



Oxidation stability of biodiesel from different feedstocks: Influence of commercial additives and purification step



Marta Serrano, Abderrahim Bouaid, Mercedes Martínez, José Aracil *

Department of Chemical Engineering, Faculty of Chemistry, Complutense University, 28040 Madrid, Spain

HIGHLIGHTS

- Influence of raw material on oxidative stability of biodiesel is tested.
- Commercial antioxidants are used and their effectiveness is compared.
- Two different washing agents in methyl ester purification processes were used: distilled water and a citric acid solution.
- Citric acid enhances the oxidative stability of methyl ester and retards oxidation in presence of copper.
- Correlations can help to predict oxidative stability of methyl ester samples.

ARTICLE INFO

Article history:

Received 9 October 2012

Received in revised form 22 May 2013

Accepted 23 May 2013

Available online 6 June 2013

Keywords:

Biodiesel

Antioxidants

Oxidative stability

Rancimat method

Citric acid

ABSTRACT

The present study investigates the effectiveness of three commercial synthetic (AO1, AO2 and AO3) and one natural (AO4) antioxidants to improve the oxidation stability of various biodiesel fuels produced from different vegetable oils: soybean methyl ester (SBME), rapeseed methyl ester (RME), high oleic sunflower methyl ester (HOSME) and palm methyl ester (PME) and prepared by two different purification steps, using distilled water and acidified distilled water (0.1 M citric acid solution) wash methods. The results of this study have shown that different biodiesel samples have different levels of oxidative stability. Antioxidants can improve the oxidation stability and the antioxidant effect increases as a function of its concentration.

This study showed that the use of citric acid (0.1 M) instead of distilled water in the purification step improved the oxidative stability of biodiesel from different feedstocks, and the washing agent volume required resulted reduced.

Results obtained were fitted to an equation in order to predict the minimum antioxidant dosage to meet EN 14214.

The information generated in this study could be used to better understand the oxidation stability and its effect on the quality of pure biodiesel.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The need to replace fossil fuels as a source of energy is a problem that is becoming even more patent through the years. In addition to the limited stock and the environmental issues associated with fossil fuels, price rising and the problems derived from the foreign energetic dependence are gaining weight in these last years. In this context, biodiesel is one of the most promising alternatives, not only for its low emissions and renewable properties but also for the wide range of raw materials from different origin that can be used for its production [1].

Chemically, biodiesel is fatty acid methyl or ethyl esters and they are called biodiesel only when used as fuel in diesel engines and heating systems [2]. The transesterification process combines

the oil with an alcohol in the presence of suitable catalysts; the alcohol employed in the transesterification is generally methanol. Biodiesel is commonly made with methanol and vegetable oils.

In order to ensure customer's acceptance, standardization and quality assurance are key factors for the market introduction of biodiesel as fuel for transport and heating. One of the major problems associated with the use of biodiesel as supply for diesel engines is poor oxidative stability. The problems arising from the deterioration of the fuel properties of biodiesel during storage are expected to be more severe than for commercial diesel fuel. Resistance to oxidative degradation during storage is an increasingly important issue for the successful development and viability of alternative fuels.

Fatty acid methyl ester (FAME) is more prone to oxidation than typical petroleum diesel unless it is treated with antioxidants. The oxidation mechanism of FAME is generally well understood [3]. Fatty acid alkyl chains have varying numbers of double bonds.

* Corresponding author. Tel.: +34 91 394 4167.

E-mail address: jam1@quim.ucm.es (J. Aracil).

Nomenclature

A	parameter (h), in Eqs. (1) and (2)	HOSME	high oleic sunflower methyl ester
AO1	Antioxidant 1 hindered phenol based antioxidant	IP	induction period (h)
AO2	Antioxidant 2 hindered phenol/amine based antioxidant	IP ₀	induction period of sample without antioxidant added (h)
AO3	Antioxidant 3 propyl gallate based antioxidant	PME	palm methyl ester
AO4	Antioxidant 4 mixed tocopherols based antioxidant	RME	rapeseed methyl ester
B	parameter (ppm), in Eq. (1)	SBME	soybean methyl ester
C _{AO}	antioxidant concentration (ppm)		
FAME	fatty acid methyl ester		

Generally, the rate of oxidation of fatty acids alkyl esters depends on the number of double bonds and their position on the chain. Common FAME such as soybean, rapeseed, sunflower and palm oils based methyl ester are primarily composed by carbon chains with 16–18 carbon atoms and zero to three unsaturations. For C18 carbon chains, oleic acid contains one double bond, two for linoleic and three for linolenic acid.

Oxidation of unsaturated esters in biodiesel occurs by contact with air and other pro-oxidizing conditions during storage period. Thus, oxidative stability is an important issue that biodiesel research must address since oxidation product may impair fuel quality and, subsequently, engine performance.

The need to obtain a product which is stable against oxidation both during its use and storage, has led to make different approaches. The election of the best raw material cannot always been done, due to economic reasons. The use of additives can improve the oxidation stability, in order to satisfy the corresponding standard, which is established by the EN 14214 in Europe (with a minimum induction period requirement of 6 h) and by ASTM 6751 in United States (where an induction period of 3 h is required).

Sterically hindered phenols and secondary aromatic amines are considered *primary* or free radical scavenging antioxidants that inhibit the oxidation via chain termination reactions. They contain one or more highly labile hydrogen (OH or NH group) that can be removed by a peroxy radical more easily than one's from fatty oil ester. The resulting antioxidant radical (phenolic or aminic) is very stable and leads to stable molecules without removing a proton from the fatty acid chain.

Tocopherols and flavonoids are natural substances that occur as minor constituents in vegetable oils but they are removed during the refining process. They are also classified as primary antioxidants. Tocopherol content and profile depends on the raw material (botanical source, climatic and geographical factors) and processing procedure, including storage time and conditions.

Secondary antioxidants do not convert free radicals into stable molecules, as primary antioxidants do. They act by binding metal ions, scavenging oxygen, decomposing hydroperoxydes to nonradical species, etc.

The use of natural and synthetic antioxidants to retard the oxidative degradation of lipids, such as edible oils and biodiesel has been subject to evaluation on numerous occasions [4–8]. Commercial antioxidants are a combination of different substances. Usually a secondary antioxidant is mixed with a primary antioxidant, in order to enhance the antioxidant activity. The recommended concentration depends on the raw material used, based on its fatty acid profile and its antioxidant substances content. Antioxidants will not improve the quality of a deteriorated lipid system, so they have to be added at an early stage of the processing.

One of the most commonly used methods for purifying biodiesel is to wash out the impurities with water. Other effective, though archaic, ways to wash biodiesel are agitation, mist and bubble washing. Water has a very low affinity for biodiesel and absorbs excess alcohol, catalyst and soap suspended in the fuel.

After the biodiesel is washed, it has to be dried. This is usually done via vacuum flash drying with an evaporator, or it can dry when left in settling tanks. Spent process water can be pretreated for evaporation or sent to a distillation column to be recycled in the process.

But water washing has its drawbacks. It is a time-consuming step that requires many hours for the biodiesel and water to completely separate. And, since virtually all biodiesel processes use a homogeneous catalyst like sodium or potassium methoxide, the presence of soap can create emulsification problems, which impair the separation of the water and biodiesel during the wash.

The water used in the methyl ester washing process can be slightly acidified with H₂SO₄ or HCl. As an alternative of biodiesel washing stage, in the current study a 0.1 M citric acid solution was used as washing agent.

Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) is found as a constituent of a variety of citrus fruits. Nowadays, most citric acid is obtained by fungal fermentation [9] and has a variety of applications [10]. Due to its solubility in lipids and its innocuous nature, it is used as preventive antioxidant in foods [7]. It is added to edible oil after deodorization in order to enhance superior stability against oxidation. Several studies have evaluated synergetic effects of mixing citric acid with other antioxidant substances, especially with primary antioxidants [11]. Consequently, the addition of citric acid to biodiesel during its production is expected to result in an increment of oxidative stability. Citric acid can also chelate metal ions by forming bonds between the metal and the carboxyl or hydroxyl groups of the citric acid molecule [12]. Traces of metal can catalyze the autooxidation of oil and consequently, methyl esters. Knothe and Dunn measured the decrease of *Oil Stability Index (OSI)* at 90 °C of methyl oleate in the presence of metals, by concluding that copper has the strongest effect of three metal investigated [13]. Sarin et al. and Santos et al. also tested the oxidative stability of contaminated Jatropha and soybean biodiesel, respectively. Among the tested metals, copper has the most negative effect in induction period of the samples [14,15].

The aim of this study is to evaluate the effectiveness of a series of synthetic and natural commercial antioxidants in biodiesel prepared from different feedstocks, by means of Rancimat method according to European Standard EN 14214. Biodiesel was obtained by using two different washing agents: distilled water and a citric acid solution. Results of neat and samples with additives were compared.

Finally, ability of citric acid in delaying biodiesel oxidation in presence of copper has also been tested.

2. Experimental

2.1. Materials

Soybean, rapeseed, high oleic sunflower and palm oils were supplied by Gracomsa Alimentaria (Valencia, Spain). The fatty acids composition and physicochemical properties of the oils are

Download English Version:

<https://daneshyari.com/en/article/6639716>

Download Persian Version:

<https://daneshyari.com/article/6639716>

[Daneshyari.com](https://daneshyari.com)