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Effects of biodiesel composition on its long term storage stability

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HIGHLIGHTS

- Biodiesel with higher saturated methyl ester is stable after 10 months storage.
- Unsaturated methyl ester content increases the rate of biodiesel degradation.
- Biodiesel density, kinematic viscosity increased beyond standard specifications.
- Bio-mix and blending with diesel reduces the rate of biodiesel degradation.

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ABSTRACT

Biodiesel is accepted worldwide as an alternative for diesel fuel in compression ignition engine applications as it is renewable, non-toxic, biodegradable, safe to store, handle and transport, locally available, has zero sulfur content and a higher cetane number. Upon these advantages, the poor storage stability of biodiesel owing to its unsaturated methyl ester constituents is a major concern. The fatty acid methyl ester composition of biodiesel fuels vary significantly according to the nature of vegetable oil feedstock used in their production process and are found to influence fuel stability upon long term storage. In the present work, experiments are done to investigate the effects of changes in biodiesel composition on its long term storage stability. For this study, two biodiesel fuels with significantly different compositions, viz. Coconut biodiesel having a higher proportion of saturated methyl esters (~90%) and Karanja biodiesel with higher amounts of unsaturated methyl esters (~70%) are chosen. The different blends of these two biodiesel fuels are prepared (referred herein as bio-mix) to alter their composition. The fuel blends are also made by mixing Karanja biodiesel with petro diesel. Six fuel samples with two neat biodiesel fuels and four blends are made by using this approach and are stored under four different storage conditions for a period of 10 months. The changes in compositions and the important properties of these fuel samples are measured at regular intervals to assess their rate of degradation. The obtained results show that the rate of degradation is higher for neat Karanja biodiesel as compared to all other fuel samples due to its higher unsaturated methyl ester contents. Further, it is observed that by blending Karanja and Coconut biodiesel, the rate of degradation is reduced on long term storage. Surprisingly, blending with diesel results in a higher rate of degradation as compared to bio-mix. Among the different storage conditions investigated, the direct exposure to air and sunlight results in a higher rate of biodiesel degradation.

1. Introduction

Continued use of petroleum based fuels is now widely recognized as unsustainable because of their depleting supplies and their contribution to the accumulation of carbon dioxide in the environment. Renewable, carbon neutral transport fuels are the need of time for environmental and economic sustainability [1]. Biodiesel fuel derived from vegetable oil (edible and non-edible), animal fat, used frying oil is considered as a potential renewable and carbon neutral replacement to petroleum fuels. Biodiesel is a multi-component mixture of long chain mono-alkyl esters of fatty acids [2]. The vegetable oil and animal fat derived feed stocks used to produce biodiesel are known as triacylglycerides (TAGs), or simply triglycerides. Biodiesel is produced by a chemical process known as transesterification wherein the triglycerides are reacted with alcohol in the presence of a catalyst to produce fatty acid alkyl esters [3]. Since methanol is the most widely used alcohol in the transesterification process, the biodiesel thus produced are commonly referred as fatty acid methyl esters (FAME).

The poor storage stability of biodiesel is one of the major concerns for its commercial applications since the fuel quality gets

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degraded with an increase in storage period. The stability of biodiesel fuel primarily depends upon the fatty acid profile of the vegetable oil feedstock used for its production. The biodiesel fuels having a higher concentration of unsaturated methyl esters are found to be more prone to oxidation [4,5]. Besides the unsaturated contents, the other parameters which affect the rate of degradation of biodiesel are the nature of the storage container and the storage conditions [6]. The oxidative stability of biodiesel is not affected by the presence of zinc, whereas, the use of tin or aluminum die casting for storing biodiesel is found to decrease the stability within a week [7]. The methylene groups (CH_2) present adjacent to the double bonds (allylic position) in the unsaturated methyl esters form a free radical upon hydrogen abstraction which then react with atmospheric oxygen to form hydroperoxides which are the primary oxidation products of biodiesel oxidation [8,9]. The methylene carbons between the olefinic carbons are found to be the sites of first attack during the primary oxidation process [9]. The greater the availability of methylene carbons nearer to the double bonds, the greater is the rate of oxidation of biodiesel fuel. The relative rates of oxidation for the different unsaturated methyl esters are found to be 1 for oleate, 48 for linoleate and 98 for linolenate [3,10]. The hydroperoxides thus formed decompose and inter react to form numerous secondary oxidation products including aldehydes, alcohols, shorter chain carboxylic acids and higher molecular weight polymers [8]. A higher acid value of biodiesel is an indication of its higher degree of degradation [11].

The presence of acids in biodiesel could cause corrosion and wear in the fuel pump, injector and the other engine parts [12]. The oxidative polymerization reactions in biodiesel upon long term storage leads to the formation of insoluble gums and sediments that cause problems in the fuel supply systems, especially, in the fuel injection pump [4]. An extensive degradation of biodiesel may produce insoluble higher molecular weight polymers that can clog fuel lines and filters or may lead to injector coking, incomplete combustion and engine deposits. Thus, the long term storage stability of biodiesel is a major concern to be addressed for its applications in automotive engines [4,13].

Bouaid et al. [14] in their study stored biodiesel fuels having different saturated and unsaturated methyl ester contents for around 30 months. They found that the physical and chemical properties of the fuels varied due to the changes in storage conditions and degree of unsaturation. Christensen and McCormick [15] in their study on long term storage stability of biodiesel and its blends found that the production, purification, storage methods and the concentrations of unsaturated methyl esters affect the storage stability. They also concluded that the direct contact of biodiesel fuel with heat, metal and sunlight accelerated its degradation. Mittelbach and Gangl studied the effects of long term storage of biodiesel exposed to air and sunlight and found that the viscosity and neutralization numbers rose during storage owing to the formation of dimers and polymers and also due to the hydrolytic cleavage of methyl esters into fatty acids [4]. Hoekman et al. [16] found that the variations in biodiesel properties upon long term storage are correlating well with their unsaturated methyl ester contents. Anand et al. [17] concluded from their study on Karanja biodiesel stored in a mild steel container for 500 days that both the fuel properties and engine performance change significantly due to ageing of biodiesel. Bannister et al. [18] found that the oxidative stability of biodiesel is related to its fatty acid methyl ester profile, temperature, presence of sunlight and contaminants such as metal, water and presence of antioxidants. Karavalakis et al. [19] studied the stability of biodiesel-diesel blend and found that a lower sulfur content in the diesel fuel decreases the oxidative stability of the blend.

Although, there are numerous investigations concerning the storage stability of biodiesel fuels, there are no systematic investigations on how the changes in biodiesel composition affect its storage stability. This study attempts to fulfill this gap by carrying out experimental investigations to study the effects of variations of biodiesel composition on its long term storage stability.

2. Materials and methods

2.1. Test fuel samples

For this study, two biodiesel fuels with significantly different compositions, viz. Coconut biodiesel having a higher saturated content of ~90% and a Karanja biodiesel with a higher unsaturated content of ~70% are chosen. The Karanja biodiesel was purchased from Mint Karanja, Pune, India and the Coconut biodiesel was supplied by the Southern Railway, Tamilnadu, India. The different blends of these two biodiesel fuels (bio-mix) are prepared by mixing them in different volumetric proportions to alter their compositions. The fuel blends are also prepared by mixing Karanja biodiesel with diesel to study the stability of blends which are commercially used. Six different fuel samples thus obtained are provided in Table 1.

2.2. Fuel storage containers and test conditions

For the long term storage of biodiesel, bio-mix and biodiesel–diesel blends it is necessary to find out a suitable storage container. For the present work, glass containers are chosen owing to the fact that it would not react with biodiesel and its blends and also it is possible to create different storage conditions. The glass containers are cleaned with acetone and are left open for a day before they are filled with the test fuel samples. To avoid contact with the metal lid closures of the containers, the fuel samples are filled only up to the half of the total volume of the containers. For exposing the test fuel samples to direct contact with air, drilled metal lid closures are used. To avoid contact with sunlight, the fuel samples are kept closed in the dark rooms. The four different storage conditions simulated using the glass containers with drilled/closed metal lid closures are as follows: direct contact with both air and sunlight, direct contact with air and closed to sunlight, direct contact with sunlight and closed to air and non contact with air and sunlight. All the test fuel samples are stored under these storage conditions for a period of 10 months.

2.3. Measured biodiesel properties and test standards

To investigate the stability of the fuel samples upon long term storage, their properties, viz. density, kinematic viscosity, calorific value, acid value, iodine value and peroxide value are tested at regular intervals after every 4 months. The cetane number of the fuel samples are estimated based on their measured composition following Ref. [20]. All the properties of the fuel samples are tested according to ASTM D6751 standard specifications [21]. The ASTM test procedures followed for the individual property measurements along with the international and Indian standard specifications for biodiesel fuel are provided in Table 2.

Table 1
Test fuel samples.

Fuel samples	Nomenclature
Sample 1	Neat Karanja biodiesel
Sample 2	Neat Coconut biodiesel
Sample 3	20% Karanja and 80% Coconut blend
Sample 4	50% Karanja and 50% Coconut blend
Sample 5	20% Karanja and 80% diesel blend
Sample 6	50% Karanja and 50% diesel blend