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Corrosion testing of a diesel engine common rail system using various types of biodiesel

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Abstract. In this paper, the behavior of different types of biodiesel (from rapeseed, soybean, coconut and palm oils) in contact with different parts of a common rail injection system was evaluated. Stability tests were carried out by static immersion of test pieces in biodiesel at two different temperatures, 50ºC and 75ºC. After 15 days of immersion, interaction between pieces and biodiesel was evaluated considering two parameters: mass variation of pieces and biodiesel acid value (AV). A mass loss in both injector and pipes was found, no matter which biodiesel was used. In case soybean oil biodiesel was used, a slightly lower loss was achieved. On the other hand, coconut oil biodiesel showed a significant acid value increase with respect to the others. The temperature increase influenced mass loss and acid value increase.

Key words

Biofuel, materials compatibility, acid value variation, mass loss, oxidation.

1. Introduction

Biodiesel is mainly a biofuel derived from vegetable oils and animal fats that is synthesized by a transesterification with a short-chain alcohol, generally methanol or ethanol, to yield fatty acid alkyl esters (biodiesel) and glycerol, as a by-product [1]. Among others, its main features are its renewability, its high flash point and its ability to be mixed with diesel fuel. However, diesel fuel and biodiesel have a very different chemical composition. In this sense, diesel fuel is composed of saturated hydrocarbons (primarily paraffins and isoparaffins, including cycloparaffins) and aromatic hydrocarbons compounds (including naphthalenes and alkylbenzene). This disparity in terms of chemical composition presumes differences in fuel stability and engine oxidation. Double bonds present in fatty acids that make up fatty acid alkyl esters are reaction points where atmospheric oxygen may influence biofuel quality.

In this sense, biodiesel oxidation has been studied by different authors. Tsuchiya *et al.* ensure that biodiesel oxidation process increase with free water content. Moreover, esters may become different carboxylic monoacids such as acetic acid and propionic acid, among others, which are responsible of corrosion. The above acids can generate pitting process on the metal surface. However, most of them could be reduced with the help of antioxidants [2].

Another study carried out by Labeckas and Slavinskas showed that rapeseed oil biodiesel presents a free water content value about 2.7 times higher than others. This fact can lead to an increase in both density and viscosity values, stimulating acidity, as well as reducing cetane

number, thus increasing corrosion [3].

On the other hand, Fazal et al. studied the corrosion of aluminum (99% commercially pure), copper and stainless steel in contact with palm oil and palm oil biodiesel. After an exposure time of 1200 h, it was found that the corrosion rate of copper and aluminum in contact with biodiesel was greater than that presented by diesel fuel, while the stainless steel did not show significant changes. The corrosion rates of copper, aluminum and stainless steel were approximately 0.586, 0.202 and 0.015 mm/year, respectively [4].

Singh and Singh found that biodiesel is much more corrosive than diesel fuel when used in metals and elastomers, while stainless steel do not show pitting corrosion [5]. Also, other authors report that unsaturated double bonds make biodiesel more susceptible to oxidation.

Along the different parts of the engine feeding system, biodiesel comes into contact with metallic and non-metallic materials. They are ferrous metal materials, such as casting and steel, and non-ferrous metals, such as aluminum alloys. The aforementioned authors have studied commercially pure metals, but there are few studies on actual pieces or in use. These pieces are mostly metal alloys, also affected by forming processes, thermal treatments, surface treatments and other typical manufacturing techniques which may further affect their reactivity with biodiesel. Studies considering the use of biodiesel in diesel engines only consider corrosion of Cu, but degradation of biodiesel and corrosion or alteration of materials goes beyond. This raises the undeniable need to further study the compatibility of different biodiesel types with different engine materials [6].

2. Materials and methods

2.1 Materials

2.1.1 Vegetable oils

Soybean oil was purchased from Guinama (Alboraya, Valencia, Spain), coconut oil from Acofarma (Terrassa, Barcelona, Spain), palm oil from Químics Dalmau (Barcelona, Spain) and rapeseed oil was provided by IFAPA (Instituto de Formación Agraria y Pesquera, Córdoba, Spain).

2.1.2 Reagents

Potassium hydroxide and methanol for biodiesel production were acquired from Panreac Química (Barcelona, España). To determine acid and peroxide values, PA absolute ethanol, diethyl ether stabilized with 6 ppm of BTH PA-ACS, phenolphthalein solution (10 g/L), methanol PA-ACS-ISO and potassium hydroxide (85% purity), acetic acid, PA-ACS water, soluble starch, potassium iodide, 0.1 N sodium thiosulfate and trichloromethane stabilized with ethanol were used, all supplied by Panreac Química. To determine water content, an anodic solution containing sulfur dioxide, imidazole and potassium iodide, using methanol as solvent and a cathodic solution were used. Reagents were purchased from Sigma-Aldrich (Steinheim, Germany). Finally, hexane and sodium methylate, from Panreac, were used for fatty acid determination.

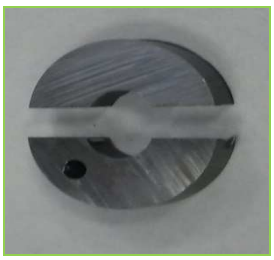
2.1.3 Chromatographic analysis

A Perkin gas chromatograph instrument provided with a flame ionization detector (GC-FID) model Clarus 500 was used. The equipment was purchased from Perkin-Elmer (Shelton, Connecticut, USA) provided of a SGE BPX70 capillary column (30 m length, 0.32 mm inner diameter and 0.25 µm film).

2.1.4 Injector and pipes

Corrosion tests were carried out using a Bosch common rail injector, manufactured in Korea with model number 0445110269 for Chevrolet vehicles and its associated pipe. Figure 1 shows both injector and pipe.

a



b

Fig. 1. (a) Pipe pieces and (b) injector pieces

2.2 Methods

2.2.1 Biodiesel production

Biodiesel production for each type of oil were conducted based on previous optimization studies in batch process [7], as shown in Table I.

Table I - Biodiesel synthesis optimal conditions

Oil	Catalyst (% wt.)	Methanol to oil molar ratio	Temperature (˚C)	Reaction time (min)
Rapeseed	1.7	6.6:1	60	60
Soybean	1.8	6.2:1	65	40
Coconut	1.5	6:1	60	50
Palm	1.5	6:1	60	50

2.2.2 Vegetable oil and biodiesel characterization

Physical tests consisting of density and kinematic viscosity were performed according to EN ISO 3675 and EN ISO 3104, respectively. Acid value was determined according to ISO 660, while peroxide value was determined by EN ISO 3960. Water content was determined according to EN ISO 12937, using a Karl Fischer Coulometer DL32 (Schawerzenbach, Switzerland). Flash point was measured using a Seta Flash series 3 plus following the standard EN ISO 2719, from Instrumentación Analítica (Madrid, Spain). High calorific was measured by an Optika SRL calorimeter pump, model IKA C200 (Ponteranica, Italy). The analyses were carried out following ASTM D240 standard.

2.2.3 Fatty acid determination

Fatty acid content was determined by GC-FID, following EN 14103 standard.

2.2.4 Preparation of metal samples

Pieces were cut using a metallographic cutting machine, cooled with water and showing a slow advance to avoid changes in metallic surfaces. Samples were washed with water and surfaces were polished mechanically with a polisher, using abrasive papers of silicon carbide (400 and 1200 μm) to provide a fine surface finish. Samples were quickly washed with distilled water and acetone. Finally, they were dried with compressed air and introduced into glass bottles containing biodiesel (Figure 2).

2.2.5 Static immersion tests

These tests consisted in placing pieces of both injector and pipe in glass bottles containing biodiesel, into a thermostated water bath, at 50ºC and 75ºC, 360 h (15 days). Previously, pieces were weighed and the acid value of each type of biodiesel was determined (Figure 3). After the tests, each piece was weighed and biodiesel acid value was determined.

Fig. 2. Glass bottles containing both biodiesel and metal samples

Fig. 3. Glass bottles in the thermostated water bath at 75ºC during the test

3. Results and discussion

Oil and biodiesel chemical composition, physical and chemical properties were determined. Results are shown in tables II y III.

Table II - Oil chemical composition

PROPERTY	RO[5]	SO[6]	CO[7]	PO[8]
FATTY ACID COMPOSITION (%)				
Caprylic (C8:0)	0	0	9.5	0
Decanoic (C10:0)	0	0	8	0
Lauric (C12:0)	0	0	41	0.5
Miristic (C14:0)	0	0.05	18	1.5
Palmitic (C16:0)	3.87	11.05	9	45.5
Stearic (C18:0)	2.12	3.87	3.8	4
Oleic (C18:1)	66.73	25.85	7.5	38
Linoleic (C18:2)	17.19	52.83	2.7	10
Linolenic (C18:3)	10.09	6.55	0.5	0.5
Arachidic (C20:0)	0	0.2	0	0
Behenic (C22:0)	0	0.2	0	0
HYDROCARBON CHAIN PROPERTIES				
LC (%)[1,9]	17.92	17.89	13.37	17
TUD (%)[2,10]	131.38	151.16	14.4	59.5
PUD (%)[3]	64.65	125.31	6.9	21.5
MUD (%)[4]	66.73	25.85	7.5	38

[1] Length of chain (LC); [2] total unsaturation degree (TUD); [3] polyunsaturation degree (PUD) and [4]monounsaturation degree (MUD); [5] RO (rapeseed oil); [6] SO (soybean oil); [7] CO (coconut oil); [8] PO (palm oil); [9] LC = Σ(*nCn/100*), where *n* is the number of carbon atoms of each fatty acid and *Cn* is the weight percentage of each methyl ester in the given fatty acid; [10] TUD = (1%*MU* + 2%*DU* + 3%*TU)*/, where *%MU* is the weight percentage of monounsaturated methyl esters, %DU is the weight percentage of diunsaturated methyl esters and %TU is the weight percentage of triunsaturated methyl esters.

European biodiesel standard EN 14214 limits for viscosity, density and acid value are 3.5-5 mm^2/s, 860-900 kg/m^3 and 0.5 mg KOH/g, respectively.

Table III - Biodiesel properties

Property	ROB[1]	SOB[2]	COB[3]	POB[4]
Kinematic viscosity, μ (mm^2/s) at 40ºC	4.2	3.9	4.8	4.7
Density, ρ (kg/m^3) at 15ºC	884	884	897	890
Acid value (mg KOH/g)	0.369	0.0663	0.0714	0.0663

[1] ROB (rapeseed oil biodiesel); [2] SO (soybean oil biodiesel); [3] COB (coconut oil biodiesel) and [4] POB (palm oil biodiesel)

3.1 Mass variation

Results show that after the test at 50°C, each piece of injector reduced its mass 0.00004 g for rapeseed oil biodiesel, 0.00001 g for soybean oil biodiesel, 0.00002 g for coconut oil biodiesel and 0.00006 g for palm oil biodiesel. Likewise, at 75°C, it was reduced 0.00015 g for rapeseed oil biodiesel, 0.00009 g for soybean oil biodiesel, 0.00014 g for coconut oil biodiesel and 0.00048 g for palm oil biodiesel. The variation of the mass of each piece of pipe after the test is shown in Figures 4 and 5.

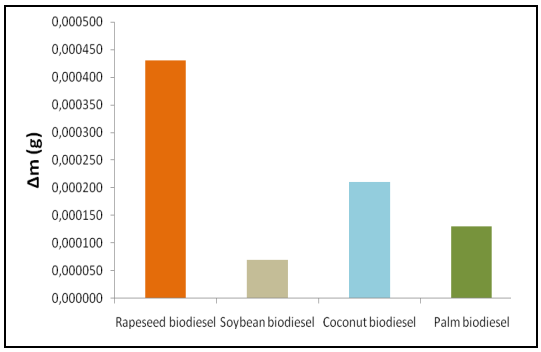


Fig. 4. Mass variation (Δm) of pipe at 50ºC

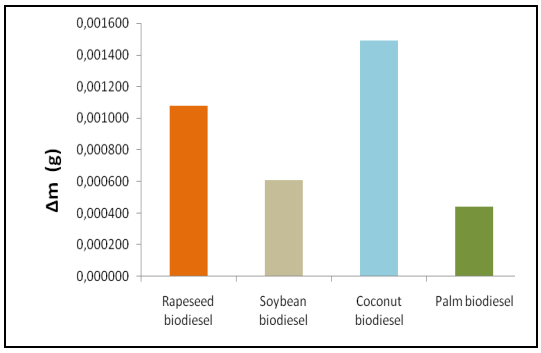


Fig. 5. Mass variation (Δm) of pipe at 75ºC

3.2 Acid value variation

The variation of biodiesel acid value after the test is shown in Figures 6-9.

As can be seen, there is not a clear trend of the influence of the fatty acid composition in both mass loss and acid value increase. Influence of biodiesel from unsaturated

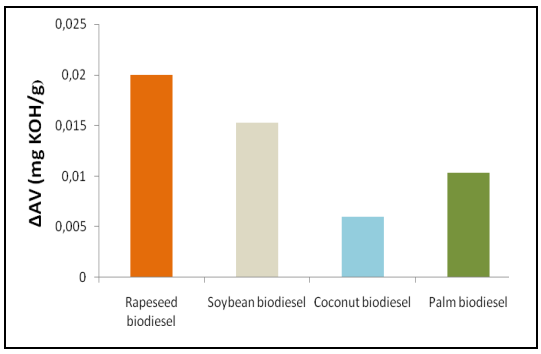


Fig. 6. Biodiesel acid value variation (ΔAV) when an injector sample is placed at 50ºC

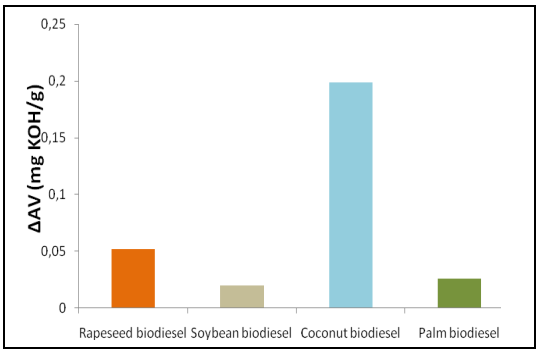


Fig. 7. Biodiesel acid value variation (ΔAV) when an injector sample is placed at 75ºC

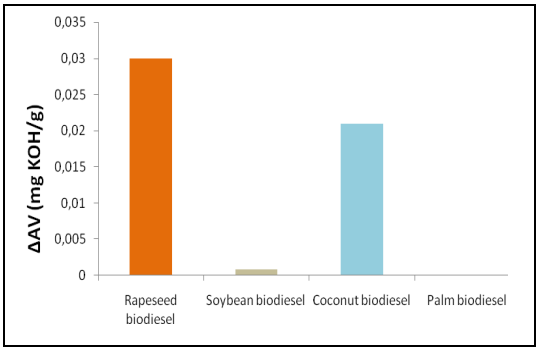


Fig. 8. Biodiesel acid value variation (ΔAV) when a pipe sample is placed at 50ºC

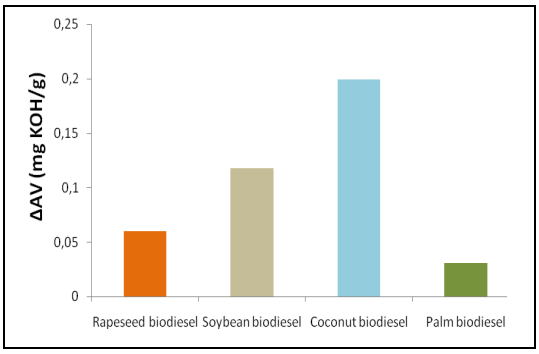


Fig. 9. Biodiesel acid value variation (ΔAV) when a pipe sample is placed at 75ºC

fatty acids (rapeseed and soybean oils) is indistinguishable from saturated ones (coconut and palm oils) either in terms of mass loss or acid value increase.

However, temperature significantly affects both biodiesel acidity and metal loss of mass. It has been shown that injector and pipe are made from different materials, thus influencing biodiesel in different ways. In this sense, palm oil biodiesel produces the greatest loss of mass of the injector, although it is the less degraded biodiesel. Rapeseed oil biodiesel produces the greatest loss of mass of the pipe, being also the most degraded biofuel at 50ºC; this position is conquered by coconut oil biodiesel, when temperature increases to 75ºC.

4. Conclusion

This paper investigated the corrosion behavior of metallic pieces of a diesel engine common rail injector system by static immersion, at different temperatures, in four types of biodiesel (from coconut oil, rapeseed oil, palm oil and soybean oil). After 15 days of immersion tests, it was found that there is a mass loss in both injector and pipe samples and an increase of biodiesel acid value. On the other hand, the increase of temperature, from 50°C to 75°C, show a significant influence on both metal mass loss and biodiesel acid value increase.

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