



Storage stability of commercially available biodiesels and their blends under different storage conditions



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HIGHLIGHTS

- Acid values increased but induction time decreased for samples without copper.
- Copper affected the measurement of acid value and induction time.
- Water did not significantly alter acid values and induction time for all samples.
- Presence of any impurities did not affect the degradation rates of FAMES.
- FAMES in blended samples degraded faster than that in pure biodiesels.

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ABSTRACT

The present study investigated the storage stability of two commercially available biodiesels and their blends with diesel spiked with different impurities, which were stored at two different temperatures (15 and 40 °C) with air tight and light screen. These samples were periodically monitored during the whole storage period by measuring a number of properties, such as acid value (AV), induction time (IT) and composition of fatty acid methyl esters (FAMES). It was found that (1) acid values increased but induction time decreased with the extension of storage for all samples without copper; however, both IT and AV values kept nearly constant for all samples with copper; (2) the presence of water did not contribute significantly to the degradation of all tested samples over time; and (3) higher temperature (40 °C) was favorable to the degradation of unsaturated FAMES, accompanying with the altered acid values and induction time in comparison with the same samples stored at 15 °C. Faster degradation of FAMES in blended samples than those in pure biodiesels may be partially due to the diluting effects of antioxidants in biodiesel. However, the presence of any impurities did not affect the degradation rates of FAMES, which was not in agreement with the above mentioned AV and IT time series. This suggested that the addition of copper affected the measurement of AV and IT. Therefore, for samples with copper, FAME profiles can represent their quality more appropriately than IT or AV.

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1. Introduction

Biodiesel, as an alternative diesel fuel consisting of alkyl monoesters of fatty acids prepared from vegetable oils or animal fats, has attracted more and more focuses because it is renewable and envi-

ronmental-friendly. Storage stability of fuel is the ability of liquid fuel to resist change in its physical and chemical characteristics brought about by its interaction with its environment [1]. However, biodiesel can be very sensitive to oxidative and thermal degradation due to its chemical structure, especially for polyunsaturated fatty acid alkyl esters, they are very susceptible to degradation, polymerization and gum formation caused by oxidation during storage or by complex oxidative and thermal polymerization at the higher temperature and pressure of combustion. The oxidation can result in the formation of corrosive acids and deposits, which may cause increased wearing engine fuel pumps. Therefore, the long-term storage conditions is a key issue for its markets concerning.

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The deterioration of biodiesels under different storage conditions has been investigated by evaluating several commonly-used physicochemical parameters, such as, peroxide values (PV), acid value (AV), iodine value (IV) viscosity (ν), insoluble impurities (II) [1–4], and total fatty acid methyl ester (FAME) concentration [2]. It is generally concluded that the storage stability of biodiesel is a very complex process that is affected by a variety of factors, which includes the composition of the fuel itself and conditions of storage, such as: the exposure to air, light, water, metal contaminants, and temperature [1,2,5–7]. Bouaid et al. [1] found that AV, PV, ν , and II increased, while IV decreased with increasing the storage time of freshly-prepared biodiesel samples. However, the difference between samples exposed and not exposed to daylight became significantly after 12-month-storage. High temperature (e.g., 40 °C) combined with air exposure was considered to accelerate the degradation of biodiesel greatly relative to those stored at lower temperature (5 or 20 °C) [2]. Contact with metallic materials such as copper, zinc, lead, tin and bronze will increase the rate of degradation through metal catalyzed oxidation [5,8]. Therefore, care was taken to ensure that fuel was stored in a container that would not facilitate degradation. The presence of water in biodiesel may deteriorate the fuel quality [9–11] by decreasing the heat of combustion, due to the incomplete combustion and decreased percentage of combustible components. The presence of water will also cause engine corrosion and the development of microbe colonies which can plug fuel system. At the same time, some researchers [12–14] have tried to increase the oxidation stability of biodiesel by adding various synthetic antioxidants.

Unfortunately, most above research focused on the freshly-prepared, not on commercially available biodiesels [15,16], therefore, no synthetic antioxidants were present in these studied samples. For commercially available biodiesels, they are generally mixed with diesel to be used; some natural and synthetic antioxidants have been added for improving the oxidative stability of the final products. In 2003, Bondioli et al. [6] simulated the biodiesel stability under commercial storage conditions over year, where samples were also self-made. Recently, Karavalakis et al. [17] evaluated the impact of biodiesel source material and biodiesel concentration in diesel fuel on the stability of the final blends with commercially available biodiesels and diesels. Therefore, very few studies have focused on the storage stability of commercially available biodiesel and biodiesel/diesel blends with long term storage under different conditions. For example, the effect of impurities on their physicochemical properties, and the relationship between the variations of induction time (IT) or AV and FAME composition over storage time are still necessary to be fully understood. Furthermore, the reliability of using IT or AV to express the oxidative stability of biodiesel and its blends with diesel is still pending, especially for some specific samples.

In order to clearly understand the aging mechanism of biodiesel and biodiesel/diesel blends over long term storage, the storage stability of commercially available biodiesel products from two feedstocks (soybean and canola oil) and the corresponding blends with diesel under different storage conditions were evaluated by simulating different storage conditions in the present study. The variation of petroleum hydrocarbons, FAME composition, induction time and acid value were compared at predetermined time intervals. The effects of the storage temperature, impurities and oil types on above mentioned parameters were evaluated. The feasibility of using above physicochemical properties to assess the stability of biodiesel and its blends was verified. This work is very important because it substantially enriches the knowledge on the storage stability of the finished biodiesel and its blends with diesel based on the variation of several physicochemical parameters and FAME composition.

2. Experimental procedures

2.1. Materials and chemicals

The solvents used (including hexane, dichloromethane (DCM), acetonitrile, and methanol) were obtained from Caledon (Georgetown, ON, Canada) at the highest purity available and used without further purification. Silica gel (100–200 meshes) was obtained from Sigma–Aldrich (Milwaukee, WI, USA).

Normal alkane calibration standards from n -C₉ to n -C₃₆, 5 α -androstane, and polycyclic aromatic hydrocarbons (PAHs) calibration certified standard mixtures were purchased from Restek (Bellefonte, PA, USA) and the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), respectively. Deuterated internal and surrogate n -C₂₄- d_{50} (C₂₄D₅₀), PAH standards including [²H₁₄] terphenyl (terphenyl- d_{14}), [²H₈] naphthalene (naphthalene- d_8), [²H₁₀] acenaphthene (acenaphthene- d_{10}), [²H₁₀] phenanthrene (phenanthrene- d_{10}), [²H₁₂] benz [a] anthracene (benz [a] anthracene- d_{12}), and [²H₁₂] perylene (perylene- d_{12}) were purchased from Supelco (Bellefonte, PA, USA). And biomarkers terpane and sterane standards were obtained from Chiron (Trondheim, Norway).

FAME mixtures including 37 FAME standards ranged from C₆ to C₂₄ with different saturated degree, surrogates (13-methyl, methyl myristate (13-methyl, C14:0)), and internal standards (methyl heptadecanoate (C17:0)) purchased from Sigma–Aldrich (Bellefonte, PA, USA) were employed for identification and quantification of target FAMES. Refer to Ref. [18] for the detailed chemical information for FAME standards used for calibration and identification, including their composition, formula, shortened name/synonym, molecular weight, CAS number, and quantitation ions.

Two biodiesel samples sourced from soybean and canola oil and one commercial ultra low sulfur diesel (ULSD) sample were supplied by a commercial supplier in Canada. All of them and their physicochemical properties were generously provided by Debbie Rosenblatt of the Emissions Research and Measurement Division of Environment Canada. Their physicochemical properties and the corresponding standard measurement methods are described in the supporting Tables 1 and 2. All samples were stored in a dark cold room at 4 °C to avoid storage degradation.

2.2. The preparation of fuel mixtures

The ULSD was well characterized prior to experiments [18]. Two pure biodiesel (B100) samples sourced from canola oil and soybean oil were designated as B100_{can} and B100_{soy}, respectively. Biodiesel blends, B20_{soy} and B20_{can}, were prepared by mixing 20% biodiesel with 80% diesel by volume. The densities of the ULSD, B100_{can}, and B100_{soy} were determined to be 0.904, 0.899, and 0.864 g/mL, respectively. The samples used for the exposure experiments included the following set of four biodiesels: B100_{can}, B100_{soy}, B20_{can}, and B20_{soy}. ULSD was also used to act as a control sample to assess the variation of petroleum hydrocarbon during the storage test.

2.3. Storage test procedures

Each set of sample was divided into 8 samples with 500 mL each. These 8 samples were further divided into two groups in two temperature-controlled shakers (15 °C and 40 °C). Each group consisted of 4 samples: the first sample was stored directly; the second sample was spiked with 5% (mass/mass) water, the third sample was spiked with 5% copper granule (–10 to +40 mesh), the fourth sample was spiked with 5% of water and 5% copper granule (mass percent). Two pure ULSD samples without any spiking

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