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Corrosion inhibition of aluminum in biodiesel by ethanol extracts of Rosemary leaves

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ABSTRACT

Rosemary extract was used to control aluminum corrosion in biodiesel. Weight loss and polarization methods were used to test corrosion inhibitor efficiency. Surface morphology was tested by scanning electron microscopy (SEM). The inhibition efficiency increased with increase in extract concentration and decreased with temperature, suggesting the occurrence of physical adsorption. Adsorption of extract on aluminum surface is spontaneous and obeys Langmuir's isotherm. Polarization measurements revealed that Rosemary extract act as a mixed-type inhibitor with predominant anodic effectiveness. The activation energy as well as the heat of adsorption were calculated and discussed.

1. Introduction

Biodiesel (diesel derived from renewable biological sources such as vegetable oil or animal fat by a transesterification process) is currently in regular use as an alternative fuel over conventional oil derived diesel (petrodiesel) [1–5]. The use of vegetable oil as an alternative renewable fuel to compete with diesel oil was proposed in the early 1980 [6]. Although biodiesel has many properties that assist in good yield as a fuel as a relatively high flash point and good lubricating properties compared to diesel, some of these properties facilitate its self-oxidation, and oxidation of the metallic materials which they are in contact [7]. The metallic corrosion becomes extremely important since many of the engine parts are composed of variety metals such as aluminum, copper, stainless steel and alloys. The percent of aluminum in engine parts includes piston (100%), cylinder heads (70%), and engine blocks (19%) [8].

The metallic corrosion may occur due to the following factors:

(a) Biodiesel is an ester so makes hydrogen bonds with water; then it becomes much more hygroscopic compared to diesel which is composed by hydrocarbons. Water acts on the corrosion of metallic materials, or it causes the hydrolysis of biodiesel, resulting in fatty acids and glycerol which increases metallic corrosion or it promotes microbial growth and thereby microbial corrosion [9–12].
(b) The presence of impurities like water, methanol, free glycerol, and free fatty acid, catalyst residues (Na and K) due to incomplete conversion or inadequate purification can also result in metallic corrosion [12].
(c) Due to its good lubricity, biodiesel dissolves more metallic parts than diesel, and these trace metals in solution enhance biodiesel degradation and promote metallic corrosion [12].
(d) Metals into biodiesel like brass, copper and aluminum act as catalysts for biodiesel oxidation. Therefore, the acid number of biodiesel increases proportionally with the corrosion rate for different metals [12–14].

Though the serious consequences of corrosion can be controlled to a great extent by selection of highly corrosion resistant materials, the cost factor associated with the same, favors the use of cheap metallic materials along with efficient corrosion prevention methods in many industrial applications. In this aspect, corrosion inhibitors have ample significance as individual inhibitors or as a component in chemical formulations [15].

Considerations of cost, toxicity, availability and environmental friendliness are of considerable importance. Accordingly, the replacement of some toxic, expensive chemical inhibitors by inhibitors obtained from natural sources is necessary [16–18].

Recently, there are numerous successful reports on the using of natural additives to biodiesel, such as corrosion inhibitors or antioxidants [19–21].

The main aim of the present work was to investigate the corrosion inhibition of aluminum exposed to biodiesel by ethanol extracts of Rosemary leaves using weight loss, polarization measurements and scanning electron microscopy (SEM).

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Table 1
The physicochemical properties of the biodiesel.

Property	Unit	Biodiesel
Appearance	–	Clear, light yellow
Odor	–	Mild
Physical state	–	Liquid
Boiling point	°C	235
Kinematic viscosity at 40 °C	mm^2/s	4.19
Specific gravity at 25 °C	–	0.865
Flash point	°C	165
Pour point	°C	0
Water content	wt%	0.05
Total acid number	mg KOH/g	0.39
Solubility in H_2O	–	Insoluble
pH	–	Not applicable

2. Experimental

2.1. Materials

Corrosion tests were performed on aluminum sheets of the following percentage composition: Al (99.89%), Si (0.03%), Cu (0.02%), Mg (0.03%) and Zn (0.01%). Prior to each experiment, the aluminum electrodes were first briefly ground with different grades of emery paper (120, 400, 800, 1000 and 1200) and washed thoroughly with distilled water and degreased with acetone.

2.2. Inhibitor

Leaves of Rosemary were obtained from local market in Egypt. 10 g of Rosemary leaves were dried, grounded and soaked in 300 mL of ethanol solution (95%) for 48 h at 313 K. After 48 h, the samples were cooled and filtered. The filtrates were further subjected to evaporation at 352 K in order to leave the sample free of the ethanol. The remaining extract was finally dried in oven at 323 K for 3 h to ensure the removal of any residual ethanol solution. The calculated extracted yield was about 11.3%. The stock solutions of different concentrations of the extract were obtained by dissolving 0.1, 0.2, 0.3, 0.4 and 0.5 g of the extract powder in 10 mL ethanol (95%) and biodiesel was added until a total volume of 1.0 L was reached.

2.3. Test solution

The tests were performed in biodiesel with the addition of various concentrations of Rosemary extract. Biodiesel samples were derived from waste cooking oils. The biodiesel used in this work was supplied by Egyptian Petroleum Research Institute. The main components of biodiesel are saturated fatty acid ester (methyl stearate) and unsaturated fatty acid ester (methyl oleate). The physicochemical properties of biodiesel are listed in Table 1.

For each run, a freshly prepared solution was used. During the experiments, the test solutions were opened to the air and experiments were performed under static conditions.

The temperature of the test solution was controlled by immersing the cell in a water thermostat.

2.4. Weight loss measurements

Rectangular specimens of aluminum with dimensions 3.0 × 2.0 × 0.2 cm were used for weight loss measurements. The cleaned and dried specimens were weighed before immersion into the respective test solutions of biodiesel using an analytical balance (GM1502-Sartorius). Tests were conducted with different concentrations of inhibitor. After immersion period (2000 h), the specimens were carefully washed with double-distilled water and degreased with AR grade ethanol, and then reweighed. Triplicate experiments were performed in each case and the mean values reported.

Table 2
Corrosion rate (C_R) and inhibition efficiency (η_w%) values for the corrosion of aluminum in biodiesel in the absence and presence of different concentrations of Rosemary extracts at 298 K.

Rosemary extracts conc. (g/L)	C_R (mg/cm^2 h) × 10^{-5}	η_w%
Blank (biodiesel)	1.785	–
0.1	0.665	62.7
0.2	0.424	76.2
0.3	0.308	82.7
0.4	0.155	91.3
0.5	0.075	95.7

2.5. Potentiodynamic polarization measurements

Electrochemical measurements were conducted in a conventional three electrodes cell assembly. A non-aqueous Ag/AgCl/EtOH/LiCl electrode was used as a reference electrode, and a platinum wire was used as a counter electrode. The working electrode was prepared from aluminum, mounted in polyester in such a way that the area exposed to solution was 0.450 cm^2. The polarization curves were obtained potentiodynamically between potential ranges from −0.90 to −0.10 V with scan rate of 0.125 mV/s. The electrochemical experiments were performed using a potentiostat/galvanostat (EG and G model 273) coupled to a computer equipped with the software 273 Soft Corr^{TM}. Prior to the electrochemical measurement, a stabilization period of 30 min was allowed, which was proved sufficient to attain a stable value of E_{corr}.

0.10 mol/L lithium perchlorate was added to biodiesel solution in order to increase fuel conductivity. This salt was chosen in order to avoid anion adsorption on the metal surface.

2.6. SEM and digital photos

Surface morphology of aluminum surface was examined after the required experiments using scan electron microscopy (SEM) (model: JOEL-JEM-1200 EX II ELETRON MICROSCOPE).

The stability and appearance of the biodiesel with and without Rosemary extract were characterized by a digital camera (KODAK EASYSHARE P850 zoom digital camera).

3. Results and discussion

3.1. Weight loss measurements

3.1.1. Corrosion rates and inhibition efficiency

From the weight loss measurements of aluminum specimens in biodiesel in the absence and presence of different amounts of different concentrations of Rosemary extract at 298 K, the inhibition efficiency and corrosion rate were calculated and the results are given in Table 2.

The inhibition efficiency η_w% and the corrosion rate C_R are calculated using Eqs. (1) and (2), respectively [22,23]:

$$\eta_W\% = \frac{C_{R0} - C_R}{C_{R0}} \times 100 \quad (1)$$

$$C_R = W/At \quad (2)$$

where C_R is the corrosion rate (mg cm^{-2} h^{-1}) in the presence of inhibitor, C_{R0} in the absence of inhibitor, W is the weight loss (mg), A is the exposed surface area (cm^2) and t is the exposure time (h).

The stability and appearance of the biodiesel with and without Rosemary extract were investigated for fresh samples and after storage time 1000 h. The digital photos are represented in Fig. 1. It is clearly observed that the addition of Rosemary extract to biodiesel does not affect the biodiesel clarity but causes slight increase in the