



## Research article

## Re-additization of commercial biodiesel blends during long-term storage

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## ABSTRACT

Commercial biodiesel blends were aged at 43 °C while monitoring stability. The oxidation stability—or oxidation reserve expressed as Rancimat induction period (IP)—gradually decreased from its initial value. At a pre-determined IP threshold, an antioxidant was used to restore IP to the ASTM D7467 specification minimum of 6 h, referred to as re-additization. At lower IP values, the amount of antioxidant required increased significantly, and the effectiveness tended to be reduced. Once IP fell to essentially zero, the acid content increased to above the allowable limit and insoluble material was also detected. Storage life was increased relative to the as-received fuels as evidenced by longer time to produce acids. Experience in the field may vary based on storage conditions; however, these results indicate re-additization can significantly increase storage life of biodiesel blends when used with regular monitoring of IP and acid number. An assessment of the storage stability of the as-received fuels showed that the initial IP did not predict storage behavior, although fuels above the specification minimum remained stable for > 12 weeks accelerated aging (1 year simulated).

## 1. Introduction

Biodiesel is a renewable compression-ignition fuel blendstock derived from fats and oils [1,2]. The triglycerides that compose the oils are converted to alkyl esters via transesterification with an alcohol, most often methanol, yielding fatty acid methyl esters (FAMES) [3]. This product retains the fatty acid carbon chains of the triglycerides, which tend to be a combination of saturated and unsaturated chains [4]. Unsaturated carbon chains, particularly polyunsaturated chains, are susceptible to oxidation under mild conditions when exposed to air over time (autoxidation) [5,6]. If oxidation occurs to a large enough degree, it can lead to deleterious changes in fuel properties, such as the production of acids and insoluble polymers [7–9]. This is of concern for fuel storage, given that acids can cause corrosion of storage tanks and engine fuel systems [10,11] and insoluble materials can cause filter blocking and injector fouling [12].

The ability of a fuel to resist changes in physico-chemical properties caused by interaction with the environment is known as its storage stability [9]. The length of time biodiesels and blends with hydrocarbon diesel can be stored before problematic changes occur (storage life or shelf life) is largely dependent on its rate of oxidation, which depends on many factors that are related to both fuel properties and storage conditions [13,14]. The most reactive sites in the fatty acid structure are adjacent to two unsaturated carbons, known as bis-allylic positions; therefore, the concentration of polyunsaturated esters has a large influence on stability [15,16]. Antioxidant additives slow the process of

oxidation by interrupting the free radical mechanism, increasing storage life [9,17–24]. Sustained exposure to heat, air, light, or oxidizing metals accelerates oxidation and reduces storage life [9,13,17,22,25–27]. The overall stability can be thought of qualitatively as the oxidation reserve, the proportionality of factors that prevent oxidation to those that promote it [28].

## Oxidation Reserve

$$\propto \frac{\text{Antioxidant Concentration}}{\text{Radical Initiator Concentration} + \text{Bisallylic Site Concentration}}$$

The inherent oxidation reserve of biodiesel and biodiesel blends is assessed by test method EN 15751 (commonly known as the Rancimat test, or oxidation stability index) in which a sample is exposed to heat and air to accelerate oxidation and generate degradation products. An induction period (IP) is reached once the sample has broken down to form volatile acids, expressed in hours (h). The higher the IP value, the greater the resistance to oxidation or the greater the inherent oxidation reserve. Oxidation stability measured by this test is specified in US specifications ASTM D6751 for biodiesel at a minimum of 3 h and in ASTM D7467 for B6–B20 blends at a minimum of 6 h. These limits have been established to ensure biodiesel blends have sufficient stability to prevent problematic changes during normal storage for up to 6 months [29].

The majority of diesel fuel is consumed relatively soon after production, but some low-use applications require longer-term storage, i.e., longer than one year. Storing diesel fuel for longer than one year

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requires additional considerations to ensure adequate fuel quality at the time of use, including high initial oxidation reserve and monitoring for signs of degradation during storage [30]. Long-term storage of biodiesel and its blends raises some concerns given differences in oxidation stability relative to hydrocarbon diesel. Although chemical or physical property limits that indicate the end of storage life of biodiesel have not been well defined, a limit on the acid number (also called total acid number) is included in the ASTM specifications. ASTM D6751 limits the acid number of pure biodiesel to a maximum of 0.5 mg KOH/g, and ASTM D7467 limits B6–B20 blends with hydrocarbon diesel to 0.3 mg KOH/g. These limits are included to ensure free fatty acids have been removed during production; however, it is recommended that the acid number be monitored for increases during long-term storage to detect evidence of oxidation [2,29]. An acid number increase to above the specification limit as a result of oxidation indicates that a fuel is no longer fit for use. For example, Bouilly and coworkers studied injector failure when operating on oxidized B20s [12]. Although they found that acid number did not correlate well with injector failure time, their results showed that failures occurred after the acid number had increased above 0.3 mg KOH/g and IP had fallen below 3 h. In another study, biodiesel blends stored in vehicle fuel tanks in a hot climate were shown to be equivalent to a hydrocarbon diesel when the acid number remained below the limit of 0.3 mg KOH/g and IP remained above 3 h; high-pressure fuel pumps showed no signs of abnormal wear and filters showed no signs of deposits when operating on the stored fuel [31]. A practical limit for defining the storage life of biodiesel and blends would therefore be the acid number limit included in the specifications.

Studies on the long-term storage of pure biodiesel have demonstrated 6 months to one year prior to out-of-specification acid number with adequate initial oxidation reserve [13,14,20,26,32]. Tang and coworkers found that with the use of antioxidants soybean-based biodiesel could be stored up to 30 months prior to detecting high acid number [33]. Biodiesels having low oxidation reserve can become problematic in much shorter timeframes, within 4 months [8], but the use of antioxidants has been shown to be effective at stabilizing low IP samples and increasing storage life [21,22,34]. Re-additization—adding antioxidants after detecting a decrease in IP—was studied by Christensen and coworkers and shown to be effective at increasing B100 biodiesel storage life [28].

Pure biodiesel is not typically stored for long periods as it is primarily used as a blend with hydrocarbon diesel. Blending biodiesel with hydrocarbon diesel tends to improve its stability significantly [35]. The stability of a blend is largely influenced by the stability of the biodiesel and blend concentration [36]. Studies of biodiesel blend storage stability have used accelerated testing, given the longer storage lives encountered with primarily hydrocarbon fuels, following ASTM method D4625 for storage stability of middle distillate fuels [8,28]. In this test, the fuel is kept in vented glass jars in an oven at a constant temperature of  $43\text{ °C} \pm 1\text{ °C}$ . This test method states that at this temperature, the rate of oxidation is accelerated roughly by a factor of four compared to storage at a constant ambient temperature of  $21\text{ °C}$ , which the method describes as normal ambient conditions. One week of this test being approximately equivalent to one month in “typical” storage conditions [37]. This method was developed to evaluate potential storage stability of diesel fuels prior to the advent of ultra-low sulfur diesel or biodiesel. Currently, this fourfold acceleration in aging has not been verified with modern fuels. Additionally, given the large influence of environmental factors that vary depending on the storage scenario, such as heat, air exposure, fuel tank materials, and contamination, storage life may vary considerably in the field compared to a laboratory test. However, this test method provides a consistent basis for evaluating the storage stability of diesel-range fuels. The results from this test – 1 week accelerated simulating 1 month – will be referred to as potential storage life.

Accelerated tests have shown that blends prepared with biodiesel having an initial IP  $\geq 3$  h result in B5 and B20 blends with sufficient

stability for storage lives  $> 12$  weeks (a simulated year of storage), but blends prepared with low-IP biodiesel had high acid number within 6 weeks (simulated 6 months) [8]. Blends prepared with biodiesel having an IP of 6 h resulted in B5 and B20 blends that still met the IP minimum for blends by the end of 36 weeks of accelerated aging, simulating storage stability of  $> 3$  years [28]. Yang and coworkers studied storage of B20 blends at  $15\text{ °C}$  and  $40\text{ °C}$  in which blends prepared with biodiesel having IP  $> 5$  h remained below the acid number limit after 300 days of storage at both temperatures, indicating the storage lives of these fuels were longer than the time studied [38].

Previous studies on biodiesel and blend stability have shown promising results for long-term storage with lab-prepared blends. It has been demonstrated that high oxidation reserve indicates longer storage lives, potentially allowing for blends to be stored for multiple years without problematic changes to fuel properties. Here we report on the long-term storage stability of commercial biodiesel blends collected from across the United States. During storage, the potential for stabilization via re-additization is explored with addition of an antioxidant at pre-determined IP thresholds followed by continued aging.

## 2. Experimental

### 2.1. Biodiesel blends

Twelve nominally 20% biodiesel blends (B20s) were collected from 12 different states, and one sample was prepared in the lab using a distilled B100 and a biodiesel-free hydrocarbon diesel (B0). Blends were tested for ASTM specification D7467 properties; these results are provided in Table 1. The test methods listed in Table 1 were followed as written except for peroxide number; ASTM D3703 was modified for endpoint detection by potentiometry in place of colorimetric titration. Properties of the distilled B100 and B0 were reported previously [31] and are provided in the supporting information in Table S1. Sample A did not meet the minimum value for oxidation stability. This sample met the specification for acid number, indicating the fuel had not yet degraded, so was included in storage stability experiments.

FAME profiles of biodiesels in the blends were determined using heart-cutting two-dimensional (2D) gas chromatography (GC) using the GC parameters described by McCurry and Wang [39]. Samples were prepared according to method EN 14103 for determination of ester content of biodiesel. The samples were injected onto an Agilent 7890A GC equipped with a Deans Switch microfluidic valve. A non-polar column (DB-5;  $15\text{ m} \times 0.25\text{ mm ID} \times 0.1\text{ }\mu\text{m}$ ) was used for initial separation, and FAMES were transferred to a polar column (HP-INNOWax  $30\text{ m} \times 0.25\text{ mm ID} \times 0.5\text{ }\mu\text{m}$ ) using the Deans Switch for separation from hydrocarbons. FAMES were then quantified using the procedure of EN 14103. FAME profiles are provided in Table 2 along with the calculated bis-allylic position equivalents (BAPE). This value indicates the number of positions on the polyunsaturated FAME molecules, which are susceptible to oxidation, providing a relative measure of reactivity [40]:

$$\text{BAPE} = \%C18: 2 + 2 \times \%C18: 3$$

To place the BAPE values in context, a typical soy-derived biodiesel would have a BAPE of approximately 60 to 75, a canola-derived biodiesel would have a BAPE between 30 and 40, and a pure tallow-derived biodiesel would typically have a BAPE below 10 [41].

### 2.2. Storage stability and re-additization

Each as-received B20 was subdivided into three separate 400 mL aliquots that were held in vented 500-mL glass jars in an oven at  $43\text{ °C}$ , per ASTM method D4625 to assess middle distillate storage stability. Sample D was tested in duplicate (six jars). Samples were tested monthly by EN 15751 to track changes in IP. When IP reached  $< 4$  h, one jar was removed from the oven and re-additized with butylated hydroxytoluene (BHT, purchased from Sigma Aldrich), to a

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