

An electrochemical study of carbon steel API 5L X-52 exposed in biodiesel

Vivi A Fardilah, Yustina M Pusparizkita, M Tauviquirrahman, AP Bayuseno

Abstract— Biodiesel is an alternative fuel consisting of Fatty Acid Methyl Ester (FAME) and is currently widely used. However, one disadvantage of biodiesel is that it is hygroscopic, making it easy to corrode various materials, especially metals. Carbon steel is a material commonly used as a distribution pipe, both flowline and pipeline. The use of carbon steel in various operating tools often faces significant problems related to corrosion resulting in damage. Therefore, it is necessary to investigate corrosion tests for carbon steel material due to biodiesel exposure. This study investigated the corrosion resistance of carbon steel API 5L X-52 using electrochemical monitoring techniques such as Open Circuit Potential (OCP) and Tafel plot. For the experiment, the carbon steel was exposed to a mixture of biodiesel and 3.5% NaCl solution for 168 hours at 30°C. The electrochemical results indicated that high biodiesel concentration potentially accelerates the corrosion rate of API 5L X-52. Meanwhile, the SEM/EDS images depicted the form of damage as localized corrosion. The corrosion products formed on the metal surface are FeO, Fe₂O₃, and Fe₃O₄.

Index Terms— Electrochemical, carbon steel, biodiesel, SEM, XRD, hydrocarbon, tafel polarization.

1 INTRODUCTION

The corrosion resistance of materials for casings, pipes and other installations is increasingly becoming a concern when biofuels such as biodiesel are gaining worldwide attention as an alternative fuel to replace mineral diesel derived from conventional fossil sources [1] [2]. Biodiesel is considered chemically stable in pure form. However, it can become more corrosive than diesel fuel, according to previous studies, due to its greater hygroscopicity, higher electrical conductivity, higher polarity, higher solvency, the presence of water and oxygen in biodiesel, which promotes microbial growth, and finally, its auto-oxidation, which produces corrosive agents [3]. Higher susceptibility to degradation and contamination causes significant issues in the problem of biodiesel utilization. The situation became more complicated when the contact of biodiesel with different metals [4]. Carbon steel is currently the most widely used engineering material because the material is strong, readily available, and relatively cheap [5]. Carbon steel plays an irreplaceable role in modern life and production, but it suffers from both abiotic and biotic corrosion damage, which will bring severe safety and economic problems.[6]

Corrosion is a phenomenon of degradation of material properties in an environment such as soil, water, and atmosphere due to the interactions that occur between them [7]. The result of the electrochemical reactions of corrosion, namely chemical reactions that occur involving the transfer of electrons, is the loss of material and damage. The electron transfer process takes place through a series of oxidation reactions at the anode and reduction at the cathode. Electrons will be released from the anode side and captured on the metal cathode side. The reactions that occur at the cathode can vary according to the environment, but the most common is the reduction of oxygen which occurs at neutral or alkaline pH [8]. Under acidic conditions, protons can act as cathodic reactants [9]. In the case of biodiesel, the persistence of mono- and di-glycerides generated from an incomplete reaction in the syntheses of methyl es-

ters make it possible to absorb water. The molecules can act as an emulsifier and promote water to be mixed with biodiesel. The presence of water is a crucial trigger of reactions that leads to corrosion. The water content of biodiesel was initially high, and after 7 months of storage, it significantly increased at an average of 59%. Not only water content, but the acidity of biodiesel also increased with storage time. The increase in acid value resulted from the oxygen content of biodiesel and molecule interactions during storage duration. A larger quantity of free fatty acid present in fuel will not only lead to greater acid value but can also be the reason for rusting in the fuel pipeline [10]. Some researchers suspect that the presence of biodiesel as fuel causes an increase in the acidity of the fuel and contributes to an increase in corrosion rate [11][12]. There are various investigations in the literature concerning the corrosion of different metals in biodiesel [13]. The objective of this study aims to investigate the corrosion behavior of carbon steel API 5L X-52 in palm biodiesel with different concentrations during storage time, and to evaluate its influence on the degradation of the fuel properties using electrochemical measurements, SEM, and X-ray diffraction.

2 MATERIAL AND METHODS

2.1 Preparation of Biodiesel and Material

Commercial diesel oil was purchased from PT Pertamina gas station and palm oil-based biodiesel (B100) was obtained from APROBI (Indonesia Biofuel Producer Association) through PT Wilmar. The physical and chemical properties of the prepared biodiesel and commercial diesel fuel are shown in Table 1 and Table 2.

The metal used in this research is carbon steel (CS) API 5L X-52 with the composition shown in Table 3. The size of each specimen has a diameter of 15 mm and a thickness of 20 mm. The CS sample used in the work was prepared following ASTM G 31-72 standards by polishing using coarse (240), me-

dium (600), and fine (1200) grid silicon carbide (SiC) abrasive paper, rinse in water and ethanol. The cleaned samples were stored in desiccators.

TABLE 1
PHYSICAL AND CHEMICAL PROPERTIES OF THE PREPARED BIODIESEL FAME

Test	Results	Standard Specification	Standard Method
Density at 40 °C	857	850-890	ASTM D 1298
Viscosity Kinematic at 40°C (mm ² /s (cSt))	4,5	2,3-6,0	ASTM D445
Cetane number (Min)	58	51,0	ASTM D613
Flash Point (covered bowl) (oC, Min)	158	130	ASTM D93
Copper Plate Corrosion (3 hours at 50oC) (Max)	1a	No 1	ASTM D130
Carbon Residue:			
100% Sample (% mass, Max)	0.004	0.05	ASTM D4530
10% Distillation Dregs (% mass, Max)	0.16	0.3	
Distillation Temperature 90% (oC, Max)	352	360	ASTM D1160
Sulfated Ash (% mass, Max)	0.006	0.02	ASTM D874
Sulfur (mg/kg, Max)	2.2	10	ASTM D5453
Phosphorus (mg/kg, Max)	ND	4	AOCS Ca 12-55
Acid Number (mg-KOH/g, Max)	0.3	0.4	ASTM D664
Free Glycerol (% mass, Max)	0.005	0.02	AOCS Ca 14-56
Total Glycerol (% mass, Max)	0.06	0.24	AOCS Ca 14-56
Methyl Esters Content (% mass, Min)	98.4	96.5	Calculated
Iodine Number (g-I ₂ /100g, Max)	46.6	115	AOCS Cd 1-25
Oxidation Stability :			
The induction period of the raincoat method (minutes, Min)	760	600	EN 15751
ASTM Color (Max)	1.0	3	ASTM D1500
Monoglycerides (% by mass, Max)	0.27	0.55	AOCS Cd 11-57
Water Content (mg/kg, Max)	139	350	DIN EN ISO 12937:2002
CFPP (Cold Filter Plugging Point (oC, Max)	12.2	15	DIN EN 116:1998
Metal I (Na+K) (mg/kg, Max)	2.8	5	EN 14108/14109, EN 14538
Metal II (Ca+Mg) (mg/kg, Max)	ND	5	EN 14538
Total Contaminant (mg/L, Max)	15	20	ASTM D2276, D5452, D6217

2.2 Carbon Steel Immersion

Immersion of CS was carried out in a 500 ml reactor made of glass containing 400ml of pure biodiesel medium (B100) or a mixture of 40% v/v biodiesel (B40). A reactor could accommodate 4 specimens. During the immersion, each reactor was covered with acrylic. The period of immersion was 7 days (168 h) at room temperature. After soaking during the specified time, several analyzes are carried out.

2.3 Electrochemical Measurements

All electrochemical measurements were carried out with the Potentiostat/Galvanostat (CorrTest Type CS 300), which was controlled by a computer running the CS Studio5 software. OCP and Tafel analysis tests were conducted to determine the corrosion behavior and corrosion rate of ordinary carbon steel. Due to the high resistance of the biodiesel solution, the tests were conducted in three-electrode cells. that included platinum (Pt) as a reference electrode, silver-silver chloride (SSCE) / (Ag/AgCl) as counter electrodes, and a reference electrode and carbon steel as working electrodes. The carbon steel was degreased with acetone and rinsed with de-ionized water before being immersed. All the electrodes were placed in form of perfect triangular geometry and faced each

other. The solution used for this measurement was 3.5% NaCl since this electrolyte supports an oxidation-reduction reaction and completes the electrical circuit between the anode and cathode. The setup of the electrochemical cell test was as shown in Figure 1.

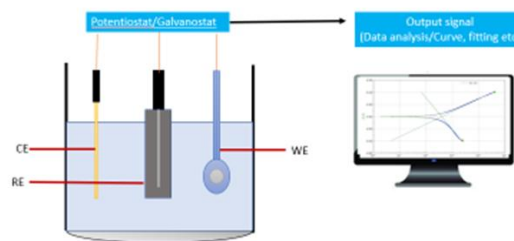


Figure 1 Electrochemical measurements set up.

The parameters obtained from electrochemical measurement are corrosion potential (E_{corr}), the corrosion current density (i_{corr}), and Tafel slopes (anodic b_a and cathodic b_c). According to Faraday's law, the corrosion rate of an anode is proportional to the corrosion current. The corrosion rate is usually expressed by the area weight reduction rate and the depletion rate, the unit commonly used is mpy (miles per year). The relationship between current density and corrosion rate can be calculated by Eq. 1. (Fontana, 2006).

$$R = 0,129 \frac{i_{corr} (ew)}{\rho} mmpy \quad (1)$$

where the R = corrosion rate (mmpy), i_{corr} = corrosion current density ($\mu A/cm^2$), E_w = equivalent weight (grams/equivalent) and ρ = indicates density (g/cm^3).

TABLE 2
PHYSICAL AND CHEMICAL PROPERTIES OF THE PREPARED COMMERSIAL BIODIESEL

No.	Characteristics	Unit	Limitation		Standard Method
			Min	Max	
1	Cetane Number and	-	53		D613
	Cetane Index	-	48		D 4737
2	Specific Gravity at 15 °C	kg/m ³	820	860	D 4052/ D1298
					D445
3	Viscosity at 40 °C	mm ² /sec	2,0	4,5	D2622/D4294
4	Sulfur content	% m/m	-	0,05	D86
5	Distillation:	Place at 90	°C	-	340
		Place at 95	°C	-	360
		Final boiling point	°C	-	370
		Flashpoint	°C	55	-
7	Pour point	°C	-	18	D97
8	Carbon Residue	% m/m	-	0,3	D4530
9	Water content	mg/kg	-	500	D6304
10	Oxidation Stability	gr/m ³	-	25	D2274
11	Biological Growth	-	Nihil		
12	FAME Content	% v/v	-	10	
13	Methanol and ethanol content	% v/v	Not detected		D4815
14	Copper blade corrosion	Merit	-	Class 1	D130
15	Ash Content	% m/m	-	0,01	D482
16	Sediment Content	% m/m	-	0,01	D473
17	Strong Acid Number	Mg	-	0	D664
		KOH/gr			
18	Total Acid Amount	Mg	-	0,3	D664
		KOH/gr			
19	particulate	Mg/l	-	10	D2276
20	Lubricity (HFRR wears her scar.@60 °C)	Mikron	-	460	D6079
21	Visual Appearance	-	Clear and Bright		
22	Colour	No.	-	1,0	D1500
		ASTM			

2.4 Characterization of Carbon Steel Surface

The observation procedure using SEM began with rinsing the specimen using aqua dm and ethanol (concentrations of 20%, 50%, 75%, and 98%). Then, the sample was dried and stored in a desiccator. Observational research was carried out using the FEI Quanta 650 FEG SEM at various magnifications. Moreover, Energy Dispersive Spectroscopy (EDS) for elemental mapping in microanalysis is also carried out. The corrosion products on biodiesel exposed on metal surfaces were investigated using XRD by scanning the material with Cu-K α radiation ($\lambda=0.154\text{nm}$) at a speed of $1^\circ/\text{min}$ at an angle range of $5\text{-}100^\circ$. XRD uses high score plus software to process XRD data with ICSD and ICDD PDF-2 2018 databases.

TABLE 3
CARBON STEEL API 5L X-52 CHEMICAL COMPOSITION (%WT)

Material	C	Mn	Ti	Al	Si	Cr	Ni	Cu	Co	Fe
API 5L X-52	0.14	0.662	0.087	0.047	0.011	0.207	<0.005	0.087	<0.033	Balance

3 RESULT

3.1 Tafel Polarization

The corrosion rate of the sample was determined by the Tafel polarization method which provides a polarization curve by applying different potentials in the positive and negative ranges concerning the open-circuit voltage. The result of the Tafel plot contains anodic and cathodic areas. The logarithm plot of the current Vs potential and the extrapolated current in the two Tafel regions (with the same voltage difference on both sides) gives the corrosion potential and corrosion current [14]. Figure 1 Tafel, for coupon CS API 5L X-52 shows that the corrosion rate of B100 is greater than all mixtures than B40 and the percentage of bio diesel continues to increase, the corrosion rate increases But, due to its unsaturated molecules and compositional effects, it is more oxidative and causes enhanced corrosion and material degradation [15] This also shows that the icoor value shifts to the right which indicates it is getting more corrosive [16].

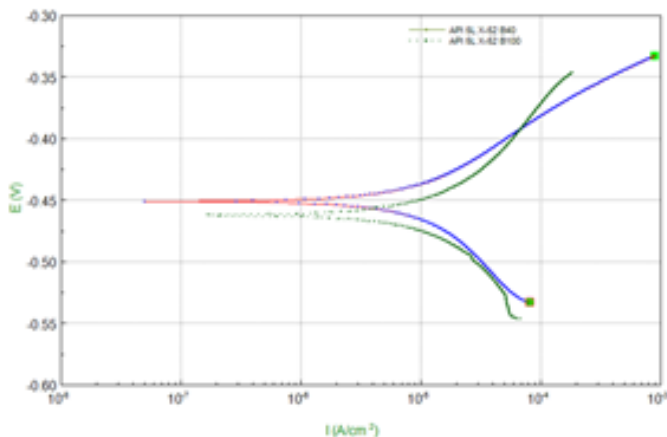


Figure 2. Polarization graph of API 5L X-52 carbon steel in contact variations B40 and B100

TABLE 4
RESULT OF CORROSION ANALYSIS OF CS API 5L X-52 VARIATIONS B40 AND B100

No.	Material	Biodiesel Concentration	Corrosion rate (mmpy)	Current density ($\mu\text{A}/\text{cm}^2$)	Potential (mV)	OCP (mV)
1	API 5L X-52	B40	0.12423	1.0657	-451.12	-382
2	API 5L X-52	B100	0.38534	3.3058	-462.36	-409.2

The results of the carbon steel polarization test for CS API 5L X-52 Specimen with concentrations of B40 and B100 can be seen in Figure 2. Based on table 1, it can be seen that the increase in biodiesel content in the addition of FAME vegetable oil will increase the corrosion rate of CS API 5L X-52. Figure 2 shows that with increasing levels of FAME, the anodic test of iron in 3.5% NaCl was in accordance with Tafels' law. Electrochemical analysis showed that carbon steel material quickly corroded when exposed to a mixture of biodiesel and a 3.5% NaCl. As biodiesel becomes the more dominant fuel source for transportation, these findings offer a new way to rapidly characterize the electrochemical corrosion of metals and provide insights for developing corrosion prevention strategies [17]. Short-term laboratory experiments such as these in a simulated environment are limited in their ability to predict long-term corrosion rates in the desired natural environment. [18]. For the highest corrosion rate value in the B100 variant, with a value of 0.38534 mmpy and the lowest value in the B40 diesel variant with a value of 0.12423. mmpy.

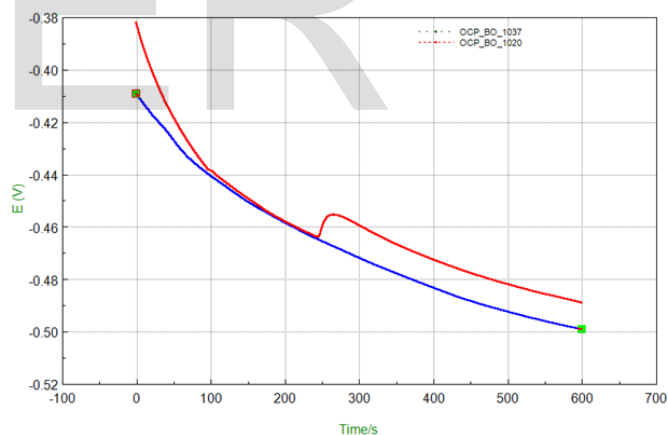


Figure 3. Open Circuit Potential

When the sample is placed in a series of cells, giving some delay per iod of about 600 seconds, obtain the OCP value. Therefore the OCP must be stable first and then proceed to electrochemical tests. Stable potential value gives supporting information for electrochemical impedance spectroscopy. Unfortunately, in this study, EIS testing was not carried out. Picture. 4 clearly shows that the OCP B100 is greater than mix B40 in case of coupon API 5L X-52 It also shows that B100 takes more time to stabilize, i.e. B100 has more stabilizing potency than B40.

3.2 Scanning Electron Microscope (SEM)

Coupons upon exposure in biodiesel were then cleaned with soft toothbrush in deionized water and then degreased

by acetone. The SEM micrographs of steel carbon after exposure in biodiesel are shown in Figure 5. The exposed coupons were then cleaned and SEM micrographs taken for further investigation CS API 5L X-52 B40 and CS API 5L X-52 B100 Figure 4 and Figure 5. A number of small holes were found to form randomly on the carbon steel surface exposed to biodiesel for 168 h. These holes increase in size with increasing immersion time. The tendency of pits also seems to increase with the addition of biodiesel content.

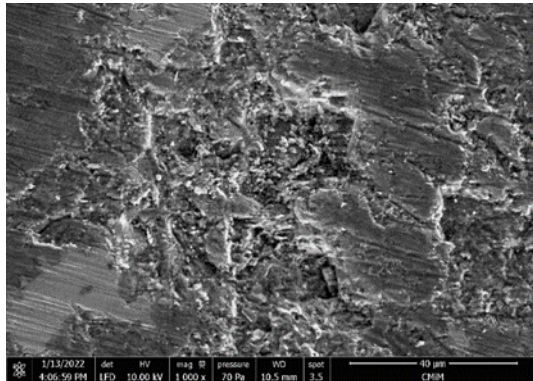


Figure 4. SEM CS API 5L X-52 B40

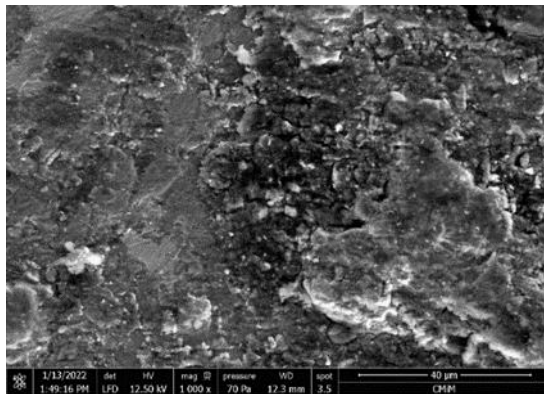


Figure 5. SEM CS API 5L X-52 B100

3.3 X-Ray Diffraction (XRD)

Shows XRD analysis on the surface of CS API 5L X-52 B40 and CS API 5L X-52 B100 after immersion test for 168 hours. XRD analysis was performed with an angle of incidence of 1.0, positions from 30° to 90° and a step size of 0.1. Both CS API 5L X-52 B40 and CS API 5L X-52 B100 show the formation of oxides. XRD CS API 5L X-52 B40 results revealed the presence of metal compounds, namely FeO, Fe₂O₃ and Fe₃O₄. FeO compounds are found at an angle of 2θ 41.6°. In Fe₂O₃ find it at an angle of 2θ 43.4° and Fe₃O₄ 73.7°. On the exposed surface of B100, the Xrd results for Fe compounds at an angle of 2θ are 44.65 and 82.28. then followed by Fe₂O₃ compounds 43.8 and 78. It was also detected for the next compound Fe₃O₄ at 2 theta angles 59.54 and 65.42. According to XRD analysis, the presence of Fe₂O₃, FeO and Fe₃O₄ compounds on the surface of API 5L steel immersed in palm biodiesel, where Fe²⁺ was in high proportion when it was on the API 5L surface. [3].

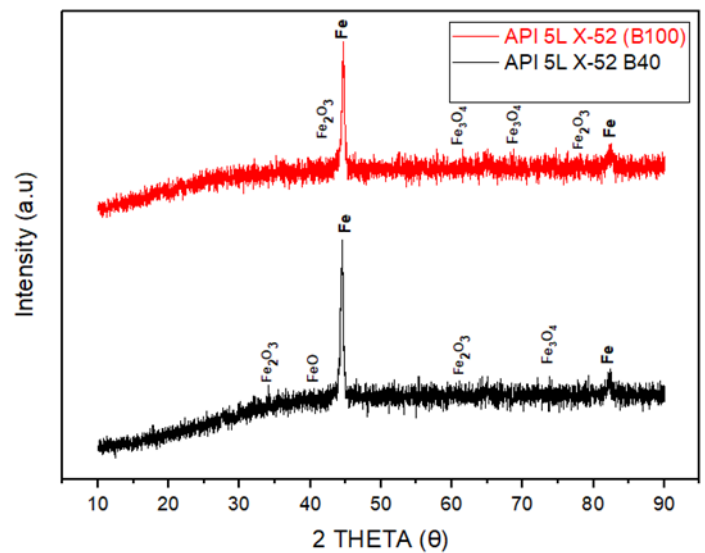


Figure 6. XRD analysis of corrosion products formed on CS API 5L X-52 B40 and CS API 5L X-52 B100 surface exposed biodiesel at 25C for 168 h

This indicates that each corrosion product formed on the surface of B40 and B100 is sufficiently formed to be detected by XRD technique. It has been seen previously that the corrosion rate of the two metals slightly increased with the different percentages of immersion biodiesel content. This indicates the possibility of the formation of some kind of protective layer on the metal. However, this layer appears to be too thin for XRD to detect. Further investigations with surface analysis techniques have been planned for future studies.

4. CONCLUSION

1. Compared with the conditions of concentrations of B40 and B100, it was found that the corrosion rate was lower in conditions without B40 biodiesel mixture than in B100 conditions where the corrosion rate increased. The higher oxygen concentration when exposed to biodiesel from diesel fuel makes biodiesel more corrosive due to fatty acids.
2. The corrosion rate values for API 5L X-52 B40 and API 5L X-52 B100 is 0.12423 mmpy and 0.38534 mmpy
3. SEM clearly shows that the surface degradation is severe at B100, compared to B40 mixture
4. The corrosion mechanism of biodiesel is caused by chemical corrosion and corrosion products such as metal oxides that produce compounds (FeO, Fe₂O₃, Fe₃O₄).
5. The respective order of degradation is B100 > B40. the degradation shown was similar for all test durations of 168 days.

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- Vivi Aisah Fardilah is a undergraduate student in the department of mechanical engineering in Diponegoro University, Jl. Prof. Soedarto SH Tembalang Semarang, phone/fax : +62(024)7460059. E-mail: aisahfardilahvivi@gmail.com
 - Yustina M. Pusparizkita is a lecturer and researcher in the department of environmental engineering in Diponegoro University, Jl. Prof. Soedarto SH Tembalang Semarang, phone/fax : +62(024)7460059. E-mail: ympusparizkita@lecturer.undip.ac.id
 - Athanasius Priharyanto Bayuseno is a lecturer and researcher in the department of mechanical engineering in Diponegoro University, Jl. Prof. Soedarto SH Tembalang Semarang, phone/fax : +62(024)7460059. E-mail: apbayuseno@gmail.com
 - Mohammad Tauwqiirrahman is a lecturer and researcher in the department of mechanical engineering in Diponegoro University, Jl. Prof. Soedarto SH Tembalang Semarang, phone/fax : +62(024)7460059. Email: mtauwqi99@lecturer.undip.ac.id