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Influence of blending soybean, sunflower, colza, corn, cottonseed, and residual cooking oil methyl biodiesels on the oxidation stability

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HIGHLIGHTS

- Biodiesels with low oxidation stability (OS) were blended with soybean biodiesel.
- Residual cooking oil and cottonseed oil biodiesels had their OS improved.
- Sunflower oil biodiesel had its OS improved by blending with colza oil biodiesel.
- Binaries mixtures meet ASTM D6751 and EN 14214 requirements of OS values.

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ABSTRACT

Binary mixtures of soybean (SbMB), sunflower (SfMB), colza (CzMB), corn (CoMB), cottonseed (CsMB), and residual cooking oil (RMB) methyl biodiesels were prepared and the oxidation stability (induction period, IP) was measured. CoMB, SbMB, and particularly CzMB improved the oxidation stability of the binary mixtures, which was in agreement with measurements of polyunsaturated fatty acid content and antioxidants (TBHQ) originating from the vegetable oils used for biodiesel production. The oxidation stability of biodiesels with low oxidation stability such as CsMB and RMB was improved through blending with 90% (w/w) SbMB to satisfy EN 14214 (IP > 6 h). Considering ASTM D6751 (IP > 3 h), the oxidation stability of SfMB (0.88 h) was improved by blending with 60% (w/w) SbMB while RMB only required 10% (w/w) SbMB in order to attend ASTM requirements. CzMB presented the highest IP value and therefore is the most effective blender to biodiesels with low oxidation stability. On the other hand, soybean oil is one of the major feedstocks for biodiesel production in the world and the use of SbMB as a common blending to other biodiesels such as CsMB, RMB and SfMB is demonstrated to be an alternative solution to prepare biofuels with improved oxidation stability.

1. Introduction

Biofuels originating from renewable sources are considered emerging alternatives to fossil fuels due to economic, social and environmental advantages. Biodiesel is a renewable fuel composed of a mixture of saturated and unsaturated esters typically produced by the transesterification reaction of vegetable oils, animal fat or waste cooking oil with short chain alcohols, such as methanol or ethanol, in the presence of a catalyst [1].

Brazil has a wide diversity of fauna and flora thus the country has a large variety of potential feedstock for biodiesel production [2]. Most biodiesel produced in Brazil is obtained from soybean oil; however, the Brazilian production is not enough to fulfill the demands for food and energy simultaneously. Therefore, other oil sources have been exploited for biodiesel production such as sunflower, soybean, colza, cottonseed due to its favorable physical–chemical properties [3–5].

Although biodiesel is considered chemically stable, its chemical properties can be altered during storage and transportation. The presence of unsaturated fatty acids in vegetable oils, animal fat or recycled oils contributes proportionally to oxidation instability of biodiesels [6,7]. Oxidation processes are accelerated in the presence of water and oxygen (exposure to air), heat and light (environmental conditions), and trace metals from corrosion of containers and automotive materials [8]. As a result of oxidation processes, increase in viscosity, density and polymer content in biodiesel occurs.

For this reason, the measurement of oxidation stability is one of the required parameters for the quality control of biodiesel established by the European norm (EN 14214). A minimum of 6 h of induction period (IP) measured by a Rancimat equipment is

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obligatory for further distribution of biodiesels [7]. The increase in oxidation stability of biodiesels can be obtained by adding antioxidants [4–10]. Synthetic phenolic antioxidants have been reported to be efficient on the enhancement of oxidation stability of different biodiesels with special attention to tert-butylhydroquinone (TBHQ) as the most efficient antioxidant for B100 (100 % v/v biodiesel) [4–10]. Phenolic antioxidants such as TBHQ contain a highly labile hydrogen that is easily abstracted by a peroxy radical than a fatty oil or ester hydrogen and then stop the free radical oxidation process.

Instead of adding antioxidants to improve the oxidation stability of biodiesels, the use of blends of biodiesel can be an alternative to solve this parameter. As previously stated, the composition of unsaturated fatty acids in oil sources is proportional to oxidation instability of biodiesels [6,7], and consequently the use of blends of biodiesel of opposite properties (in this case containing low and high content of unsaturated fatty acids) can provide a final biofuel with improved oxidation stability. Freire et al. [11] evaluated thermal and oxidation stability of pure vegetable oils (cottonseed, babassu, soybean, and jatropha) and their blends up to quaternary mixtures using pressurized differential scanning calorimetry, Rancimat and Petro-Oxi methods. The authors suggested the use of a quaternary mixture of oil sources for biodiesel production with improved thermal and oxidation stability instead of biodiesel production of a single raw material [11].

Sarin et al. [12] reported the feasibility of blending Jatropha biodiesel with palm biodiesel, once South and South-East Asian countries have surplus palm and Jatropha crops. Jatropha biodiesel has low oxidation stability oppositely to palm biodiesel that, on the other hand, has poor low temperature properties. Thus the use of this blend provided an improved biodiesel. Beyond Jatropha oil, other non-edible oil sources such as Pongamia were exploited for biodiesel production and their blends with palm biodiesel evaluated [13]. It was found a minimum dosage of 40 wt.% and 20% of palm biodiesel into Jatropha and Pongamia biodiesels, respectively, in order to provide oxidation stability values higher than 6 h [13]. Similarly, Chen et al. [14] investigated the modification of Jatropha biodiesel properties by blending with soybean and palm biodiesels. The oxidation stability and cold filter plugging point of Jatropha biodiesel were improved by adding palm and soybean biodiesels, respectively. However, both properties cannot meet the EN 14214 requirements simultaneously, in such a way that addition of antioxidants was necessary [14]. More recently, Jatropha biodiesel was combined with soapnut oil biodiesel (a tree generally found in tropical and subtropical climates) and this combination was considered very promising to fulfill both oxidation stability and cold filter plugging point [15].

Moser [16] studied the influence of blending colza, palm, soybean, and sunflower oil biodiesels on fuel properties. The oxidation stability of soybean biodiesel was increased by blending with colza, palm and sunflower biodiesels while the cold filter plugging point of palm biodiesel was improved by blending with colza, soybean and sunflower biodiesels. In this study Moser also has found statistically significant relationships between IP values and saturated fatty acid methyl ester content, IP values and cold filter plugging point, and saturated fatty acid methyl ester content and cold filter plugging point. Biodiesels obtained from colza and palm oil were blended with tung (*Vernicia montana*) oil biodiesel in order to improve its oxidation stability. The production of biodiesel from this non-edible oil is greater than Jatropha biodiesel due to the long-term plantation of tung trees [17]. On the other hand, meadowfoam seed oil methyl esters, which present an extremely high induction period (66.2 h), were used for blending with biodiesels obtained from soybean and waste cooking oils to enhance their oxidation stability [18].

In this work we investigated the influence of blending soybean (SbMB), sunflower (SfMB), colza (CzMB), corn (CoMB), cottonseed (CsMB), and residual cooking oil (RMB) methyl biodiesels on the oxidation stability.

2. Experimental

2.1. Synthesis of biodiesel

Refined oils of colza (Sinhá, Brazil), corn (Sinhá, Brazil), sunflower (Liza, Brazil), soybean (ABC Mines, Brazil), cotton (Cargill, Brazil), and residual cooking oil (collected at a local restaurant) were used for biodiesel production through with methanol (Vetec 99.8%, Brazil) performed at room temperature (27 °C). The transesterification reaction was carried out following the 6:1 M ratio (alcohol/oil) during 1 h in the presence of 1% (w/w) of KOH as catalyst. Glycerin, which is formed as the main byproduct during biodiesel production, was properly separated and stored for further treatment. The biodiesel purification process was performed with successive washes of distilled water at 85 °C. The amount of water used varied depending on the raw material and according to the pH after each wash until reaching a final pH value close to 7. The water and methanol remaining in the biodiesel were removed in the drying process using a rotaevaporator under reduced pressure. The remaining water was removed by adding anhydrous sodium sulfate (Merck) followed by simple filtration.

The blends were prepared by mixing biodiesels in different proportions from 10 to 90 (% w/w) and homogenized with the aid of magnetic stirrer for 30 min. The following binary mixtures were prepared: SbMB/CsMB, SbMB/CzMB, SbMB/SfMB, SbMB/CoMB, SbMB/RMB, SfMB/CoMB and SfMB/CzMB.

2.2. Physico-chemical characterization of biodiesel

The physico-chemical analyses for biodiesels were performed according to the recommendations proposed by the ANP. The parameters determined were acid number (ASTM D664), oxidative stability (EN 14112), kinematic viscosity at 40 °C (EN ISO 3104), water content (EN ISO 12937), flash point (EN ISO 3679), peroxide index, free glycerin (ASTM D6584) and total glycerin (ASTM D6584).

A Plus848 Titrino automatic titrator (Metrohm) was used for determining the acid value and peroxide value. For the first titration, biodiesel samples (3.0 g) were diluted in a 1:1 (v/v) toluene (Merck):ethanol (Merck) solution. The second titration involves sample (5.0 g) dilution in a 3:2 (v/v) acetic acid (Vetec):chloroform (Merck) solution.

The viscosity of biodiesel was analyzed using an automatic viscometer (CAP ISL Instruments). The flash point was determined using a Cleveland device. Gas chromatography was performed using a Model 7890A gas chromatograph for the determination of free and total glycerin, and saturated and unsaturated fatty acids. The oxidative stability was evaluated using a Rancimat 873 (Metrohm), in which 3 g of biodiesel sample was subjected to an oxidation process at a temperature of 110 °C.

Producers of commercial vegetable oils (used for biodiesel production in this work) declared on labels the addition of citrate and tert-butylhydroquinone (TBHQ). Additionally, natural antioxidants such as tocopherols may be present in the vegetable oils. Thus these three antioxidants were analyzed in all the obtained methylic biodiesels.

High-performance liquid chromatography (HPLC) measurements were performed using a Shimadzu LC-10 VP equipped with an UV–Vis detector that was fixed at 280 nm (SPD-10AV), a LC column (Lychrispher 100 A8 RP18-C18, 250 mm × 4.6 mm, 5 mm), a