had been used to measure the degree of unsaturation in vegetable oil and fats. Determination of the IV is important in preventing problems in engines such as polymerization and deposit formation on engine nozzles, piston rings and piston rig grooves. With high IV, degradation of product can negatively affect engine efficiency and reduce the quality of lubrication. Iodine value measures the unsaturation of esters present in the biodiesel and it is determined by the quantity of grams of iodine that reacts directly with double or triple bonds between carbon atoms [25]. With high unsaturation degree leads to lessening of cetane number and of oxidative stability of the biofuel [22].

2.5 Transportation of biodiesel

Biodiesel can degrade due to oxidation, contact with water, and/or microbial activity. It is occur when the biodiesel that leaves the production plant in good condition but become unacceptable during distribution because without proper care and attention

Generally, biodiesel will degrade more quickly than petro-diesel. A biodiesel spill will biodegrade quickly and not cause as many environmental problems as a petro-diesel spill. Nevertheless, both fuels will eventually degrade, and the same good housekeeping practices that apply to petro-diesel will also keep biodiesel in good condition.

Another problem is that biodiesel has a tendency to gel (freeze) at higher temperatures than petro-diesel. Since biodiesel gels at low temperatures, it is difficult to transport biodiesel like any other diesel fuels at low temperatur Therefore, some of the methods recommended for transportation of biodiesel designed to deal with this tendency (13) are:

- Kept hot in tank cars for immediate delivery,
- Kept in insulated rail tank cars equipped with steam coils (the tank cars are melted with steam at the final destination as needed)
- Kept in 20 percent blends with available winter diesel
- Kept in a 50 percent blend with diesel No. 1 (kerosene). A 50:50 blend of soy biodiesel and kerosene has a pour point of 0° F in most cases.

Figure 1 Transportation of Biodiesel blends

2.6 Handling of biodiesel

Blending of biodiesel can cause irritation and a burning sensation to sensitive body parts, so it is advisable to wear rubber gloves while dealing with biodiesel. Spontaneous combustion may be a problem because the fuel can oxidize in the air; consequently, rags that contain biodiesel and other combustible material should be put in clo ed metal cans or dried individually (14,15). Biodiesel is also considered essentially nontoxic (16).

2.5 Solvency of biodiesel

Biodiesel is a mild solvent, it may help to remove engine deposits that settle in the storage tanks of vehicles and also in the systems. As a result, fuel filters in vehicles may become plugged, giving a false impression that biodiesel plugs filters, while it actually helps clear out sediments deposited in storage tanks. If biodiesel or a biodiesel blend is used in an engine where diesel No. 2 was previously used, fuel filters will initially get clogged as the biodiesel cleans out deposits left by diesel No. 2. It is recommended that one should read the guidelines provided for that kind of biodiesel before using higher biodiesel blends in their vehicles. Since biodiesel can also act as a solvent for certain elastomers and natural rubber compounds, thereby affecting engine components like gaskets and seals as well as older fuel dispensing equipment. As is true with recent engine designs, fueling station systems have started using materials that are compatible with biodiesel. One fuel dispenser manufacturer states that there should be no problems with low-blend biodiesel blends (17). It should be noted that the Department of Defense has concluded that biodiesel is fully compatible with military specification diesel No. 2 (18). Biodiesel can act as a solvent on painted surfaces, so spills on painted surfaces should be wiped immediately (19).