

Evaluation of the Oxidation Stability of Diesel/Biodiesel Blends using the Modified Rancimat Method

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ABSTRACT

This study describes the effect of different types of biodiesel (fatty acid methyl esters, FAME) on the oxidative stability of low and ultra low sulfur automotive diesel fuels. Eight different samples of FAME were employed to create blends of 2, 3, 4, 5, 7, and 10% v/v with four different types of diesel fuels. The samples were analyzed using the modified Rancimat method (EN 15751). The aim of this paper was to evaluate the impact of biodiesel source material and biodiesel concentration in diesel fuel, on the oxidation stability of the final blend. Moreover, the effect of sulfur content and the presence of cracked stocks in the base diesel fuel, on the oxidation stability of the final blends were also investigated.

INTRODUCTION

The world-wide biofuels industry and notably biodiesel production have experienced a tremendous annual growth in the last years. An important stimulus for these developments was legislation promoting the partial substitution of petroleum based automotive fuels with biofuels, such as the European Union Directive 2003/30. Biodiesel is defined as the mono alkyl esters of long chain fatty acids, derived by transesterification from vegetable oils, used frying oils and animal fats [1]. Although biodiesel tends to improve lubricity, has a high flash point and is practically free of sulfur and non-toxic, its chemical nature makes it more sensitive to oxidation or auto-oxidation than petroleum diesel during long-term storage [2]. The sensitivity varies, depending on the

feedstock and the presence of naturally occurring antioxidants in the fuel. Therefore, biodiesels with high content of unsaturated methyl esters, such as methyl linoleate (C18:2) and methyl linolenate (C18:3) can be easily oxidized. The rate of oxidation depends on the number and position of bis-allylic methylene (CH_2) moieties (adjacent to the double bond) on the backbone of olefinic compounds (i.e. $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$). Polyunsaturated methyl esters are more vulnerable to oxidation than monounsaturated esters because they contain more allylic methylene configurations [3-4]. Oxidation stability does not correlate with the total number of double bonds, but with the total number of bis-allylic sites [5]. The main oxidation products of double bonds are peroxides and hydroperoxides. During further degradation these products form shorter-chain compounds such as acids, aldehydes, ketones and alcohols [6]. Further reactions of the unstable hydroperoxide species with another fatty acid chain may occur to dimerize or trimerize into higher molecular weight materials [7-9]. Another aspect that can have an impact on the overall oxidation stability of biodiesel is the conformational *cis/trans* isomerization. It is important to note that while a *trans* unsaturation is more stable than a *cis* unsaturation, conjugated *trans* unsaturations are more sensitive to oxidation than *cis* unsaturations. Figure 1 describes the order of stability for different alkene isomers.

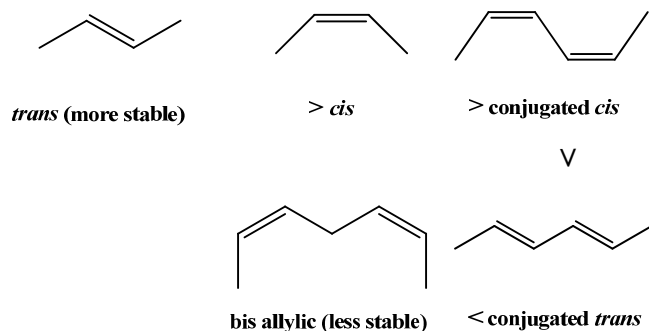


Figure 1: Order of stability for different alkene isomers.

Oxidation stability is thus a parameter that describes the degradation tendency of biodiesel and is of great importance in the context of possible problems with engine parts. Fuel deterioration can take place in the fuel supply chain and in the vehicle fuel system. Fuel ageing is accelerated in the presence of heat, oxygen, water, metal ions and other impurities. The presence of low molecular weight acids and aldehydes decreases the flash point and the presence of acids (mainly formic and acetic acids) increases the acid number. Moreover, the oxidized biodiesel gives rise to polymers often classified as sediments, gums and residues, which may lead to filter blocking and injector failures [10-11].

As a result, the European Committee for Standardization (CEN) already discusses a limit change of a minimum induction period of 8 h instead of 6 h to be included in the revised EN 14112 standard. An additional change was also included in the most recent version of the European Standards for automotive diesel (EN 590:2008), which now requires the determination of oxidation stability of diesel/biodiesel blends in order to guarantee long-term engine performance. The finished blends of diesel fuel with biodiesel shall comply with a minimum induction period of 20 h at 110 °C. The US standard ASTM D 7467 also provides for minimum oxidative stability albeit less severe than the European standard. The latest revision of the oxidation stability standard (EN 15751) using a modified Rancimat apparatus, is the test method that determines the stability of biodiesel blends with automotive diesel fuel. The modified Rancimat EN 15751 method will be an alternative to the 16 hour long EN 12205 sludge test specified in EN 590. The oxidation stability of biodiesel blends with ultra low sulfur diesel, which is already available in most parts of the EU, was also a major concern among the vehicle manufactures.

This work is important because it substantially increases knowledge on the fuel characteristics of automotive diesel/biodiesel blends. The purpose of this study was to provide results on the effect of biodiesel concentration in diesel fuel together with the effects of certain physicochemical parameters, such as those of sulfur

content, distillation characteristics, and polycyclic aromatic hydrocarbons content of the diesel fuels, on the oxidation stability of the final blends. In addition, the impact of biodiesel source material on the oxidation stability of the final blends will be addressed.

EXPERIMENTAL

FUELS – Four commercial diesel fuels were selected as the base fuels (D-1, D-2, D-3, and D-4). The first three samples were low sulfur diesel (up to 50 ppm sulfur content) and the fourth sample was an ultra-low sulfur diesel (up to 10 ppm sulfur content), which conforms with the fuel quality requirements for diesel vehicles (EN 590:2008).

D2 and D3 were hydrotreated straight run atmospheric gasoils, while D1 and D4 included streams from cracking processes as middle distillate fuel extenders. The main physicochemical properties of the diesel fuels are listed in Table 1.

Eight different types of commercially available FAME were also employed to create blends of 2, 3, 4, 5, 7, and 10% v/v with the base fuels. The neat biodiesels were examined according to the automotive FAME standard EN 14214, published by the European Standard Organization (CEN) that establishes specification for biodiesel use as a blendstock for conventional diesel fuel. The properties of the biodiesels and the test methods used are shown in Tables 2 and 3. All fuel samples were supplied by the four Greek refineries, which are responsible for the blending and the fuel supplying chain to the retail stations and to Petroleum trading companies.

Information data on the raw materials used for the production of the biodiesel samples were not available except for the first three samples (B-1, B-2, and B-3). The feedstocks used for the production of B-1 were 65% refined rapeseed oil and 35% used frying oils. B-2 feedstocks were 36% used frying oils, 20% palm oil and 44% soybean oil, while B-3 feedstocks were 32% used frying oils, 32% soybean oil and 36% rapeseed oil. These samples were free of anti-oxidant additives. The fatty acid composition profile (Table 4) of the other biodiesel samples was an indication of the raw materials used for the production of the methyl esters. B-4 was a palm-based biodiesel probably blended with coconut oil because of the high amount of lauric acid (C12). B-5, B-6 and B-7 samples were soy-based methyl esters probably blended with palm oil and/or used frying oils. The last four biodiesel samples contained a commercial anti-oxidant (probably BHT-based). B-8 was obtained from pure rapeseed oil and was free of anti-oxidant.

FUEL PROPERTIES – The physicochemical properties of the four base diesel fuels fulfilled the European standard EN 590. The first three samples, those of D-1, D-2 and D-3 respectively, were of low sulfur content (max 50 ppm-S) and were of summer grade.

by the CFPP analysis. On the contrary, D-4 fuel sample was of ultra low sulfur content (max 10 ppm-S) and was of winter grade. It is worthy of note that D-1 fuel has a relatively higher density and close to the upper limit of the specification, compared with the rest of base fuels. Moreover, the base fuels present significant differences in term of their polycyclic aromatic hydrocarbon (PAH) content. D-4 fuel had a fairly low content of PAH, followed by D-3.

Most of the physicochemical properties of the methyl ester samples were found to agree with the EN 14214 specifications. However, 3 biodiesel samples had oxidation stability below the 6h limit, 3 had excessive water, and one sample exceeded the limit for both acid number and iodine number.

Table 1: Physicochemical properties of the base diesel fuels

Property	D-1	D-2	D-3	D-4	EN 590 Limits	Test Method
Viscosity (mm ² /s, 40 °C)	2.9	3.2	2.94	2.84	2.00-4.50	EN ISO 3104
Density (g/cm ³ , 15 °C)	0.8439	0.834	0.8308	0.8355	0.820-0.845	EN ISO 3675
Flash point (°C)	65	82			55 min	EN ISO 2719
Sulfur content (mg/kg)	37	44.6	44	4	50 max 10 max (EN 590:2008)	EN ISO 20846
Water content (mg/kg)	46	100	86	52	200 max	EN ISO 12937
Cold Filter Plugging Point, (°C)	-5	-7	0	-20	-10 min	EN 116
Distillation						EN ISO 3405
IBP	163	197	177	163.9		
10	209	238	213	202		
20	233	253	230	219		
50	276	282	277	271.7		
65	295	296	299	296.5		
85	325	321	336	332		
90	337	333	348	342		
95	356	353	363	354.7		
FBP	375	367	370	363		
Recovery (%)	99.2	97.8	97.8	98.7		
Cetane index	49.7	58.3	56.1	52.3	46.0 min	EN ISO 4264
Copper strip corrosion (3h at 50 °C, rating)	1A	1A	1A	1A	Class 1	EN ISO 2160
Polycyclic aromatic hydrocarbons (% m/m)	4.6	4.5	2.98	1.2	11 max	EN 12916
Lubricity, corrected wear scar diameter (wsd 1.4) at 60 °C	445	345	-	-	460 max	EN ISO 12156-1

Table 2: Biodiesel quality parameters

Property	B-1	B-2	B-3	B-4	EN 14214 Limits	Test Method
Viscosity (mm ² /s, 40 °C)	4.4	4.5	4.6	3.67	3.50-5.00	EN ISO 3104
Density (g/cm ³ , 15 °C)	0.884	0.8839	0.8847	0.8763	0.860-0.900	EN ISO 3675
Flash point (°C)	182	176	179	>140	120 min	EN 22719
Sulfur content (mg/kg)	2.3	4	3	1.4	10 max	EN ISO 20846
Water content (mg/kg)	352	356	300	270	500 max	EN 116
Cold Filter Plugging Point, (°C)	-2	-1	-10	2	+5 max	EN ISO 12937
Iodine Number	123	109	115	42	120 max	EN 14111
Acid Number (mgKOH/g)	0.14	0.11	0.14	0.32	0.50 max	EN 14104
Oxidation stability, 110 °C (Hours)	3.51	5.72	6.59	17.38	6 h min	EN 14112
Monoglyceride content (% m/m)	0.33	0.22	0.32	0.57	0.80 max	EN 14105
Diglyceride content (% m/m)	0.094	0.05	0.052	0.08	0.20 max	EN 14105
Triglyceride content (% m/m)	0.087	0.086	0.083	0.02	0.20 max	EN 14105
Free glycerol (% m/m)	0.003	0.003	0.006	0.00	0.02 max	EN 14105 EN 14106
Total glycerol (% m/m)	0.111	0.076	0.105	0.15	0.25 max	EN 14105
Ester content (% m/m)	95.9	97.8	97.9	98.4	96.5 min	EN 14103
Linolenic acid methyl ester (% m/m)	3.3	3.1	4.4	0.12	12 max	EN 14103