NABC National Advanced Biofuels Consortium
Biofuels for Advancing America
Developing cost-competitive, sustainable biofuels for today's transportation infrastructure.

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Effect of Bio-Oil on Materials Used in Production and Storage

Selection of materials with acceptable corrosion resistance is a critical element in the design of biomass processing systems. Within the NABC, we are examining corrosivity and materials of construction in the catalytic fuel production processes. The goal of our work is to identify suitable materials so that implementation of these technologies is not limited because of materials issues.

The production of liquids from biomass can be accomplished through a number of processes, of which fast-pyrolysis is probably the most frequently mentioned. But even in the NABC technologies like Catalysis of Lignocellulosic Sugars, Hydrothermal Liquefaction (HTL), or Hydropyrolysis (HYP), production of water and oxygen-containing compounds is a common trait, and carboxylic acids are among the oxygen-bearing species that are produced. While the different technologies produce intermediates with a range of acidity, the biomass-derived oil streams create unique problems in selection of the structural materials used in the production, processing, storage, and transport of the as-produced bio-oil or its derivatives. As a result, several projects have been undertaken at Oak Ridge National Laboratory (ORNL) to further characterize the bio-oil, to conduct laboratory corrosion studies, to examine corrosion samples exposed in process vessels, and to conduct examinations of system components that have undergone significant degradation.

The chemical characterization of the bio-oil has included measurement of the Total Acid Number (TAN), which is an indication of the level of acidity, and use of the capillary electrophoresis (CE) method, which separates and quantifies the amount of low molecular weight carboxylic acids present in the bio-oil. An example of CE results from a fast pyrolysis bio-oil sample is shown in Figure 1 where it is evident that acetic and formic acids are the most common carboxylic acids in that particular sample. Studies for other projects include efforts to identify the "other organic acids".

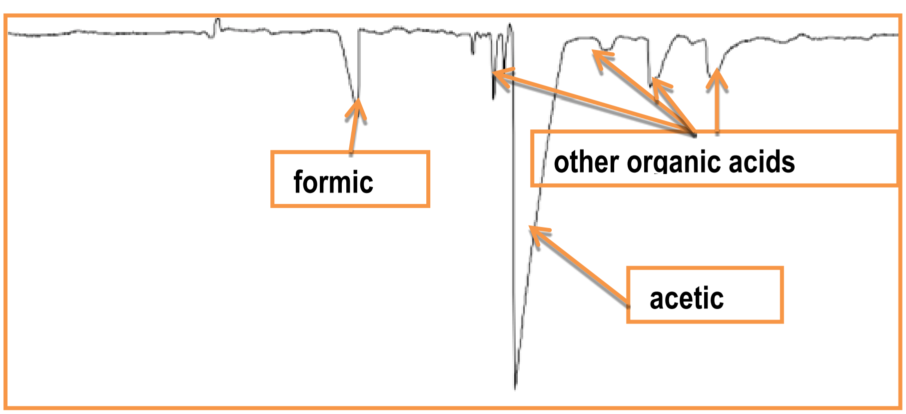

Figure 1. Example of capillary electrophoresis results identifying acid contents

Laboratory corrosion studies conducted for other biomass projects have primarily been conducted at 50°C since this is expected to be the absolute maximum temperature that the bio-oil would experience during transport or storage. Five alloys which are frequently used as structural materials are exposed in most tests, and the two least expensive and least highly alloyed – carbon steel and 2¼Cr-1Mo steel – almost always have corrosion rates in excess of an acceptable level. Materials are tested as flat corrosion coupons and as highly stressed U-bend samples to look for evidence of stress corrosion cracking or stress accelerated corrosion. Typical samples are shown in Figure 2, and examples of both stress corrosion cracking and stress-accelerated corrosion are shown in Figure 3. These studies should help identify corrosion resistant alloys for both NABC process and non-NABC process environments.

Figure 2. General and U-bend stress corrosion cracking samples

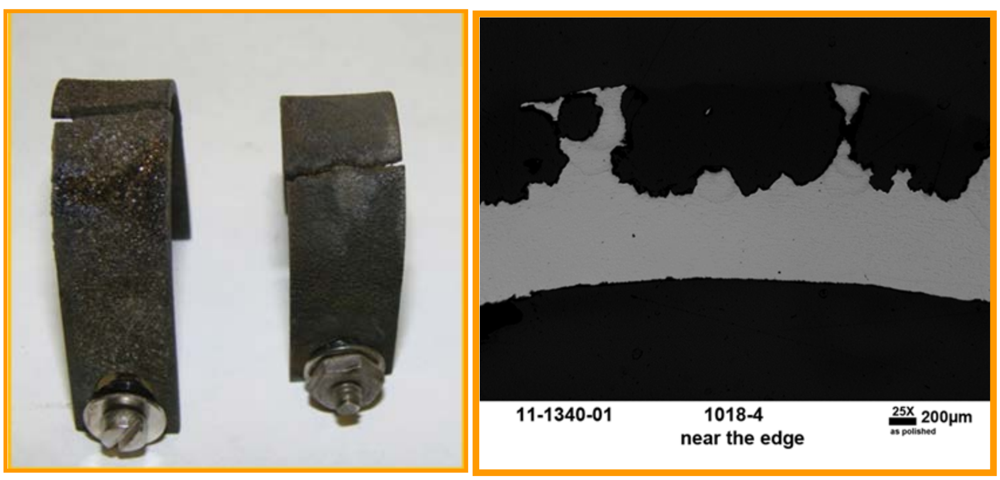

Figure 3. Examples of stress corrosion cracked U-bend samples and cross section of a sample that experienced stress accelerated corrosion

It is understood that the oxygen content of biomass-derived oils must be reduced to make these oils suitable for the anticipated applications. Corrosion tests using fast pyrolysis oils that have been hydrotreated to reduce the oxygen concentration to 3.3% (and, consequently, the carboxylic acid content) have been conducted at 50°C, and negligible corrosion was observed on all five materials. Another sample hydrotreated to reduce the oxygen content to <0.5% was tested at 50°C, 200°C, and 350°C, and this bio-oil was non-corrosive under these test conditions even for the least corrosion resistant alloys. The organic products of the HTL and HYP processes have lower oxygen contents, so it is reasonable to expect these products would require less processing to reduce the oxygen and carboxylic acid content to acceptable levels.

Examination of components exposed in operating systems is providing considerable information about the conditions under which bio-oils are corrosive. For example, a stainless steel tube fitting developed a leak, so it was sent to ORNL for failure analysis. Cross sections of the fitting were examined microscopically, and extensive cracking, as shown in Figure 4, was observed. On the basis of these observations and elemental analysis, chloride stress corrosion cracking was identified as a possible cause of this cracking.

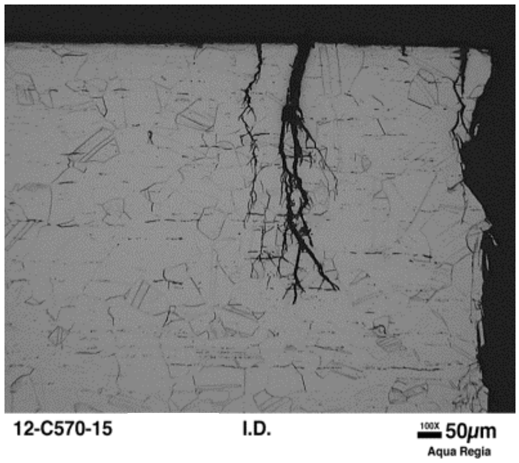

Figure 4. Stress corrosion cracking seen in stainless steel fitting

Another example of a component examination was inspection of an approximately 3 feet long thermowell which had been removed from service. Cross sections of the thermowell were taken every 2 inches along the length. Figure 5 shows the thermowell and the locations where samples were taken. Measurement of the wall thickness of each sample showed significant variation along the length of the thermowell – the approximately 10% variation in wall thickness as a function of position is shown in Figure 6 which indicates the most corrosive environment in this vessel was about midway along the length of the vessel. This thermowell was in service for less than a month, so it is an obvious conclusion that this nickel-base alloy would not be suitable for long-term service in this application.

Figure 5. Multipoint thermowell exposed less than a month

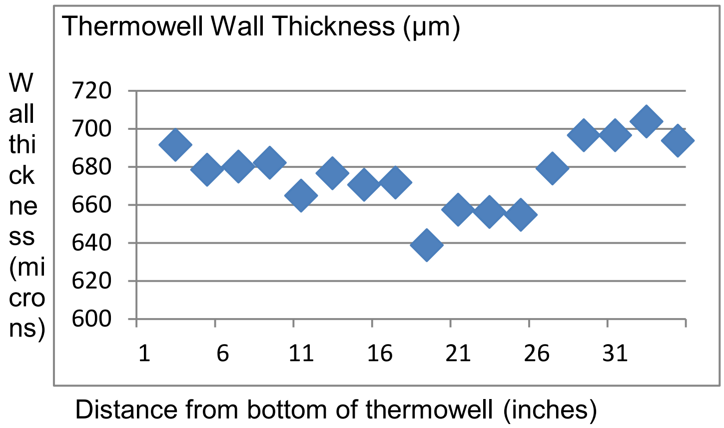

Figure 6. Variation in wall thickness showing thinning near center of the thermowell

The presence of carboxylic acids as well as some sulfur and chlorine-containing compounds make the biomass-derived oils corrosive to potential containment materials. Selection of materials with acceptable corrosion resistance is a critical element in the design of biomass processing systems. The goal of our particular task in the NABC project is to identify suitable materials so that implementation of these technologies is not limited because of materials issues.