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Screening of antioxidant additives for biodiesel fuels

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ABSTRACT

One of the major issues associated with the use of biodiesel is to maintain the fuel at specified standards for a longer period. Biodiesel is more prone to oxidization than a mineral diesel, and it starts turning rancid within a week or less, and complete degradation occurs after a period of 4 weeks. The final products of oxidation alter the physical and chemical properties of fuel which results in the formation of insoluble gums that can plug fuel filters. This instability of biodiesel is a long-standing issue, and it has not as yet been satisfactorily resolved. As the use of biodiesel has increased massively, this oxidation issue could become a significant barrier to market expansion. One very promising and cost-effective approach to improving the stability of biodiesel is that the addition of appropriate antioxidants to the biodiesel fuels. Antioxidants perform better or worse in different biodiesel fuels, and there is no unique inhibitor that suit for every kind of biodiesel fuels. To screen the antioxidants for a specific biodiesel, it is necessary to understand the chemistry of antioxidants and the key factors that influence their effectiveness against biodiesel oxidation. Most of the published studies had been carried out solely with some common antioxidants, and still, hundreds of antioxidants are out there for testing. This article provides an insight into the factors to be considered for the selection of antioxidants to improve the storage stability of biodiesel fuels.

1. Introduction

Biodiesel is a renewable fuel that reduces engine emissions and provides greater lubrication when compared to mineral diesel. Despite its many advantages, it has a poor oxidation stability and increased NOx emitting tendency over the conventional diesel fuel. Oxidation of biodiesel leads to the formation of hydroperoxides which can produce insoluble gums and sediments that can plug fuel filters or make deposits on the fuel injector. The final products of oxidation also increase the viscosity of the fuel that leads to poor fuel atomization. This consequently leads to the biodiesel getting into the crankcase and making sludge with the lubricating oil which can lead to catastrophic engine failure [1]. In general, biodiesel is considered as a safe fuel because of its higher flash point. However, in oxidized state, it reacts with water and makes micro-explosion that can cause fire hazards [2]. Karavalakis et al. [3] observed a sharp increase in emissions of human carcinogens such as formaldehyde, acetaldehyde, acrolein, and PAHs when the engine is fueled with oxidized biodiesel blends. Moreover, the unsaturated biodiesel fuels have more reactivity towards oxygen that leads to the formation of more prompt NO during combustion which results in increased NOx emissions [4].

1.1. Factors affecting the oxidation stability

Hydrolytic, ketonic, microbiological and oxidative deterioration are the common degradation processes of fatty acids. It is generally accepted that, apart from microbial deterioration, oxidation is the primary process by which fatty acid or its ester degrades [5]. Autoxidation, photooxidation, thermal and enzymatic oxidation are the major oxidation processes that cause quality deterioration in biodiesel fuels. Among all, autoxidation is the most common process and it is defined as the spontaneous free radical reaction of fatty acids with atmospheric oxygen [6]. Factors that influence the oxidation rates of biodiesel fuels include the FAME composition and its structure, presence of natural antioxidants, exposure to heat, light, air and moisture, the presence of metal ion catalysts, enzymes and other impurities [7].

1.1.1. Chemical composition

There are two types of fatty acids, viz. saturated fat and unsaturated fat. The stearic, palmitic and hydroxystearic acids are saturated fatty acid group while the oleic, linoleic, ricinoleic, palmitoleic, linolenic and eicosenoic acids are unsaturated fatty acid group [8]. In general, the rate of oxidation of saturated fatty acids is extremely slow when

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compared to unsaturated ones and their contribution to the oxidation of biodiesel has usually been considered insignificant. Therefore, fuel stability research is primarily focused on the study of the reactions of unsaturated fatty acids. Though Iodine Value (IV) is an indicator of unsaturation, it cannot be a predictor of oxidative stability [9]. Knothe and Razon [9] reported that the oxidation rates of biodiesel increases with the total number of the bis-allylic sites (methylene CH directly adjacent to the two double bonds) in its structure and not with the total number of double bonds or Iodine value. The allylic position equivalent (APE) and bis-allylic position equivalent (BAPE) value are important parameters that decide the oxidation stability which can be calculated by using the following relations [10].

$$\text{APE} = 2\ (A_{C18:1} + A_{C18:2} + A_{C18:3}) \tag{1}$$

$$\text{BAPE} = (A_{C18:2} + A_{C18:3}) \tag{2}$$

Where A is the amount of each fatty acid compound.

C18:1 – Oleic acid
C18:2 – Linoleic acid
C18:3 – Alpha-linolenic acid

The BAPE value is the more significant than the APE value since a higher rate of oxidation occurs in bis-allylic positions only [9]. The linoleic and linolenic acids contain bis-allylic sites in their structure (linoleic – 1 and linolenic – 2) and are more susceptible to oxidation than saturated acids. The relative oxidation rates of the fatty acid series stearic, oleic, linoleic and linolenic acid are to be in the ratio of 1:100:1200:2500 [11]. Kumar et al. [12] reviewed the possibilities of improving the stability of biodiesel by increasing the saturated fatty acid content of the feedstock. However, higher saturation leads to poor cold flow that can cause choking of fuel lines and filters [13].

1.1.2. *Presence of natural antioxidants*

The results of many researches show that even highly saturated ester loses its stability rapidly if it contains a low level of natural antioxidants. Though the biodiesel fuels produced from land animal fats such as lard and beef tallow contain large amounts of saturated fats they have poor stability because they contain a lesser amount of natural antioxidants [14]. Moreover, Lima et al. [15] reported that the highly unsaturated Amazonian buriti oil (80% unsaturation) has more oxidation stability irrespective of its high oleic acid content because of the presence of large amounts of tocopherols and carotenoids. Most of these natural antioxidants might be reduced or destroyed during the transesterification or in the refining process.

1.1.3. *Storage temperature*

It has been well established that the rates of most oxidation reactions increase when the temperature is increased. Typically, oxidative stability measured by Rancimat method is based on the principle that degradation rate linearly increases with temperature. Xin et al. [16] reported that the degradation rate of biodiesel fuel is low when it is stored at a lower temperature. On the other hand, in real-world conditions, low-temperature storage of fuels has more practical difficulties and usually stored at ambient temperature. During the storage periods, the fuels are not subjected to higher temperature and the effect of temperature on oxidation is nominal. However, the engine spray nozzles and needles, the combustion chamber walls and piston are subjected to a higher temperature which leads to rapid oxidation of fuels that cause deposits on them. The sludge deposition rate is high within a range of temperature and is dependent on the type of fuel. Beyond this range, sludge formation rate decreases due to the increase of vapor pressure of the fuel and decrease in partial pressure of oxygen [17].

1.1.4. *Presence of transition metals*

All biodiesel fuels contain small amounts of transition metals such as copper, iron, and nickel that accelerate the rate of autoxidation even at quite low concentrations. Iron and copper are the most common transition metals found in biodiesel fuels and they decompose the peroxides into free radicals. When the transition metal ions in their lower valence state (M^{n+}), it reacts rapidly with hydroperoxides (ROOH) and produces free radicals RO* and ROO* [18].

$$\text{ROOH} + M^{n+} \rightarrow \text{RO}^* + -\text{OH} + M^{(n+1)+} \tag{3}$$

$$\text{ROOH} + M^{(n+1)+} \rightarrow \text{ROO}^* + H^+ + M^{n+} \tag{4}$$

The Eq. (4) shows that metal ions are regenerated and generates more RO* and ROO* radicals which result in a reduction of the induction period (IP). This catalytic effect can be suppressed with the use of Metal chelators or deactivators. They form catalytically inactive complexes with the metal cations making them unavailable to promote oxidation.

1.1.5. *Other factors*

It has long been known that exposure to light accelerates the oxidation rate of organic materials. In liquids like biodiesel, light penetrates in depth which results in larger portions of FAME become deteriorated. The carotenoids naturally present in vegetable oils helps to protect oils against light-induced oxidation [19]. The biodiesel sensitivity to light depends on the type and amounts of sensitizers present, FAME composition and other constituents. The pigments such as chlorophylls and pheophytins act as a photo-sensitizer when exposed to light and promote photooxidation and in the dark, they show antioxidant activity [20]. Biodiesel with a high content of mono- and diglycerides or glycerol absorb more water and is potentially subject to hydrolytic degradation. During this process, biodiesel is reconverted into alcohols and free fatty acids [21]. High initial acid value, free fatty acid content and humid and warm climate aggravate this hydrolytic reaction. The water content of biodiesel reduce its calorific value, increase corrosion rate and can serve as a breeding ground for microbes [21].

1.2. *Methods to improve the stability of biodiesel fuels*

A wide variety of oxidation inhibiting techniques is being pursued, including vacuum technology, inert gas packaging, low-temperature storage, enzyme deactivation, reducing the partial pressure of oxygen in contact and the use of antioxidants. Structural modifications such as changing the location of unsaturation closer to the ester head group, lessening the number of double bonds, removal of hydroxyl groups and the conversion of cis unsaturation to trans are some of the advanced techniques to improve the stability of the biodiesel fuels [22]. Sundus et al. [23] have discussed in detail about the methods to enhance the oxidation stability of biodiesel. In order to avoid the water contact they suggested using membrane technology for the purification of biodiesel.

Preventing or delaying the oxidation process with the use of small quantity antioxidants is the most cost-effective way than any other methods. Antioxidants donate an electron or hydrogen to the free radicals to neutralize the oxidation reaction. There is no universal antioxidant that prolongs the shelf life of all kinds of biodiesel fuels. With the abundance of available antioxidants, it is necessary to find the most appropriate antioxidants or its combination to optimize the storage stability of each biodiesel fuel. The objective of this paper is to identify the main factors that influence the effectiveness of antioxidants which can be considered in the screening of antioxidants for biodiesel fuels.