Corrosion Behaviour of Automotive Materials in Biodiesel from Sunflower Oil

DIANA CURSARU*, SONIA MIHAI
Universitatea Petrol – Gaze Ploieşti, 39 Bucureşti Blv., 100520, Ploieşti, România

The effect of biodiesel fuel synthesized by catalytic transesterification of the fatty glycerides existing into sunflower oil in the presence of methanol, on the corrosion properties of mild carbon steel, stainless steel and Monel steel was investigated and compared with those of classic diesel fuel. It was also studied the effect of the replacement of different (1, 5 and 10) volume percents of classic diesel fuel with biodiesel on the corrosion rates of the metals. The corrosion behaviour of biodiesel, diesel fuel or mixtures biodiesel-diesel fuel was evaluated by conventional electrochemical techniques. It was found that the corrosion rates of the metals immersed in commercial diesel fuel were relatively lower than corresponding to the corrosion rates of the metals immersed in biodiesel. In addition, it was observed that by rising the percent of biodiesel in diesel fuel the corrosion raises. The corrosion rates of mild carbon steel, stainless steel and Monel steel in biodiesel were decreased in order.

Keywords: biodiesel, corrosion, automotive materials, engine parts

The rapidly exhausted fossil sources coupled with increasing price of petroleum together with the public awareness concerning the environmental protection, are the main reasons that have made many scientists to search for alternative and renewable energy sources. The Directive 2003/30/EC of the European Union known also as biofuels directive imposes from 2010, for all member states, the replacement of 5.75% of all transport fossil fuels (petrol and diesel) with more environmentally friendly biofuels [1].

Promotion of the production and use of biofuels contribute to a reduction in energy import dependency and in emissions of greenhouse gases. Nowadays, biodiesel is successfully used as alternative biofuel for classic diesel fuel due to the enhanced biodegradability, reduced toxicity and superior lubricity in comparison with diesel fuel derived from fossil fuel.

Biodiesel is an unconventional engine fuel consisting of mixture of mono-alkyl esters of saturated and unsaturated long chain fatty acids derived from renewable feed stocks such as vegetable oils, waste frying oils, animal fats and biomass sources.

Most commonly method used for biodiesel production is catalytic transesterification of the fatty glycerides existing into vegetable oils (rapeseed oil, soybean, sunflower, canola, palm oil, olive oil, canola oil, pomace oil, cotton oil, hazelnut oil, etc.), in the presence of the primary alcohols using a strong base like KOH or NaOH as catalyst [2-6].

After transesterification process the crude biodiesel and glycerol are separated by gravity. In order to improve the quality of biodiesel, the residual glycerol, catalyst and free fatty acids were eliminated by hot water washing, the washing step being repeated for several times.

As a result of technological advances, most vehicles currently in circulation in the European Union were adapted to be able of using biofuel blend without any problems. The most recent technological developments make it possible to use higher percentages of biofuel in the blend and probably until 2020 most of the European Union countries should be prepared to use biofuel blends of 10 % and higher.

A large number of studies presented in the literature illustrate mostly the advantages of biodiesel such as higher lubricity than conventional fuels, biodiesel is 100% renewable when the alcohol used in the synthesis process is also renewable, it is biodegradable, non-toxic, has higher flash point, and has superior potential to reduce emissions, especially the particulate, CO, aromatic and polyaromatic compounds, from the exhaust pipes of the cars [7]. Besides being an eco-friendly fuel, biodiesel has some unfavorable characteristics such as oxidative instability, can provide slightly lower engine performances such as engine power and torque and higher fuel consumption [8-10, 19, 20].

However, due to its excellent solvent properties, utilization of biodiesel can contribute to the formation of deposits that lead to fuel filter and injector plugging. It is generally known that biodiesel is more corrosive than diesel fuel and there are few investigations which claim the corrosive potential of biodiesel on the automotive materials, probably because of the impurities such as water, methanol, glycerol or catalyst left over into biodiesel after processing.

Utilization of biodiesel in automotive applications imposes the direct contact of biodiesel or biodiesel blends with a large variety of materials which can be grouped in three categories: (i) ferrous alloys, (ii) non-ferrous alloys and (iii) elastomers [11].

It was reported that materials like bronze, brass, copper, lead, tin and zinc may oxidize biodiesel in certain working conditions and could generate sediments [12-16]. In the literature, only aluminum and stainless steel have been reported as biodiesel or biodiesel blends compatible materials [17].

The main aim of the present work is to investigate the corrosion behavior of automotive materials such as mild carbon steel, stainless steel and Monel steel in biodiesel synthesized from sunflower oil. The corrosion of biodiesel was initially measured by copper strip tarnish test according to ASTM D 130 and secondly was evaluated by conventional electrochemical technique.

* email: dianapetre@yahoo.com; Tel.: 0244556445, 0742124146

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS OF DIESEL FUEL

Tests	Diesel fuel	Methods
Density (25°C, kg/m^3)	838.0	ASTM D-1298
Sulfur (wt%)	0.0016	ASTM D-2622
Viscosity at 40°C, mm^2/s	3.6	ASTM D-455
Cetane number	51.9	ASTM D-613
Pour point, °C	-17	ASTM D-2500
Copper corrosion	1a	ASTM D-130
Distillation	°C	ASTM D-86
T 90%	334.7	
T 95%	354.9	
Hydrocarbon type	% vol	ASTM D-1319
Aromatics	22.1	
Polyaromatics	6.2	
Lubricity WS1.4, μm	535	ASTM-D6079

Table 2
PHYSICO-CHEMICAL CHARACTERISTICS OF VEGETABLE OIL AND FATTY ACID METHYL ESTERS

Tests	Results		Methods
	Sunflower oil	FAME	
Density (25°C, kg/m^3)	918	857	ASTM D-1298
Viscosity (40°C, mm^2/s)	4.81	4.48	ASTM D-455
Lubricity WS1.4, (μm)	123	210	ASTM D-6079
Acid value (mgKOH/g)	0.12	0.30	ASTM D-1980
Pour point, (°C)	-13	-5	ASTM D-2500
Water content (mg/kg)	-	-	EN ISO-12937
Methanol content (wt.%)	-	0.1	EN ISO-14110
Ester content (wt.%)	-	97	EN ISO-14103
Cetane index	-	55	ASTM D-976
Copper corrosion (3h at 50 ^{0}C)	-	1a	ASTM D-130
Oxidation stability (at 110 ^{0}C)	-	min 6h	EN ISO-14112
Flash point (^{0}C)	-	>110	EN ISO-2719

Experimental part

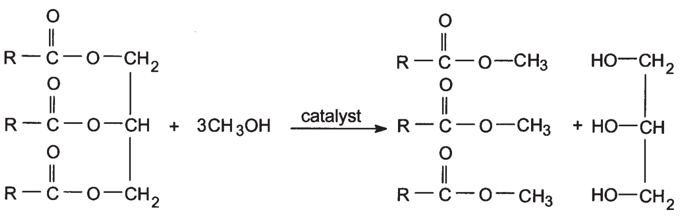
Materials and methods

Diesel fuel used for our investigations was obtained by hydrodesulphurization of diesel fuel from atmospheric distillation plant and it was delivered by Petrotel-Lukoil Refinery. The biodiesel used in the present work was synthesized from commercially sunflower oil (food-grade) and anhydrous methanol (99.8%) using potassium hydroxide (KOH) of analytical grade as catalyst. The physico-chemical characteristics of diesel fuel are depicted in table 1 and for vegetable oil are presented in table 2.

Sample consisting of 99.999% pure mild steel, stainless steel and Monel steel were used as electrodes.

Synthesis and characterization of biodiesel

The fatty acid methyl esters, known also as biodiesel, were synthesized by transesterification reaction of the fatty glycerides existing into sunflower oil. The over all transesterification reaction is:



R=8-18 C-atoms

The transesterification process was realized in a batch reactor using potassium hydroxide as catalyst via a method given elsewhere [2-6]. The reaction was carried out at 60°C, atmospheric pressure, for 2 h, under vigorous agitation in order to achieve the maximum conversion. It was used 100% excess methanol, keeping the molar ratio sunflower oil to methanol at 1:6 and the catalyst concentration of 1%.

The crude methyl esters were separated by glycerol by gravity and the catalyst was eliminated by hot water washing. The residual water in biodiesel was removed by distillation at 120°C and reduced pressure for 30 min. Finally, the unrefined biodiesel was refined by vacuum distillation at 10 mm Hg and temperature above 250 ^{0}C. The properties of fatty acid methyl esters (FAME) were determined according to ASTM and EN standards and are given in table 2.

Strip corrosion tests

The standard for biodiesel EN 14214 imposes as method to measure the corrosion of biodiesel by strip tarnish test according to ASTM D130. This test method covers the detection of corrosiveness to copper of biodiesel, biodiesel blends or diesel fuel. During the test, a polished copper strip is immersed into the fluid being evaluated and heated for a specified time and temperature after which the corrosion is rated by visual comparison to the ASTM Copper Strip Corrosion Standards. The tests run for 3 h at 50^{0}C.

Electrochemical measurements

Electrochemical experiments were carried out using a Princeton Applied Research potentiostat in conventional three electrode cells. Graphite bar was used as counter electrode, saturated calomel electrode (SCE) was the reference electrode and various alloys (mild carbon steel, stainless steel and Monel steel) bars with a surface 1.013cm^2 were used as working electrodes. The working electrodes were polished with 1500 grit SiC abrasive paper, degreased with acetone and rinsed with distilled water.

The working electrode was immersed into biodiesel solutions, and then the open circuit potential was measured after 30min. Polarization studies were performed with a scan rate 1mV/s in the potential range from -400mV to 600mV. All potentials were recorded with respect to the SCE. The I_{corr} and E_{corr} were obtained by fitting the experimental data and performing Tafel analysis.

Table 3
COPPER STRIP CORROSION TEST AND TOTAL ACID NUMBER RESULTS

Fuel	Cu strip corrosion test results	Test method	Total acid number (TAN), mgKOH/g	Test method
Diesel	1a	ASTM D-130	-	
B1	1a	ASTM D-130	0.18	ASTM D-1980
B5	1a	ASTM D-130	0.20	ASTM D-1980
B10	1a	ASTM D-130	0.21	ASTM D-1980
B100	1a	ASTM D-130	0.30	ASTM D-1980

Results and discussions

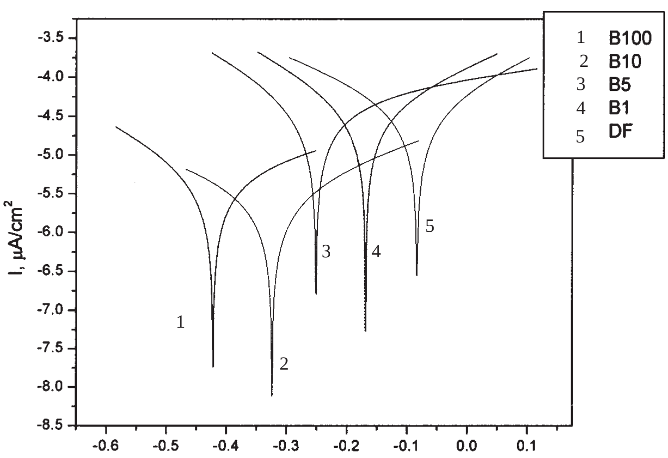
The corrosive nature of biodiesel was initially investigated by copper strip corrosion test according to EN ISO-2160. The results of these investigations are summarized in table 3 and by comparison with standardized references we observed a slight tarnish, which classify our samples in 1a corrosion class.

This method indicates only marginal corrosion and cannot make a convincing distinguish between different concentrations of biodiesel in blends. Therefore, the copper strip corrosion test was coupled with total acid number test (TAN). The TAN method is related to the free fatty acid content which together with impurities such as water, methanol, glycerol or catalyst remaining after transesterification process, is the source of corrosion. For a higher fatty acid content correlated with a higher TAN we observe an increasing in the corrosiveness of the fuel and from table 3 we observed that the corrosiveness of biodiesel rises with the concentration of biodiesel in the blend.

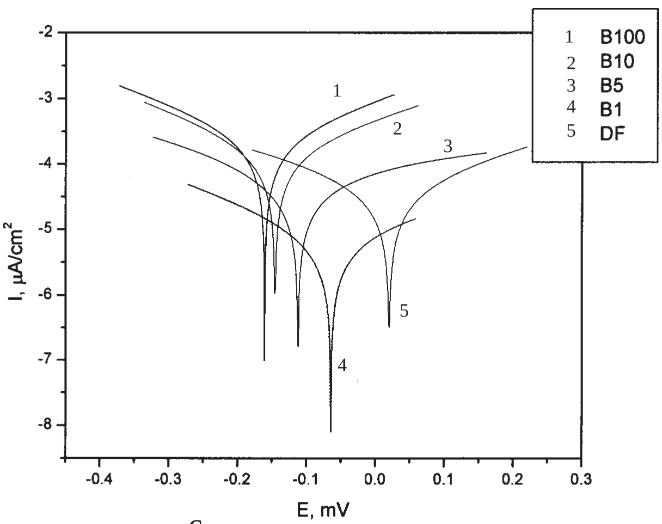
Besides of being convenient methods, the copper strip corrosion test and the total acid number test were not effective enough and for rigorous investigation on the corrosive effect of biodiesel we used conventional electrochemical technique in order to measure the yearly corrosion rate.

Figure 1 shows typical polarization curves of mild carbon steel (fig.1a), stainless steel (fig.1b) and Monel steel (fig.1c) exposed to biodiesel, diesel fuel or biodiesel blends. All these figures clearly show that the corrosion potential (Ecorr) was negative for biodiesel and biodiesel blends and was shifted to positive values for diesel fuel. These investigations performed so far are in agreement with others [18] which assume that biodiesel is more corrosive than diesel fuel and the corrosiveness of biodiesel increases with the concentration of biodiesel in the blend.

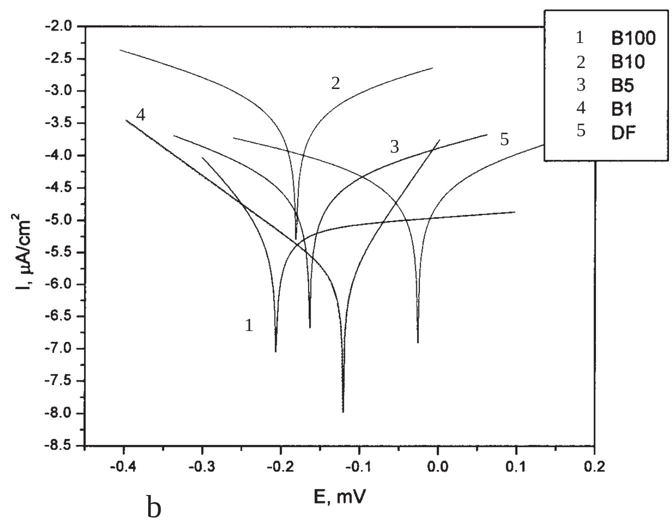
A comparison between the ferrous materials used in our investigation make an obvious distinguish between the



a



c



b

Fig. 1. The typical polarization curves of mild carbon steel (fig.1a), stainless steel (fig.1b) and Monel steel ((fig.1c) exposed to biodiesel, diesel fuel or biodiesel blends

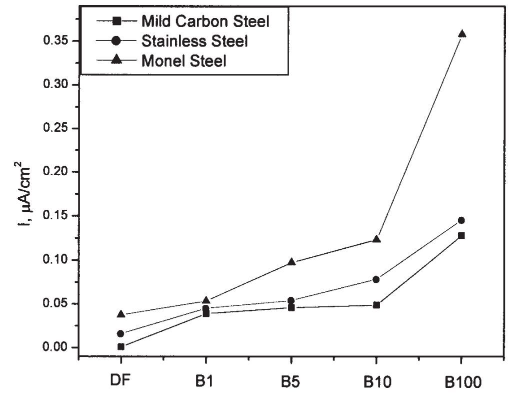


Fig. 2. Corrosion current density of different ferrous alloys exposed to biodiesel, diesel fuel or biodiesel blends

corrosion effects of biodiesel on mild carbon steel, stainless steel and Monel steel. The circuit potential moved to positive values for Monel steel, suggesting a decrease of the electrochemical action, in consequence a diminishing of the corrosion activity.

In figure 2 is presented the corrosion current density of different ferrous alloys exposed to diesel fuel, biodiesel or biodiesel blends.

The corrosion current density increases with biodiesel content in blend. The lowest corrosion current density was observed for diesel fuel, while the highest value was noticed for pure biodiesel (B100). This suggests that biodiesel, together with its possible contaminants, are responsible for the corrosion.

The corrosion reaction of metals is one of the most restrictive conditions of biodiesel when is used as engine fuel and the corrosive characteristics of biodiesel are very important for long term durability of engine components. Therefore, it is essential to establish the effect of biodiesel over different materials such as mild carbon steel, stainless steel and Monel steel, by calculating the corrosion rates.

In table 4 are presented the corrosion speeds for our ferrous alloys immersed in diesel fuel, biodiesel and diesel blends.

Table 4

CORROSION SPEED FOR DIFFERENT FERROUS ALLOYS IMMERSED IN BIODIESEL, DIESEL FUEL OR BIODIESEL BLENDS

	Mild steel	Stainless steel	MONEL steel
	Corrosion speed mm/year	Corrosion speed mm/year	Corrosion speed mm/year
DF	82.33 E-6	61.74 E-6	20.58 E-6
B1	52.62 E-6	10.29 E-6	3.673 E-6
B5	17.18 E-5	4.52 E-5	1.837 E-5
B10	0.535 E-4	0.266 E-4	0.109 E-4
B100	0.514 E-3	0.421 E-3	0.045 E-3

The corrosion of mild carbon steel and stainless steel were more severe than those of Monel steel in biodiesel: 0.000514 mm/year, 0.000421 mm/year and 0.000045 mm/year, respectively. Similarly, the corrosion rates of three metals were lower in diesel fuel and rises with the biodiesel content in blends.

A comparison between three metals used in our investigations shows that the corrosion effect of biodiesel on Monel steel were minor, because Monel is high alloy steel, resistant to corrosion and acids, its surface is hardly oxidized and a film of metal oxide is formed which prevent the oxidation of metal allowing lower corrosion rates.

Conclusions

The corrosion behavior of biodiesel produced from sunflower oil was evaluated according copper strip corrosion test as recommended by ASTM D-130 coupled with TAN method. The copper strip corrosion test shows no corrosion effect for all samples investigated but, an increase in TAN number with the concentration of biodiesel in the blend, indicate the oxidation of biodiesel sample and biodiesel blends, which can be correlated with an increasing of the corrosion effect with the concentration of biodiesel in the blend.

The corrosion process of different ferrous materials such as mild carbon steel, stainless steel and Monel steel was estimated by conventional electrochemical technique. The corrosion effects on mild carbon steel are more severe than those on stainless steel and Monel steel, probably because of the chemical corrosion that is acting more easily on the mild carbon steel surface because of the reaction of the mild ferrous material with the species from biodiesel. The corrosion rates of mild carbon steel, stainless steel and Monel steel in biodiesel are 0.000514 mm/year, 0.000421 mm/year and 0.000045 mm/year.

Acknowledgements: The authors of the present work are grateful for financial support to Postdoctoral project CNCSIS-UEFISCSU, project number PN II-RU 6/2010.

References

1. *** http://ec.europa.eu/energy/res/legislation/doc/biofuels/en_final.pdf
2. KULKARNI, M.G., DALAI, A.K., BAKHSHI, N.N. Bioresource Technology 98, 2007, 2027-2033.
3. LANG, X., DALAI, A.K., Bioresource Technology 80, 2001, 53-62.
4. KANSEDO, J., LEE, K.T., BHATIA, S., Biomass and Bioenergy33, 2009, 271-276.
5. HU, J., DU, Z., LI, C., MIN, E., Fuel 84, 2005, 1601-1606.
6. HANCSOK, J., BUBALIK, M., BECK, A., BALADINCZ, J., Chem. Eng. Research and Design 86, 2008, 793-799.
7. KEGL, B., Bioresource Technology 99, 2008, 863-873.
8. BUYUKKAYA, E., Fuel 89, 2010, 3099-3105.
9. RAKOPOULOS, D.C., RAKOPOULOS, C.D., GIAKOUMIS, E.G., DIMARATOS, A.M., KYRITSIS, D.C., Energy Conversions and Management 51, 2010, 1989-1997.
10. RAKOPOULOS, C.D., RAKOPOULOS, D.C., HOUNTALAS, D.T., GIAKOUMIS, E.G., ANDRITSAKIS, E.C., Fuel 87, 2008, 147-157.
11. HASEEB, A.S.M.A., FAZAL, M.A., JAHIRUL, M.I., MASJUKI, H.H., Fuel 90, 2011, 922-931.
12. KAUL, S., SAXENA, R.C., KUMAR, A., NEGI, M.S., BHATNAGAR, A.K. GOYAL, H.B., GUPTA, A.K., Fuel Processing Technology 88, 2007, 303-307.
13. HU, E., XU, Y., HU, X., PAN, L., JIANG, S., Renewable Energy 37, 2012, 371-378.
14. HASEEB, A.S.M.A., MASJUKI, H.H., ANN, L.J., FAZAL, M.A., Fuel Processing Technology 91, 2010, 329-334.
15. FAZAL, M.A., HASEEB, A.S.M.A., MASJUKI, H.H., Energy 36, 2011, 3328-3334.
16. ALMEIDA, E. S., PORTELA, F.M., SOUSA, R.M.F., DANIEL, D., TERRONES, M.G.H., RICHTER, E. M., MUNOZ, R.A.A., Fuel 90, 2011, 3480-3484.
17. DIAZ-BALLOTE, L., LOPEZ-SANSORES, J.F., MALDONADO-LOPEZ, L., GARFIAS-MESIAS, L.F., Electrochemistry Communications 11, 2009 41-44.
18. *** Biodiesel handling and guidelines. 3rd ed. US Department of Energy, DOE/GO-102006-2356; 2006
19. IVANOIU, I.A., BANDUR, G., RUSNAC, L.M., Rev. Chim. (Bucharest), **61**, no. 9, 2010, p. 872
20. DUMITRU, M.G., GRECU, D.R., TUTUNEA, D., POPESCU, A., Rev. Chim. (Bucharest), **61**, no. 9, 2010, p. 882

Manuscript received: 8.06.2012