

Influence of Organic Acids Released During Hydrothermal Liquefaction of Biomass on Corrosion of Candidate Reactor Alloys

Minkang Liu¹, Yimin Zeng², Xue Han², Jing-Li Luo¹

¹ Dept. of Chem. & Mat. Engineering, University of Alberta, Edmonton, AB T6G 1H9

² CanmetMATERIALS, 183 Longwood Rd South, Hamilton, ON L8P 0A5

ABSTRACT

Hydrothermal liquefaction (HTL) is a promising thermochemical pathway developed to convert wet biomass or waste biomass into valuable bio-oil and biochemical products in hot pressurized water medium. Over the past few years, some studies have initiated to investigate the corrosion challenges under the HTL processes for the industrial-scale deployment of this conversion technology. Among them, the impact of organic acids generated during HTL processes on the corrosion of refinery reactor alloys remains as a puzzle. In this work, static autoclave tests under organic acid-containing HTL conditions were performed on candidate stainless alloys. The formed corrosion products after each exposure were characterized using advanced microscopic characterizations techniques to obtain the related corrosion modes and extents of the alloys. This paper presents the preliminary findings on this aspect.

Keywords: hydrothermal Liquefaction, biomass, biofuel, corrosion, organic acids, nickel-based alloys

INTRODUCTION

Hydrothermal liquefaction (HTL) is a thermochemical process in which hot pressurized water is used as the reaction medium for one-step conversion of wet biomass and waste streams (e.g., municipal waste, black liquor, and hog fuel) into bio-fuels.¹⁻⁹ To-date, most of the HTL studies focused on the impacts of biomass feedstocks, residence durations and operating temperatures on conversion efficiency and products chemical properties.¹⁰⁻¹⁵ Little attention and effort has been employed to address impacts of organic corroders produced by various biomass feedstocks, along with conversion catalysts, intermediates and final bio-products on the corrosion of HTL reactors. In fact, the produced crude bio-oils contain a range of corrosive inorganic and organic compounds, such as organic acids, aggressive sulfur and/or chlorinated compounds which have the potential to introduce serious corrosion damage on the HTL core equipment, especially conversion reactors, in the hot pressurized water.¹⁶⁻¹⁸

The corrosivity of organic acids produced from the HTL coherently relates to the biomass feedstocks and processing conditions. For instance, saturated short-chain organic acids, such as formic acid (HCOOH), acetic acid (CH_3COOH) and butyric acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$) are likely to be present during the conversion of conventional forest and agricultural biomass streams.¹⁹⁻²⁴ Acetic acid, a weak reducing acid, is one of the most common acids produced from aforementioned biomass feedstocks and with the typical concentration of 8 - 10 wt.% in the final products.²⁰ The corrosivity of acetic acid in water at room temperature is negligible to most alloys. However, acetic acid could become quite corrosive under HTL conditions as indicated by previous studies.²⁵⁻²⁸ For instance, Cheng *et al.* reported the structure of the passivation film formed on UNS S31603 would be decreased significantly at temperatures above 55°C when exposed to 60 wt% acetic acid solution. Sekine *et al.* also found that the corrosion rates of UNS S31600 increased with prolonged immersion time in 5-80 wt% acetic acid solutions at both room temperature and boiling temperature (117.9°C).²⁶ It seems that certain conventional stainless steels would not be able to provide good corrosion resistance under organic-acid containing conditions and thus alternatives are needed.

Unfortunately, little information is available to describe alloy performance under organic acid-containing HTL conditions. The produced organic acids shall make the conversion condition more complicated, and thus it is required to identify their roles on the corrosion of candidate constructional materials. Note that alkaline catalysts, such as potassium carbonate (K_2CO_3), potassium hydroxide (KOH) and sodium carbonate (Na_2CO_3), are applied to enhance the liquefaction efficiency and conversion rate during the HTL processes. Their synergetic effect with organic acids introduces other issues to be solved.^{8,21,23,29,30}

UNS N08811 was recognized as a promising candidate reactor material due to its extensive application, decent corrosion resistance and mechanical properties in various high temperature reaction pathways such as high temperature gas-cooled reactors (HTGR).³¹ It was also tested and shown decent corrosion resistance in similar high-temperature water environment.³²⁻³⁴ Therefore, the corrosion of candidate reactor material Alloy 800HT (UNS N08811) under HTL conditions with or without the presence of acetic acid was investigated using high temperature high pressure autoclave and

advanced microscopic characterization techniques. It is anticipated to advance the mechanistic understanding of how organic acids affect materials corrosion under HTL conditions.

EXPERIMENTAL PROCEDURE

Test Sample Preparation

Rectangular test coupons (20 mm long × 10 mm wide × 2 mm thick) were machined from UNS N08811 plate. The composition of the alloy was obtained from the mill test report (Table 1). A small 4 mm diameter hole was drilled near the top of each coupon to facilitate mounting on the sample holder. For each corrosion test, four freshly prepared coupons were used to ensure the accuracy and precision of test results. All test coupons were polished with a series of SiC papers up to a final 600 grit in deionized water to completely remove possible contaminations and defects introduced during coupon machining. The samples were then cleaned using ethanol in an ultrasonic bath for 10 minutes and dried using pressurized air. Prior to each autoclave test, the test coupons were weighed using a Mettler Toledo micro-balance with the precision of 1 µg and measured using a digital caliper with the precision of 10 µm.

Table 1
Composition of Candidate Alloy

Alloy	Composition (wt%)							
	Cr	Mo	Ni	Mn	C	Si	N	Fe
UNS N08811	22.6	0	34.8	1.2	0.02	0.02	0.01	39.5

Static Autoclave Tests

Static tests were carried out in an autoclave made of UNS N10276 at 310 °C. A liner made of pre-oxidized UNS N00625 was used to accommodate the samples and sample holder to mitigate the potential influence of autoclave material on testing solution. The freshly prepared coupons were hung on the sample holder (made of pre-oxidized UNS N00625) with pre-oxidized nickel-chromium wires to avoid potential galvanic effect between the coupons and the holder, as shown in Figure 1. Detailed testing conditions used in the autoclave are summarized in Table 2. Reagent grade acetic acid and potassium carbonate was used. The solution was deaerated by purging with Ar gas prior to starting the test. The temperature and pressure in autoclave was monitor continuously during the test.

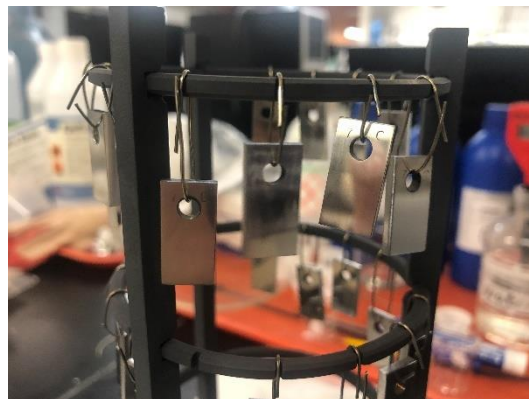
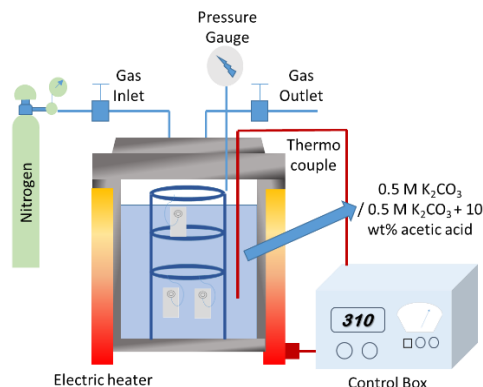


Figure 1: Schematic and Photographic images of static autoclave testing facilities used for the study.

Table 2

Testing Conditions of Static Autoclave

Testing Temperature (°C)	Testing Pressure (MPa)	Solution	Duration (hrs)
310	10	Deaerated 0.5 M K ₂ CO ₃ solution	240
310	10	Deaerated 0.5 M K ₂ CO ₃ + 10 wt% acetic acid solution	240

Corrosion Rate Assessments

During the high temperature corrosion testing, corrosion products dissolution and/or the re-deposition of cations and anions from the testing solution may occur on testing coupons in high temperature water medium. Thus, weight loss was considered as a more appropriate approach to assess corrosion rates of the candidate alloy compared to weight gain method. The de-scaling procedure has been established and described in our previous study.³⁵ The weight loss measurement was conducted according to ASTM G1 standard and corrosion rate was calculated based on Equation 1.³⁶

$$Corr.Rate = \frac{3.45 \times 10^6 \cdot \Delta m}{dAt} \quad (1)$$