Fuel Processing Technology 177 (2018) 75–80

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

The effect of metals and metal oxides on biodiesel oxidative stability from promotion to inhibition

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ARTICLE INFO

Keywords:
Biodiesel
Fatty acid methyl esters
Metals
Metal oxides
Oxidative stability

ABSTRACT

Biodiesel, usually the methyl esters of plant oils or other triacylglycerol-containing materials, has become an established alternative to conventional, petroleum-derived diesel fuel. Several technical problems persist when using biodiesel, one of which is oxidation stability upon exposure to oxygen in air. Factors affecting oxidation stability are not only the composition of the fuel with polyunsaturated fatty acid methyl esters being more susceptible to oxidation but also temperature, presence of light, storage headspace, and presence of extraneous materials such as pro- and antioxidants, metals, and other substances. In case of metals, it has been stated/shown that some metals are especially effective in promoting oxidation of biodiesel, especially copper. In this work, studies on the effect of metals are expanded to include a total of 26 metals for their effect on biodiesel in form of soybean oil methyl esters. The metals included in this study are Ag, Al, Au, Co, Cr, Cu, Fe, In, Mg, Mn, Mo, Nb, Ni, Pd, Re, Rh, Ru, Sc, Si, Sn, Ta, Ti, V, W, Zn and Zr. Besides these neat metals, the oxides of 29 metals were studied. These oxides are those of Ag (I), Ag (II), Al (III), Au (III), Ba (II), Ca (II), Co, Cr (III), Cr (VI), Cu (II), Eu (III), Fe (II), Fe (III), In (III), La (III), Mg (II), Mn (III), Mn (IV), Mo (IV), Mo (VI), Nb (II), Nb (IV), Nb (V), Ni (II), Sc (III), Si (IV), Sn (IV), Sr (II), Pd (II), Re (VI), Re (VII), Ru (IV), Ta (V), Ti (II), Ti (III), V (V), W (IV), W (VI), Zn (II), Zr (IV). As experimental procedure the Rancimat method, which is included in biodiesel standards, was used. The results confirm that Cu indeed is the metal most strongly promoting oxidation, while most other metals gave results in which the induction time in the Rancimat test did not differ widely from that of the used biodiesel. Some metals, notably Mo and Re, showed an inhibitory effect on biodiesel oxidation. The metal oxides usually show similar effects on biodiesel oxidation from promotion to inhibition with oxides of Ag, Au, Cr, Cu, Re and Ru showing the greatest promoting effect and oxides of Mo the greatest inhibiting effect.

1. Introduction

With vacillations in production and price of petroleum and the eventual depletion of petroleum reserves a certainty, although it remains unknown when this will eventually occur, the search for and development of alternative energy sources remains of paramount importance as future events are unforeseeable. One of the most prominent alternative fuels in this connection is biodiesel [1–3], defined as the mono-alkyl esters (usually methyl esters) of vegetable oils, or, more generally, plant oils, animal fats or other materials composed primarily of triacylglycerols.

While biodiesel is generally competitive with petroleum-derived diesel fuel, several issues have continued to beset biodiesel which have been addressed by the establishment of stringent fuel quality standards such as ASTM D6751 [4] in the United States, EN 14214 [5] in Europe and many others elsewhere around the world. Among these issues is oxidative or storage stability as biodiesel contains unsaturated fatty acid methyl esters which are prone to oxidation in presence of air (oxygen). The oxidation of fatty compounds is a complex multi-step process, leading to a variety of different products such as aldehydes, ketones, shorter-chain fatty acids, polymers and others. Numerous articles have dealt with oxidation of biodiesel, some monographs and reviews being [6–8]. Oxidative stability of biodiesel is most commonly assessed with the so-called Rancimat instrument in which the sample is heated to a specified temperature (usually 110 °C) with air flowing through the sample tube. Volatiles formed under the conditions are swept with air flow into a water bath, the conductivity of which is constantly measured. The maximum rate change of the conductivity of the water is then what is termed the induction time (or oxidation stability) of the sample. This method comprises the standard EN 14112 [9] and EN 15751 [10] for blends of biodiesel with conventional petrodiesel fuel. In biodiesel standards, minimum induction times of 3 h [4] and 8 h [5] are prescribed.

The oxidation of biodiesel is influenced by a variety of factors. The most important factor is, of course, the presence of the unsaturated

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https://doi.org/10.1016/j.fuproc.2018.04.009
Received 21 February 2018; Received in revised form 10 April 2018; Accepted 11 April 2018
0378-3820/ Published by Elsevier B.V.

fatty acid methyl esters themselves, so that the extent of oxidation depends on the amount of the unsaturated fatty acid methyl esters. Polyunsaturated fatty acid methyl esters (≥2 double bonds in the chain) are especially susceptible to reaction with oxygen due to the presence of bis-allylic CH_2 positions. Thus relative rates of oxidation of polyunsaturated FAMEs are 41 for C18:2, 98 for 18:3 and 195 for 20:4 if the relative rate of oxidation for C18:1 is set to 1 [6]. The concentration of the more oxidations-susceptible polyunsaturated fatty acids also plays a role with minor amounts of polyunsaturated fatty acids affecting oxidative stability more strongly than the minor amounts would appear to indicate [11]. On the other hand, oxidative stability can be improved by the addition or presence of natural or synthetic antioxidant additives [12–22].

Besides the composition of the biodiesel fuel itself, parameters affecting oxidative stability [6,23,24] are the presence of air, including the headspace/surface-to-air ratio/contact area with the air [25], presence of light, elevated temperature, as well as the presence of extraneous materials such as residual catalyst or carry-over constituents from the feedstock. These extraneous materials may also include the metals a fuel container may be constructed of and biodiesel can be exposed to different metals during storage, for example, metal containers may be produced using different steels containing various metals.

In prior literature concerned with the effect of different metals on biodiesel oxidative stability [11,26–29], copper has been shown to be especially effective in promoting oxidation compared to the other metals studied which were Fe, Ni, [11] and Zn, Co and Mn [26–29] studied. In case of metal ions, Fe (III) showed stronger pro-oxidant activity that Cu (II), Zn (II) and Mn (IV) [26]. The oxidation is catalytic as trace amounts of metal have more effect than the low amounts may indicate [11,27]. As the number of metals studied for their effect on biodiesel oxidation has been limited, the present work expands on that work utilizing the Rancimat method [9,10].

Besides exposure of biodiesel to metals through metal containers or other extraneous sources, such work is important because many alternative catalysts used for transesterification/producing biodiesel also contain metals and virtually no information is available regarding their effect on oxidative stability. Furthermore, many "new" transesterification catalysts contain metals not directly covered in standards. Thus the question is how remaining catalyst/metal could affect oxidative stability. It also needs to be considered that the metals are bound in various compounds whose moieties other than the metal may possibly have their own effect on impairing or enhancing oxidative stability. Metal-containing catalysts may also be used in polymerization reactions producing polymers from vegetable oils as well as production of hydrocarbons from fatty compounds by hydrodeoxygenation. Testing all these catalysts individually for their effect on oxidative stability would be an enormous task and well beyond the scope of the present work.

These aspects may play a role even for other uses. Fatty acid alkyl esters (or other fatty materials) when used as lubricants come in contact with metal parts in various machinery/engines. Even solvents, which may be fatty acid alkyl esters, may be stored in containers at least partially consisting of metals.

Oxides are overall the most common compounds in which elements/metals exist besides the neat form. Numerous oxides have been used in biodiesel production as "alternative" heterogeneous transesterification catalysts [30,31]. Traces of catalyst may remain in a biodiesel fuel, possibly influencing its properties with oxidative stability being among these properties. Other catalysts may also contain oxygen, even if they are not formally oxides. Among the oxides, calcium oxide has been a "popular" alternative transesterification catalyst [32]. Ca is contained in biodiesel standards. Other oxides, for example SrO [33] and others [34] have also been used as "alternative" catalysts, providing an incentive to investigate such materials. Furthermore, metal oxides nanoparticles have also been mixed with biodiesel with the objective of improving combustion [35,36] although this additization has not been evaluated for its effect on oxidation and catalysts used for reducing exhaust emissions.

The present work expands on the previous research dealing with effect of metals on oxidation, investigating if any other metals have the same oxidation-promoting effect as Cu or, indeed, others may have an opposite effect and including metal oxides which, to the best of our knowledge, have not been studied yet. The results also serve to evaluate the influence of metals in "alternative" transesterification catalysts as a more comprehensive evaluation of this kind is, to the best of our knowledge, not yet available. The results may also be of interest for other applications such as lubricants, polymers, etc. in which fatty compounds may be exposed to metals or metal-containing materials.

2. Experimental

2.1. Materials

Commercial biodiesel (as soybean oil methyl esters; brand name: SoyGold) was obtained from AGP (Sergeant Bluff, IA, USA). According to information from the manufacturer, the soybean oil methyl esters (SME) were additive-free. Details of the fatty acid profile of the SME determined by GC and GC–MS as described previously [37] as well as fuel quality analyses provided in the certificate of analysis from the manufacturer are given in Table 1. Metals and metal oxides were obtained from Sigma-Aldrich (St.

Table 1
Analysis of soybean oil methyl esters (SME) used in this work.

Fatty acid profile		
Fatty acid	Amount in SME used (%)	
C16:0 (palmitic)	10.4	
C18:0 (stearic)	3.9	
C18:1 Δ9 (oleic)	20.9	
C18:1 Δ11 (asclepic)	1.7	
C18:2 (linoleic)	55.6	
C18:3 (linolenic)	7.5	
Analytical data		
Specification	SME used[a]	Limits in ASTM D6751 [4] and EN 14214 [5]
Free glycerol	0.001	0.02% mass max; 0.02% mass max
Total glycerol	0.062	0.24% mass max; 0.25% mass max
Acid number	0.13	0.50 mg KOH/g max; 0.50 mg KOH/g max
Moisture	0.0135	0.05% volume as water and sediment max; 500 mg/kg
Methanol	0.04	0.2 mass % max; 0.2 mass % max
Soap	0 ppm	–
Kinematic viscosity; 40 °C	4.10	1.9–6.0 mm^2/s; 3.5–5.0 mm^2/s

[a] Analytical values per certificate of analysis of the manufacturer of the commercial SME used in this work.