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Investigation of the effect of detergent–dispersant additives on the oxidation stability of biodiesel, diesel fuel and their blends

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ARTICLE INFO

Article history:

Received 3 December 2013

Accepted 23 March 2014

Available online xxx

Keywords:

Biodiesel

Oxidation stability

Additive

Detergent–dispersant

Rancimat

Diesel fuel

ABSTRACT

Basic materials of biodiesels and molecular structure of different biodiesels were discussed with special focus on their oxidation stability and post-additization. Commercial biodiesels produced from rapeseed oil and used cooking oil were blended to diesel fuel in 5%, 7%, and 10% mass fraction. The samples were stored at ambient temperature for one year to simulate the effects of strategic storage and/or long stock turnover rate. Following the one year storage period the samples were treated with BHT antioxidant and/or succinic type detergent–dispersant additives in 300 mg kg⁻¹, 600 mg kg⁻¹ and 900 mg kg⁻¹ concentrations. BHT was applied as antioxidant additive, while the detergent–dispersant additives were either newly developed additives (polyisobutylene succinic anhydride derivatives containing fatty acid methyl ester in their molecular structure) or commercial ones. Structure of the developed additives and their mechanism is described in detail. Rancimat and Seta TOST devices were applied to evaluate the effect of the additives on the oxidation stability of the samples. It was found that the decrease of oxidation stability during storage can be partially compensated with post-additization by suitable detergent–dispersant additives. Oxidation of biodiesels during Rancimat measurement was investigated with infrared spectroscopy. The results showed that during the thermal oxidation fatty acid methyl esters decompose to carbonyl, carboxyl and hydroxyl compounds, while cis-trans isomerization also occurs.

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1. Introduction

Application of fuels containing bio-components is supported by several European Union directives, 2003/30/EC (Biofuels), 2009/28/EC (Renewable Energy Directive) and 2009/30/EC (Fuel Quality Directive). Nowadays, bio-components blended to diesel fuel are almost exclusively fatty acid methyl esters

(FAME) produced by catalytic transesterification of natural triglycerides (e.g.: vegetable oils, used cooking oils) [1–5]. The EN 590:2010 standard allows blending of biodiesel to diesel fuel up to 7% volume fraction. It also requires that the blended biodiesel in all cases shall fulfil the requirements of the EN 14214:2012 standard. Nevertheless according to the literature and our experience the use of biodiesels can cause many problems, for example higher CFPP (cold filter plugging point),

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<http://dx.doi.org/10.1016/j.biombioe.2014.03.050>

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Table 1 – Fatty acid composition of biodiesel feedstock.

Feedstock	Fatty acid composition, ^a m/m%							
	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C22:1
Babassu	44-45	15-17	56-9	3-6	12-16	1-3		
Canola			4-5	1-2	55-63	20-31	9-10	1-2
Coconut	44-51	13-19	8-11	1-3	5-8	1-3		
Corn			7-13	2-3	31-43	39-52	1	
Cottonseed		1-2	22-24	2,6-5	19	50-53		
Linseed			6	3-4	13-37	5-23	26-60	
Olive		1	7-18	1-3	56-85	4-19		
Palm		1-2	32-46	4-6	37-53	6-12		
Peanut		1	6-13	2-6	37-61	13-41		
Rapeseed		2	1-5	1-4	13-38	10-22	1-10	40-64
Safflower			6-7	2-29	10-14	75-81		
Safflower (high oleic acid)			4-8	2-8	74-79	11-19		
Sesame			7-9	6-8	35-46	35-48		
Soybean			2-11	2-6	22-31	49-53	2-11	
Sunflower			4-6	1-6	14-43	44-69		
Beef tallow		3-6	25-37	14-29	26-50	1-3		

^a The first number after the carbon atom indicates the number of carbon atoms in the fatty acid, the second number indicates the number of double bonds.

higher viscosity, sensitivity to hydrolysis (corrosion), poor thermal and oxidation stability, storage problems, lower energy content [6–12]. The storage stability of biodiesels is influenced by several factors: molecular structure of fatty acids, storage temperature, presence of oxygen and its partial pressure, presence of peroxides, metal ions, antioxidants etc. Generally, during biodiesel degradation carboxylic acids and polymers are formed. Acid formation can occur in two ways: on one hand by hydrolysis in the presence of water, on the other hand by oxidation in the presence of oxygen [13–16]. In the presence of water in neutral pH the hydrolysis of esters takes place slowly, but the presence of acid or base catalyses the process, therefore it is essential during the production of biodiesel to remove adequately the catalyst from the product.

Nowadays only limited information is available in Europe on the storage stability of the higher than 5% volume fraction of FAME and diesel fuel blends. One of the future aims of the European Committee for Standardization (CEN) is to amend the EN 590:2010 standard to allow the use of blending 10% volume fraction of fatty acid methyl esters to diesel fuel. This idea is not fully supported by the car manufacturers, professional organizations and institutions due to the overloading of particulate filters, higher engine oil quality deterioration, incompatibility with some structural materials, etc. [1,15–19].

Antioxidant additives applied in biodiesel can be divided into two categories: natural and artificial. Natural antioxidants are compounds which can be found naturally in the raw material of biodiesel, such as vitamin E, carotene, tocotrienols (α , β , γ , δ) and tocopherol (α , β , γ , δ). The most common synthetic antioxidants applied in biodiesels are TBHQ (tert-butyl hydroquinone), BHA (di-tert-butyl-hydroxy-anizol), BHT (di-tert-butyl hydroxy toluene) and PG (propyl-gallate) [10]. Antioxidant additives are typically applied in a concentration of 100–1000 mg kg⁻¹, their efficiency depends on their molecular structure, for example how they can release a proton to neutralize free radicals.

The oxidation behaviour of fatty acid methyl esters mostly depends on their molecular structure: number and location of

double bonds. The relative order of the oxidation rate of the 18-carbon fatty acid esters (methyl-, ethyl ester) is the following: oleates 1, linoleates 41, linolenates 98 [9]. The relative oxidation rate is crucial, since biodiesels - depending on their raw material - can contain 1%–85% mass fraction of stearates, 5%–85% mass fraction of oleates and 1% to 81% mass fraction of linoleates. As Table 1 shows, the fatty acid composition of oils obtained from different plants can vary significantly [2–7]. In the oleic acid (C18: 1) the double bond is located at the 9th carbon atom, thus the adjacent carbon atoms are in allyl position. In the linoleic acid (C18: 2) the double bonds are located at the 9th and 12th carbon atoms, thus the 11th carbon atom is in bis-allyl position resulting in lower oxidation stability. In linolenic acid (C18: 3), the double bonds are located at the 9th, 12th and 15th carbon atoms, in such a way two carbon -atoms are in allyl and two are in bis-allyl position.

The radicals formed during the oxidation of plant oils and the geometry of double bonds strongly affect the structure of the resulting decomposition products, and therefore their properties also. The primary oxidation products of molecules having a double bond are the allyl hydroperoxides. In these products the double bonds can migrate or cis-trans isomerization can occur. Hydroperoxides are not stable, they can form several types of secondary oxidation products - such as aldehydes, acids, dimers-through complex decomposition processes.

In the temperate climate zone two oil plants can be grown in industrial quantities: sunflower and rapeseed. Among the two feedstock rapeseed is the most widely used raw material for biodiesel production. Conventional rapeseed oil has better oxidation properties than the sunflower oil, since rapeseed oil has lower unsaturated fatty acid content. The number and location of the double bonds in the fatty acid methyl ester molecular structure have high importance regarding the oxidation stability. When selecting the raw material for biodiesel production it is also important to note that the cetane number of fatty acid methyl esters increases with increasing

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