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Highlights

- Corrosion characteristics of blends of RME, GTL and ULSD were investigated upon exposure to Aluminium and Copper
- Tests were carried out at 80°C and at room temperature for 600 and 5760 hours respectively
- Effects of dissolved oxygen and absorbed water on corrosion process were studied
- Fuels were analysed for changes in kinematic viscosity, TAN and composition
- Damage inflicted on metals were investigated using SEM/EDS, XRD and changes in weight

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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Abstract

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 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, 600h) and long-term (room temperature, 5760h). 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 presence of dissolved oxygen and absorbed water are key factors 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.

Keywords: Corrosion, RME, GTL, ULSD, GCMS, XRD, SEM/EDS, Degradation, TAN

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 NO_x pollution of the fuels [1, 2]. Biodiesel has always been considered as one of 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 is 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 sulfur and aromatic content in its chemical composition, the GTL 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 are more destructive than regular diesel. Similarly, it is known that these types of fuel have greater tendency to adsorb water which leads to enhancement in oxidation rate on metals 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 hours 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 hours 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 hours) of operation with biodiesel at 70°C. In another study, the corrosion attack (weight loss) was observed after performing the 115 days 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 while 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 months 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 hours) immersion test of copper at room temperature (25-27°C) was performed. They found that, the rate of corrosion increases initially until reaches a maximum at around 900 hours 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%. The major chemical composition of Al alloy were silicon with a (0.30-0.6 wt. %), iron (0.10-0.30 wt. %) and magnesium (0.035-0.6 wt. %).

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.

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

3. Experimental

3.1 Static Immersion Test

Corrosion characteristics of prepared metals (aluminum 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 hours) 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 (aluminum, 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 hours 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 by bubbling pure oxygen from oxygen bottle through the sampling containers. In this method, the oxygen flow process must be conducted at an extraordinarily low rate in order to achieve the optimum quality of enhancement and prevent any evaporation of the sample. Therefore, the flow rate of 1 ml/min has been deemed appropriate and was chosen for this work. On the other hand, de-oxygenating process was done in two steps: bubbling pure nitrogen through the fuel samples at very low flow rate followed by heating up the fuel to evaporate the residual saturated oxygen followed by rapidly cooling down the fuel to minimise any fuel molecules loss. Oxygen will leave the system without condensation. Schematic diagram of the process is shown in Figure 1.

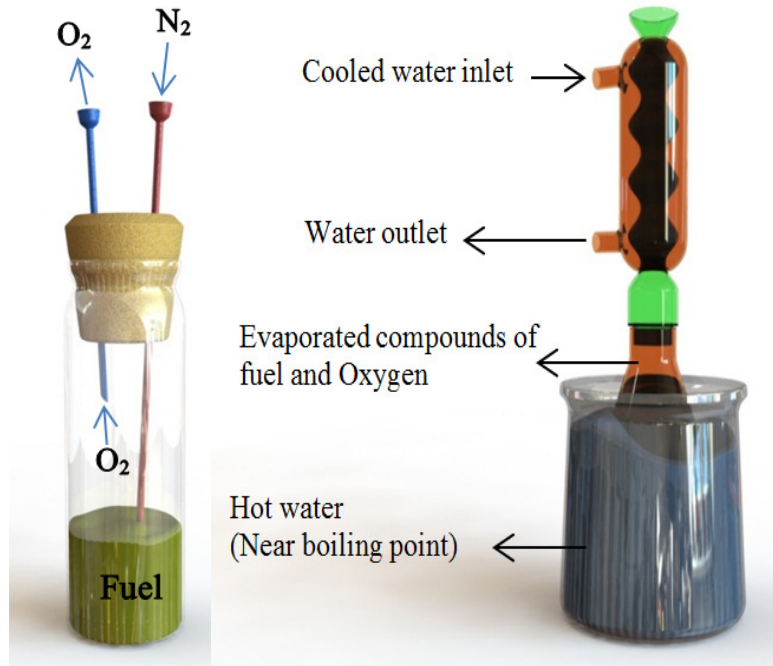


Figure 1 Deoxygenating Process

Likewise, based on literature [15] the presence of water in the fuel may increase the total rate of corrosion in metals exposed to these fuels. Water may be absorbed into the fuel during the storage and also due to the both fuel properties and environmental issues. Therefore, effects of excess water in fuel were investigated by adding up water into the blends. Water with blend at a ratio of 5 % was added to the mixture of fuels. Likewise, in order to prevent any external influence (such as pressure and environmental impact) on the metal coupons, test samples were kept in closed pressure resistant glass bottles. Moreover, a calibrated Carbolite® laboratory oven ($\pm 0.2^{\circ}\text{C}$ temperature stability) was employed for controlling and monitoring the temperature within desired limit.

3.2 Surface and Fuels Analyses

The surface pit morphology and elemental composition were scrutinized by scanning electron microscopy linked to an energy dispersive X-ray spectroscope (SEM/EDS) device (Jeol 6060 SEM with Oxford EDS). Also, X-ray diffraction (XRD), (Bruker D8 FOCUS), was employed at ambient temperature for oxide layers identification, elemental analysis and also identification of corrosion products on the surface of samples. In addition, after the immersion tests reconnaissance of changes in fuel composition was performed by Perkin Elmer Clarus 600 Gas Chromatography / Mass Spectrometry (GC-MS). Besides, the level of acidity of the fuels was investigated using total acid number (TAN) measurement. Both PH and colour change measurement methods were employed simultaneously for obtaining reliable results. Before and after the immersion tests, the viscosities of

solutions were also examined according to ASTM standard D-455 using CANNON FENSKE ROUTINE (PSL ASTM-IP 50) viscometer at 40°C.

4. Results and Discussion

4.1. Corrosion Rate

Analysis of corrosion damage on metals was performed using equation (1). This is currently used in many studies by other researchers [25].

$$\text{Corrosion rate } (R) = \frac{K \times W}{A \times T \times D} \quad (1)$$

Where W is weight loss of metal pieces in (g), A is the metals exposure area in (cm²), T is the exposure time in (hours), D is density of the sample in (g/cm³) and finally, K is the constant which can be calculated for several units such as mils (0.001 inch) per year (mpy) with value of 3.45×10⁶.

Results of corrosion rate calculations at 80°C are given in Figure 2. As can be seen, corrosion damage has occurred in all samples during the immersion test. However, copper coupons experienced more reduction in weight and therefore larger corrosion rate in comparison with aluminium samples. Investigation of results reveals that additional water and oxygen cause a significant increase in corrosion rates whilst absence of oxygen leads to reduction in loss rates for total weight. Moreover, an increase in concentration of biodiesel means higher proportion of fatty acids in fuel compounds. Therefore, more biodiesel resulted in larger corrosion. These explanations are in good agreement with experiment of Kaul et al. [16] who reported that higher corrosivity of biodiesel is caused by higher concentration of unsaturated fatty acids in fuel compositions. Besides, other investigators corroborated the enhancement in corrosion rates of specimens [15, 24].

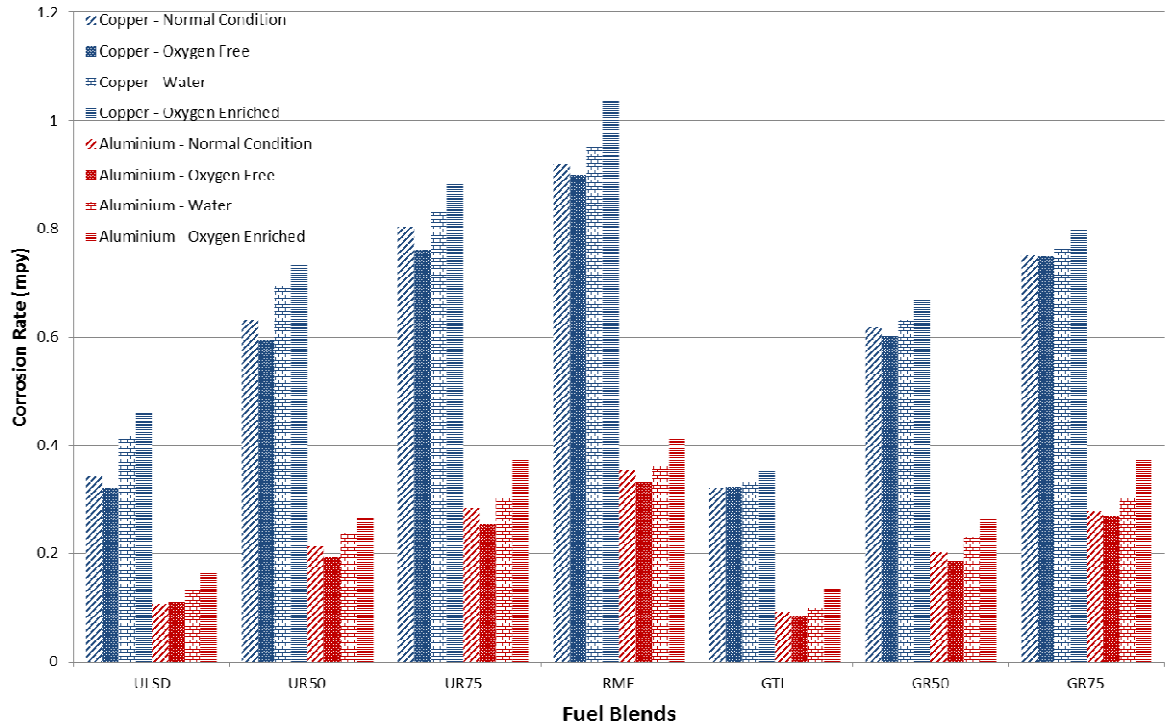


Figure 2 Corrosion rates of samples at 80°C

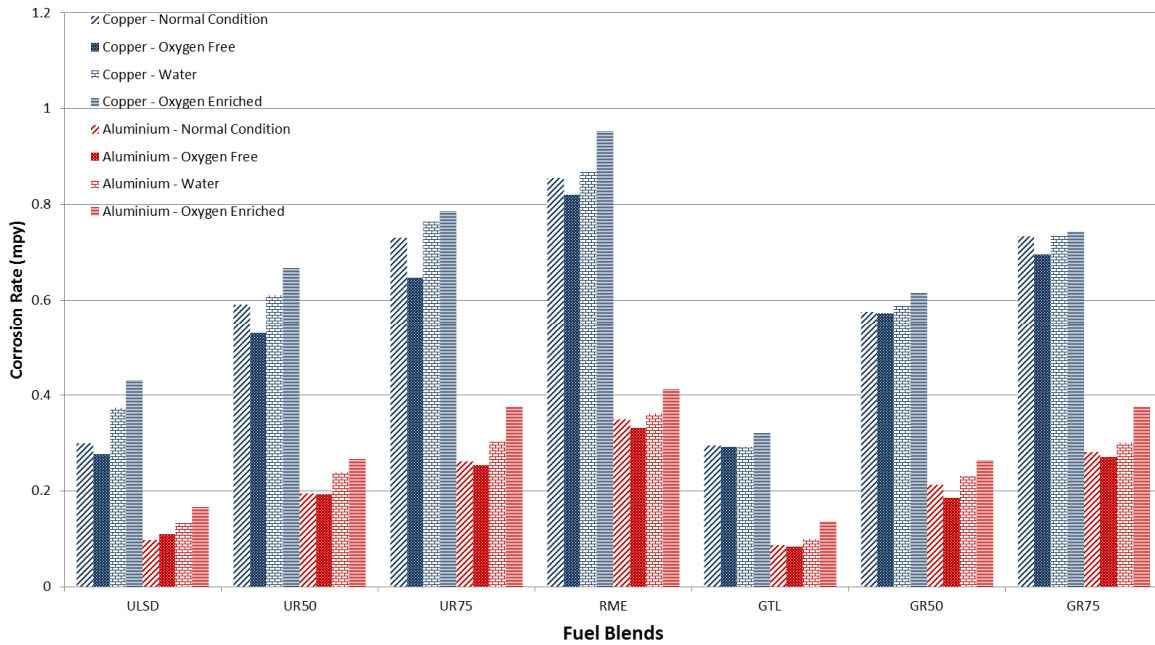


Figure 3 Corrosion rates of samples at room temperature

Results of corrosion rate calculation for metal samples at room temperature for long period of time are also shown in Figure 3. These results showed almost similar trend as those with higher temperature, but the corrosion rates were lower for all samples. For better analysis of effect of temperature and exposure time on corrosion damages, copper samples were kept at room temperature for different exposure times. Results of corrosion rates of copper samples exposed to three main fuels for different periods of times are shown in Figure 4. It was found that corrosion rates increased with increase in exposure time to a maximum and then decreased gradually to the final values reported in Figure 3. This can be due to equilibrium state occurrence for corrosion process and also decrease in rate of corrosion product layer dissolution at the surface of metals which results in generation of a protective layer on the surface.

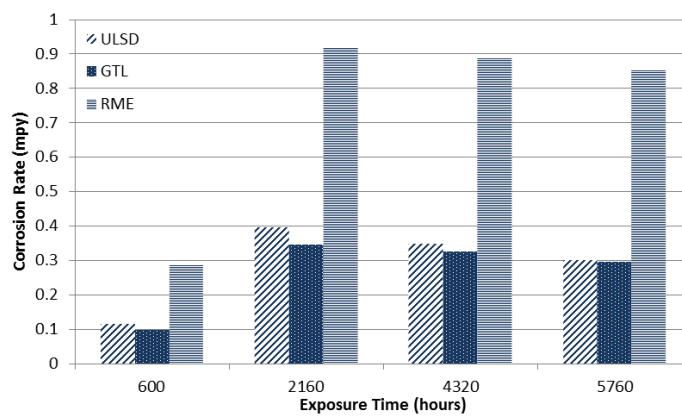


Figure 4 Corrosion rate of copper samples exposed to pure fuels for various immersion times

Also by comparison of results of corrosion rates for 600 hours at both room and elevated temperature it can be found that temperature has a significant role in enhancement of corrosion rate. It should also be noted that for both test conditions (high and room temperature) The GTL (gas-to-liquid) was found to be the least corrosion-aggressive fuel compared with the other two.

4.2. Total Acid Number (TAN)

TAN value as a part of examination of fuel characteristics was measured with by titration to find the amount of base required neutralize the sample and thus determining the extent of acidity in solution [26]. Figure 5 indicates the attained TAN values for the different fuel mixtures. The limit for TAN number of biodiesel is specified by ASTM D6751 standard and has a value of 0.5 mg KOH/g [14]. As it can be observed, higher concentration of biodiesel resulted in higher TAN values after execution of immersion tests. Furthermore, notably higher TAN values were experienced with those blends exposed to copper coupons compared to those exposed to aluminum. Moreover, results show that

absence of oxygen in fuel can cause a lower TAN value, while presence of water as well as oxygen leads to increases in TAN number. Additionally, corrosion phenomenon can be accelerated through the consideration of temperature parameter. Higher temperature permitted to formation of adequate conditions for compounds to getting involved in probable reactions. However, in this experiment slightly higher quantity of TAN value were obtained by those samples which participated in room temperature test. Although higher temperature results in higher TAN, this can be due exposure to fuels for a long time. These consequences are in good agreement with obtained results from M. A. Fazal et al. [14] According to their research; TAN value of copper exposed in palm diesel was increased with increasing exposure time. In another research by Fernandes et al. [27] the TAN value of biodiesel with soaked carbon steel, initially decreased and followed by slight enhance due to the formation of organic acid. Results from room temperature tests had exactly similar pattern to the high temperature ones, but the numbers were slightly higher due to higher exposure time.

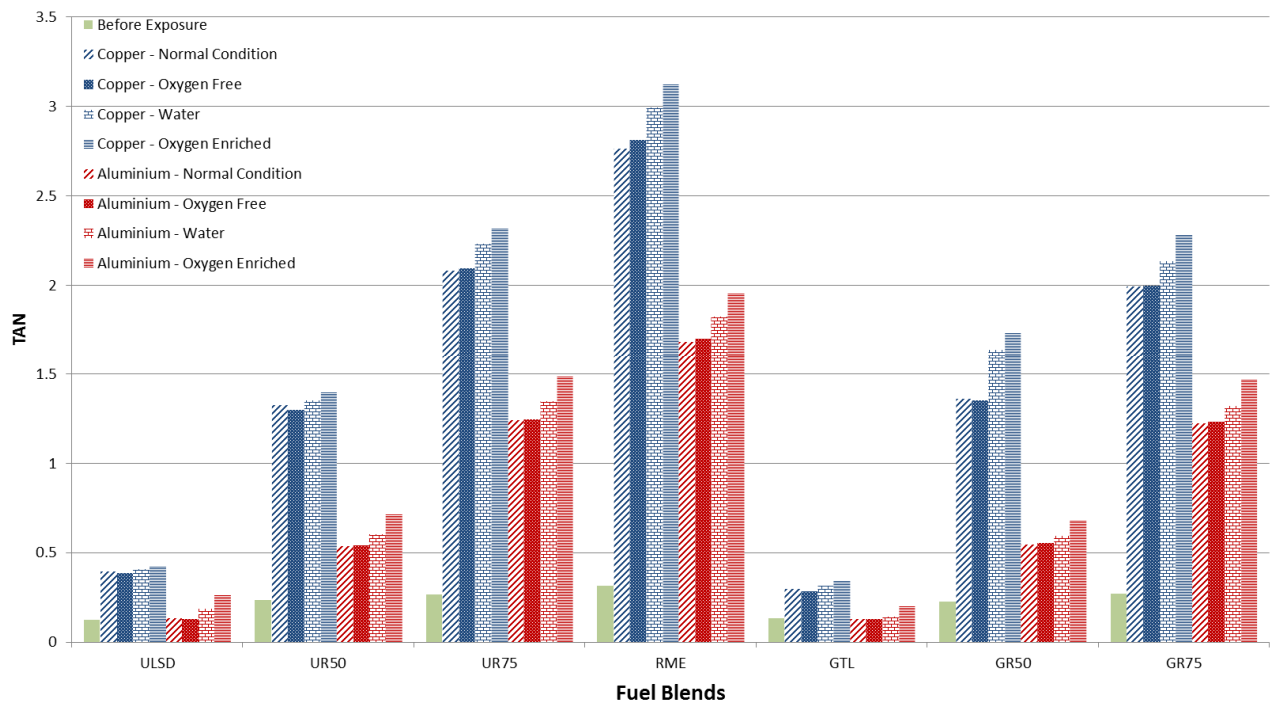


Figure 5 TAN values of the fuels blends exposed to metals at 80°C

4.3. Kinematic viscosity

Change in viscosity value indicates that the fuel composition changed as a result of corrosion product generation as well as formation of other compounds during the tests [24] In general, viscosity of the fuels must be located within the previously proposed standards (ASTM D6751 for biodiesel, 1.5-6 mm²/s) and (ASTM D975 for diesel, 1.5-4 mm²/s) in order to prevent fuel leakage and increase in combustion process quality [28] Kinematic viscosities of all blends before and after immersion for 600 h at 80°C are listed in Table 2. Investigation of results indicates that viscosities of all fuels have grown slightly as a result of new corrosion products and compounds formation. In addition, solutions that contain copper corrosion products species have experienced this enhancement slightly more in comparison with others.

Table 2 Kinematic Viscosity of Blends Exposed to Cu and Al

	Normal Condition		Added Water		Oxygen	
	Before	After	Before	After	Free	Enriched
Blends Exposed to Cu						
ULSD	2.503	2.786	2.391	2.561	2.546	2.845
B50	3.417	3.657	3.232	3.395	3.523	3.897
B75	3.961	4.328	3.721	3.984	4.194	4.568
RME	4.518	5.135	4.233	4.862	4.974	5.456
GTL	3.497	3.539	3.312	3.398	3.576	3.698
GB50	4.023	4.368	3.782	4.008	4.206	4.512
GB75	4.25	4.451	3.980	4.195	4.398	4.687
Blends Exposed to Al						
ULSD	2.503	2.637	2.391	2.465	2.516	2.703
B50	3.417	3.597	3.232	3.284	3.516	3.784
B75	3.961	4.194	3.721	3.913	4.098	4.367
RME	4.518	4.846	4.233	4.721	4.782	5.132
GTL	3.497	3.567	3.312	3.364	3.541	3.621
GB50	4.023	4.208	3.782	3.905	4.168	4.412
GB75	4.25	4.316	3.980	4.120	4.316	4.498

4.4. Composition of fuels

Gas Chromatography Mass Spectrometry analysis is used to evaluate the compositional alteration in fuels exposed to aluminum and copper. The separation is accomplished using a capillary column (Perkin Elmer, Elite-1, dimethyl Polysiloxane). Results from GCMS indicate that under different conditions (additional oxygen and water) no significant change has occurred on biodiesel exposure to aluminum coupons.

Table 3 illustrates the concentration of major compounds in terms of abundance percentage of each parameter for biodiesel samples exposed to both metals at different conditions. As can be realized, biodiesel exposed to copper has experienced higher disintegration compared with other blends. Methyl oleate (18:1), Methyl linoleate (18:2) and Methyl Gamma linoleate (18:3) as the main compounds in rapeseed methyl ester biodiesel are the main esters that have reduced sharply in fuels exposed to copper. Besides, several different compounds such as alcohols (Heptatriacontanol), acids and esters with various concentrations were formed once immersion test has been conducted. Some of these compounds are listed in Table 4.

Table 3 Main composition of B100 before and after exposure

Chemical Name	Commercial Name	Relative Chromatogram Area %								
		As received	Al	Cu	Al Oxygen Enriched	Cu Oxygen Enriched	Al Added Water	Cu Added Water	Al Oxygen Free	Cu Oxygen Free
Tetradecanoic acid methyl ester	Methyl myristate (14:0)	0.0970	0.2631	0.1133	0.0453	0.0854	0.0470	0.0685	0.2836	0.0998
Hexadecanoic acid methyl ester	Palmitate (16:0)	4.3510	4.5528	4.0857	3.9916	2.6840	4.1369	3.0346	4.2985	3.9987
Octadecanoic acid methyl ester	Methyl stearate (18:0)	1.8380	1.9190	1.6504	1.3564	0.8470	1.4058	1.0367	1.7896	1.6649
9-Octadecanoic acid methyl ester	Methyl oleate (18:1)	63.2210	59.1348	55.7087	55.6273	42.1870	57.6521	46.3571	60.3610	56.3218
9-12-Octadecadienoic acid methyl ester	Methyl linoleate (18:2)	19.5470	13.1489	9.3654	13.2982	5.1235	13.7823	6.3815	15.3942	11.1240
6-9-12-Octadecadienoic acid methyl ester	Methyl Gama linoleate (18:3)	8.6870	6.1894	4.4398	6.8453	1.0325	7.0945	3.3647	7.1239	5.3028
Cis-11-Eicosenoic Acid acid methyl ester	Gadoleic (20:1)	0.6600	0.1365	0.8915	0.3126	0.2546	0.3240	0.4529	0.3648	0.5413
Cis-13-Docosenoic acid	Erucic (C22:1)	1.4590	1.2549	0.9978	0.9955	0.6781	1.0317	0.8896	1.2630	1.2364

Table 4 New produced and highly changed compounds in B100 after exposure

	Relative Chromatogram Area %							
	Al	Cu	Al Oxygen Enriched	Cu Oxygen Enriched	Al Added Water	Cu Added Water	Al Oxygen Free	Cu Oxygen Free
Cyclopropanoic acid, 2-methyl ester		0.7926		0.3256		1.035		0.6845
Heptatriacotanol		0.1264				0.364		0.1033
11,14-Eicosenoic acid methyl ester	0.0034	0.1062	0.0095	0.2031	0.013	0.3821	0.0065	0.0980
10-Octadenoic acid methyl ester	0.0031	0.0852	0.009	0.1365	0.0084	0.215	0.0098	0.1025
N-hydroxymethyl-2-phenylacetamide		0.0065		0.03485		0.1328		
2-Methyl cyclopentanol		0.0076		0.009748	0.0064	0.0129		
Heneicosanoic acid methyl ester	0.2958		1.036		0.864	0.0398	1.0326	
Nanoic acid		0.864		0.982		0.865		0.6589
Decanedioic acid		0.6479		1.369	0.097	1.416		0.3468
Methyl 9-oxononanoate		2.654		2.3178		2.034		2.1354
Hexadecanoic acid		0.0035		0.0136		0.00954		
Methyl 12-oxo-9-dodecenoate		1.035	0.3462	0.9874	0.316	0.9453		0.8457
Methyl 11-oxo-9-undecenoate	0.148	0.9548	1.06	1.036	0.978	1.0654		0.7485
Pentadecanol					0.097	0.364		
Myristic acid		0.2158		0.32158	0.26	0.12		
Methyl 9,10-epoxyoctadecanoate		1.259	0.64	1.0367		0.9864		
Methyl linolenate		2.365	1.64	3.0321	1.42	2.948		1.987
2-undecanone				0.9548		1.035		

4.5. Corrosion process

Oxide layer on the surface of a metal appears as a result of chemical reaction between oxygen atoms and metal components. In addition, oxygen is identified as a potent oxidizing agent by way of possessing high electronegativity. Therefore, oxide films on the surface of metal act as anodic film, which has a capability of charging metal species as well as creating potential difference between the various metal components. Accordingly, as long as oxygen atoms are introduced, corrosion products will be formed and oxide layers will be simultaneously dissolved into the fuel composition. In this manner, more oxygen stands for more corrosion and pitting. On the other hand, water can also be classified as a corrosive agent as it consists of oxygen and hydrogen elements in its elemental composition. Besides, it is discovered that the presence of H^+ in liquids can diminish the pH value of the fuel (enhancement in acidity). The larger is acidity of the fuel the greater corrosion rate is achieved.

It can be concluded that presence of water has a significant effect on corrosiveness of fuels. Oxygen and hydrogen in water can cause increase in acidity and corrosion product layer formation.

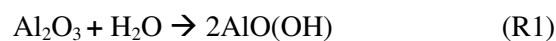
GTL fuel is produced through the Fischer-Tropsch process by conversion of syngas into single alkane chain [29] Besides, alkanes are naturally chemically strong and virtually nonpolar and these

characteristics caused them to have lower tendency to react with other compositions (saturated). Therefore, as expected no significant reactions between GTL and metals were observed throughout the immersion tests. However, reaction of aromatic rings present at low percentage together with alkyl groups (C–H bonds) leads to formation of aryl groups (R) in the supplied ultra-low sulfur diesel, since aromatics are usually reactive agents in the fuel. Therefore, ULSD exhibits greater readiness to react with metal molecules in order to engender the deterioration compared with GTL which has smaller reactivity.

Overall, due to the presence of oxygen and amount of diluted water and volatile acids (such as acetic and formic acid) in biodiesel composition, a lower pH value is obtained, which eventually could result in metal degradation. In addition, it was reported in other works [14, 15] that the corrosion process depends on factors such as materials, biodiesel properties and temperature condition.

4.5.1. Corrosion process of Aluminum

It is reported that the oxide layer on the surface of aluminum has an extremely low solubility and conductivity. In addition, temperature parameter should be considered as it is always as an important factor in formation of oxide film. Furthermore, it has been discovered by researchers that anodic films which form on the surface of aluminum are usually thin and have high density. However, these properties usually depend on physical and chemical attributes of the solution. Mostly, passive films on aluminum surface are characterized as n-type semiconductors [30]. The rate of corrosion in the metal is directly related to the existence of n-type semiconductors. Formation of aluminum oxide (Al_2O_3) film on the surface of metal takes place promptly; however, the dissolution procedure of passive layer is performed gradually. This results in less dissolution of aluminum as well as the delay in corrosion process of this element in aqueous solutions. Aluminum is by its nature an active element. Therefore, it rapidly reacts with oxygen in early stages of the process to form Al_2O_3 which finally can result in creation of white crystal of boehmite (AlOOH). This type of aluminium oxyhydroxide is formed at high temperature. Furthermore, due to the presence of water another corrosion product $\text{Al}(\text{OH})_3$ is generated on the surface of metal. Possible reactions mentioned above are listed below in R1 and R2.



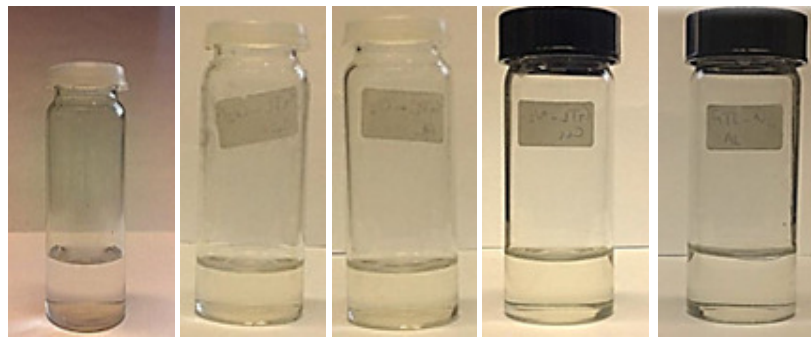
4.6.2 Corrosion process of Copper

The color change from reddish brown into blue-greenish occurred in metallic samples in contact with fuel due to the formation of different oxide layers on the surface of metal. Copper in presence of oxygen reacts and produces Copper (I) oxide (Cu_2O), (R3). However, due to the instability of this component it reacts with oxygen to eventually form cupric oxide (CuO), (R4). Moreover, the creation of hydroxyl groups (OH) from the reaction of oxygen and hydrogen at the initial stages could ultimately result in formation of Copper (II) hydroxide ($\text{Cu}(\text{OH})_2$), (R5). The existence of Copper (II) carbonate (CuCO_3) due to the presence of carboxylate anions (COO^-) is also reported by M. A. Fazal [24]. According to their research, the amount of CuCO_3 was increased with immersion time while the concentration of other components such as Cu_2O and CuO were decreased. This is in good agreement with the obtained XRD results presented in Figure 9 and Figure 10.

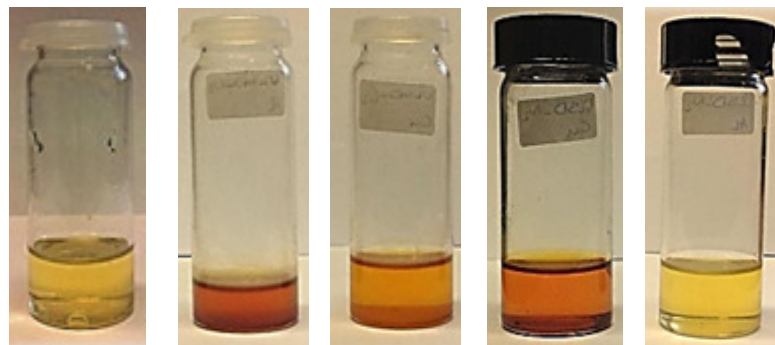


The corrosion process of copper is much faster than aluminum. This is due to the formation of corrosion product films and their dissolution in biodiesel with faster rate on the surface of copper. Likewise, copper acts as a catalyst for oxidation of fuel along with its extraordinary detrimental effects on oils. However, due to the rise in passive layer and formation of protective film on the surface of metal, corrosion rate reduces gradually. On the other hand, the formed oxide layer on the surface of aluminum acts as a protecting layer which prevents the oxygen and fuel component atoms to have contact with metal surface. Copper and aluminum do not have any carbon content in their compositions. Thus, an increase in carbon content through the corrosion process confirms the reaction accomplished between the oxide layer and available fatty acids in the biodiesel. Moreover, the production of salts can result from the occurrence of these reactions [30].

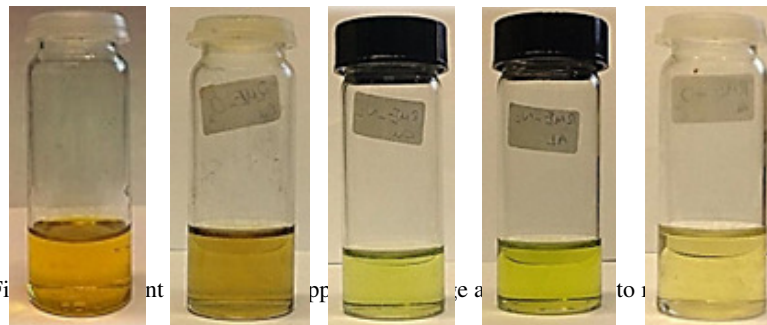
No significant color changes were observed at bottles containing GTL fuel. However, the color alteration in both biodiesel (RME) and ULSD shows the emphasis on the formation of new compounds as a result of oxidation along with corrosion process. The color of ULSD has been changed into opaque reddish orange as a result of the formation of CuO and other equivalent compounds. Moreover, even low percentage of sulfur can be a reason for this change. Besides, color alteration from clear yellow into bright pale green for RME fuel occurred by reason of CuCO_3 formation as a result of fuel degradation. The color changes in different blends can be seen in Figure 6.



GTL As Received GTL O₂ enriched, Exposed to Cu GTL O₂ enriched, Exposed to Al GTL O₂ free, Exposed to Cu GTL O₂ free, Exposed to Al



ULSD As Received ULSD O₂ enriched, Exposed to Cu ULSD O₂ enriched, Exposed to Al ULSD O₂ free, Exposed to Cu ULSD O₂ free, Exposed to Al



RME As Received RME O₂ enriched, Exposed to Cu RME O₂ enriched, Exposed to Al RME O₂ free, Exposed to Cu RME O₂ free, Exposed to Al

4.7. Surface Analysis

In reality, corrosion is basically identified as a surface phenomenon. Therefore, the evaluation of the extent of generated damage on the surface of metals has been accomplished by utilizing image analysing procedures.

4.7.1. SEM/EDS Analysis

Figure 7 shows the SEM images of different metals soaked in mentioned fuels using various rate of magnification for clearer corrosion understanding (100 μm and 10 μm per unit length as shown). As can be seen, the corrosion is much smaller for the metals that were in contact with diesel compared to those exposed to biodiesel. According to the visual inspection, the colours of copper coupons were turned into dark brown which confirms the formation of oxide layers (such as CuO and Cu_2O) on the surface of the sample. On the other hand, the rate of deterioration of aluminium was relatively minor as it was protected by passive films on its surface. Based on SEM illustrations, the intensity of corrosion attack increased with concentration of RME. On the other hand, according to the results from EDS (Energy Dispersive Spectroscopy), the peak intensities of the oxygen component formed on the surface were observed higher for the metals exposed to biodiesel in comparison with those exposed to ULSD. Figure 8 demonstrates the EDS results of different samples exposed to pure biodiesel only. Based on graphs, the increase in abundance of oxygen and carbon elements confirms the accumulation of oxide layer formed on the samples surfaces while the quantity of carbon can also be enhanced as a result of fatty acids salts presence. It should be noted that due to existence of the same pattern in elemental change of samples exposed to all fuel blends only samples exposed to pure biodiesel B100 at different conditions are shown.

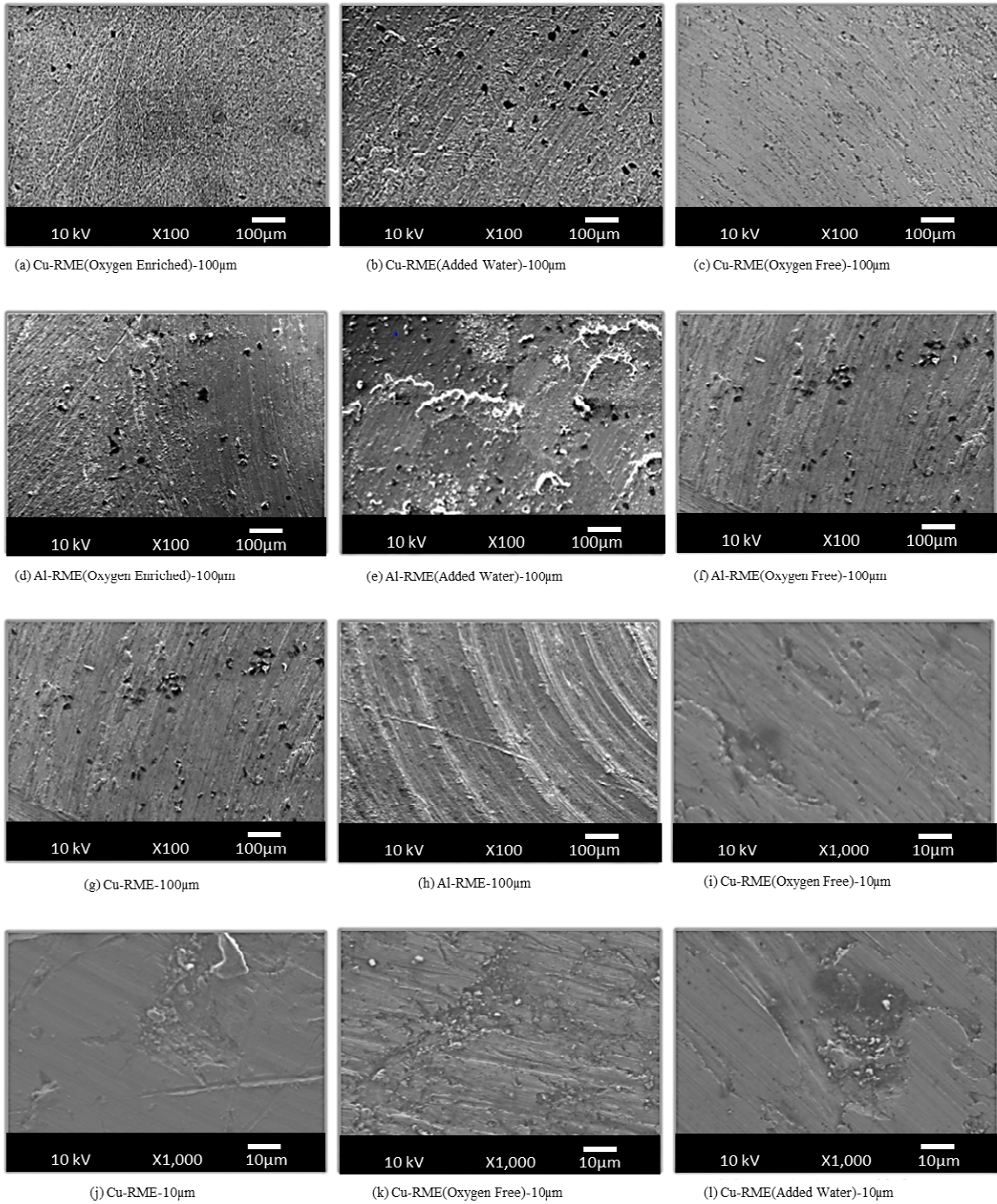


Figure 7 SEM images (100 µm unit) of exposed metal surface after immersion test (a-h) and SEM photographs of exposed copper in RME fuel with magnification of 1000x (10 µm unit) for better visualisation of corrosion damages (i-l).

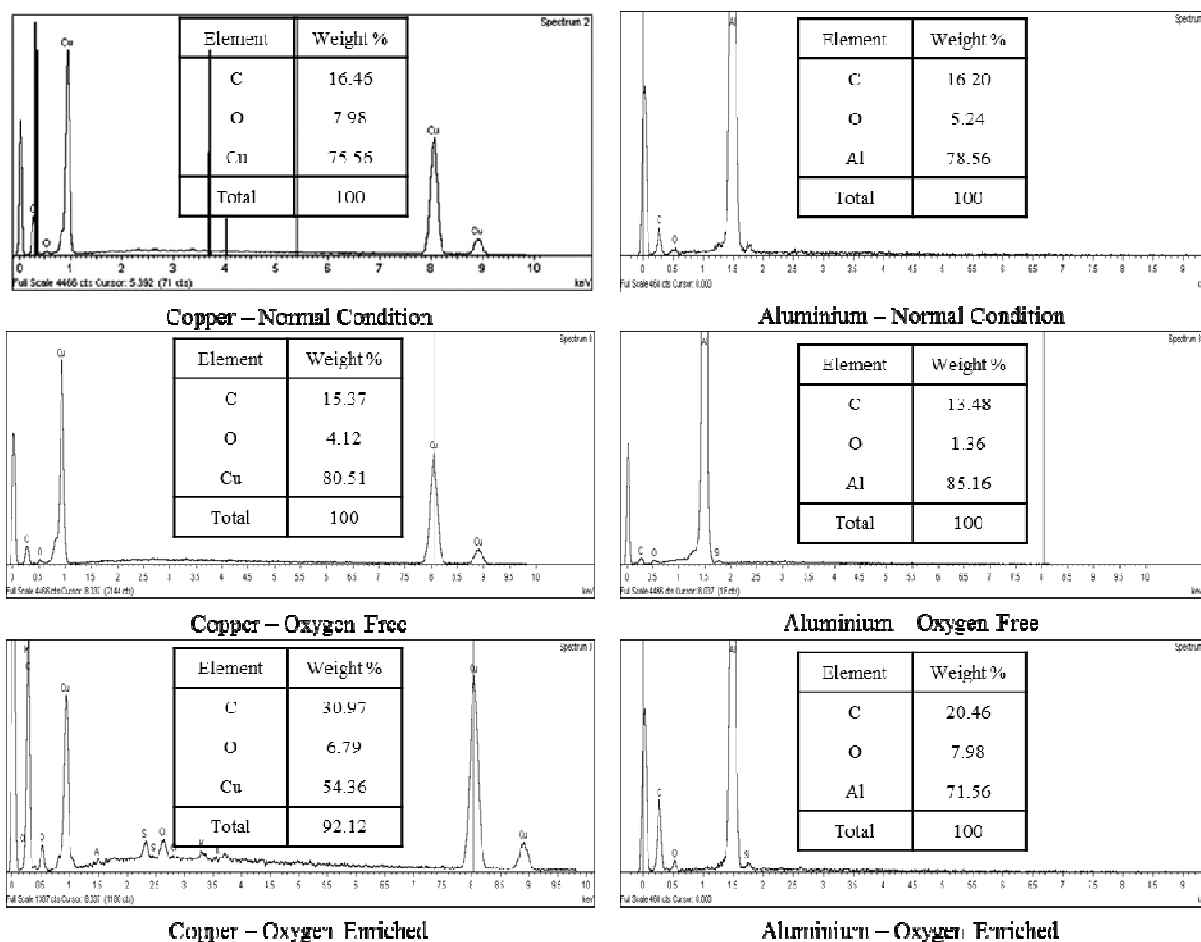


Figure 8 Elemental analysis of metal surfaces after exposure to B100 in three conditions (Oxygen enriched fuel, Oxygen free fuel and as received fuel)

4.7.2 XRD Analysis

Composition difference, types of corrosion products, oxide layers and also the distribution analysis of contributing elements were investigated using the x-ray diffraction (XRD) apparatus. XRD results shown in Figure 9 revealed that dense layers of Cu_2O and CuO are observable on the surface of copper coupon exposed to biodiesel after 600 hours immersion. Moreover, CuO and Cu_2O were also detected on the surface of other copper samples exposed to both the ULSD and GTL fuels. This is in good agreement with Feng et al. [31]. However, low concentration of these compounds is attributed to the inferior rate of oxidation as well as to minor rate of corrosion. In contrast, metal that was exposed to RME (containing dissolved water) showed higher concentration of $\text{Cu}(\text{OH})_2$, which seems to be an argument for the reactions between water and oxide layer. Besides, high intensity of CuCO_3 is clearly perceptible on the surface of copper coupon submerged in oxygen enriched RME. Moreover, cleaning the coupon sample before XRD determination can lead to elimination of some unstable particles from the surface of metal. These compounds include CuCO_3 , $\text{Cu}(\text{OH})_2$ and Cu_2O .

Furthermore, formation of Al_2O_3 as well as Boehmite (AlOOH) was confirmed through the XRD examination technique. Results of XRD analysis for aluminium samples and those for copper samples exposed to B100 with different test conditions (oxygen content) are shown in Figure 10. As the results of aluminium samples have shown the same compounds only one of them is shown in the Figure.

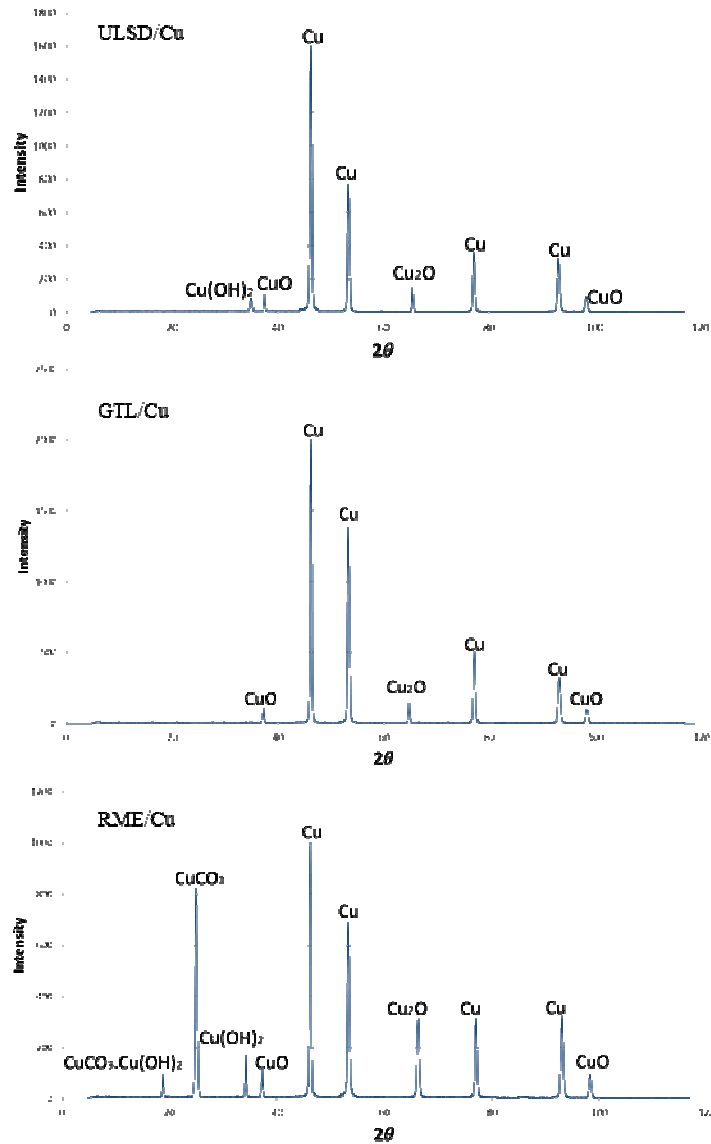


Figure 9 XRD analysis of copper samples exposed to pure fuels

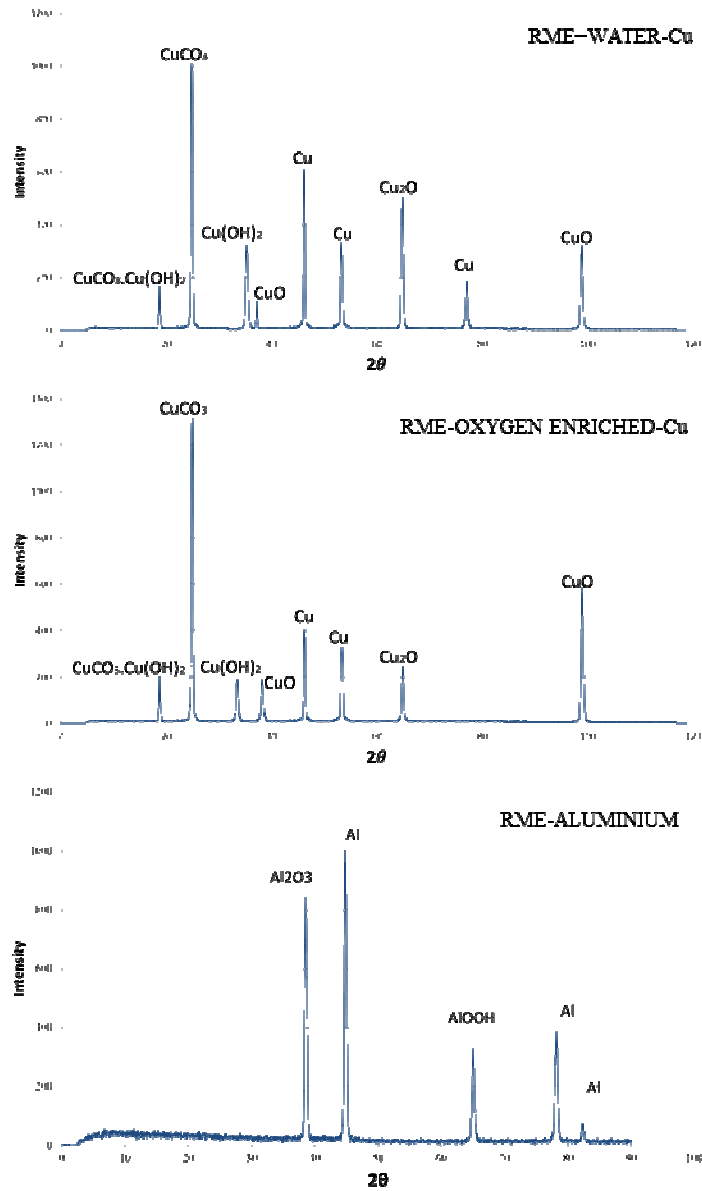


Figure 10 XRD results of copper samples at water and oxygen added condition (Top, Middle) and aluminium sample exposed to B100 (Bottom)

5. Conclusion

The corrosion behaviour of Aluminium and Copper in diesel, biodiesel and GTL blends with diverse concentrations has been investigated at varying conditions (long and short terms) and following consequences were found:

- For all specimens augmentation in corrosion rates was observed with an enhancement in concentration of biodiesel in blends.
- No significant changes were detected on the metals exposed to diesel and GTL fuels. Moreover, higher tendency for corrosion has been detected for copper coupons compared with aluminium. Besides, corrosion damage in all specimens has been assessed by SEM/EDS measurement technique.
- The reason behind the larger deterioration of copper coupons can be reasoned due to the lower resistance of formed oxide layer on the surface of this metal, also due to copper action as a strong catalyst to oxidise the biodiesel samples. on the contrary, the passive films generated on the surface of aluminium act as a protective layer which eventually enables it to form an efficient corrosion resistance.
- Results by XRD analysis on corrosion layer of the samples revealed that various oxide layers were formed on the surface of copper samples. CuO , Cu_2O , $\text{Cu}(\text{OH})_2$, CuCO_3 . $\text{Cu}(\text{OH})_2$ are the identified films generated on the surface. Likewise, various test conditions (such as different percentage of biodiesel concentration) resulted in changes in intensity of each oxide layer. Protective films formed on the surface of aluminium samples were found to be Al_2O_3 and AlOOH .
- Fuel degradation analysis showed that disintegration of existing fatty acid esters along with formation of new organic acids in the fuel can result in an increases in TAN of fuels exposed to metallic samples. Besides, formation of these new products has been confirmed via GCMS analysis apparatus.
- Kinematic viscosity of the fuels increased during the immersion tests. However, no significant changes beyond the standard values were attained for this parameter.

It can also be concluded that oxygen and absorbed water are the major factors in enhancement of corrosion as well as in fuel degradation. Therefore reduction of these elements in fuels can leads to smaller fuel corrosivity. Furthermore, higher temperature can be recognized as another crucial reason for increasing in rates of corrosion.

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