Fuel 235 (2019) 269–276

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Effects of accelerated oxidation on the selected fuel properties and composition of biodiesel

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ARTICLE INFO

Keywords:
Biodiesel
Oxidation stability
Viscosity
Acid value
Density
Fatty acid methyl esters

ABSTRACT

Oxidative stability reflects an ability of biodiesel to resist degradation caused by reactive (oxidative) species, which may lead to further changes in other fuel properties. The aim of this paper was to measure and analyze changes of selected physical and chemical properties of biodiesel produced from different raw materials during the intensive (accelerated) contact with air at elevated temperature (110 °C). The samples were subject to accelerated aging for 1, 2, 3, 4, 5, 6, 9, 12 and 24 h, and the following properties were analyzed: kinematic viscosity, acid value, density and content of total saturated, mono- and poly-unsaturated fatty acid methyl esters. After only few hours of exposure (1–4 h) to accelerated oxidation, viscosity, acid value and density exceeded the standardized (EN 14214 and ASTM 6751) maximum limits in the case of biodiesel samples obtained from vegetable oils. The observed changes in the methyl ester contents proved the highest rates of the compositional degradation in these first hours, particularly of polyunsaturated esters, which obviously led to failing certain property specifications. Lard-based biodiesel, containing about 30% of saturated, 40% of monounsaturated and 24% of polyunsaturated methyl esters, retained the viscosity value under the standardized EN 14214 maximum limit for ~6 h and under the ASTM 6751 limit for ~17 h of the accelerated oxidation.

1. Introduction

Biodiesel is a biomass-derived fuel considered as renewable, biodegradable, non-toxic, sulfur-free and non-aromatic substitute of petroleum-derived diesel. It is composed of mono alkyl esters of fatty acids originating from vegetable oils or animal fats. Most commonly, biodiesel is produced in the process of alkaline transesterification, when triglycerides from oils or fats react with alcohols (most often methanol); besides bases, acids and enzymes can also be used as catalysts [1,2].

One of the most prominent disadvantages of using biodiesel as a diesel engine fuel, is its low oxidative stability. The term, oxidative stability“ refers to the tendency of biodiesel to react with oxygen at room temperature and it describes its relative susceptibility to degradation by oxidation. During processes of oxidative degradation various products are formed, such as aldehydes, alcohols, shorter chain carboxylic acids, insoluble gums, and sediments [3]. The details on the oxidation mechanisms could be found elsewhere [4–8]. In brief, deterioration of biodiesel composition by oxidative degradation starts with the removal of hydrogen in (bis)allylic position relative to double bond in polyunsaturated fatty acid chains in the presence of reactive (initiator radical) species, creating radicals that are further involved in a multi-step reaction process. The explanation of mechanism of oxidation is based on the primary and secondary oxidation, and formation of unstable primary oxidation products – peroxides and hydroperoxides, which further form a variety of the secondary oxidation products due to reactions such as rearrangement, fission and dimerization; the complex variety of secondary degradation products includes monomeric, oligomeric and short chain compounds [7,8]. Thus, the direct consequence of biodiesel oxidation instability is its compositional change, which influences deterioration in standardized fuel composition and properties [9]. The studies that have been focused on the analysis of oxidative stability of biodiesel [7,10–15] discovered that acid value and viscosity increase during the oxidation process. Manufacturers of Fuel Injection Equipment (FIE) are particularly concerned with the change of kinematic viscosity of biodiesel [16,17], as increased kinematic viscosity has adverse effect on fuel dispersion, fuel and air mixing, and consequently on the combustion process [18]; biodiesel with the increased levels of the oxidation products can drastically reduce the service life of

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https://doi.org/10.1016/j.fuel.2018.07.123
Received 26 February 2018; Received in revised form 11 June 2018; Accepted 25 July 2018

the FIE [4,17]. Companies that transport and store biodiesel are concerned that biodiesel may form sediment during storage. Vehicle and equipment operators need assurances that sediment and gums will not form in equipment during biodiesel use [17,19]. Hence, degree of oxidative degradation of biodiesel can be determined by analyzing the changes of its composition and physical characteristics [17].

The latest version of the European standard EN 14214 on the quality of fatty acid methyl esters (MEs) intended to be used in diesel engine, defines minimum of 8 h for oxidative stability (determined as induction period by the standard method EN 14112), which is more rigourous than the previous requirement of 6 h; contrary to that increased demand for the biodiesel oxidative stability in European Union, the US standard specification for biodiesel, ASTM 6751, is less demanding setting 3 h as a minimum for the oxidation stability.

The level of biodiesel composition deterioration by oxidation due to the presence of short or long-chain oxidation products depends on several factors like fatty acid structure, production procedure, storage and transport conditions. More specifically, factors that influence the oxidation process of biodiesel are the content of unsaturated MEs that primarily reflect composition of the oily feedstock, presence of certain metals and extraneous materials, peroxides, light or pressure, elevated temperature, level of antioxidant additives, as well as the exposed surface area between biodiesel and air [7,20–24]. In general, the rate of oxidation of saturated fatty acids is extremely slow when compared to unsaturated ones and their contribution to the oxidation of biodiesel has usually been considered insignificant [25]. Antioxidants significantly slow down the biodiesel degradation processes by inhibiting or stopping the oxidation and polymerization of unsaturated fatty acids in fuel [4,6], while the presence of metals reduces oxidative stability, but this effect is considered less than the effect of polyunsaturated fatty compounds [26]. Therefore, biodiesel stability is primarily related to the unsaturated MEs and it reduces with increased total number of double bonds and increased number of double bonds per molecule [9,26].

Although oxidation stability of biodiesel has been studied extensively, most existing studies focus on measuring the induction time and discussing its correlation with properties of the feedstocks or with the added antioxidants. There are only few studies that quantified temporal changes of selected fuel properties induced by oxidative degradation, either under realistic conditions of long-term storage [11,27] or under controlled accelerated conditions [28]. The aim of this study was to contribute to these previous efforts made to better understand the influence of the oxidation degradation on the biodiesel composition and properties. The main objective was to determine levels, rates and trends of changes in selected physico-chemical properties of biodiesel produced from different feedstocks caused by simulated, accelerated oxidation using the lab-scale equipment. Properties chosen to be analyzed are those known to be changed as a consequence of the oxidation instability of biodiesel: kinematic viscosity, density, acid value and MEs composition. Temporal changes of these properties during the exposure to air blowing and heating at 110 °C, which can be noted as the fuel deterioration rates, were determined and compared, discussing the importance that starting biodiesel composition has on them. Special attention was given to the changes observed within the exposure periods of 3 and 8 h, representing a minimum induction periods specified as the lowest preferable oxidation stability by ASTM D6751 and EN14214, respectively.

2. Material and methods

Oxidative stability was determined in biodiesel produced from rapeseed (RS), sunflower (SU) and soybean (SO) oil as well as from lard (L). All types of oils were obtained from Serbian domestic grains: rapeseed variety “Kata”, sunflower hybrid “Somborac”, soybean variety “Zlata”. Rapeseed variety “Kata” contains about 46% ($m \cdot m^{-1}$) of oil and its seed yield potential is over 4.5 $t \cdot ha^{-1}$ [29]; this variety of rapeseed belongs to the “canola“ group and its oilcake can be used as animal feed (without erucic acid and with low glucosinolate content). Seed of domestic sunflower hybrid “Somborac” contains 48–51% ($m \cdot m^{-1}$) of oil and its seed yield potential is 4.6 $t \cdot ha^{-1}$ [29]. The soybean variety “Zlata” has high content of oil (23–25% ($m \cdot m^{-1}$)) and its seed yield potential is over 4 $t \cdot ha^{-1}$ [29]. The seeds were cold pressed in order to obtain the mentioned oils. The pork lard was obtained from a local farm with individual production of meat products. The pork lard was heated in a pan without the presence of water at 110 °C for 1 h (under atmospheric pressure) to remove water, and after that the melted fat was filtered to remove the insoluble materials [30].). The vegetable oils and pork fat was stored in air tight opaque plastic jars to prevent oxidation before transesterification.

Table 1
Fatty acid composition, molar mass and iodine value of oily feedstock materials (RS – rapeseed, SU – sunflower, SO – soybean, L – lard) used for biodiesel production in this study.

Acid		Formula	RS	SU	SO	L
Fatty acid composition (% (mm^{-1}))						
C14:0	Myristic	$C_{14}H_{28}O_2$	0.08	0.07	0.07	1.99
C16:0	Palmitc	$C_{16}H_{32}O_2$	4.75	5.95	9.41	22.34
C18:0	Stearic	$C_{18}H_{36}O_2$	1.49	2.41	4.23	11.11
C18:1	Oleic	$C_{18}H_{34}O_2$	66.96	28.28	26.86	43.23
C18:2n6c	Linoleic	$C_{18}H_{32}O_2$	16.79	61.85	51.05	13.21
C18:3n3	Linolenic	$C_{18}H_{30}O_2$	7.80	0.06	7.20	1.23
C20:0	Arachidic	$C_{20}H_{40}O_2$	0.49	0.20	0.34	0.87
C20:1	Eicosenoic	$C_{20}H_{38}O_2$	1.04	0.19	0.26	0.91
C22:0	Behenic	$C_{22}H_{44}O_2$	0.37	0.61	0.41	< LOD
C22:1n9	Erucic	$C_{22}H_{42}O_2$	0.06	0.12	0.06	< LOD
C24:0	Lignocerinic	$C_{24}H_{48}O_2$	0.17	0.24	0.30	< LOD
Total saturated			7.35	9.48	14.76	36.31
Total unsaturated			92.65	90.5	85.43	58.58
Total monounsaturated			68.06	28.59	27.18	44.14
Total polyunsaturated			24.59	61.91	58.25	14.44
Molar mass ($g \cdot mol^{-1}$)			881	878	875	863
Iodine value ($g\ I_2 \cdot 100\ g^{-1}$)			107.9	131.8	130.6	64.00
LOD-limit of detection						

The fatty acid composition of used oily feedstocks for biodiesel productions, as well as their molar masses and iodine values, are shown in Table 1. The oil and lard composition was determined in the commercial laboratory according to the standardized methods on ISO 5508:2009 and ISO 12966-2:2011.

Transesterification of mentioned feedstocks (4 batches per feedstock) with methyl alcohol and KOH as a homogeneous catalyst was performed in a Parr 4520 batch reactor with volume of 2 dm^3. After separation from the glycerine layer, the obtained crude fatty acid methyl esters (biodiesel) were neutralized with acetic acid and washed with water. After the purification procedure, remaining water was removed using silica gel. The biodiesel batches produced from particular feedstock were mixed in order to obtain the homogenized starting material for testing the effects of accelerated oxidative degradation on selected fuel properties. The biodiesels were marked as RSME (methyl esters obtained from rapeseed oil), SUME (methyl esters obtained from sunflower oil), SOME (methyl esters obtained from soybean oil) and LME (methyl esters obtained from lard). None of the investigated biodiesel contained synthetic antioxidants.

Accelerated degradation of biodiesel fuels was performed in equipment presented in Fig. 1: biodiesel was simultaneously subjected to heating at 110 °C and blowing with air at flow rate of 10 $dm^3 \cdot h^{-1}$ following the requirements of the EN 14112 standard that specifies method for determination of biodiesel oxidative stability.

Biodiesels were divided into multiple aliquots of 100 mL (exactly 27 per biodiesel type). After taking particular aliquot, the bulk of biodiesel stored in opaque plastic vessel was purged with nitrogen before tight closing in order to be preserved for later use [27]. The same aliquots of biodiesel samples (100 mL) were subjected to the oxidative degradation