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Research article

Improvement on oxidation and storage stability of biodiesel derived from an emerging feedstock camelina

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ABSTRACT

Camelina is recognized as a promising feedstock for biodiesel production. Similarly to biodiesel derived from other vegetable oils, the oxidative stability is not satisfactory. This issue can be addressed by treating biodiesel with synthetic antioxidants to increase its resistance to oxidation. This study examined the effectiveness of four commonly used antioxidants, butylated hydroxytoluene (BHT), butylated hydroxyanisol (BHA), tert-butylhydrooquinone (TBHQ) and propyl gallate (PrG) on both oxidation stability and storage stability of camelina biodiesel. The antioxidative activity of four antioxidants was found to be in the order of BHA < BHT < PrG < TBHQ; The oil stability index (OSI) of camelina biodiesel was increased (≥8 h), meeting the stability requirement regulated in EN 14214:2014, through adding either 2000 ppm BHT, 1000 ppm PrG or 1000 ppm TBHQ. Regarding the long term storage, it was predicted that treating camelina biodiesel with 3000 ppm TBHQ was enable satisfactory oxidation stability to be maintained for one year.

1. Introduction

Biodiesel, a renewable, biodegradable and environmentally innocuous biofuel, has attracted great interest as a promising substitute for petro-diesel. Biodiesel is typically defined as a mixture of fatty acid alkyl esters obtained through a transesterification process. Currently, >95% of biodiesel worldwide is derived from traditionally edible vegetable oils such as soybean, canola and sunflower [1,2]; however, this competes with the food and feed supply, raising a heated debate on "fuel vs food". Numerous efforts have been made to evaluate the feasibility of biodiesel production from alternative oil crops that are less competitive with traditional oil crops, including *Adansonia digitata L.* [3], *Hodgsonia macrocarpa* [4], *Hibiscus esculentus* [5], *Jatropha curcas* [6], and *Sapindus mukorossi* etc. [7].

Recent research has recognized *Camelina sativa* as a promising and sustainable oilseed crop for biodiesel production in North America [8–11]. Camelina seed has a high oil content (35–43% on a dry matter basis), a short growing season, and is tolerant to drought, cool weather and insect pests, thus it becomes a favourable low-cost feedstock for biodiesel production [12,13]. The camelina oil yield can be expected to be between 500 and 700 L per hectare [14,15]. The price of biodiesel derived from plant oils is generally higher than that of petroleum diesel [16] and risk-averse farmers would grow camelina for biodiesel production if the price of petro-diesel equals or exceeds $1.31 per liter [17]. Our previous work has demonstrated that a high camelina biodiesel product yield (97%) with a fatty acid methyl ester (FAME) purity of 98.9% could be achieved through an one-step alkali-catalyzed transesterification process under optimum reaction condition settings [18]. Most of the fuel properties of camelina biodiesel were in agreement with the American Society for Testing and Materials (ASTM D6751) and European Committee for Standardization (CEN EN14214) standard specifications; however, the oxidative stability of camelina biodiesel was not satisfactory due to a high percentage of unsaturated fatty acids (about 90%) in the camelina oil such as linolenic acid (C18:3; 32.6–38.2 wt.%), linoleic acid (C18:2; 16.9–19.6 wt.%), oleic acid (C18:1; 14.5–19.7 wt.%) and gadoleic acid (C20:1; 12.4–16.2 wt.%) [15,19].

Biodiesel is generally more sensitive to oxidative degradation than petro-diesel and this has become a major drawback of biodiesel derived from vegetable oils. This is attributed to an inherently high percentage of unsaturated long chain fatty acids in the parent vegetable oils, which is highly susceptible to oxidation [20–22]. The rate of biodiesel oxidation is dependent on the number of allylic and bis-allylic sites in the unsaturated fatty acid ester chains [23,24]. Oxygen is able to readily attach to those reactive allylic and *bis*-allylic sites, and therefore initiates the primary free-radical chain reaction and forms intermediate compounds (hydroperoxides). On the stage of the secondary oxidation, the resulting hydroperoxides are further decomposed, forming volatile organic acids, alcohols, ketones, and aldehydes etc. [25] There are a number of measures used to assess the oxidation stability of biodiesel, including iodine value (IV), peroxide value (PV), oil stability index (OSI) and induction period (IP) [26]. The newly released European

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biodiesel standard (EN 14214:2014) specifies an accelerated biodiesel oxidation testing method, which requires a determination of the oxidative stability of biodiesel at 110 °C with a minimum induction time of 8 h by the Rancimat method. The parameter of OSI is equivalent to IP, which can be tested by an oxidative stability instrument as described in the American Oil Chemists' Society (AOCS) method Cd 12b-92 [21,27,28]. The OSI testing method monitors the appearance of the secondary products from oil degradation. It is conducted under an isothermal condition (110 °C) while purging a steady stream of dry air through the oil sample, the oil degradation takes place and its secondary products (such as volatile organic acids) are swept into a test tube containing deionized water and a conductivity probe. The conductivity of water is periodically measured and the OSI is defined as the time point where maximum conductivity of water is reached [21]. Alternatively, PV is also commonly used to evaluate the oxidation stability of oil through the determination of the amount of primary oxidation products (such as hydroperoxides) by titration or other testing methods. Although the PV provides information concerning the extent of oil oxidation, it might not be suitable for monitoring oil or biodiesel storage stability over a long period of time. This is because the PV tends to increase at the early stage of oxidation and then decreases as hydroperoxides further decompose to the secondary oxidation products [29].

The long term storage stability of biodiesel is defined as how well it will resist to changes caused by the external storage environment. During long term storage, autoxidation of biodiesel is initiated by air exposure [30], excessive metals [28], storage tank [31] resulting in legitimate concerns with respect to monitoring and maintaining fuel quality. The ASTM D4625 (Diesel Storage Stability at 43 °C) has been reported as a reliable aging method to monitor biodiesel quality during storage [32–34]. Bondioli et al. [33] stated that the ASTM D4625 was generally recognized as the best way to simulate storage behaviour. However, this aging method is not suitable for biodiesel quality control because of its relatively long aging time (4–24 weeks). In 2004, Bondioli et al. [35] proposed a quick testing method to predict biodiesel storage stability. The method uses a modified Rancimat apparatus to speed up the rate of the aging processes by exposing 3 g of biodiesel sample at 80 °C with an airflow rate of 10 L/h for 24 h.

Biodiesel properties such as acid number, kinematic viscosity, OSI and PV of biodiesel are also adversely or unfavorably changed by the extensive degradation during storage [29,31]; Polymers generated from the biodiesel oxidation process could clog fuel lines and pumps [36]. Hence, eliminating the undesirable effect of fuel autoxidation on the biodiesel quality is critically important for biodiesel fuel producers, suppliers and consumers [21]. Treating biodiesel with oxidation inhibitors (antioxidants) is a common and effective approach used by the edible vegetable oil and biodiesel industry to increase autoxidation resistance [20,21,37,38]. There are generally two groups of antioxidants. Antioxidants which occur naturally in vegetable oils, such as tocopherols, are called natural antioxidants. The types and concentration of natural antioxidants existing in biodiesel vary with feedstocks and oil refinery processes [39]. Synthetic antioxidants are derived from petroleum and have been utilized to improve the oxidation and storage stability of biodiesel, such as butylated hydroxytoluene (BHT), butylated hydroxyanisol (BHA), *tert*-butylhydrooquinone (TBHQ) and propyl gallate (PrG) [20,27,40]. The chemical structures of these commonly used antioxidants are illustrated in Fig. 1.

Those synthetic antioxidants are able to stop the free radical chain reaction and thus delay the oxidation initiation as their active hydroxyl groups (—OH) provide protons for the oxidized free radicals and form stable radicals. Dunn [27] reported that PrG, BHT and BHA were the most effective antioxidants for stabilizing soybean biodiesel, while *a*-Tocopherol was recognized as the least effective one. This study indicated that 3000 ppm of BHA added to biodiesel could sufficiently suppress the auto-oxidation during long term storage. However, Liang et al. [41] reported that adding only 50 ppm TBHQ was enough to obtain satisfactory oxidation stability of palm oil biodiesel. Osawa et al. [40]

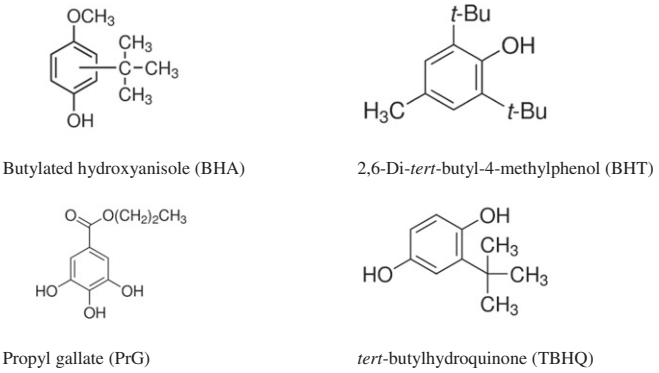

Fig. 1. The chemical structures of synthetic antioxidants (BHA, BHT, PrG and TBHQ).

demonstrated that the oxidation stability index of *Croton megalocarpus* biodiesel treated with 1000 ppm PrG and BHA decreased by 12.2% and 20.59% respectively after 8 weeks' storage. Several reviews also illustrated that the effectiveness of antioxidants on oxidation and storage stability of biodiesel largely depended on the concentration of the antioxidants, the unsaturation degree of FAMEs, storage conditions and the presence of metal etc. [21,24,25,36]. Supriyono et al. [26] suggested that dedicated studies should be conducted to determine the appropriate type and concentration of antioxidants when considering the use of antioxidants for improving oxidation and storage stability of biodiesel derived from different parent oils.

The oil stability index (OSI) of camelina biodiesel determined in our previous work [15] was 1.9 h, much lower than a minimum value of 3 h and a minimum value of 8 h specified in ASTM D6751 and EN 14214 respectively. However, to our knowledge, there is no research with a focus on the stability improvement of camelina biodiesel in the literature. Moreover, most studies related to biodiesel stability only focused on either oxidation stability or storage stability. The objective of the present work is to comprehensively evaluate the effects of synthetic antioxidants (BHA, BHT, PrG and TBHQ) with varying loading concentrations (from 500 ppm to 3000 ppm) on both oxidation stability and storage stability of camelina biodiesel. OSI and PV parameters were used for assessing the stability of biodiesel, and the suitable dosage of the most effective antioxidant was determined. This research would provide valuable information for commercial applications of this emerging biodiesel feedstock in the near future.

2. Materials and methods

2.1. Materials

Camelina oil was cold pressed from *Camelina sativa* L. Crantz CDI007 seeds grown in Canning, Nova Scotia, Canada. Potassium hydroxide in the form of pellet, 1 N hydrochloride (HCl), analytical grade methanol, spectroscopy grade isooctane, isopropanol and butanol were purchased from Fisher Scientific Ltd. Canada. Cumene hydroperoxides, ammonium thiocyanate, barium chloride ($BaCl_2$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), butylated hydroxyanisole (BHA), 2, 6-Di-*tert*-butyl-4-methylphenol (BHT), propyl gallate (PrG), *tert*-butylhydroquinone (TBHQ) were purchased from Sigma Aldrich, Canada. A standard reference solution of camelina methyl esters (GLC 937, >99%) was purchased from Nu-Chek Prep. Inc. USA.

2.2. Characterization of fatty acid composition of camelina oil

Camelina oil was methylated according to ISO 5509 standard (Animal and vegetable fats and oils - Preparation of methyl esters of fatty acids). As such prepared sample was injected into an Agilent 7890A GC equipped with a Flame Ionization Detector (FID) at 260 °C and an Agilent DB-23 column (50%-Cyanopropyl-methylpolysiloxane; 30 m