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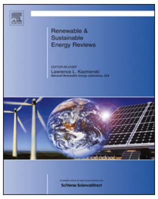

Effect of antioxidants on oxidation stability of biodiesel derived from vegetable and animal based feedstocks

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ABSTRACT

The increase of energy demand coped with utilization of fossil resources have engendered serious environmental impact. The progressively stringent worldwide emission legislation and increasing greenhouse gas emission require significant research effort on alternative fuels. Therefore, biodiesels are becoming important increasingly due to its ease in adaptation, environmental benefits and prospect in energy security. Biodiesel derived from vegetable oils, waste cooking oils and animal fats are long chain fatty acid alkyl esters, which contains unsaturated portions that are susceptible to oxidation. Biodiesel oxidation is a complex process having a number of mechanisms involved. Autoxidation radical chain reactions are the primary cause of biodiesel degradation that leads to formation of hydroperoxide, which, after that decompose to form an array of secondary oxidation products like aldehydes, ketones, carboxylic acids, oligomers, gum, sediment etc. Antioxidants are often used to inhibit biodiesel oxidative degradation. The present review attempts to cover the inhibition action of natural and synthetic antioxidants, methods used to analyze biodiesel oxidation and their effect on biodiesel derived from various feedstocks. Phenolic antioxidants are more effective compared to amine antioxidants. Pyrogallol is found to be the most effective antioxidant to improve the oxidation stability in case of almost all biodiesels reviewed.

Contents

Abbreviations: AO/AH, antioxidant; AOCS, American Oil Chemists' Society; BHT, butylated hydroxytoluene; BHA, butylated hydroxyanisole; CSOME, cottonseed oil methyl ester; CA, caffeic acid; DTBHQ, 2,5-di-*tert*-butyl-1,4-dihydroxybenzene; DPD, *N,N*′-diphenyl-*p*-phenylenediamine; EHN, 2-ethylhexyl nitrate; FA, feluric acid; FAAE, fatty acid alkyl ester; FAME, fatty acid methyl ester; FFA, free fatty acid; FTIR, Fourier transform infrared; h, hour; IB, Ionol BF200; IP, induction period; IPR, relative change in IP; MD, metal deactivator; NMR, nuclear magnetic resonance; OBPA, octylated butylated diphenyl amine; OS, oxidation/oxidative stability; OSI, oil stability index; OT, onset temperature; PDSC, pressurized differential scanning calorimetry; PG, propyl gallate; PY, Pyrogallol; TBHQ, *tert*-butylhydroxyquinone; TG, thermo gravimetric; UFOME, used frying oil methyl ester; YGME, Yellow grease methyl ester; α-T, α-Tocopherol

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1. Introduction

The replacement of fossil fuel-derived energy is one of the most pressing technological issues nowadays [1]. The detrimental impact on environment due to burning of fossil fuel, the unsteadiness in both demand and supply of fuels, and the rising cost of production of petroleum products are intensifying this issue. Thus, biofuels especially biodiesels are receiving significant attention because of these environmental as well as energy concerns [2–4]. The use of biodiesel is becoming popular due to its adaptation with current transportation infrastructure and requires minimal modification for its use [5,6].

Biodiesel, which refers to the fatty acid alkyl esters (FAAEs), are derived from lipid substances originated from vegetable oil, animal fats, waste greases, recycled cooking oils etc. In order to produce biodiesel, vegetable oils of edible source were treated as one of the potential feedstocks. However, due to criticism on edible-based oil use for fuel production, other sources e.g. non-edible oils of plant origin, waste fats with high free fatty acid (FFA) content etc. are now being used for biodiesel production. Researchers are also in quest for newer feedstock of biodiesel production [7–19]. Triglyceride molecules that are the main constituents of these oils are tranesterified with addition of alcohols, for example, methanol in presence of a suitable catalyst to form FAAE [10,13,20–27]. The fatty acid profile i.e. the chain length and the level of unsaturation of the produced FAAE corresponds to that of parent oil [28]. It is the fatty acid profile, which influences the physicochemical properties of biodiesel.

Fuel instability is the susceptibility of fuel to degradation processes by alteration of fatty acid composition that form undesirable species. Although biodiesel is thermodynamically stable, its instability primarily occurs from contact of oxygen present in the ambient air that is referred to as oxidative instability. The term ‘oxidation stability’(OS) is a general term, which differs from ‘storage stability’ and ‘thermal stability’, as the oxidative degradation may occur during extended storage period, transportation and end use [29]. Other instabilities of the fuel could occur if the fuel is exposed to air and/or light, experience higher temperature and if the presence of metallic compound incites catalytic degradation process. During shipping and use in transport vehicles, biodiesel come across different fuel line components, namely, fuel tank, feed pump, fuel lines, fuel filter, fuel pump, fuel injector cylinder, piston assembly, etc. which are made of various transition metals and elastomers [30,31], shows prooxidant behavior on it. As the oxidation occurs to biodiesel, a series of changes in its properties occurs. Properties like the density, kinematic viscosity, acid value, and peroxide value increase, while the iodine value and methyl esters content decrease [32]. Accelerated oxidation of biodiesel also results in an increase in polymer content that initiates the gum and sediments formation. It influences the corrosion of engine components, too through which the fuel comes in contact up to combustion chamber like injector, piston ring, piston liner, etc. [29,33–35]. Other physicochemical properties that are sensitive to biodiesel oxidation include cetane number, flash point, refractive index, and di-electric constant [36–38]. Biodiesel admixed in the lubricating oil during crankcase dilution tends to be persistent within it due to less volatility and begins to degrade and oxidize. This causes a significant increase in viscosity of the sump oil, thereby, resulting the decrease of performance, greater engine wear and necessitates a premature oil change [39].

Oxidation stability of biodiesel has been a subject of considerable research for last two decades [40–50]. Numerous methods, including various physicochemical properties like induction period, viscosity, iodine value, peroxide value and acid value monitoring, analyzing the methyl ester content, thermo gravimetric (TG) and pressurized differential scanning calorimetry (PDSC), nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), etc. have been applied in oxidation stability studies of biodiesel [32,51–55]. Several published articles focused on stability of biodiesel [46,56–62] without using antioxidants by monitoring the physicochemical properties which generally recommended the use of antioxidants for good storage stability. Some of the published articles also studied the stability of blends of biodiesel along with diesel [63–65]. The interesting part of antioxidants action is that its action depends on the fatty acid methyl ester (FAME) composition [66,67]. Previous reviews [37,68–70] on oxidation stability of biodiesel was focused on detailed discussion on oxidation mechanism, characterization of stability, effects of biodiesel oxidation in diesel engine operation and emission with little discussion on antioxidant chemistry. Hence, this article attempts to review the antioxidant inhibition mechanism on biodiesel and its effect on oxidative and storage stability of biodiesels derived from various feedstocks.

2. Oxidative degradation chemistry

Biodiesels are more susceptible to degradation compared to fossil diesel because of the presence of unsaturated fatty acid chain in it (carbon double binds C=C) [37,71]. The mechanisms of degradation are: (a) autoxidation in presence of atmospheric oxygen; (b) thermal or thermal-oxidative degradation from excess heat; (c) hydrolysis in presence of moisture or water during storage and in fuel lines; and (d) microbial contamination from contact with dust particles or water droplets containing fungi or bacteria into the fuel [37,38,49]. This degradation is exasperated if there is at least two or higher number of carbon double bonds (polyunsaturation) are extant in their fatty acid chains [72]. More than half of a century has been elapsed after the establishment of autoxidation mechanism of polyunsaturated fatty acids as a radical chain reaction [73–75]. This was followed by interpretation on role of antioxidants as inhibiting agent [76].