Corrosion performance of different alloys exposed to HTL conditions

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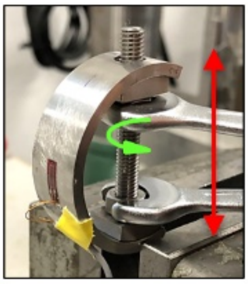
BL2F is a Horizon 2020 project with focus on production of drop-in biofuels for aviation, and shipping, using black liquor, a side stream of the chemical pulping industry as raw material.

Hydrothermal liquefaction (HTL) is a thermochemical conversion process that uses compressed water as reaction medium at temperatures between 200-400 °C and pressures between 10-40 MPa. To make HTL a viable industrial process, especially with black liquor as feedstock, the corrosion resistance of the processing materials is important and must be clarified. There is not much literature, nor experience, available on corrosion in black liquor processing systems operating at supercritical conditions. Available literature data covers temperature ranges of 100-200°C, i.e., not supercritical[2]. Hence, it has been aimed to investigate the behaviour of certain commercial steel qualities at supercritical conditions as basis for construction of a small-scale pilot system. Here, the suitability of different types of alloys as reaction vessel- and process component material was evaluated by testing in simulated- and in real process conditions with focus on resistance to corrosion, inclusive stress corrosion cracking. To simulate the hoop-stress from the high inside pressure in the real process, as well as external loads and residual stresses from e.g., welding, the C-ring test specimens for the different materials were stressed to their respective actual yield strength, $R_{P0.2}$, at the test temperature. Prior to testing in real supercritical HTL conditions, screening testing of the candidates was carried out in simulated water-based black liquor and then examined for corrosion and cracking. Then, to mimic the real conditions, the most promising alloy candidates were exposed in the same electrolyte in SINTEF Energy Research continuous HTL reactor at super critical conditions (both flowing and stagnant).



Expanding the C-ring

A selective dissolution (dealloying) of essential alloying elements (Ni, Mo, Fe) has been observed in the supercritical region for certain Ni-based super alloys. A subsequent transformation of metal into scale is accompanied by reduction in the wall thickness. Intergranular grain attack (corrosion) precedes the dissolving of alloying elements and causes sub-surface damage[3].

The corrosion- and materials evaluation study in a) water-based simulated black liquor and b) water-based simulated black liquor at super-critical conditions was successful. The conclusion from the testing program was that the most corrosion resistant alloy for the defined conditions is the chrome-rich carbon steel candidate P91 (UNS K91560). This is a type of creep strength enhanced ferritic (CSEF) alloy, which are steels designed to retain strength at extremely high temperatures. The P91 abbreviation represents the material's chemical composition, i.e., 9% chromium (Cr) and 1% molybdenum (Mo). Further work is required to at conclude on corrosion resistance for the P91 quality at supercritical conditions in the **welded** condition, including the heat affected zone (HAZ), and to better understand caustic corrosion mechanisms for safe design of future full-scale plants.

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[1] https://www.bl2f.eu/

[2] https://doi.org/10.1590/1980-5373-MR-2017-0148

[3] DOI 10.1002/xrs.1297