

Corrosion of Candidate Alloys in Supercritical Water Gasification (SCWG) Reactor under Batch-mode Operation

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ABSTRACT

Supercritical Water Gasification (SCWG) is a promising thermochemical conversion technology in which supercritical water (SCW) is used as a conversion medium to gasify wet biomass feedstocks, such as raw forest biomass, black liquor, crude bio-oils and bio-wastes, into syngas (a mixture of CO and H₂). Despite that considerable studies have been done on the development of SCWG technology, the optimum SCWG conversion conditions have not yet been well defined due to the complexity of raw feedstocks and

conversion chemistry. From the corrosion perspective, few information is available to determine which alloys are suitable for the construction of SCWG core components (e.g., reactor and gas lines) to avoid catastrophic disaster under harsh operating conditions, e.g., high temperature ($>450^{\circ}\text{C}$) and high pressure ($>22.1\text{MPa}$). Thus, the corrosion of two candidate alloys with high Cr contents $> 20\%$ (UNS S31000 and UNS N06625), which exhibit high corrosion resistance in SCW environments, were investigated in a batch SCWG reactor containing supercritical water and a typical biomass model compound at 500°C and 34.4 MPa . To obtain reliable results, a test of 12 SCWG cycles was completed, and the duration of each cycle was one hour. The gasification products were collected and analyzed to advance the fundamental understanding of how the organic compounds released during the conversion affect the corrosion performance of the alloys in the SCWG environments. CO_2 was found to be the main gas product, along with certain amounts of H_2 and CH_4 , and a trace contents of CO and C_2H_4 . Acidic phenolic compounds are the major volatile compounds. Both alloys exhibited general and nodular oxidation. Furthermore, UNS N06625 alloy experienced more obvious localized oxide breakdown.

Keywords: supercritical water gasification, biomass model compounds, Cr-bearing alloys

INTRODUCTION

Gasification is a thermochemical technology for the conversion of coal or biomass or organic solid wastes into gaseous products (H_2 , CH_4 , CO , and CO_2) using suitable gasifying agents such as air, oxygen, steam or supercritical water (SCW), at temperatures ranging from 400°C to 1400°C .¹ Oxygen gasification is a process that uses partial combustion of enriched oxygen and biomass to provide the required heat for pyrolytic reduction to generate the gas. Its reaction essence is the same as that of air gasification, but without N_2 . Steam Gasification involves the reaction of steam with solid feedstocks such as coal, coke, biomass, or carbon-containing wastes to produce syngas. Gasification has shown a great promise in replacing conventional waste treatment processes such as landfills, incineration, and recycling for organic wastes disposal or utilization. Landfills are occupied by a large area of land, of which decomposition cycle is long, and the decomposition products also pollute the environment. The incineration which is limited by temperature, feedstock, diffusion and other factors, causes toxic gases, such as dioxin and other substances, which also pollutes the environment. Recycling and reuse of organic waste are limited by screening, separating, cleaning and hot melting. Gasification can accept a wide variety of low-quality feedstocks, such as agricultural/forestry residues, wastewater sludge or algal biomass, and produce useful products – syngas that can be used for the production of clean energy (fuel cells or gas engines), liquid transportation fuels, or chemicals (via Fischer–Tropsch synthesis).^{2, 3} Over the past few decades, biomass gasification has attracted intensive attention due to the depletion of fossil resources and the serious environmental concerns on combusting fossil fuels.

Supercritical water gasification (SCWG) is a high-efficient pathway for syngas production.⁴ Compared with conventional gasification, a SCWG process has the following advantages:

- i) The high solubility of the intermediates in SCW can prevent tar and char formation that is commonly the major problem of conventional biomass gasification in air/oxygen/steam media.⁵
- ii) Feedstock does not need to be dried. Wet biomass such as algae, sludge, and black liquor, can be directly loaded into the reactor without any drying process.
- iii) Organic matters can dissolve in SCW and react in the same phase. Therefore, the reaction efficiency is higher.
- iv) Heteroatoms (S, N, Cl, etc.) in the feedstock are mainly present in the liquid phase after reaction in the form of inorganic salts, hence not affecting the purity of produced gases.⁶

Moreover, depending on the operating temperatures, SCWG can efficiently convert wet biomass or high water content organic wastes into methane-rich (at temperatures < 500°C) or hydrogen-rich (at temperatures > 600°C) gaseous products without the need of costly dewatering/pre-drying operation.^{7,8,9}

Although SCWG is a promising thermochemical technology, significant knowledge gaps need to be addressed for its industrial applications. Among them, optimum reaction conditions and cost-effective construction materials for reactors need to be determined based on the types and compositions of biomass feedstocks and the quality of the desired gaseous products. Several studies have been done to investigate long-term corrosion performance of Fe-based steels and Ni-based alloys in supercritical water environments for the development of next-generation supercritical water nuclear reactors.^{10,11,12} However, it is unclear whether Cr-bearing alloys, such as UNS S31000 and UNS N06625, still show acceptable performance under biomass SCWG conditions due to the existence of complicated organic compounds and reducing gaseous products. Therefore, it is necessary to investigate the corrosion performance of these alloys under biomass SCWG and determine their application potential for the construction of SCWG reactors. This paper presents our recent and preliminary findings in this area.

EXPERIMENTAL PROCEDURE

Testing Materials Preparation

Table 1

Bulk Compositions of Testing Alloys

Alloy	Composition (wt%)							
	Cr	Mo	Ni	Mn	C	Si	N	Fe
UNS S31000	24.2	0	21.8	1.6	0.02	0.20	0.10	Bal.
UNS N06625	22.40	8.79	64.0	0.01	0.01	0.10	N/A	0.56

Rectangular corrosion testing samples (20 x 10 x 2 mm) were machined from two commercial Cr-bearing alloys plates (UNS S31000 and UNS N06625), and their chemical compositions are listed in Table 1. All the testing samples were polished using a series of SiC papers up to 600 grit with water as a lubricant. The coupons were then rinsed with deionized water, subsequently submerged in an ethanol ultrasonic bath for 15 minutes, and finally dried with pressurized air. Each prepared sample was stamped with an ID. Prior to SCWG corrosion testing, the prepared samples were weighed using a micro-balance with the precision of 1 μ g and measured using a digital caliper with the precision of 0.01 mm.

SCWG Experimental Procedure

As shown in Figure 1, all the SCWG experiments were carried out in a 75 mL batch reactor with the maximum working temperature and pressure of 540°C and 7900 psi respectively. Cellulose was used as a model biomass feedstock. In a typical SCWG run, 1.2 g of cellulose and 12 g distilled water were thoroughly mixed and then loaded into the reactor. In each run, three coupons of an alloy were hung on a customized sample holder and then accommodated inside the reactor vessel (see Figure 2).

After loading the alloy coupon samples and biomass/water mixture, the reactor was sealed, vacuumed, and then flushed with pure nitrogen repeatedly for at least 3 times to ensure the removal of the residual air inside the reactor. Following that, the reactor was pressurized with 300 psi pure nitrogen. It was then heated at approx. 10°C /min to 500°C where the pressure was about 5000 PSIG as evidenced in Figure 3 and kept for 1 h duration. After the gasification, the reactor was cooled rapidly to room temperature using a fan. The gaseous products were collected using a gas bag for GC analysis followed by pressure releasing. The reactor was then opened, and the liquid and solid products were poured into a beaker. Note that the residual products on the reactor inside the wall were also rinsed off with ethyl acetate (reagent-grade) and distilled water, and then combined with those in the beaker. Afterward, the combined reaction mixture was filtered under a vacuum with a pre-weighed filter paper to separate the solid residue, which was dried at 105°C overnight. The oil phase (including ethyl acetate and the extracted oil) in the filtrate was separated from water using a separating funnel and was subject to GC-MS analysis to determine volatile compositions.

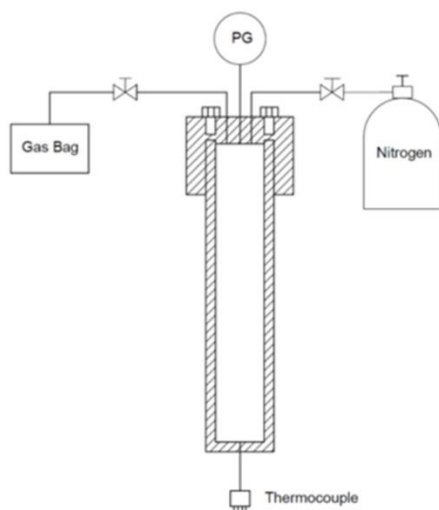
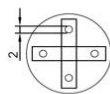
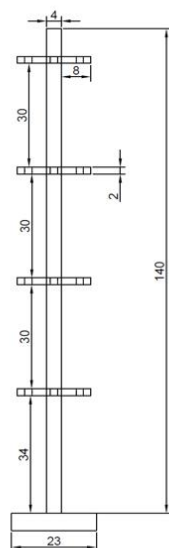


Figure 1: Schematic diagram and a photo image of the 75 mL batch-mode SCWG reactor setup used in this study



unit: mm

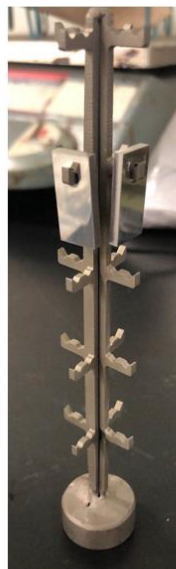


Figure 2: Schematic diagram and a photo image of testing coupons and sample holder