

Evaluation of Corrosion Susceptibility of Structural Steels in Biomass Derived Pyrolysis Oil

Jiheon Jun, Dino Sulejmanovic, James R. Keiser, Michael P. Brady and Michael D. Kass
Material Science and Technology Division, Oak Ridge National Laboratory,
One Bethel Valley Road, Oak Ridge, TN 37831, USA

ABSTRACT

Biomass derived pyrolysis oil is a promising renewable energy source. Due to the variety of biomass feedstocks, the bio-oils could contain a wide range of organic constituents which would provide unique corrosive environments for structural materials. A preliminary work exposed different classes of steels and stainless steels to selected organic constituents of biomass pyrolysis oils and found that corrosion susceptibility, assessed using electrochemical impedance spectroscopy (EIS), was prominent in the steels with Cr lower than 11 wt.%. Although this result suggests stainless steels will resist corrosion by certain organic constituents, it may not be sufficient to predict the corrosion performance in real bio-oils. Therefore, this study attempted electrochemical measurements on Cr-alloyed steels and stainless steels directly exposed to a biomass derived pyrolysis oil. To overcome the low conductivity of bio-oils, a customized Luggin capillary was designed to minimize the ohmic path in bio-oils. The results of this work will be reported.

Key words: biomass pyrolysis oil, stainless steels, bio-oil storage, Electrochemical Impedance Spectroscopy, corrosion

INTRODUCTION

Biomass-derived pyrolysis oil, or simply bio-oil, is a renewable energy source that could substitute for fossil derived fuel. One concern for bio-oils is their potential corrosivity attributed to the water and organic acid contents.¹⁻⁵ Therefore, the corrosion compatibility of structural steels used to transport, and store bio-oils should be investigated to avoid any maintenance issue or failure caused by corrosion. Previous studies reported that raw bio-oil exposure tests caused significant mass loss of plain steels but minimal or no loss in different grades of stainless steels.^{6,7}

While the mass loss measurement allows direct and quantitative comparison of alloy corrosion resistance, it usually involves long exposure times. To determine the corrosion resistance for various ferrous alloys in shorter time, electrochemical impedance spectroscopy (EIS) was attempted using selected constituents of bio-oils.⁸⁻¹⁰ These works clearly distinguished corrosion

susceptibility of low Cr steel from high corrosion resistance of stainless steels in three aggressive bio-oil constituents by comparing the resistance elements determined from the impedance spectra. However, the results obtained from the previous work are not sufficient to assess the corrosivity of bio-oils that have more complex compositions. In present work, EIS measurements were conducted on the alloys immersed in a bio-oil with a customized electrochemical cell to minimize the ohmic drop due to the low conductivity of the bio-oil. Per author's best knowledge, this is the first reported attempt to electrochemically assess the corrosion behavior of structural steels in a real bio-oil. Similarly, another work presented by the authors for this conference also assessed corrosion behavior of Cr-Mo alloyed steels in real bio-oils.¹¹

EXPERIMENTAL METHODS

The alloy specimens for EIS measurements were machined from raw materials, 2.25Cr-1Mo steel and type 430F stainless steel in round bar form and type 430 stainless steel in sheet form. The composition of raw materials determined by inductively coupled plasma optical emission spectroscopy and combustion techniques are summarized in Table 1. 2.25Cr-1Mo and type 430 were chosen as commercial ferritic alloys with low and high Cr contents. Type 430F was also used to investigate sulfur effect on corrosion resistance. To characterize microstructures, the alloy specimens were cross-sectioned, epoxy-mounted, polished to mirror surfaces and observed with and without chemical etching. The etchant used was a mixture of 33% glycerol, 17% HNO₃ and 50% HCl in volume ratio. The etching time was less than 30 s at room temperature.

Table 1

Elemental composition of 2.25Cr-1Mo steel and 430 stainless steels, normal and F-grade with high sulfur content, in mass percent, N, O and S contents are in ppm. No measurement was made for O and N in 430 stainless steel.

Alloy	UNS No.	Fe	Cr	Ni	Mn	Mo	Cu	Si	C	N	O	S	Other
2.25Cr-1Mo	K21590	95.69	2.22	0.14	0.51	1.01	0.09	0.17	0.092	45	9	50	0.01Co
Type 430	S43000	81.82	16.92	0.15	0.26	0.05	0.13	0.33	0.035	-	-	20	0.08V
Type 430F	S43020	80.43	17.5	0.3	0.43	0.33	0.17	0.32	0.032	420	91	3260	0.06V

EIS measurements were conducted in a custom designed cell that schematically described in Figure 1 using High Ash and High Moisture (HAHM) bio-oil produced by National Renewable Energy Laboratory (Golden, CO, USA).¹² The conductivity of HAHM oil, measured by a commercial conductivity meter, was $\sim 120 \mu\text{S}\cdot\text{cm}^{-1}$ that is less than one half of a tap water conductivity, $\sim 270 \mu\text{S}\cdot\text{cm}^{-1}$. A teflon-made holder was used to expose 1 cm^2 of alloy surface which was prepared by 600 grit finish. A mercury sulfate electrode was loaded on a glass Luggin capillary filled with saturated K₂SO₄ as reference electrode. Platinized rhodium mesh was placed between the alloy surface and the Luggin capillary as counter electrode. The distances between the alloy surface, Luggin capillary and rhodium mesh were kept within 10 mm so that the ohmic drop would be minimized. For each measurement, corrosion potential (E_{corr}) of alloy specimens in the bio-oil was monitored for 1 h first, and then EIS was conducted at E_{corr} using the potential amplitude of $\pm 10 \text{ mV}$ and frequencies from 200 kHz to 5 mHz. All electrochemical measurements in this work were conducted at room temperature with the bio-oil open to air.

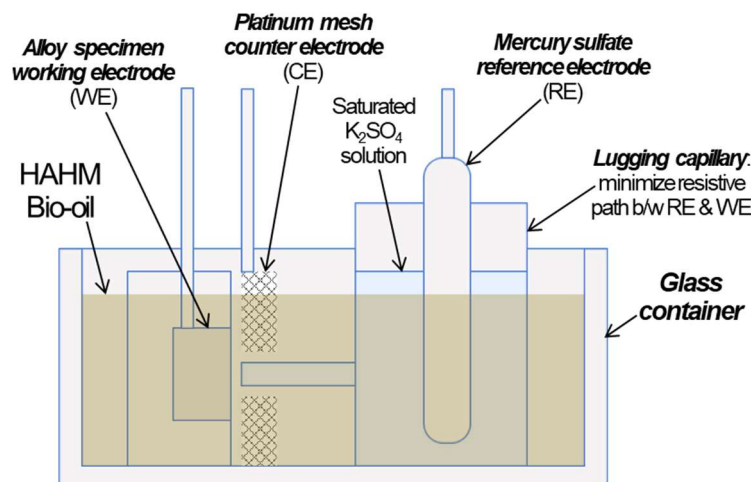


Figure 1: Schematic of electrochemical cell custom-designed for bio-oils. The volume of bio-oil in the glass container was approximately 100 mL.

RESULTS

The surfaces of type 430 and 430F are shown for as-polished and etched conditions in Figure 2. Type 430 exhibited polygonal inclusions with the size up to 10 μm (Figure 2a) and ferritic microstructure (Figure 2b). Type 430F, on the other hand, showed fiber-shaped inclusions along the direction of extrusion throughout ferritic grains and their boundaries (Figure 2c and 2d). The surface of 2.25Cr-1Mo steel was previously analyzed,⁸ which showed fewer inclusions in its ferritic microstructure.

The composition of inclusions analyzed by EDS is presented in Figure 3 for type 430 and 430F. The polygonal inclusions in type 430 were identified as TiN, while a distinctive region inside TiN contained other metals and oxygen (Figure 3a and 3b). The compositional differences in the sub-sections of a single inclusion has also been reported for type 304 stainless steels.¹³ Meanwhile, the fiber-shape inclusions in type 430F can be characterized as a mixture of Cr and Mn sulfides (Figure 3c and 3d), which is not surprising due to the high S content of the stainless steel. Sulfide inclusions were reported to increase corrosion susceptibility of stainless steels in aqueous solutions containing chlorides.^{13,14} However, it is an open question as to whether the sulfide inclusions would promote corrosion in HAHM bio-oil used in this work. Therefore, type 430 and 430F, almost identical in composition but sulfide inclusions only in F-grade, would make reasonable comparison to confirm the sulfide effect on corrosion susceptibility in HAHM oil.

The Nyquist impedance spectra of type 430 and 430F in HAHM oil are presented in Figure 4. The impedance values at the lowest frequency, i.e. the end point of each spectra on the right, were higher and close to $1 \times 10^{-5} \text{ ohm} \cdot \text{cm}^2$ (Figure 4a and 4b). This is indicative of high corrosion resistance of these alloys because such a high impedance value was observed in type 201 stainless steel that did not corrode in aggressive constituents of common bio-oils.⁸ The effect of oil immersion time appeared to increase imaginary impedance (Z'') but slightly decrease real impedance (Z') in the lower frequency regime in both type 430 and 430F.