

## **Corrosion Behavior of Alloy Structural Steels in Catechol and Biomass-Derived Pyrolysis Oils**

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### **ABSTRACT**

Electrochemical impedance spectroscopy (EIS) was used to assess the corrosion behavior of three steels, 2.25Cr-1Mo, 5Cr-1Mo and 9Cr-1Mo (UNS K21590, S50200 and K90941) in bio-oils and catechol, an organic constituent commonly found in bio-oils. Two types of biomass pyrolysis oils produced from selected forest residue feedstocks, classified as high-ash and high-moisture (HAHM) and low-ash and low-moisture (LALM) types and 10 wt.% catechol, were used to test the alloys. According to previous results, 10 wt.% catechol in a water and methanol mixture was corrosive to 2.25Cr-1Mo but not to 9Cr-1Mo, highlighting that increasing Cr content in the steels resulted in improved corrosion resistance. 5Cr-1Mo, a steel with an intermediate Cr content, was tested in catechol solutions to better estimate the critical value of Cr for corrosion resistance under these conditions. Also, the three alloys were tested in both HAHM and LALM bio-oils to assess corrosion susceptibility. For EIS measurements, a customized electrochemical setup was employed to minimize the ohmic path through the bio-oils. The corrosion susceptibility was evaluated by determining the resistance at the alloy-corrosive medium interface.

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

### **INTRODUCTION**

Biomass-derived pyrolysis oil, a renewable energy source, has corrosivity originating from its water and organic acid contents.<sup>1-5</sup> For example, a plain carbon steel and 2.25Cr-1Mo steel suffered from severe pitting attack, causing some pits deeper than 500  $\mu\text{m}$ , after 1000 h exposure to a pine sawdust bio-oil at 50°C.<sup>6</sup> To avoid corrosion attack by bio-oils, the use of stainless steels can be a practical, but expensive solution.

It was previously reported that mixed hardwood bio-oil exposure resulted in relatively small and essentially no corrosion mass loss for types 409 and 316L stainless steels (UNS S40900 and UNS S31603), respectively, as opposed to the greater mass losses measured in a plain carbon

and 2.25Cr-1Mo steel.<sup>7</sup> Lower or no mass loss of stainless steels was also observed in a similar study that used a different bio-oil.<sup>8</sup>

Besides the direct bio-oil exposure and corrosion loss measurements, electrochemical impedance spectroscopy (EIS) was used to evaluate the corrosion resistance of various ferrous alloys in selected constituents of bio-oils, i.e. formic acid, catechol and lactobionic acid.<sup>9-11</sup> Based on the resistance values determined from the impedance spectra, both 2.25Cr-1Mo and 9Cr-1Mo (UNS K21590 and K90941) steels were susceptible to corrosion in 10 wt.% formic and lactobionic acids, but in 10 wt.% catechol, 9Cr-1Mo steel exhibited a high resistance to corrosion reaction(s) whereas 2.25Cr-1Mo steel did not.<sup>11</sup> These results suggest that there is a critical Cr content in between 2.25 and 9 wt.% to achieve corrosion resistance in catechol solution.

It is important to compare the corrosion behavior of the alloys not only in bio-oil constituents but also in real bio-oils. To address this, three Cr-Mo alloyed steels with increasing Cr contents were tested in 10 wt.% catechol solution and two types of bio-oils to determine the corrosion resistance or susceptibility of each using EIS. To enable EIS measurements in low-conductivity bio-oils, a custom-designed electrochemical cell was utilized. With another concurrent paper,<sup>12</sup> this is one of the initial attempts where EIS measurements were directly made in raw bio-oils for the evaluation of alloy corrosion behavior.

## EXPERIMENTAL METHODS

The three alloys used in this work were 2.25Cr-1Mo, 5Cr-1Mo (UNS S50200) and 9Cr-1Mo steels with their measured or nominal compositions presented in Table 1. Disks with 16 mm diameter and 2-3 mm thickness were machined from each alloy. All alloy disks were finished with 600 grit, water-rinsed and dried prior to EIS measurements.

**Table 1**

**Chemical composition of 2.25Cr-1Mo, 5Cr-1Mo and 9Cr-1Mo steels in mass percent, while N, O and S contents are in ppm. Inductively coupled plasma optical emission spectroscopy and combustion techniques were used for the composition analysis.**

| Alloy      | UNS No. | Fe   | Cr   | Ni   | Mn   | Mo   | Cu   | Si   | C     | N  | O | S  | Other         |
|------------|---------|------|------|------|------|------|------|------|-------|----|---|----|---------------|
| 2.25Cr-1Mo | K21590  | 95.7 | 2.22 | 0.14 | 0.51 | 1.01 | 0.09 | 0.17 | 0.092 | 45 | 9 | 50 | 0.01Co        |
| 5Cr-1Mo*   | S50200  | 94   | 5    | -    | -    | 1    | -    | -    | -     | -  | - | -  | -             |
| 9Cr-1Mo    | K90941  | 88.4 | 9.08 | 0.09 | 0.56 | 0.99 | 0.03 | 0.61 | 0.07  | -  | - | 50 | 0.08Co, 0.06V |

\*nominal composition

The custom designed cell for EIS measurements is described in detail elsewhere.<sup>12</sup> In short, the basic principal is to place the working, counter and reference electrodes very close to each other to minimize ohmic drop. The alloy disks in a holder with a defined exposure area and platinum mesh were the working and counter electrodes, respectively. The exposed areas were 1 cm<sup>2</sup> for 2.25Cr-1Mo and 9Cr-1Mo steels and 0.58 cm<sup>2</sup> for 5Cr-1Mo steel. The reference mercury sulfate electrode (MSE) was used with a glass Luggin capillary filled with saturated K<sub>2</sub>SO<sub>4</sub>. 10 wt.% catechol solution was prepared using a mixture of 85 wt.% DI water and 15 wt.% ethanol as the solvent. The catechol solution was kept in a closed container at room temperature over 60 days

before use in order to allow the oxidation of catechol in the solution. After this storage period, it was considered that the catechol oxidation is mostly complete thereby not significantly changing the solution composition.

Two bio-oils derived from Low Ash Low Moisture (LALM) and High Ash High Moisture (HAHM) forest residue biomass were used for this work. These LALM and HAHM bio-oils were produced by the National Renewable Energy Laboratory (Golden, CO, USA), and their chemical and combustion properties can be found elsewhere.<sup>13</sup> The conductivities of LALM and HAHM oils, measured by a commercial conductivity meter, was  $\sim 30$  and  $\sim 120 \mu\text{S}\cdot\text{cm}^{-1}$ , respectively. These values are lower than the conductivity of common tap water,  $\sim 270 \mu\text{S}\cdot\text{cm}^{-1}$ . A photo of the assembled electrochemical cell filled with HAHM bio-oil is shown in Figure 1.

A sequence of corrosion potential ( $E_{\text{corr}}$ ) and EIS measurement steps was used multiple times per each steel specimen. The term *immersion time* is defined as the time for which an alloy was exposed in catechol solution or bio-oils prior to each EIS step. The first EIS measurement only counts the initial  $E_{\text{corr}}$  step as the immersion time, but the following EIS measurements take all the previous  $E_{\text{corr}}$  and EIS steps to determine the immersion time. EIS measurements were conducted using  $\pm 10$  mV with respect to  $E_{\text{corr}}$  and the frequencies from 200 kHz to 5 mHz. For the entire measurements, the catechol solution and bio-oils were open to air at room temperature. For each test, the volume of catechol or bio-oil (LALM or HAHM type) was approximately 100 mL.

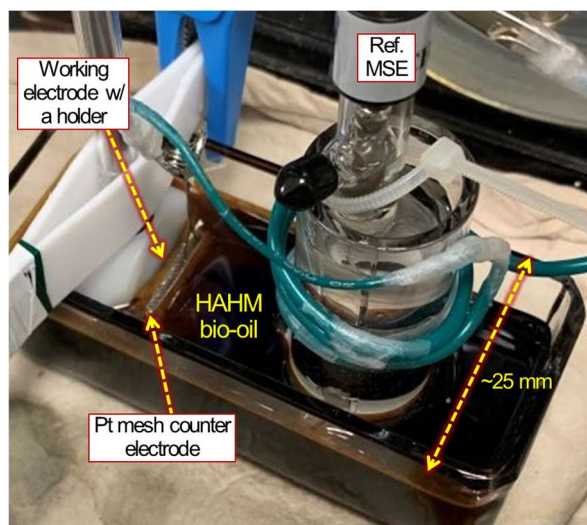


**Figure 1: A photo of electrochemical cell filled with HAHM bio-oil. The volume of bio-oil in the glass container was about 100 mL.**

## RESULTS

The impedance spectra of a 2.25Cr-1Mo steel specimen are shown in the  $Z'$  and  $Z''$  (real and imaginary impedances) plane in Figure 2 for 2 h and 19.5 h immersion times in 10 wt.% catechol and LALM bio-oil. On the left and right sides of the  $Z'$  axis, there are imperfect arcs and depressed semi-circles which correspond to the impedance responses of the electrolyte (bio-oil or 10 wt.% catechol) and the corrosion reaction at the alloy interface, respectively, as previously noted.<sup>11</sup> The