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Experimental study of the factors affecting the oxidation stability of biodiesel FAME fuels

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ABSTRACT

Oxidative stability of fatty acid alkyl esters or biodiesel during storage is very important as it yields products that degrade biodiesel quality and consequently affect engine performance. Accurate measurement, prediction and control of the oxidative stability of biodiesel from different feedstocks remain a challenging problem in biodiesel research. The current study relates to the investigation of the impacts of variation in feedstock on the oxidative stability of biodiesel, efficacy of various stability models (APE, BAPE, and OX) at predicting biodiesel oxidative stability, and the impacts of antioxidant loads in controlling oxidative instability of biodiesel. Firstly, oxidation stability for twelve different fatty acid methyl ester (FAME) biodiesels was measured to establish the effects of feedstock type on it. Then, fatty acid compositions were measured to establish the efficacy of the various models known as APE, BAPE, and OX proposed for characterizing the susceptibility of FAME to oxidation. Results showed oxidative stability and stability indices did not correlate well indicating that these models are inaccurate indicator for biodiesel stability. The response of the four biodiesel (Palm, Olive, Soyabean, and Jatropha) to the loading of the antioxidant (tertiary butyl-hydroquinone, TBHQ) was investigated to establish antioxidant threshold loading for delaying needed to delay oxidative degradation. It was found that biodiesel with high polyunsaturated fatty acids showed little improvement in oxidative stability to the same antioxidant dose. Finally, the efficacy of Rancimat methods in predicting the storage life of biodiesel was carried out by developing and extrapolating the oxidative stability Arrhenius temperature curves. The results for Sesame and Rapeseed FAME kept at 40 °C showed under prediction of the storage life by the Rancimat method than obtained in real conditions.

1. Introduction

Biodiesel is a drop-in replacement for petro-diesel that can be derived from renewable sources, including a wide range of plant-seed oils, animal fats and even certain lipid-rich algal species. Biodiesel is made via the transesterification of the range of vegetable feedstock oils or animal fats with alcohol; usually methanol to yield fatty acid methyl esters (FAME). Therefore, the chemical composition of biodiesel can vary significantly resulting in extremely varied physical properties. However, biodiesel is biodegradable, less toxic and can reduce harmful tailpipe combustion emissions (CO_2, CO, UHC and PM) relative to petro-diesel [1]. Biodiesel is miscible with petro-diesel, compatible with fuel delivery infrastructure, has high flashpoint for safer handling, and can be used in standard diesel engines requiring no engine modification. Biodiesel also offers improved lubricity over certain low-sulphur petro-diesels and thus can help reduce wear of engine components [2]. Running diesel-engine equipment on biodiesel can be beneficial in terms of environmental impact and energy security.

Biodiesel is susceptible to a process called autoxidation. Autoxidation process in biodiesel occurs when biodiesel is exposed to and reacts with ambient oxygen, and this is accelerated by elevated temperatures exposed to and reacts with ambient oxygen, and this is accelerated by elevated temperatures. Oxidative degradation can occur when biodiesel is kept in storage, or when circulating in an engine fuel system, or even when biodiesel is present as a contaminant within engine oil (after dilution of lube oil with unburned fuel). Biodiesel tends to be less resistant to oxidation than petroleum diesel [3], due to its chemical composition and results in the degradation of fuel properties which can affect on engine performance. A measure of the resistance of fuel to degradation by oxidation is referred to as it's 'oxidation stability'.

A recent detailed review by Pullen and Saeed [5] on the previous research efforts related to biodiesel oxidation stability identified the areas which need urgent research attention to address oxidative degradation [5].

Degradation of biodiesel due to auto-oxidation can cause fuel properties to significantly alter, including: flash point, ester content, the amount of insoluble contaminants (polymeric species), heating value

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of the fuel, Cetane number, acid value, kinematic viscosity and density. Changes in these properties and in colour from yellow to brown can thus indicate the progress of oxidation [5,6]. The products of biodiesel oxidation such as acids and polymer sediments cause engine fuel filters and injector blockages. Most polymers forming from degradation of biodiesel are difficult to filter out, rendering useless many industry standard stability tests for insolubles in diesel fuels. Formation of acids and polymer sediments [7] can block engine fuel filters and injectors, while acids form a corrosive environment for fuel injection equipment. Degraded biodiesel has been observed to result in coking of injectors due to an increase in viscosity caused by the formation of polymeric species in the degraded fuel. Undesirable oxidation products can affect the performance of fuel pumps and injectors due to increased wear [5,8]. Fuel lines, filters, pumps and orifices can clog [9] and exhaust emissions are performance affected [10]. Such concerns have also been expressed by leading manufacturers of fuel injection equipment [11] who declared that the resistance to oxidation is an inherent characteristics of any biodiesel, since degraded biodiesel has acids and polymers that significantly reduce fuel injection equipment performance and life. Sediments and gums can form plugging pump orifices, fuel filters and leave deposits on fuel system components [12]. Clearly, in order to deliver confidence in the quality of biodiesel fuels it is imperative to understand oxidative degradation and how to prevent associated problems. Clearly, in order to deliver confidence in the quality of biodiesel fuels it is imperative to understand oxidative degradation and how to prevent associated problems.

Exact modelling of oxidative stability of biodiesel is problematic because many factors can play significant roles in it such as fatty acid (FA) composition (unsaturation configuration, molecular weight), impurities (metals, free fatty acids, additives and antioxidants, water), physical parameters (sample mass, agitation, viscosity, temperature, light and air exposure), as well as the degree of prior sample ageing [6,10,16,19,22]. Decoupling and establishing the effects of individual effects can lead to a better understanding and prediction of oxidative stability of biodiesel. Bannister et al. [6] observed that oxidation is exacerbated (catalysed) by the presence of metals (e.g. Zn, Cu) that can be present in an engine fuel system [6]. The effect of alcohol type was investigated by Stavinoha et al. [23] who found that the OS of Soybean ethyl ester was slightly more than for Soybean methyl ester. However, the opposite was found for Sunflower-oil-based alkyl esters; currently there is no clear indication that methyl and ethyl esters have different oxidative stabilities. The blending of the biodiesel and diesel also causes improvement in the oxidative stability of the blend fuel due to the presence of sulphur in diesel fuel [6]—which acts as inhibitor to oxidative degradation of biodiesel [6], and because it is diluted from its neat form.

Recent review by the present authors [5] providing the underlying oxidation chemistry and the implications of oxidation for biodiesel use. It showed that the underlying chemistry of oxidative degradation is fundamentally a consequence of fatty acid composition and structure of the biodiesel FAME. The degree of chain unsaturation i.e. carbon double bonds ($C{=}C$) present undergo free radical attack causing hydroperoxide formation. The process of biodiesel oxidation is a self-sustaining chain reaction, proceeding by the general mechanism: initiation, propagation and termination [5]. Hydroperoxides form and decompose to problematic secondary products (acids, polymers). The allylic sites in a fatty acid chain (a methylene CH_2 adjacent to only one double bond) are vulnerable to oxidation. Similarly, a methylene CH_2 group present between two double bonds called bis-allylic sites is twice vulnerable to oxidation. Linolenic acid has two bis-allylic sites and two allylic sites. Linoleic acid has one bis-allylic site and two allylic sites; oleic acid has two allylic sites. For these unsaturated fatty acid components the order of greatest susceptibility to oxidation is linolenic > linoleic > oleic. Hence the levels of unsaturated fatty acids that are present in biodiesel FAME shall fundamentally determine relative susceptibility to oxidation. Therefore, it is necessary to decouple and establish the exact impact of biodiesel FAME composition and structure on oxidative stability to understand the role of individual feedstock types on its biodiesel oxidative stability. Researchers have developed different oxidative stability indices based upon fatty acid composition, which are discussed in detail in Section 2. Efficacy of these indices in predicting oxidative stability of biodiesel fuel has been fully established yet and needs detailed investigations.

Research has shown that it is extremely difficult to completely prevent oxidation in biodiesel and it can only be delayed. Therefore, a number of strategies to delay have been proposed in the literature which includes such as managing the impurities, storage conditions, fatty acid composition and antioxidant dosing in the biodiesel. Previous experimental studies carried out by several authors [4,21,24] have examined biodiesel oxidative stability at varying conditions of storage. Generally, similar trends of deterioration were recorded in oxidative stability and other important fuel properties (ester content, kinematic viscosity, acid value, insoluble contaminants) over extended storage periods. It was found that degradation could occur relatively rapidly in storage. For example Bondioli et al. [25] found that biodiesel stored at 43 °C deteriorated significantly on several key properties after only a few weeks. More detailed study of influencing factors (fatty acid composition, water content, storage temperature, exposure to air, agitation, and light) would be useful to understand biodiesel behaviour in storage. Researchers have investigated loading of anti-oxidants as a potential strategy for delaying biodiesel oxidative degradation during storage.

Typically, antioxidant addition in biodiesel acts to inhibits the oxidation process which can be used to control the oxidation of biodiesel. In the literature, authors have investigated the effects of different antioxidants loading on biodiesel oxidative stability [9,13–20] ranging from naturally occurring Tocopherols, to synthetic tertiary butylhydroquinone (TBHQ), pyrogallol (PY), propyl gallate (PG), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) antioxidants. It has been found that the concentration between 200 and 1000 ppm is where most of these antioxidants are most effective. A detailed review on the efficacy of biodiesel anti-oxidants has been presented by Dunn [19]. Commercially, synthetic antioxidants (TBHQ, BHA, BHT and PG) have been preferred over natural antioxidants because of their better effectiveness as 1000 ppm dosing of TBHQ improves the oxidative stability of biodiesel by more than two times [20]. TBHQ is therefore considered most effective antioxidants amongst synthetic antioxidant [21]. Also, addition of anti-oxidants in high quantity did not alter the other properties of the biodiesel [20] except slight increase in acid value. However, in the literature the relationship, if any, between the fatty acid composition of biodiesel and amount of the antioxidants have not been fully investigated and established. Establishing this relationship will be useful to establish the threshold limits for antioxidants for different biodiesel types in order to attain the same high level of oxidative stability (OS).

Accurate method for determining biodiesel storage life is urgently needed to predict the biodiesel stability under certain storage conditions. Typically, oxidative stability measured by Rancimat method shows a linear relationship between $\log_{10}$(oxidative stability) vs. temperature, which is Arrhenius equation describing increased reaction rate at higher temperature. Xin J et al. [17] extrapolated oxidative stability results obtained at higher temperatures (T) to predict oxidative stability at lower temperatures. Storage life estimates can be obtained by this method, however such estimates may not represent real time conditions as the process of oxidation may be different in real lower temperature conditions than assumed by Xin J et al. [17] be unreliable since it is assumed that the oxidation mechanism does not alter under less severe conditions. Xin J et al. [17] concluded that biodiesel fuel stored at lower temperature is favourable for long time storage of biodiesel without degradation. However, in real-world storage conditions at temperatures nearer ambient may result in different oxidation behaviour. Study of the reliability of storage life estimates derived from Rancimat oxidation stability measurements represents a promising strategy which needs to be investigated further to establish its