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Long term storage stability of biodiesel: Influence of feedstock, commercial additives and purification step

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ABSTRACT

In the present work, the effect of four commercial additives, three synthetic (AO1, AO2 and AO3) and one natural based antioxidant (AO4), on the oxidation stability of biodiesel after six months of storage was investigated. Biodiesel fuel was obtained from different vegetable oils: Soybean, rapeseed, high oleic sunflower and palm methyl ester (SBME, RME, HOSME and PME, respectively). The influence of the washing agent used in the purification step (distilled water or a citric acid solution) was also studied. Samples were stored for a 6 month period at room temperature and not exposed to day light. Propyl gallate based antioxidant was found to provide the best oxidative stability after the storage period. Biodiesel obtained from low unsaturated feedstocks, such as palm oil, presented more oxidative stability than higher unsaturated oils, such as soybean oil. By purifying methyl ester phase with citric acid, the washing agent volume required resulted reduced. The antioxidant characteristic of citric acid enhanced the IP values of the samples, retarding the oxidation process.

1. Introduction

Compared to diesel fuel, biodiesel is more sensible to degradation, which results in a reduction in fuel combustion efficiency. This quality is one of the most important restrictions for biodiesel market acceptance. A minimum oxidative stability is required for not only recently produced biodiesel, but also during its storage, handling and use. Biodiesel oxidative stability during storage is strongly dependant on fatty acid profile of raw material used. Polyunsaturated fraction accelerates the oxidation process [1]. Besides the unsaturation degree of biodiesel, storage conditions and presence of impurities are determinant factors for methyl ester oxidation. Temperature, exposure to air and light, tank material of construction or presence of metal traces and antioxidant substances are factors that influence the stability of biodiesel [2]. Several studies [3,4] reported the deterioration of fatty acid methyl esters (FAMEs) including changes in acid value (AV), peroxide value (PV), and viscosity (n). It was found that these parameters increased over storage time. Other studies [5,6] reported the biodiesel degradation by monitoring changes in induction period (IP), heating value, ester content, etc. Primary products of methyl ester oxidation are hydroperoxides. Their degradation results in secondary product formation: short chain products, such as aldehydes, ketones, organic acids, etc. or polymeric products. Organic acid and aldehyde formation results in acid value increment. Hydrolysis of fatty esters to free fatty acids also causes the acidity augmentation. European Standard EN 14214 fixes a maximum AV of 0.5 mg KOH/g. Peroxide content is not specified in biodiesel fuel standards. PV will increase as a result of free radical oxidation into peroxides and hydroperoxides, however PV is not suitable for monitoring FAME storage oxidation [7].

Kinematic viscosity of biodiesel increases because of the formation of long chain saturated compounds and polymers [5]. In European specifications, the kinematic viscosity is limited to a value between 3.5 and 5 mm^2/s.

Induction period (IP) is a thermal oxidative stability parameter to measure the stability of materials. Rancimat test, EN 14112, is an accelerated test used to evaluate the oxidative stability of methyl esters as alternative diesel fuels. The minimum IP value is fixed in 6 h by EN 14214 and in 3 h by ASTM D6751.

Different storage conditions have been tested in order to determine their influence in oxidative stability. Thompson et al. monitored changes in peroxide value, acidity, viscosity, density and heat of combustion of rapeseed methyl and ethyl esters over 2 years of storage. Whereas no effect was found for container type (glass or metal), samples stored indoors, where mean temperature was higher than that outdoors, degraded faster [8]. Leung et al. investigated the influence of temperature, water content and exposure to air in edible rapeseed oil based biodiesel degradation. They reported that samples stored at 0 and 20 °C showed similar resistance to oxidation (by means of acid value determination) regardless of the storage conditions, while AV of samples stored at 40 °C increased significantly after 52 weeks [6].

Mittelbach et al. evaluated the induction period, acidity, peroxide value and kinematic viscosity changes in rapeseed oil based biodiesel at different storage conditions over 150 days [9]. Exposure to air, daylight and impurities such as metal traces caused an increase in acid

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Nomenclature

AO1 Antioxidant 1. Hindered Phenol based antioxidant.
AO2 Antioxidant 2. Hindered phenol/amine based antioxidant.
AO3 Antioxidant 3. Propyl Gallate based antioxidant.
AO4 Antioxidant 4. Mixed tocopherols based antioxidant.
HOSME High oleic sunflower methyl ester.
IP Induction Period (h).
IP_0 Induction Period of fresh sample (h).
IP_6 Induction Period of stored sample (h).
IPR Induction Period Reduction (%).
PME Palm methyl ester.
RME Rapeseed methyl ester.
SBME Soybean methyl ester.

and peroxide values and viscosity, whereas induction period value decreased. The presence of metal traces results in an increase of peroxide formation rate, which leads to faster biodiesel degradation. Copper has the strongest effect on storage stability of jatropha oil based biodiesel [10].

Antioxidants delay the oxidation process of biodiesel extending its useful life. Common additives have been tested in both conventional [4,11–13] and non conventional oil based methyl esters [14,15] under different storage periods and conditions. Tang et al. measured the evolution of some quality parameters in soybean oil based biodiesel with several antioxidants, both natural and synthetic. After 9 months of storage, adding propyl gallate resulted in a good stabilization effect, only exceeded by TBHQ addition [12]. Monophenolic compounds such as BHT and BHA were not able to maintain the IP value over 6 h, whereas α-tocopherol dosage provided the lowest IP values in both fresh and aged samples.

McCornick et al. reported the ability of commercial phenolic antioxidants in preventing acids and insoluble formation [16].

In the ester washing process, the water used can be slightly acidified, normally with H_2SO_4 or HCl to remove impurities. If citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) is used, these impurities can also be removed efficiently.

As an antioxidant substance, citric acid is expected to increase the oxidative stability of FAME. Few studies investigated the effect of citric acid on long term storage of biodiesel. However, various studies have evaluated its effectiveness in vegetable and fish oils, [17,18] specially the synergies of citric acid with natural and synthetic antioxidant substances [19]. These studies concluded that citric acid was less effective than other antioxidant substances in delaying oil oxidation.

In a prior research, the effectiveness of four commercial additives in delaying FAME oxidation was studied. Two FAME purification processes were tested: in the first one, after transesterification methyl ester phase was washed with distilled water. In the second one, washing agent was a 0.1 M citric acid solution [20].

The aim of the present study was to evaluate the oxidative stability of the biodiesel samples after 6 months of storage under particular conditions. The effects of commercial antioxidants and the presence of citric acid in the purification step were investigated in terms of Induction Period measured in a Rancimat equipment.

2. Experimental

2.1. Materials

Soybean, rapeseed, high oleic sunflower and palm oil were supplied by Gracomsa Alimentaria (Valencia, Spain). Properties and fatty acid profile of vegetable oils are shown in Table 1. Methanol (99.8% purity) was supplied by Cor Química (Spain). The catalyst used in transesterification was potassium methoxide (32% purity) purchased from BASF Ibérica (Spain). Citric acid was supplied by Sigma Aldrich (Spain).

Table 1
Fatty acid composition (wt.%) and properties of vegetable oils.

Fatty acid (wt.%)		Vegetable oil			
		Soybean	Rapeseed	High oleic sunflower	Palm
Myristic	C14:0	0.3	0.1	0.0	2.5
Palmitic	C16:0	10.9	5.1	3.5	40.8
Palmitoleic	C16:1	0.0	0.0	0.1	0.0
Stearic	C18:0	3.2	2.1	3.1	3.6
Oleic	C18:1	24.0	57.9	82.7	45.2
Linoleic	C18:2	54.5	24.7	9.0	7.9
Linolenic	C18:3	6.8	7.9	0.1	0.0
Arachidic	C20:0	0.1	0.2	0.3	0.0
Gadoleic	C20:1	0.0	1.0	0.3	0.0
Behenic	C22:0	0.0	0.0	0.8	0.0
Erucic	C22:1	0.0	0.2	0.0	0.0
Lignoceric	C24:0	0.0	0.0	0.2	0.0
Saturated		14.5	7.5	7.9	46.9
Monounsaturated		24	59.1	83.1	45.2
Polyunsaturated (2,3)		61.3	32.6	9.1	7.9
Properties					
Acid number [g KOH/g]		0.18	0.17	0.24	0.17
Iodine number [gI_2/100 g]		134	104	91	56
Peroxide number [meq/kg]		1.1	2.98	2.5	4.1
Water content [mg/kg]		0.01	0.01	0.02	0.01
Induction Period [h]		7.0	9.2	10.0	25.8

Four commercial additives were tested in this study. They were identified by their main component, since they are composed of several substances. Antioxidant 1 (AO1) is mainly composed by 2,6-Di-tert-butylphenol, a hindered phenol. Antioxidant 2 (AO2) is composed of a mixture of 2,6-Di-tert-butylphenol and ethoxyquin (6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline). Propyl gallate (3,4,5-trihydroxybenzoate) is the basic substance in antioxidant 3 (AO3). Finally, mixed tocopherols composed antioxidant 4 (AO4). Tocopherols are natural phenolic substances obtained from vegetable oils. AO4 also contains propyl gallate and ascorbyl palmitate. Table 2 resumes the composition and main properties of the additives used.

2.2. Procedure

Fatty acid methyl ester produced from different vegetable oils was used in this study: soybean methyl ester (SBME), rapeseed methyl ester (RME), high oleic sunflower methyl ester (HOSME) and palm methyl ester (PME).

Experiments were carried out in a stirred batch reactor of 500 cm^3 volume. Vegetable oil, methanol and basic catalyst (potassium methoxide) were added to the reactor. The catalyst concentration was 1.5 wt.% and the methanol/oil molar ratio 6:1. Reaction conditions were: temperature 60 °C, agitation 600 r.p.m and total reaction time 60 min. Methyl ester and glycerol phases were separated by decantation and methyl ester phase was purified by two different purification processes: in the first one, distilled water was used to remove impurities from methyl ester phase and in the second one, citric acid was used as washing agent. Finally, methyl ester phase was dried under moderate vacuum in order to remove water and methanol traces [21].

After FAME purification, commercial antioxidants described in Table 2 were added to the samples. In a previous study [20], antioxidants were added to fresh biodiesel samples in a concentration range of 250–5000 ppm. Only samples with 1000 ppm of commercial antioxidants were used in the present study.