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Influence of different factors on the stability of biodiesel: A review

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ABSTRACT

Gradual depletion of fossil fuel has greatly enhanced the necessity to look for alternative fuel for automotive engine. In response to this, biodiesel is being considered as a promising solution with a number of technical advantages over conventional petroleum diesel. However, commercial use of biodiesel has been limited because of some drawbacks including corrosivity, instability of fuel properties, higher viscosity, etc. Stability of fuel properties is especially important to ensure expected engine performance as well as engine life. Most of the research papers available in public domain reported some concerns on the stability of biodiesel fuel properties. Scattered studies on different aspects often lead to confusions in understanding the adverse effects of different factors on the degradation of biodiesel. In this article, different factors that cause instability in biodiesel and their possible implications of different fuel properties have been reviewed. A special emphasis has been given to explain the possible mechanisms of biodiesel degradation. Possible remedies to improve the stability of biodiesel have also been included. Finally, some general conclusions concerning these problems are summarized and further scopes of study have been suggested.

Contents

1. Introduction

Energy has become an indispensable factor for mankind to preserve economic growth and maintain living standard [1]. In recent years, consumption of energy is increasing rapidly due to tremendous growth of transportations and industrial sectors [2].Therefore, considerable attention has been given to look for alternative fuels. Biodiesel is being considered as one of the most promising alternative fuels [3]. It is nontoxic in nature, biodegradable and produced from renewable sources such as vegetable oils or animal fats [4,5]. Biodiesel is completely miscible with diesel and thereby can also improve certain fuel qualities [6].

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For instance, addition of biodiesel in diesel can improve lubricity as inherently biodiesel has better lubricity. Biodiesel having 11% oxygen by weight [7,8] can ensure complete combustion and thereby increases the performance of engine. It also reduces the emission of exhaust gases as compared to that of diesel [9]. However, the commercial use of biodiesel has been limited due to having some drawbacks. Biodiesel has higher viscosity which may result in injector coking, moving parts sticking, fuel filter plugging, etc. [10]. Higher viscosity also causes poor atomization and less accurate operation of fuel injectors [11]. What makes the situation more complete is the fact that biodiesel is auto-oxidative and can readily influence its other fuel properties including cetane number, flash point, viscosity, density and so on.

There are many factors, which can influence the stability of biodiesel. It has been reported that biodiesel is highly sensitive to light, temperature and metal ions [12], more hygroscopic in nature [13], more susceptible to oxidation reactions [14,15] and more corrosive than diesel [16–20], unless it is modified or treated with additives [21]. Degradation of biodiesel causes its compositional changes [17–19], and consequently it changes its different valuable fuel properties [22]. Degradation of biodiesel also has strong influence on the corrosion of metals [13] as well as tribological aspects [19,23]. Therefore, it is very important to understand the influence of different factors on the instability of biodiesel and their related mechanisms. Understanding of such things is expected to contribute for improving stability of biodiesel [24].

From the recent literature studies, it has been found that the properties of biodiesel could be deteriorated by several factors including (i) auto-oxidation, (ii) thermal decomposition or thermal fluctuations, (iii) water absorption, (iv) biodegradation with microbial growth, (v) storage conditions, (vi) metal contamination, (vii) presence and absence of additives, etc. The available scattered studies do not allow understanding the real facts causing instability of biodiesel. The present study has critically analyzed these factors and come out with the possible mechanisms of instability of biodiesel.

2. Biodiesel and its specification

Globally, there are more than 350 oil-bearing crops identified as potential sources for biodiesel production [25]. The most common of them are soybean oil [26,27], sunflower, corn, used fried and olive oil [28], rapeseed oil [29–31], castor, lesquerella oil [32], milkweed (Asclepias) seed oil [33], *Jatropha curcas* [34], *Pongamia glabra* (Karanja), *Madhuca indica* (Mahua) and *Salvadora oleoides* [35], palm oil [36–38], etc. In general, biodiesel derived from these sources can be defined as mono-alkyl esters of long chain fatty acids [39]. Vegetable oils/animal fats mainly consist of triglyceride molecules. Triglycerides in the presence of catalyst react with methanol and thereby reduce methyl esters and glycerol (Fig. 1).

Glycerol is removed as by-product. The esters produced are known as biodiesel. According to ASTM D6751, standard biodiesel should have minimum 96.4% esters. The rest could be water, sediment, free glycerol, methanol, monoglyceride, diglyceride, triglyceride, alkaline metals (Na+K), alkaline earth metals (Ca+Mg), etc. The presence of these components can greatly influence the properties of fuel. As per standard, the limit of these contaminants and the level of desired fuel properties are shown in Table 1. Although the properties of biodiesel meet the given standard in as-receive condition, many properties can deviate from the standard once biodiesel is degraded. Therefore, the factors that may cause instability of biodiesel in terms of its composition as well as related fuel properties are very important to study in systematic way. In response to this, the following section has been devoted to describe the significance of fuel stability and the factors that may make it instable.

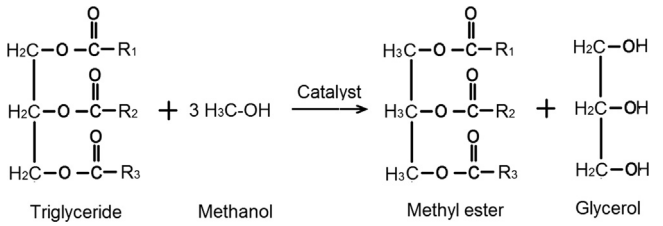

Fig. 1. Chemistry of transesterification reaction (R_1, R_2, and R_3 represent the hydrocarbon chains of the fatty acid triglyceride) [40].

3. Instability of biodiesel

Instability of biodiesel refers to the change of its original fuel composition and fuel properties. In such case, biodiesel properties can deviate from the prescribed quality standard. This can greatly affect its applicability in automotive engine. Engine performance as well as fuel consumption rate is greatly altered due to deterioration of fuel [40]. As compared to diesel, biodiesel is much more instable [41]. Therefore, manufacturers are concerned to extend the warranty of automotive while biodiesel/its blend with diesel are used as fuel.

Biodiesel is composed of different saturated and unsaturated fatty acid esters. The level of saturated and unsaturated components depends on the type of biodiesel feedstock. Fig. 2 shows the composition of different biodiesels. Unsaturated components in biodiesel chemically are more reactive. Based on the percentage of unsaturated components shown in Fig. 2, it can be said that palm and coconut biodiesel could be chemically more stable compared to others. In addition, the presence of oxygen makes it more aggressive to react with metal surface. The hygroscopic nature of biodiesel also leads to the formation of considerable amount of microorganism which alters its local chemistry [42]. Any chemical reactions occurring in biodiesel can change its fuel composition. It has been reported that biodiesel, being degraded can form different sort of acids, aldehyde, ketone, insoluble sediments etc. Formation of these compounds can greatly change its fuel properties including total acid number, viscosity, density, flash point, cetane number, etc. Degradation of these properties is directly related to engine performance and durability. For example, increased viscosity can cause fuel operation and atomization problem [2], thus increasing the tendency for coking of injector, sticking of moving parts, plugging of fuel filter, etc. Because of its instability, biodiesel is not yet being considered for commercial use in automobile engine. Interaction between biodiesel and engine oil is another concern in engine operation. During any engine operation, fuel will always penetrate into the sump (the lower part of the crankcase of an internal-combustion engine into which fuel can drain form a reservoir). The penetration of fuel is known as fuel dilution. Fuel dilution is more pronounced for in-cylinder diesel particulate filter (DPF) regeneration as post-injection of fuel to raise exhaust gas temperature in cylinder and burning off carbon-based deposits blocking diesel particulate filter (DPF) [6,43]. Biodiesel has lower volatility and causes sedimentation in the sump. As the blend ratio of biodiesel increased more with petroleum diesel in-cylinder, DPF regeneration can lead to higher fuel dilution [6]. In addition, oxidation instability of biodiesel leads to higher fuel dilution and increased viscosity of engine oil. Therefore, it is very important to study on the biodiesel stability influencing factors and necessary remedial measures to use it as an efficient and compatible diesel engine fuel.