Research article

Corrosion of stainless steels in the riser during co-processing of bio-oils in a fluid catalytic cracking pilot plant☆

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ABSTRACT

Co-processing of bio-oils with conventional petroleum-based feedstocks is an attractive initial option to make use of renewable biomass as a fuel source while leveraging existing refinery infrastructures. However, bio-oils and their processing intermediates have high concentrations of organic oxygenates, which, among their other negative qualities, can result in increased corrosion issues. A range of stainless steel alloys (409, 410, 304L, 316L, 317L, and 201) was exposed at the base of the riser in a fluid catalytic cracking pilot plant while co-processing vacuum gas oil with pine-derived pyrolysis bio-oils that had been catalytically hydrodeoxygenated to ~2 to 28% oxygen. A catalyst temperature of 704 °C, a reaction exit temperature of 520 °C, and total co-processing run times of 57–75 h were studied. External oxide scaling 5–30 μm thick and internal attack 1–5 μm deep were observed in these short-duration exposures. The greatest extent of internal attack was observed for co-processing with the least stabilized bio-oil, and more so for types 409, 410, 304L, 316L, 317L stainless steel than for type 201. The internal attack involved porous Cr-rich oxide formation, associated with local Ni-metal enrichment and S-rich nanoparticles, primarily containing Cr or Mn. Implications for alloy selection and corrosion are discussed.

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1. Introduction

Biomass is being pursued as a sustainable and renewable energy source of liquid bio-fuels, encompassing a spectrum of applications from both biomass-fired boilers to biomass-derived liquid transportation fuels [1–3]. Thermochemical pyrolysis of biomass to produce bio-oil, and subsequent upgrading to produce liquid transportation bio-fuels such as gasoline, jet fuel, and diesel is of particular recent interest due to the reliance of transportation on liquid fuels [3–11]. Due to the compositional differences between petroleum and bio-oil, production of liquid transportation fuels from bio-oil is envisioned as a separate processing pathway that enters the hydrocarbon economy at the point

of fuel blending, requiring separate capital investment that does not leverage existing refinery infrastructure [3–11]. In response, researchers have considered the requirements that must be met to co-process bio-oils in the refinery environment rather than at the point of blending [7]. However biomass-derived pyrolysis oils and their processing intermediates contain significant concentrations of organic oxygenates, including carboxylic acids (formic, acetic, etc.), which reduce the storage stability of the pyrolysis oil and result in the formation of gums and deposits when the pyrolysis oil is mixed with petroleum based feedstocks. In addition to these negative qualities, the organic oxygenates in biomass-derived pyrolysis oils can cause increased corrosion issues in the materials used for storage, transport, use and conversion to fuel [10–13].

Fluid catalytic cracking (FCC) is one of the primary hydrocarbon conversion units in modern petroleum refineries. It converts the higher molecular weight components of petroleum, such as vacuum gas oil (VGO), to gasoline, light fuel oil and petrochemical feedstocks such as propylene and butylene [14,15,16]. In the United States, FCC and the alkylation unit it supplies produce about 50% of the gasoline pool in most refineries [17]. Co-processing of bio-oils with conventional petroleum-based products such as VGO is an attractive initial option to make use of renewable biomass as a fuel source, while leveraging existing refinery infrastructure [14–15,18–24]. However, the use of untreated bio-oils as a co-processing feedstock results in processing difficulties in the FCC due

to plugging from increased coke deposition [25–28]. Hydrotreating can be used to produce higher quality bio-oil intermediates more compatible with existing refinery infrastructure, with a further benefit of lower oxygenate content to potentially reduce corrosion issues, although hydrotreating also increases cost [25–27].

Development and optimization of bio-oil co-processing is an active area of study focusing on many technical challenges (e.g. [14–15,18–24]), but little research has been pursued of potential impacts of co-processing with bio-oils on the corrosion of materials of construction used in the FCC unit. One area of the FCC unit that can experience corrosion is the riser reactor. At the base of the riser reactor, hot catalyst from the regenerator (typically between 640 and 760 °C) contacts the feedstock. This vaporizes the feed, and the mixture of catalyst and petroleum feed travels up the riser. Cracking occurs in the riser section and transport takes between 2 and 10 s, depending on unit design [16] Most riser designs are "cold-wall" where the pressure boundary of the vessel is carbon steel, with a several centimeter layer of refractory placed on top of the carbon steel to reduce its temperature and prevent abrasion from the catalyst. Stainless steel alloys are used for feed nozzles, the mesh that holds the refractory and some of the internal components of the riser [29,30]. Multiple modes of corrosion attack are potentially encountered in conventional FCC units, including oxidation, sulfidation, carburization, etc. [29–38]. Such phenomena have been studied from both an applied/materials selection/durability viewpoint [29–33] and a fundamental mechanistic perspective [32–38].

The present work took advantage of a multi-institution study by W.R. Grace, Technical Research Centre of Finland, Tesoro, Aston University, Pacific Northwest National Laboratory, Los Alamos National Laboratory, and Oak Ridge National Laboratory devoted to co-processing optimization of VGO and pyrolysis bio-oils to explore the impacts of the bio-oil constituent on the corrosion behavior of stainless steels [39]. A series of stainless steel alloy test samples were placed at the base of a FCC pilot plant riser and exposed during a series of short-term (57–75 h) co-processing campaigns using VGO and pyrolysis bio-oil that had been catalytically hydrotreated to varying degrees of hydrodeoxygenation (total run times of 75–135 h including initial FCC pilot plant run startup using 100% VGO). These exposures were too short in duration to quantitatively assess corrosion resistance of the alloys in the co-processing environment, particularly from a plant-durability component lifetime perspective. Rather the goal of this work was to gain insight into the initial stages of corrosion and the mechanism of attack, with an emphasis on advanced characterization of the scale/subscale microstructure features for several different types of stainless steels in the co-processing environment.

2. Materials and methods

A range of stainless steel alloys was exposed at the base of the riser reactor of a Grace DCR (Davison Circulating Riser) FCC pilot plant (Figure Supplemental Figure Supplemental 1). The DCR is a continuous circulating pilot plant consisting of a riser reactor, stripper and regenerator; the same vessels present in a commercial FCC unit. Typical feed rates are 1 kg/h and typical catalyst to oil ratios are between 6 and 12. A detailed description of the pilot plant can be found in references [28] and [40]. Co-processing of VGO with 3 to 10 weight% (wt.%) pine-derived pyrolysis bio-oils with different degrees of hydrodeoxygenation (HDO) (~2 to 28 wt.% oxygen) was done in the FCC pilot plant. For the majority of the co-processing work, a mid-continent VGO with a specific gravity of 0.9059 (at 16 °C) and a sulfur content of 0.35 wt.% was primarily used (nitrogen content was 0.14 wt.%, oxygen content was 0.24–0.27 wt.%). For two short experiments co-processing the severely hydrotreated bio-oil, two additional VGOs were used, VGO2 with a specific gravity of 0.927 (at 16 °C) and sulfur content of 0.93 wt.%, and VGO3 with a specific gravity of 0.927 (at 16 °C) and sulfur content of 1.41 wt.%. The catalyst used was a conventional zeolite Y (faujasite) containing equilibrium commercial fluid cracking catalyst obtained from a refinery processing a low-metals vacuum gas oil. The catalyst had <100 ppm mass each of contaminant nickel and vanadium deposited by the feedstock.

2.1. Alloys

Up to five alloys were exposed per FCC pilot plant co-processing run, representing a range of alloy content (Cr, Ni, Mn, Mo levels), cost, and stainless steel class (ferritic and austenitic). Analyzed alloy compositions are shown in Table 1.

2.2. FCC pilot plant exposures

The corrosion test samples consisted of 17.8 cm long by 0.64 cm wide alloy strips cut from sheet material, thicknesses varied from 1.1 to 1.8 mm depending on the alloy (mill surface finish retained in order to expose "real" industrial alloy surfaces). They were welded to ~23–30 cm long weld wire pieces that were used to vertically positon the test samples in the mixing chamber at the base of the riser at approximately 60° spacing (Fig. S1), which permitted exposure of up to 5 samples per co-processing run. The remaining one sixth of the FCC pilot plant mixing chamber was committed to the line introducing the hot catalyst from the regenerator to the mixing chamber. In the mixing chamber at the base of the riser, the mixture of VGO and bio-oil was

Table 1

Analyzed compositions of alloys (wt.%) as determined by inductively coupled plasma optical emission spectroscopy and combustion techniques combined with infrared analysis (listed in approximate order of least to most expensive). The 409 and 410 are ferritic grades, and the remaining alloys are austenitic. Metallic impurities <0.01 wt.% not reported.

Alloy	Fe	Ni	Cr	Mo	Mn	Si	C	Other
409	87.56	0.14	11.36	0.01	0.13	0.49	0.01	0.007 N, 0.01 Cu, 0.14 Ti, <0.001 S
410	86.49	0.15	12.05	0.03	0.43	0.44	0.14	0.014 N, 0.12 Cu, 0.07 V, 0.03 Nb, 0.001S
201	70.84	4.46	15.9	0.27	6.97	0.48	0.078	0.068 N, 0.08 Co, 0.71 Cu, 0.05 V, 0.02 W, 0.01Ti, Nb, Sn, 0.001S
304L	71.61	8.06	18.07	0.06	1.29	0.54	0.024	0.064 N, 0.03 Co, 0.01 Cu, Ti, 0.001 S
316L	69.21	10.11	16.6	2.0	1.12	0.52	0.022	0.041 N, 0.22 Cu, 0.09 V, 0.01 Ti, 0.001 S
317L	62.29	14.24	17.74	2.97	1.69	0.56	0.022	0.026 N, 0.23 Co, 0.11 Cu, 0.04 V, 0.01 Ti, 0.007 S