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Investigation on the effects of temperature, dissolved oxygen and water on corrosion behaviour of aluminium and copper exposed to diesel-type liquid fuels

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Corrosive behaviour of RME (rapeseed methyl ester) in blends with ultra-low sulphur diesel and GTL (gas-to-liquid) fuel is investigated in this study. The tests were carried out at a wide range of blending ratios and for two of the typical metals in manufacturing of engine parts in contact with fuel (aluminium and copper). Tests were divided into two main groups: short-term at elevated temperature (80 °C, 600 h) and long-term (room temperature, 5760 h). Effects of impurities such as presence or absence of dissolved oxygen and absorbed water were also investigated using the same test conditions. Before and after the tests metals and fuels have been investigated in many ways in order to understand the type and extend of the damage on both metal surfaces and fuel properties. Investigation of damages inflicted by fuel on metals was performed using scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDS). Also nature of the oxide layer formed on the surface of the metal was studied using X-ray diffraction (XRD). Degradation of fuels as a result of exposure to metals was investigated for changes in kinematic viscosity, Total Acid Number (TAN) and any compositional changes in the fuel structure using GC–MS. Results revealed that biodiesel increases the corrosiveness of fuels exposed to both metals with more effect on copper samples, also it was found that the presence of dissolved oxygen and absorbed water is a key factor for more corrosion damage to metals. TAN value, kinematic viscosity and changes in the fuel composition all confirmed the degradation of the fuels as a result of exposure to the metals. GTL was found to be the most resistant fuel to corrosion, probably due to its chemical composition.

1. Introduction

Energy has always been an influential factor in progress of humanity. In recent years, an energy crisis has taken place because of reduction of energy resources whilst escalation of environmental impact of the fuels is enlarged consequently. This issue compels researchers around the world to conduct an extensive research on acquiring new solutions for reducing total emissions and NOx pollution of the fuels [1,2]. Biodiesel has always been considered as one of the appropriate alternatives to fossil fuels. The main reasons include its production from renewable resources (vegetable oils, animal fats), lower overall emissions, less emissions of greenhouse gases, superior lubricity and biodegradability, negligible sulphur and aromatics content and also their compatibility with recently manufactured diesel engines [3]. Moreover, it is known that physical properties of biodiesel are similar to petroleum-derived diesel. Therefore, biodiesel can be utilized in both pure form (B100) or in blends with conventional diesel (B5, B10, and B20) [4–6]. In Europe, rapeseed methyl ester (RME) is the most common biodiesel. It is also stated that, due to the high oxygen content of RME the higher quality of combustion and lower quantity of dangerous emissions are attainable. Likewise, other mentionable properties of RME are its higher viscosity and boiling point as well as negligible production of sulphates at high revolutions and temperatures [7,8]. As an alternative to conventional diesel fuels GTL has been investigated during recent years; Gas to Liquid (GTL) is manufactured from natural gas or coal-derived syngas by taking advantage of the Fischer–Tropsch process. It is reported that, due to the exclusive features such as negligible sulphur and aromatic content in its chemical composition, the GTL is a superior alternative to current diesel fuel [9,10]. In general, properties of fuels can be investigated through many different aspects such as quality of combustion and level of produced pollutants. Beyond all these aspects, an important part of fuel characteristics might be their corrosiveness effects on different parts of engine which are in contact with various fuel systems fragments such as fuel delivery pipes, piston and piston rings [11]. Nowadays, several materials are employed in fabrication of different fuel delivery systems. Among all these materials copper and aluminium alloy are the base for many parts such as bearings, fuel pump and piston assembly [11–15]. It is noteworthy that biodiesel in presence of water and fatty acid is more destructive than regular diesel. Similarly, it is known that these types of fuel have greater tendency to

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adsorb water which leads to enhancement in oxidation rate on metal surfaces. Also, biodiesel is more susceptible to be oxidized when in contact with various metals at different parts of fuel system [15,16]. At present, there are a small number of studies available in literatures that reveal the effects of biodiesel on main engine components. Tsuchiya et al. [17] used long duration static immersion test (1000 h at 80 °C) to observe the effects of diesel containing low percentage of Fatty Acid Methyl Ester (FAME) on different materials. It is realized that, after degradation of FAME several organic and fatty acids such as formic and acetic acids are generated. Oleic and linoleic acids are the free acids that already existed as a raw material in production process of fuels. Furthermore, corrosiveness of biodiesel increases with the presence of these compounds. Other researchers also confirm this enhancement in the rate of acidity after performing a 25 hour immersion test (at 200 °C) [18]. The re-converting of double bonds of FAME and formation of carboxylic groups is also reported by the same researchers. According to Kaminski et al. [19] an appropriate environment for microbial growth is provided by presence of water in the oil. Therefore, beyond doubt an increase in acidity of the fuel happened following this growth, and consequently an increase in the rate of corrosion. Gellar et al. [20] scrutinized that copper and brass indicate the greatest weight loss among the other materials including stainless steel and carbon steel. However, Sgroi et al. [21] discovered that pitting corrosion occurred on the bronze sintered filter after a few hours (10 h) of operation with biodiesel at 70 °C. In another study, the corrosion attack (weight loss) was observed after performing the 115 day immersion test of carbon steel in a blend with various biodiesels (such as soybean, sunflower and petroleum diesel) [22]. M.A. Fazal et al. [14] studied the corrosiveness of different metals in both diesel and palm biodiesel at 80 °C for two different periods of time. According to their research, the rate of corrosion of copper rises with increasing time whilst this phenomenon occurred, contrary to the aluminium coupon. However, stainless steel experienced no substantial corrosion with both fuels. Hu et al. [23] agreed with Fazal. They reported that the signs of corrosion are visible after 2 month immersion of several engine materials in pure RME at 43 °C. Recently, researchers stated that corrosion rates proliferate with increasing the proportion of biodiesel. Based on research done by the authors of this work it can be said that the corrosion rate increases due to the existence of more unsaturated fatty acids. In another study from M.A. Fazal et al. [24] the long period (1200 h) immersion test of copper at room temperature (25–27 °C) was performed. They found that, the rate of corrosion increases initially until it reaches a maximum at around 900 h and then gradually decreases with time. Also as it was reported by the previous work of the authors of this work that biodiesel from rapeseed was found to be more corrosive than diesel and even more than other types of biodiesel used by researchers in their work (palm biodiesel) mainly because of higher percentage of unsaturated compounds in the structure of fuels. Furthermore, copper was mentioned as a strong catalyst to oxidise biodiesel at elevated temperature for long period of exposure time. In the present study, the corrosion characterization of aluminium (AW-6060) and copper (E-Cu 57) exposed to blends of ULSD, RME and GTL was conducted at different temperatures (25, 80 °C) and conditions (added water and oxygen) by taking advantage of immersion test methods. In addition, several surface analyses were accomplished using different apparatus such as Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS) and X-ray diffraction (XRD) to evaluate the nature of corrosion and corrosion products in nominated materials.

2. Materials and methods

2.1. Materials

Fuels used for this analysis were supplied by Shell Global Solutions UK. These fuels include ultra-low sulphur diesel (ULSD), rapeseed methyl ester (RME) and synthetic gas to liquid (GTL) fuel. The list of fuels and their physical and chemical properties can be found in Table 1. Metals utilized for the experiments were Aluminium alloy 6060 (AW-6060) with high purity and commercially pure copper E-Cu 57 99.9%. Major components of the Al alloy used are Silicon (0.3-0.6 wt.%), Iron (0.10-0.30 wt.%), Magnesium (0.035-0.60 wt.%) and Aluminium (Balance).

Table 1
Physical and chemical properties of fuels used.

Properties	Method	ULSD	RME	GTL
Cetane number	ASTM D613	53.9	54.7	79
Density at 15 °C (kg/m^3)	ASTM D4052	827.1	883.7	784.6
Viscosity at 40 °C (cSt)	ASTM D455	2.467	4.478	3.497
Distillation fraction				
50% (°C)	ASTM D86	264	335	295.2
90% (°C)	ASTM D86	329	342	342.1
Sulphur (mg/kg)	ASTM D2622	46	5	<10
Aromatics		24.4	~0	~0
O (wt.%)		~0	10.8	Na
C (wt.%)		86.5	77.2	85
H (wt.%)		13.5	12	15
H/C ratio (molar)		1.88	1.85	2.1
Water content (mg/kg)	EN ISO 12937	<200	<350	Na

2.2. Preparation of samples

Round bars of samples were cut into appropriate pieces (16 mm diameter × 4 mm length) by machining and grinding. These metal slices after being washed with distilled water were polished by silicon carbide abrasive papers (grade 400 to 1200). Afterwards, they were degreased using acetone. Finally, the washing process was performed by taking advantage of deionized water and then they were dried in air. However, before this step, metal pieces were soaked in 10% sulphuric acid for elimination of any impurities from the surface of the specimens. Furthermore, in order to avoid the unequal condition of surface oxide film creation, the preparation procedure was performed 10 min before carrying out the static immersion test.

3. Experimental

3.1. Static immersion test

Corrosion characteristics of prepared metals (aluminium and copper) were investigated using two different immersion conditions. These conditions included long-term (room temperature at 25 °C for 8 months) and short-term (80 °C for 600 h) tests. After immersion, coupons were rinsed and washed with deionized water followed by dipping in acetone for a few minutes. Also, in order to remove the corrosion products from the surfaces, the polishing process was accomplished using a polymer brush to prevent any mechanical damage to the surface of metal. Eventually, metals were rinsed and dewatered by using distilled water and acetone respectively. A list of metal weights provided before and after the immersion was obtained by using a high resolution (0.1 mg) Mettler Toledo laboratory balance. The room temperature test was performed by immersing the samples (aluminium, copper) into different blends of RME and ULSD (0, 50, 75, 100 percent biodiesel in ULSD). Gas-To-Liquid fuel was also blended with biodiesel using same blending ratios. Afterwards, metals samples were kept in a dark place in order to prevent the effect of light on oxidation of fuels. Similar approach was conducted for the corrosion tests at 80 °C for 600 h to investigate the effects of the temperature on the corrosion characteristics. In addition, the fuels brought to condition of oxygen-enriched and oxygen-free were examined to evaluate the influences of presence and absence of oxygen. The oxygen enrichment process was performed