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Full Length Article

Evaluation of the oxidation stability of biodiesel stabilized with antioxidants using the Rancimat and PDSC methods

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ABSTRACT

In this study, both the standardized Rancimat and thermoanalytical pressure differential scanning calorimetry (PDSC) methods were employed to investigate the effects of antioxidants on the oxidation stability of biodiesel. The differences in the antioxidant effectiveness between these phenolic compounds could be clearly distinguished by both methods. Results revealed that the efficiency of antioxidant was highly dependent on the test conditions used in each method. Among the five antioxidants investigated, *tert*-butylhydroquinone (TBHQ) showed the highest sensitivity to different conditions between two methods: the highest oxidation stability in Rancimat vs. the lowest efficiency in PDSC. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) acted more efficiently in PDSC than in Rancimat due to lower volatilization losses, but not as well as pyrogallol (PY) and propyl gallate (PG) in increasing the oxidation stability of biodiesel. Results from isothermal and nonisothermal PDSC methods were basically consistent with each other with respect to the antioxidant efficiency: PY > PG > BHA, BHT > TBHQ. A positive linear relationship between results obtained from both methods could be observed within each type of antioxidant, but the overall correlation for the entire data set between Rancimat and PDSC was not as strong as that between isothermal and nonisothermal PDSC methods.

1. Introduction

Over the past few decades, biodiesel has received increasing attention as a renewable alternative biofuel. Biodiesel offers many advantages over conventional petrodiesel: inherent lubricity, non-toxic and biodegradable, free of sulfur and aromatics, higher cetane number and flash point, and lower exhaust emissions such as CO_2, CO, PM, and HC, excepting higher NOx emissions [1,2]. However, biodiesel is highly susceptible to oxidative degradation because of its high content of unsaturated methyl esters. The resistance of biodiesel against oxidation has long been a critical concern to fuel manufacturers, distributors and consumers, which depends not only on the fatty acid composition profile, but also on the production process and storage conditions [3,4]. During the long-term storage of biodiesel, the presence of light, oxygen, metal ions, high temperature, etc. should be avoided as much as possible [5].

Most of the biodiesel produced requires the use of antioxidants to meet the oxidation stability requirements set forth in ASTM D6751 (3 h) or EN 14214 (8 h) [6,7]. Addition of antioxidants to biodiesel could help slow down the process of oxidation caused by free radicals. Synthetic antioxidants are generally more preferred than natural antioxidants due to higher efficiency. The most commonly used in biodiesel are the following synthetic phenolic compounds: pyrogallol (PY), propyl gallate (PG), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and *tert*-butylhydroquinone (TBHQ). These antioxidants, more easily oxidized than biodiesel itself, could interrupt the chain propagation reactions by donating hydrogen atoms to peroxyl radicals from their phenolic hydroxyl groups, with the formation of less reactive antioxidant radicals that do not initiate another free radical or propagate the oxidation process [8].

To evaluate the antioxidant efficiency on the oxidative stability of biodiesel, the following accelerated oxidation methods are most often employed: Rancimat, EN 14112, the determination of oxidation products; PetroOXY, ASTM D7545, the determination of oxygen uptake; PDSC, ASTM D6186 and E2009, monitoring of the heat evolved during the oxidation reactions [9]. These methods provide elevated temperature and/or pressure to accelerate the oxidation reaction and shorten the experimental time. Although actual storage conditions are not truly reflected by these accelerated oxidation methods, the study of oxidation stability would take too long and be unfeasible without them.

Rancimat is the only accepted method by EN 14214 standard for assessing the oxidation stability of biodiesel. The induction period

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is determined by monitoring the continual increase of conductivity, which is mainly caused by the volatile secondary oxidation products, such as formic and acetic acids [10–12]. Usually, the longer the induction period, the better the oxidation stability. The biggest disadvantage to this method is the test duration being too long: a single test will require much more time than before given that the oxidation stability specification in the EN 14214 standard has increased from the earliest 6 h to the present 8 h. To shorten the time of analysis, raising the test temperature from 110 °C to 130 °C was suggested. However, higher temperatures could yield misleading results that do not accurately reflect antioxidant performances as some antioxidants, like BHA and BHT, could easily volatilize and decompose at higher temperatures [13,14].

PetroOXY provides a fast, safe and promising alternative for measuring the oxidation stability of biodiesel. The high pressure in this method could decrease the volatilization loss of additive and saturate the sample with oxygen. The induction period is determined by monitoring the pressure drop resulting from the consumption of oxygen in oxidation reactions, which corresponds to the time required to achieve a fixed (10%) pressure drop. The fuel sample can be subjected to more severe test conditions in PetroOXY than in Rancimat: there is a maximum pressure of approx. 1000 kPa when the temperature reaches 140 °C as per ASTM D7545. This method has shown good repeatability, reproducibility, and judgement between different replicates [15–18]. However, a minimum value of induction period using the PetroOXY method has not been accepted yet, and the correlation between PetroOXY and Rancimat is still under investigation [19–21]. Note that, this method is not the focus of this article; the correlation between Rancimat and PetroOXY will be explored in detail in a separate paper.

The thermoanalytical technique, PDSC, that directly measures the heat flow associated with chemical reactions, has been widely used over the past 25 years to investigate the thermooxidative stability of lubricating oils and greases, aviation turbine oils, vegetable oils and polymers [22]. This method can be run in an isothermal mode to give an oxidation induction time (ASTM D6186) or in a programmed temperature (nonisothermal) mode to give an oxidation onset temperature (ASTM E2009) [23]. The acceleration of autoxidation could be easily detected by this method: the heat flow remains stable prior to oxidation but rises sharply to the maximum exothermic peak when oxidation reaction begins. The high temperature and pressure recommended by ASTM E2009 and D6186 (130–210 °C, 500 psi) could effectively suppress the volatilization of sample materials and shorten the experimental time to minutes instead of hours. But these recommended parameters are not suitable for evaluating the oxidation stability of biodiesel due to the fundamental differences in the chemical structures between biodiesel and lubricants. Therefore, a prior selection of appropriate temperature and pressure is required to give a measurable induction time (isothermal mode) or onset temperature (nonisothermal mode): the induction time will either be impractically too short or too long when chosen at too high or too low temperature, respectively. Lower temperatures and pressures (110 °C, 200 or 80 psi) were most often employed in previous studies, in which the PDSC method demonstrated good indication of the oxidation stability of biodiesel [2,24–28].

A pilot study using the above mentioned three methods to investigate the oxidation stability of biodiesel was carried out by Murta Valle et al. in 2014 [27]. Results showed that the sensitivity of the oxidation stability of soybean oil biodiesel to the antioxidant concentration, bisphenol and phenol, was highly dependent on the method applied; PDSC presented better sensitivity and shorter analysis time as compared to Rancimat and PetroOXY. However, most research done to date have been limited to a single test method for assessing antioxidant efficiency [4,6,7,16]. There's not much attention paid to investigating the possible differences in the antioxidant efficiency between two or more methods, and few systematic research has been carried out to verify the dependence of the sensitivity of antioxidant efficiency on the applied method. Based on this background, the standardized Rancimat and promising PDSC methods were employed in this study to investigate the efficiency of the antioxidants on the oxidation stability of biodiesel, and attempts were also made to establish the correlation between these two methods with different test conditions.

2. Materials and methods

2.1. Materials

The waste cooking oil biodiesel was used in this study, which was provided by Chengdu Hengrun Hi-tech Co., Ltd., Sichuan, China. This biodiesel did not contain any antioxidant additives, and fulfilled the EN 14214 quality specifications with the exception of oxidation stability. The main chemical and physical properties of the fresh biodiesel were given as follows: viscosity at 40 °C, 4.20 mm^2/s; density at 15 °C, 0.878 g/cm^3; CFPP, 5 °C; flash point, 159 °C; cetane number, 54.0; sulfur content, <1 ppm; water content, 300 ppm; acid number, 0.37 mg KOH/g; copper strip corrosion (~3 h at 100 °C), 1.0; oxidation stability at 110 °C, 3.01 h. The following antioxidants, purchased from Aladdin Industrial Corporation (analytical grade), were investigated for their impacts on improving the oxidation stability of this biodiesel: PY, PG, BHA, BHT, and TBHQ. These antioxidants were added into the biodiesel at the concentration of 100, 250, 500, 750, and 1000 ppm (by weight), after which the treated biodiesel was kept in the dark at room temperature.

2.2. GC/MS analysis

The fatty acid composition of the waste cooking oil biodiesel was determined by gas chromatography/mass spectroscopy (GC/MS). The chromatographic analysis was performed on Agilent 7890A GC system (Agilent Technologies) equipped with a 5975C MSD and a HP-5MS UI column (30 m × 250 μm × 0.25 μm) using Helium as the carrier gas. The column temperature was held constant at 180 °C for 3 min, ramped to 200 °C at 1 °C/min, and then held at 200 °C for 2 min, and lastly at 20 °C/min to 250 °C, where it was kept for 2 min. The transfer line between GC and MS was kept at 260 °C. The EI mass spectra (70 eV) was acquired in the *m*/*z* range 10–400. The injection volume was 1 μl and a split ratio of 100:1 was employed. The biodiesel was dissolved in tetrahydrofuran and quantification analysis was performed by internal standard calibration using methyl heptadecanoate (Sigma-Aldrich). The fatty acid profile of this biodiesel was presented as follows: myristic acid (C14:0), 0.59%; palmitic acid (C16:0), 15.53%; palmitoleic acid (C16:1), 1.27%; stearic acid (C18:0), 6.80%; oleic acid (C18:1), 41.53%; linoleic acid (C18:2), 27.78%; linolenic acid (C18:3), 1.10%; arachidic acid (C20:0), 0.41%; eicosenoic acid (C20:1), 1.44%; behenic acid (C22:0), 0.24%; erucic acid (C22:1), 2.27%.

2.3. PDSC method

The PDSC measurements were carried out using a DSC Q2000 TA Instruments, coupled to a pressure cell. The instrument was calibrated with high-purity indium before test. Approximately 3 ± 0.3 mg sample was carefully weighed in an open aluminum pan and placed in the equipment's sample chamber, and an identical empty pan was placed on the rear platform as a reference. The