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Corrosion of Reactor Alloys Under Simulated Partially Thermal Cracking of Oilsands Bitumen

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ABSTRACT

Bitumen partial upgrading methods (such as thermal treatment with diluent addition) have been developed to achieve significant economic and environmental benefits. Among them, thermal cracking is seen as a cost-effective pathway and a number of investigations have been done for optimizing cracking processes. However, little work is performed to study the corrosion under the partially thermal cracking of bitumen feedstocks, in which the involved environment chemistry is quite different from those of complete cracking processes at refining plants. Thus, this study focuses on the corrosion modes and extent of typical reactor alloys (including carbon steel UNS K02700 and stainless steel UNS S31603) in a bench top reactor under simulated partially thermal cracking processes of bitumen. Sulfidation seems to be a major mechanism for gas phase corrosion. Scale spallation likely occurs on UNS K02700 samples exposed to gas phase. The samples contacting liquid phase are covered by coke-like substances which to some extent inhibit severe damage of underneath samples. Fe oxides and Fe sulfides might form on the surface of oil-corroded UNS K02700. A thin protective surface layer is observed on UNS S31603 corroded in liquid phase, which possibly prevents the substrate from further corrosion.

Key words: corrosion, bitumen, partial thermal-cracking, refinery reactor alloys

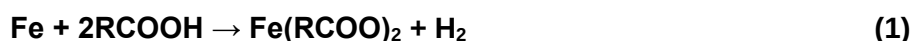
INTRODUCTION

Canada accounts for 10% of the world's proven oil reserves, 96% of which are present in the oil sands.¹ Bitumen, which is extracted from oil sands, has an API gravity of 7-10° and viscosity of over 10000 cPs, and is associated with tar sands deposits at reservoir conditions.² The transportation of refined products of Canadian bitumen and heavy crude oil for domestic use and export is limited by insufficient clean-fuel pipeline capacity. Due to the high cost of building new refining capacity in Canada, a large portion of Canadian produced bitumen is exported to the US. The raw bitumen must be converted to a fluid form to reduce the viscosity for easy transportation from field to refineries through long distance pipelines.

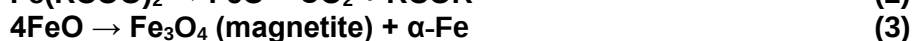
The current pipeline operation is using diluents including natural gas condensate and fully upgraded synthetic crude oil (SCO).² In order to meet the pipeline specifications of 19 °API @ 15.6 °C and 350 cSt @ 7.5 °C, 30 vol% of diluent in the bitumen-diluent mixture is typically required. The resultant bitumen blend needs to be processed at destined refineries to separate the diluent that will be shipped back to the site for reuse. This practice imposes a large economic strain on bitumen recovery.³ An alternative to dilution under consideration is partial upgrading that converts only a portion of the heavy vacuum residue fraction in bitumen to make it flow freely in pipelines. This technique reduces or eliminates the usage of diluent and is applicable for existing pipeline capacity. Moreover, *in-situ* thermal enhanced oil recovery methods make partial upgrading more attractive because the partial upgraders are easily located at the oil field.⁴ The combustion of rejected coke or other unconverted heavy products in partial upgrading processes can cover a portion of or even all the steam that is required for Steam-Assisted Gravity Drainage.⁵ In addition, due to the elimination of product distillation and secondary product treatment, the cost for constructing partial upgrading facilities is much lower than that for full upgrading facilities.⁶

Commonly used methods for viscosity reduction of bitumen include deasphalting, cracking, removing sulfur and nitrogen, adding hydrogen, and diluting with solvent or diluent.⁷⁻⁹ Among them, the conventional thermal cracking is a relatively cost-effective approach to partially upgrade bitumen. During the thermal cracking process, the long-chained, high boiling point hydrocarbons are broken into small components to significantly reduce the viscosity and density of bitumen. Based on our literature review, the investigated temperature for bitumen partial upgrading (BPU) locate in the range of 150-440 °C which is lower than the industrial operating conditions.^{3, 10, 11} The viscosity of partially upgraded bitumen can be significantly reduced by two orders of magnitude. However, the properties of upgraded liquid products do not meet the pipeline requirements until the processing temperature reaches 440 °C. An oil sand company thus has developed the Hydrogen-Donor Diluent Reduction (HDR™) technology to use thermal cracking for bitumen partial upgrading.^{12, 13}

Material degradation issues are crucial in the construction of a partial upgrading refinery. As partial upgrading of bitumen is a relatively new technology, the study on the material degradation is at the early stage. In refinery complete bitumen upgrading processes, corrosion occurs in the temperature range of 220-400 °C, with two types of well-recognized corrodents of naphthenic acids and sulfur-containing compounds such as H₂S.¹⁴ Naphthenic acid (NA) can interact with Fe in steel or alloy to generate Fe(RCOO)₂ (Equation 1) that is oil soluble, leading to localized corrosion:



The acids with smaller molecular weight and less rings are found more corrosive, and the low boiling point acids have a significant influence on condense phase corrosion¹⁵. When temperature is over 400 °C, the damage from NA is reduced, due to the thermal decomposition of Fe(RCOO)₂ and the subsequent formation of Fe₃O₄ scale (Equations 2 and 3):¹⁶



H₂S can react with both Fe and Fe(RCOO)₂ to generate a layer of FeS scale on the surface of steel or alloy (Equations 4 and 5), causing general sulfur-induced corrosion:



These corrosion pathways are not independent; which one predominates relies on the concentration of corrodents. Upgrading of Canadian bitumen was reported to follow sulfur dominated corrosion mechanism.¹⁷ Moreover, chlorides are another type of corrodent commonly seen in heavy oil refining which induce localized corrosion.¹⁸ In addition to the above corrosion modes, high-temperature erosion, fouling, material embrittlement and corrosion under insulation (CUI) which are commonly seen in the conventional crude oil upgrading processes,¹⁹ may possibly occur in the BPU process. In this paper, a Canadian oilsands bitumen was subjected to partial upgrading, under which conditions the corrosion assessment of two candidate constructional materials, carbon steel UNS K02700 and stainless steel UNS S31603, was performed to evaluate their corrosion performance and application potential for the construction of partial thermal-cracking refinery reactor.

EXPERIMENTAL PROCEDURE

Sample Preparation

Typical constructional alloys used for existing refinery systems (carbon steel UNS K02700 and stainless steel UNS S31603) were evaluated. The chemical compositions of samples are listed in Table 1. Testing sample coupons with the dimension of 20 mm long × 10 mm wide × 3 mm thick were machined from commercial steel plates. A small hole with 2 mm radius was drilled near the top of each coupon to facilitate sample mounting on the sample holder.

Table 1
Chemical Composition of Testing Materials in wt% (Balance Fe)

UNS	C	Mn	P	S	Si	Cr	Mo	Ni	Cu	N
K02700	0.167	1.15	0.008	0.007	0.34	0.036	0.014	0.028	0.03	
S31603	0.02	1.1	0.0285	0.001	0.02	16.4	2.8	13		0.1

All testing coupons were polished with SiC papers up to 600 grit. Deionized water was used during polishing to remove possible contaminations and defects introduced by coupon machining. Polished coupons were cleaned in an ultrasonic ethanol bath for 10 minutes, and then dried using compressed air. Each prepared coupon was stamped with an ID. The testing coupons were weighed using a micro-balance with the precision of 1 µg and measured using a digital caliper with the precision of 0.01 mm prior to BPU test.

Thermal Cracking of Bitumen and Products Analysis

The partial upgrading of bitumen was carried out in a Parr bench top reactor. A pre-oxidized two-level sample holder (made of UNS N00625) with coupons of candidate constructional materials was placed in the reactor for corrosion assessments. Pre-oxidized nickel-chromium wires were used to hang the sample coupons to avoid potential galvanic effect between the sample holder and testing coupons. Testing coupons were distributed on a customized sample holder: three coupons of each steel on the bottom level to investigate corrosion occurred in the liquid phase, and two coupons of each steel on the top level to examine related gas phase corrosion. A blank test without coupons addition was performed to identify the oil level at 440 °C. The schematic of coupon accommodation on the sample holder is shown in Figure 1. The reactor was initially charged with 0.1 MPa N₂. During the thermal conversion of bitumen, the reactor pressure was controlled to no higher than 10 MPa. The upgrading/corrosion test was conducted