

Impact of Oxidation on Lubricating Properties of Biodiesel Blends

George S. Dodos, Alexandros Deligiannis, Dimitrios Karonis, and Fanourios Zannikos
National Technical Univ. of Athens

ABSTRACT

The lubricating efficiency is an important property of diesel fuel since several diesel engine parts, such as pumps and injectors, are lubricated by the fuel itself only. The evolution of oxidation products during oxidative deterioration may as well affect the lubricating properties of the biodiesel fuel blends and thus the proper functioning of a diesel engine. In this study Fatty Acid Methyl Esters were produced from various types of feedstock that significantly differentiate in their fatty acid profile. Each methyl ester was blended with an Ultra Low Sulphur Automotive Diesel (ULSD) at a concentration of 7% v/v which is currently the maximum acceptable FAME content according to the European Standard EN590. The B7 biodiesel blends were evaluated regarding fundamental physicochemical properties as well as their lubricating efficiency. Oxidation stability was examined on a Rancimat apparatus according to EN 15751 standard. Moreover, the samples were subjected to oxidative deterioration by employing a Rapid Small Scale Oxidation Test (RSSOT) unit in accordance to ASTM D7545 Test Methods. Subsequently, the oxidized samples were collected from the RSSOT apparatus for further analyses. Alterations in the tribological performance of the B7 blends were assessed by measuring the lubricity of the oxidized fuels in a High Frequency Reciprocating Rig apparatus. Differences in the acidity of the oxidized samples were examined, as well, by conducting acid value tests. Finally, FTIR measurements were performed in order to try to detect relative changes that occur in the blends under oxidizing conditions. Overall, a noticeable deterioration in the lubricating performance of the oxidized blends was exhibited and the analyses showed that this could be principally attributed to FAME degradation.

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INTRODUCTION

Biodiesel is the most widely used first generation biofuel. It is a renewable alternative diesel fuel consisting of fatty acid methyl esters (FAME) of vegetable or animal origin. Nowadays, the maximum FAME concentration in European Union is 7% v/v and the mixing ratio might increase more in the forthcoming years so as to meet the new directives for further reduction in the greenhouse gases emissions.

Fatty Acid Methyl Esters are, inherently, more susceptible to oxidation than conventional diesel fuel and this feature is forwarded- to a certain extend- to the FAME/diesel blends [1, 2, 3]. FAMES contain mono- and poly- unsaturated fatty acids and as a consequence they are more vulnerable to oxidation. The rate of oxidation is proportional to the number of bis-allylic carbons present. The oxidation chain reaction is usually initiated at the positions allylic to double bounds [4, 5, 6]. Thus fatty acids with methylene-interrupted double

bonds, for example, linoleic acid (18:2), are more susceptible to oxidation because they contain methylene groups that are allylic to two double bonds. Fatty acids with conjugated double bonds, for example, linolenic acid (18:3) are even more susceptible to oxidation [7,8]. Oxidation stability of biodiesel can be accelerated under the action of oxygen, temperature, pro-oxidants such as metals and other parameters [6,9].

The lubricating efficiency is an important property of diesel fuel since several diesel engine parts, such as pumps and injectors, are lubricated by the fuel itself only. The beneficial effect of FAMES (biodiesel) on ULSD fuel lubricity is well studied. Oxygen containing compounds such as fatty acids are superior friction reducing agents as they adsorb on rubbing surfaces producing a low friction, mono-molecular layer [10, 11, 12, 13, 14, 15]. The order of oxygenated moiety that provides lubricity is suggested to be

Table 1. Physicochemical Properties of the parent oils.

Properties	Units	CO	SUNO	SEO	PALO	POMO	HEAR	Test Method
Density at 15°C	kg/m ³	922.0	922.8	923.0	916.0	918.3	915.4	EN 12185
K.V. at 40°C	mm ² /s	34.85	32.10	34.97	40.32	40.27	45.13	EN 3104
Water Content	mg/kg	300	350	215	250	400	200	EN 12937
Acid Value	mg KOH/g	0.45	0.30	0.50	0.39	0.35	1.45	EN 14104
Saponification Value	mg KOH/g	201	193	192	199	195	179	AOCS Cd3-25

$-\text{COOH} > -\text{OH} > -\text{COOCH}_3 \gg \text{C}=\text{O} > \text{C}-\text{O}-\text{C}$. In FAMES, lubricity is provided mainly by $-\text{COOCH}_3$ [15].

On the other hand the effect of the oxidation process on the tribological properties has been the subject of only a few studies. The evolution of oxidation products during oxidative deterioration may as well affect the lubricating properties of the biodiesel fuel blends and thus the proper functioning of a diesel engine. Sufficient oxidation stability is a basic requirement to guarantee a smooth operation of fuel injection equipment. Biodiesel deterioration can lead to the formation of insoluble materials, such as gums and sediments that may eventually cause plugging of filters and injector failure. The increase in acidity and the presence of hydroperoxides, both arising from the onset of oxidative processes, can cause the corrosion of fuel system components [6,7]. In a previous study by the author it was shown that the addition of 5% oxidized FAME in fresh ULSD resulted in a deterioration of the lubricity. [9]. In any case, the published data concerning the subject are limited and still few are known regarding the tribological properties of oxidized biodiesel blends.

Based on this background the aim of this study was to examine the effect of oxidation on the lubricating properties of various methylesters blended with ULSD at a concentration of 7% v/v. The blends were oxidized in a RSSOT apparatus and the changes in the tribological properties were assessed by conducting lubricity measurements in the HFRR unit. Moreover, alterations in the acid value were reported as well as modifications in the composition by FTIR spectroscopy.

For this reason cottonseed oil, sunflower oil, sesame oil, palm oil, pomace olive oil and high erucic acid rapeseed oil were utilized as source materials and were converted to the corresponding Fatty Acid Methyl Esters. The selection was made based on the different fatty acid profile and the different properties of each fatty oil. On industrial basis the type of feedstock is generally the key parameter that differentiate between the physicochemical properties and characteristics of the final product (biodiesel). The most important constituent is considered to be the fatty acid composition of the starting material. [1,16]. Finally, it should be noted that some of the above vegetable oil, such as sesame and pomace olive oil, have rarely been reported in the past as a starting material for the synthesis of renewable substitutes for diesel fuel.

EXPERIMENTAL

Materials and Reagents

Six different types of refined vegetable oils, namely Cottonseed Oil (CO), Sunflower Oil (SUNO), Sesame Oil (SEO), Palm Oil (PALO), Pomace Olive Oil (POMO) and High Erucic Acid Rapeseed Oil (HEAR) were obtained either from local oilseed milling plants or from oil importers, and were used as received without further processing. The typical properties of the oils engaged in this study are listed in Table 1. Moreover, methanol, 99.99% purity was obtained from Fisher Scientific and Sodium Methoxide, pure, anhydrous powder, was taken from Acros Organics.

Fatty Acid Methyl Esters

Production

The previously mentioned fatty oils were transesterified to their corresponding fatty acid methyl esters (FAMES). COME, SUNME, SEME, PALME, POME as well as HEARME were prepared by methanolysis of cottonseed, sunflower, sesame, palm, pomace and HE rapeseed oil respectively, using sodium methoxide (CH_3ONa) as catalyst at a concentration of 0.75wt%. In all cases the reaction was carried out in a 2L flask at 65° C for 2h using 500g of oil and a 6:1 methanol/oil molar ratio. After the completion of the transesterification, the upper methyl esters phase was separated from the glycerol phase and was purified by washing with 5% w/w sulfuric acid (H_2SO_4) followed by warm water. In some cases the washing steps were replaced by dry purification process with silica gel. The excess of methanol was removed by rotary evaporator. The purified methyl esters were dried over anhydrous sodium sulphate (Na_2SO_4) and after vacuum filtration the final FAMES were obtained.

Quality assessment

The produced methyl esters were examined regarding their use as automotive fuel for diesel engines. The analysis was performed according to the specified requirements and test methods included in the European Standard EN14214:2012. Moreover the oxidation stability was examined in a Rapid Small Scale Oxidation Test (RSSOT) apparatus as per ASTM D 7545 standard. The fatty acid composition was determined by gas chromatography using a DANI Master GC apparatus in accordance with EN14103.

B7 Blends

Preparation

Each FAME was blended with an Ultra Low Sulphur Diesel (ULSD) fuel at a concentrations of 7% v/v. In the European Union this mixing ration is the current maximum allowable FAME content in automotive diesel as designated by the Standard EN590:2009. The ULSD fuel was supplied from a Greek refinery - coming from severe hydrocracking process - and it was additive free. The fuel properties are presented in Table 2, along with the standard methods that were used for their determination. It can be seen that severe hydrocracking results in extremely low sulphur content of the fuel. In any case, all the prepared blends were examined regarding their physicochemical properties such as density, kinematic viscosity, sulphur content and acid value.

Table 2. Properties of ULSD

Property	ULSD	EN590 limits	Method
k.Viscosity (mm ² /s, 40 °C)	4.15	2.00-4.50	EN 3104
Density (kg/m ³ , 15 °C)	827.2	820-845	EN 3675
Sulfur content (mg/kg)	<1	10 max.	EN 20846
Water content (mg/kg)	12	200 max.	EN 12937
Cold Filter Plugging Point,(°C)	-14	(climate related)	EN 116
Distillation (°C)			EN 3405
IBP	207		
10%,	246		
20%	258		
50%	296		
65%	316		
85%	342		
90%	349		
95%	357		
FBP	364		EN 4264
Cetane index	46.0	46.0 min.	
Copper strip corrosion (3h at 50 °C, rating)	1a	Class 1	EN 2160
Lubricity, WS 1.4 (µm)	504	460 max	CEC F-06-A-96
Acid Value	0.06	-	ASTM D974

Oxidation stability - oxidation procedure

The two following methods were applied in order to assess the oxidative performance of the B7 biodiesel blends.

1. Rancimat method

The measurements were carried out in a Rancimat 873 apparatus (Metrohm), according to the accelerated oxidation method EN15751. Samples of 7.5g were analyzed under constant airflow of 10 L/h and at 110°C heating block temperature. The oxidation stability is designated as the Induction Period (IP) in hours elapsed between initiation of oxidation process and a rapid upright increase in conductivity measurement. Although Rancimat is an established method for determining the oxidation stability of FAME and FAME/diesel blends, it is not suitable for pure petroleum-based diesel fuels.

2. RSSOT method

In order to assess the relative resistance to degradation under conditions of higher pressure and temperature, determinations were also conducted in the Rapid Small Scale Oxidation Test (RSSOT- PetroOxy, Petrotest) according to the newly established ASTM D 7545 /EN 16091 Standard method. A 5ml sample was introduced into the pressure vessel of the apparatus which was then charged with oxygen to 700kPa at ambient temperature. The test was initiated by rapidly heating the pressure vessel to the selected temperature of 140°C. The pressure in the test apparatus was recorded continuously until it was 10 % below the maximum pressure of the actual test run (break point). The lapsed time between starting the heating procedure of the sample vessel and the break point is reported as Induction Period (IP) in minutes. In contrast with Rancimat, RSSOT is applicable to conventional petroleum products as well, and therefore a direct evaluation of the impact of biodiesel on diesel fuel oxidation stability is now possible.

In order to oxidize the FAME/ULSD blends, the RSSOT accelerated oxidation method was employed. The fuel samples were subjected to oxidative deterioration under the conditions that were described in the previous paragraph. Upon termination of the test the oxidized samples were carefully collected from the apparatus and were analyzed regarding lubricity alterations as well as evolution of acid value. In an effort to notice any modifications in the structure due to oxidation reactions, determinations were conducted by infrared spectrum (FTIR - Fourier Transform Infrared).

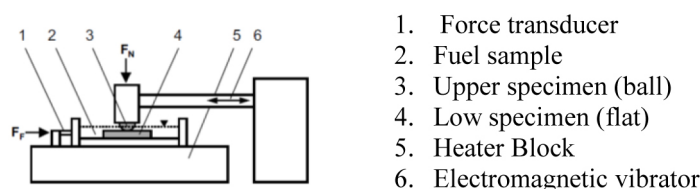


Figure 1. Description of the HFRR mechanical unit

Lubricity measurements

The alterations in the boundary lubricating properties of the fresh and oxidized fuels were determined by carrying out tribological measurements in a High Frequency Reciprocating Rig (HFRR) apparatus (PCS Instruments, Figure 1), according to the CEC F-06-A-96 method. The test conditions are presented in Table 3. The air relative humidity was kept at 45% while the ambient temperature in the laboratory was approximately 25°C. The lubricating efficiency of the fuels was estimated by measuring at the end of the test the mean Wear Scar Diameter (MWS) on the test ball, using a Leica M165C stereoscope at 120× magnification. The MWS was corrected to the standardized water vapor pressure of 1.4 kPa and the WS 1.4 value, in micrometers (µm), was reported. Additionally, at the end of each measurement the results displayed in the HFRR control

Table 3. HFRR test conditions

Parameter	Value
Fluid volume, ml	2 ± 0.2
Stroke length, mm	1 ± 0.02
Frequency, Hz	50 ± 1
Fuel Temperature, °C	60 ± 2
Applied Load, g	200 ± 1
Test Duration, min	75 ± 0.1

Table 4. Fatty acid composition of the various methyl esters

Fatty Acids		weight, %					
		COME	SUNME	SEME	PALME	POME	HEARME
Myristic	C14:0	-	0.10	0.11	1.00	-	0.13
Palmitic	C16:0	22.66	6.8	8.96	36.58	10.18	3.25
Palmitoleic	C16:1	0.58	0.25	0.15	0.24	0.89	0.22
Stearic	C18:0	2.47	2.85	6.16	4.17	3.15	0.98
Oleic	C18:1	16.36	36.57	40.98	44.44	72.49	15.25
Linoleic	C18:2	53.75	51.42	42.06	11.85	10.01	14.63
Linolenic	C18:3	0.47	0.10	0.33	0.22	0.66	9.70
Arachidic	C20:0	0.27	0.23	0.67	0.39	0.48	0.65
Gadoleic	C20:1	0.07	0.16	0.21	0.18	0.38	6.97
Behenic	C22:0	0.13	0.77	0.13	-	0.19	0.50
Erucic	C22:1	-	-	-	-	-	44.00

software concerning the average friction coefficient and the average contact resistance (film) were recorded.

FTIR spectroscopy

FTIR measurements were performed in order to try to detect relative changes that occur in the blends under oxidizing conditions. A Shimadzu IRAffinity-1 FTIR Spectrometer was utilized and the infrared spectra were taken by Attenuated Total Reflectance (ATR) sampling technique.

RESULTS AND DISCUSSION

Fatty Acid Composition

The fatty acid profile of produced methyl esters is presented in [Table 4](#). The analysis showed that COME, SUNME and SEME are abundant in poly-unsaturated fatty acids - especially linoleic acid (C18:2). COME consists mainly of linoleic, palmitic (C16:0) and oleic (C18:1) acid at a concentration of 53.75, 22.66 and 16.36 %wt. respectively. The two major fatty acids of SUNME are linoleic (51.42%wt) and oleic acid (36.57%wt), and the same applies to SEME as well, with the ratio of these two acids being approximately 1:1. On the other hand PALME contains higher levels of palmitic and oleic fatty acids, while linoleic acid concentration is considerably lower compared to the previous FAMES. Finally, mono-unsaturated fatty acids are predominant in the rest of methylesters. Oleic is the primary fatty acid in POME accounting for 72.49%wt. The other main fatty acids are palmitic and linolenic with approximately the

same content (~10%wt). HEARME contains increased levels of erucic acid (C22:1) - accounting for 44%wt - and besides unusually high concentration of linolenic acid (C18:3) was detected. (9.7%wt).

Physicochemical Properties of FAMES and B7 Blends

The quality parameters of the neat FAMES and the corresponding B7 Blends are summarized in [Table 5](#) and [Table 6](#) respectively. Regarding neat FAME properties, it is obvious that in most cases satisfy the measured applicable requirements as automotive diesel fuel outlined in the European Standard EN14214. The low levels of water and free fatty acids contained in the starting oils substantially reduced the undesirable saponification and neutralization side reactions during transesterification process. As a result the conversion was practically complete and the ester content was determined in all cases to be above the specified lower limiting value. The completion of the reaction is also depicted in the measured values of the density and the kinematic viscosity. In particular viscosity was found in all cases to be below the upper limit of 5mm²/s except for HEARME and this can be attributed to the high levels of erucic acid (longer carbon chain) contained [17].

On the other hand the water content as well as the acid value of the prepared FAMES are fairly lower than the maximum acceptable levels. Moreover, the methyl esters possess satisfactory low temperature characteristics, with the