# Corrosion Studies Evaluating Organic and Aqueous Phases From Bio-oil Processing

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## Motivation

Biomass-derived oils are a renewable resource which offers the potential for replacing a portion of the fossil derived fuels currently in use. However, processed bio-oils are composed of aqueous and organic phases containing a large number of organic compounds, many of which are oxygen containing molecules. Several of these oxygenates have been shown to degrade candidate materials utilized in the production, processing and storage of the bio-oils.

## Objectives

- Conduct systematic evaluation of the corrosive behavior of individual oxygenates
- Develop future laboratory corrosion testing methods for bio-oils

**The ultimate goal is to determine which oxygenates are most corrosive and to determine the extent of oxygenate removal necessary to make bio-oils much less corrosive**

## Methods

- Conduct 250, 500, and 1000 hr. corrosions test of selected alloys that are immersed in or suspended in the vapor space above 50° C bio-oils
- Conduct Electrochemical Impedance Spectroscopy (EIS) to quickly evaluate the effects of different oxygenates
- Weight change, cross-sectional microscopy, and XRD analysis of exposed alloys coupons and U-bends

## Bio-oil Oxygenates of Interest

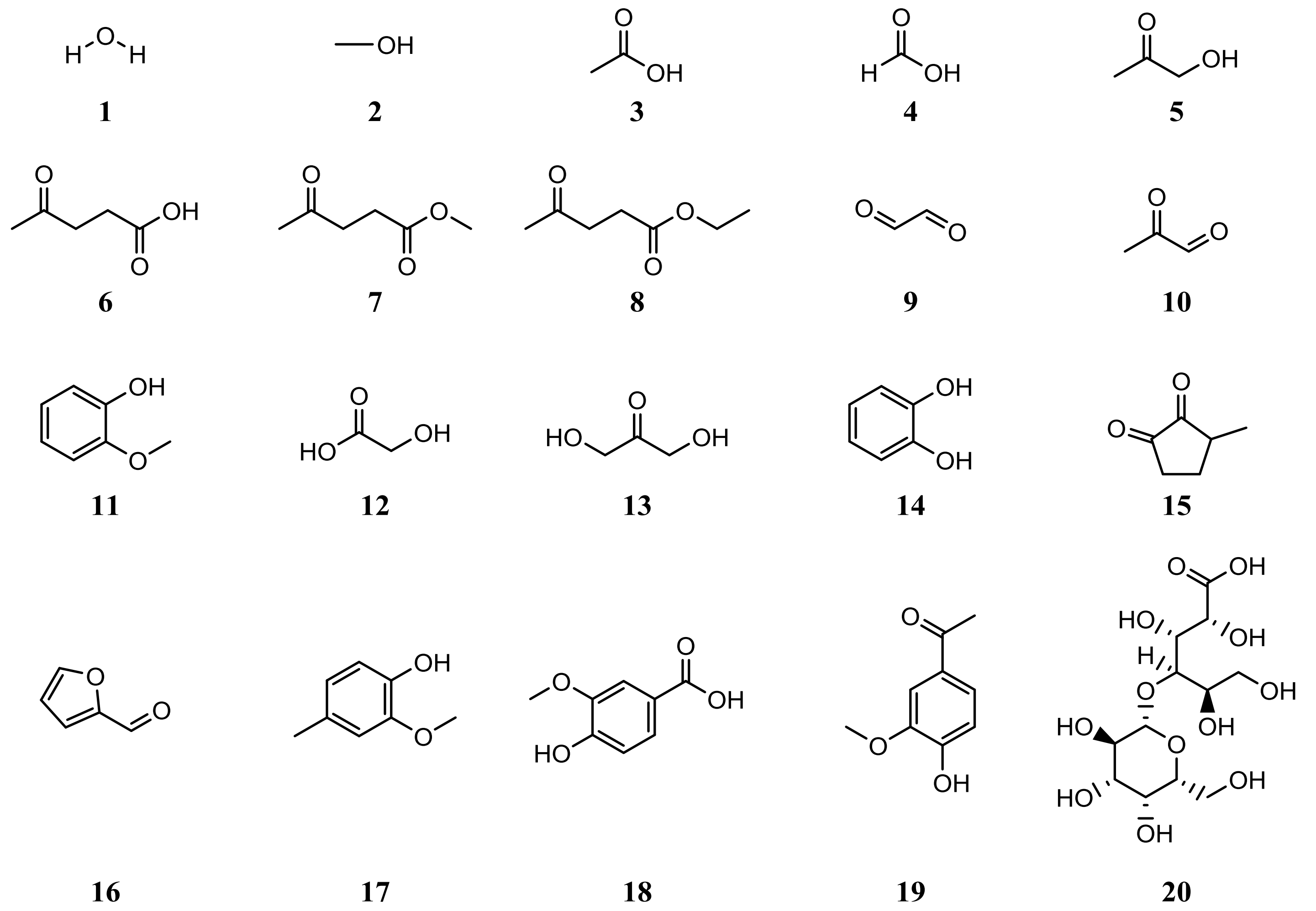

**Figure 1.** Chemical structures of oxygenates being used in oxygenate bio-oil

| | Compound | Weight % |
|---|---|---|
| 1 | water | 23.5 % |
| 2 | methanol | 4.0% |
| 3 | acetic acid | 6.0% |
| 4 | formic acid | 4.3% |
| 5 | acetol (hydroxyacetone, hydroxypropanone) | 8.0% |
| 6 | levulinic acid | 0.9% |
| 7 | methyl levulinate | 0.9% |
| 8 | ethyl levulinate | 0.9% |
| 9 | glyoxal | 0.7% |
| 10 | methyl glyoxal | 7.2% |
| 11 | guaiacol (2-methoxyphenol) | 0.5% |
| 12 | glycolic acid | 0.3% |
| 13 | dihydroxyacetone (1,3-Dihydroxypropanone) | 25.4% |
| 14 | catechol | 1.0% |
| 15 | 3-methyl-1,2-cyclopentanedione | 0.9% |
| 16 | furfural (furan-2-carbaldehyde) | 1.4% |
| 17 | creosol (2-methoxy-4-methylphenol) | 1.3% |
| 18 | vanillic acid | 2.9% |
| 19 | apocynin (acetovanillone) | 0.2% |
| 20 | lactobionic acid | 9.7% |

**Table 1.** Weight % composition of base oxygenate bio-oil

## Nominal Concentration of Alloys Used in Studies

| Alloy | Fe (wt. %) | Cr (wt. %) | Ni (wt. %) | Mo (wt. %) | C (wt. %) |
|---|---|---|---|---|---|
| 316L stainless steel | 69 | 16 | 10 | 2 | 0.02 |
| 304L stainless steel | 70 | 18 | 9 | -- | 0.02 |
| 409 Stainless steel | 87 | 11 | -- | -- | 0.015 |
| 2¼ Cr-1 Mo steel | Balance | 2.25 | -- | 1.0 | 0.1 |
| Carbon (C1018) steel | Balance | -- | -- | -- | 0.13 |

## Experimental Setup

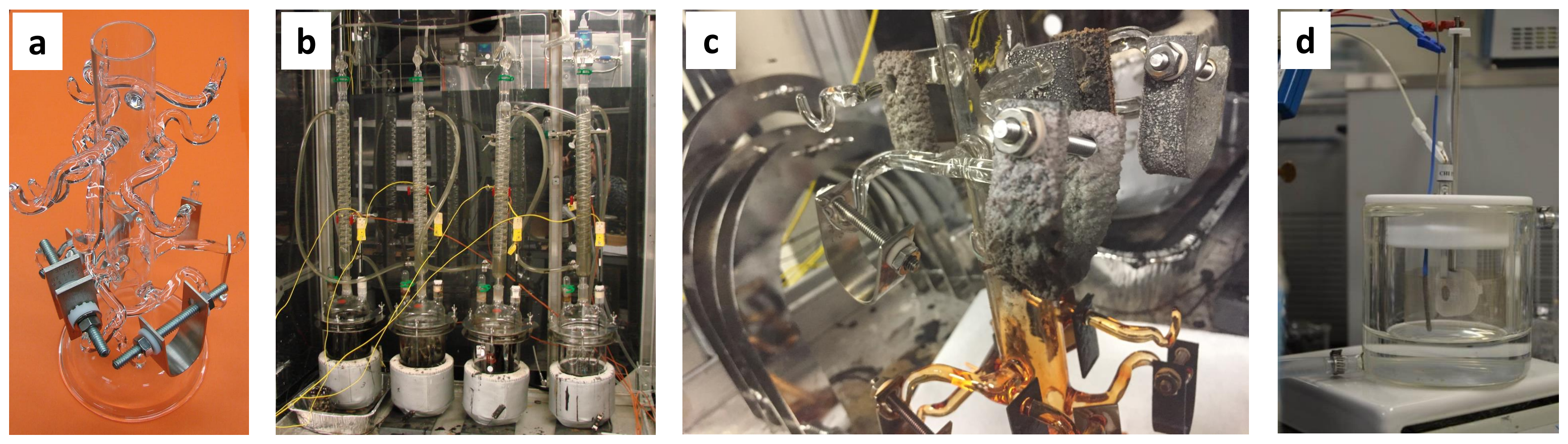

Figure 2 **a)** the sample rack for exposing samples in the 50° C corrosion tests; **b)** the 50° C corrosion tests rigs in operation; **c)** samples after 250 hr. exposure; **d)** electrochemical cell with controlled temperature bath for EIS experiments

## Calculated Corrosion Rates (mm/year) 1000hr 50°C

| Coupons | 316L stainless | 304L stainless | 409 stainless | 2¼ Cr-1 Mo steel | Carbon (C1018) steel |
|---|---|---|---|---|---|
| Base Oil Composition | < 0.001 | < 0.001 | 0.359 | 5.204 | 5.559 |
| High Acetic Acid | < 0.001 | < 0.001 | 0.098 | 3.751 | 5.655 |
| High Formic Acid | < 0.001 | < 0.001 | 1.166 | 5.340 | 4.015 |
| | | | | | |
| U-Bends | 316L stainless | 304L stainless | 409 stainless | 2¼ Cr-1 Mo steel | Carbon (C1018) |
| Base Oil Composition | < 0.001 | < 0.013 | 0.274 | 5.702 | 4.893 |
| High Acetic Acid | < 0.001 | < 0.001 | 0.079 | 4.104 | 5.214 |
| High Formic Acid | < 0.001 | < 0.001 | 0.902 | 4.645 | 4.287 |

## Electrochemical Impedance Spectroscopy (EIS)

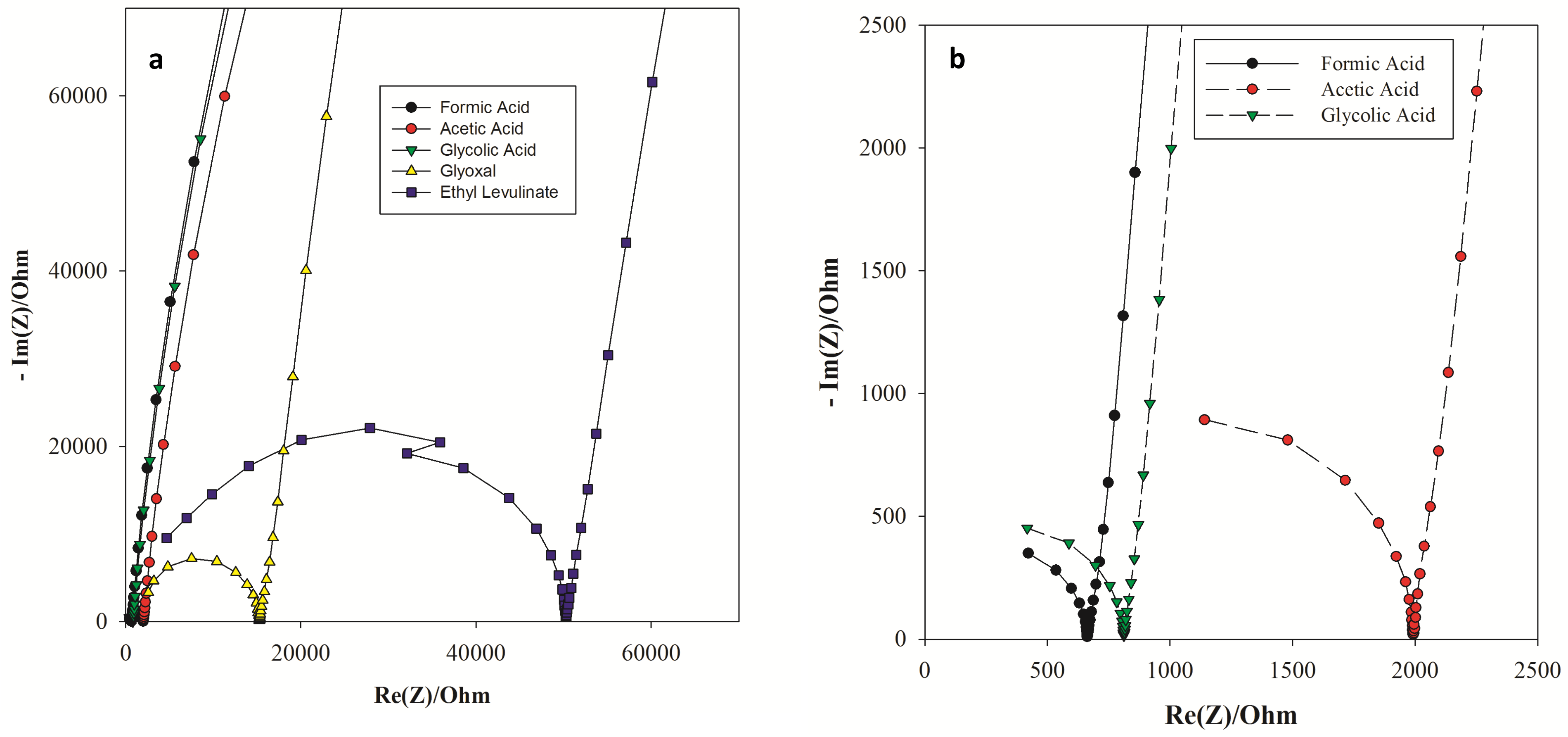

**Figure 3. a)** Subset of EIS spectra for selected oxygenates tested at 0.1 Molal oxygenate in 85 wt.% $H_2O$ – 15 wt.% Methanol solution matrix at 25°C
**b)** Zoomed in region of **3a** showing low impedance region of spectra**.**

| Compound | $R_1$ (Ohm) | $R_2$ (Ohm) | $R_{CT}$ (Ohm) | Ranking by $R_{CT}$ (small to large) |
|---|---|---|---|---|
| Formic Acid | 689.4 | 1.203E+06 | 1.202E+06 | 3 |
| Glycolic Acid | 802.6 | 1.250E+06 | 1.249E+06 | 4 |
| Lactobionic Acid | 987.2 | 8.021E+04 | 7.922E+04 | 1 |
| Acetic Acid | 1785 | 1.454E+06 | 1.452E+06 | 5 |
| Levulinic Acid | 1909 | 2.283E+06 | 2.281E+06 | 6 |
| Glyoxal | 5766 | 6.508E+06 | 6.502E+06 | 12 |
| Methyl Glyoxal | 5766 | 1.281E+07 | 1.280E+07 | 16 |
| Acetol | 15572 | 2.491E+06 | 2.475E+06 | 7 |
| Furfural | 20884 | 7.870E+06 | 7.849E+06 | 13 |
| 3-methyl-1,2-cyclopentanedione | 23746 | 3.452E+06 | 3.428E+06 | 9 |
| Dihydroxyacetone Dimer | 25608 | 2.715E+06 | 2.689E+06 | 8 |
| Catechol | 39685 | 1.131E+06 | 1.091E+06 | 2 |
| Methyl Levulinate | 39690 | 5.066E+06 | 5.026E+06 | 11 |
| Guaiacol | 44052 | 4.097E+06 | 4.053E+06 | 10 |
| Ethyl Levulinate | 49794 | 8.178E+06 | 8.128E+06 | 15 |

- The value of the charge transfer resistance ($R_{CT}$) is inversely proportional to corrosion rate
  - **small $R_{CT}$ = more corrosive**
  - **large $R_{CT}$ = less corrosive**
  - **Note**: Analysis of $R_{CT}$ must be done carefully because compounds can enhance charge transfer without being a corrosive species
- Modeling of equivalent circuits is being used to gain insight into corrosion mechanisms
- Results are guiding composition of surrogate bio-oils to be used in 50°C corrosion tests

## Summary

- The oxygenate bio-oil is significantly more aggressive than real bio-oils, but should still serve as effective means of evaluating the corrosive behavior of individual oxygenates
- Major corrosion product ($Fe(HCOO)_2(H_2O)_2$ ) from oxygenate bio-oil is the same as real bio-oils
- Carboxylic acids and Aldehydes are most corrosive
  - EIS of glycolic acid at varying concentrations is being conducted to determine what changes in glycolic acid % composition needs to be viewed as a concern
- EIS results are guiding composition of additional oxygenate bio-oils to be used in 50°C corrosion tests
- Results will help guide selection of bio-oil compatible structural materials and guide bio-oil upgrading processes at the production scale

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