

Corrosion of UNS S31603 under Partial Upgrading of Bitumen Using Thermal Cracking

Xue Han
CanmetMATERIALS
183 Longwood Rd South
Hamilton, ON L8P 0A5
Canada

Kaiyang Li
CanmetMATERIALS
183 Longwood Rd South
Hamilton, ON L8P 0A5
Canada

Yimin Zeng
CanmetMATERIALS
183 Longwood Rd South
Hamilton, ON L8P 0A5
Canada

ABSTRACT

Oil sands bitumen is partially upgraded to facilitate the pipeline transportation with environmental and economic benefits. In this work, the corrosion performance of a candidate constructional material for partial upgrading, UNS S31603, was evaluated under the environments of cyclic thermal cracking of bitumen at 360 and 400 °C. Sample coupons were exposed to gas phase and liquid phase to simulate the constructional materials for distillation tower and partial upgrader, respectively. At both temperatures, the samples are not susceptible to gas phase corrosion but liquid phase corrosion. Advanced microscopy techniques and the grazing incidence X-ray diffraction were used to examine the corrosion products. Sulfidation appears to be the major corrosion mechanism under the thermal cracking of oilsands bitumen.

Key words: Corrosion, Stainless steel, Partial upgrading, Oilsands bitumen

INTRODUCTION

With the rapid economic development and the dramatic population growth, the demand on clean energy is continuously increasing.¹ Due to the depletion of conventional crude oil reserves, the unconventional oil resources such as oil sands become more attractive.² Canada has a total estimated oil sands reserves of 161.4 billion barrels by the end of 2020, accounting for 9.3% of the global reserves.³ The bitumen in the oil sands is extracted and transported through pipelines

to the refineries with refining capabilities in Canada and the United States where the raw bitumen is processed to produce marketable synthetic crude oil (SCO). The proposed TransCanada system planned to connect the Alberta bituminous oil sands to the refineries as far as in Texas.⁴

Bitumen is highly viscous and hardly flows at ambient conditions, so the transportation of bitumen in pipelines is usually associated with the addition of diluent to achieve the viscous reduction purpose. The purchase of diluent, the separation of diluent at destination refineries, and the subsequent transportation of diluent back to the oil sand field greatly increase the operation costs. On the other hand, as the upgrading product of bitumen, SCO, has reducing competitiveness with the light crude in the US market. As a result, Canadian oil sands producers tend to partially upgrade the oil sands bitumen to target heavy crude refineries.⁵ Meanwhile, the partially upgraded bitumen has much lower viscosity compared to the raw bitumen and is easy to flow in the pipeline with less or zero amount of diluent.

A few techniques have been used for the partial upgrading of bitumen, including thermal cracking or visbreaking,⁶⁻⁸ catalytic hydroprocessing,^{5, 9} solvent deasphalting,¹⁰ cracking under supercritical water (SCW),¹¹ and methanotreating.¹²⁻¹⁴ In thermal cracking processes, the chemical bonds (C-C, C-S and C-O) in the heavy fraction of bitumen are broken with the aid of external energy (heat) without the presence of a catalyst. The produced liquid products show higher hydrogen contents than the feed bitumen, but post-processing is usually required to improve the stability of liquid products. Compared to thermal cracking, catalytic hydroprocessing to partially convert bitumen can suppress the formation of both olefins and insoluble materials while maintaining a high liquid yield. The upgrading conditions, reactor configurations and catalyst need to be carefully selected to meet the pipeline transportation requirements at a relatively low cost. In solvent deasphalting, a non-polar solvent is used to precipitate the less soluble asphaltenes, sulfur, nitrogen, metals and Conradson carbon residue out of the bitumen-solvent mixture. The resultant upgraded products could have satisfactory properties for pipeline transportation at the expense of liquid yield. For the upgrading under the SCW environment, high-yield SCO is produced through the thermal cracking pathway without the occurrence of over-cracking and polymerization. However, this process requires high capital investments. Methanotreating is a process similar to hydroprocessing but using cheap natural gas (or methane) to replace hydrogen as the reducing agent. The major challenge of methanotreating is the selection of a catalyst that can effectively trigger the cleavage of strong C-H bond in methane. Among the existing and developing techniques, thermal cracking under moderate conditions is considered as the preferred option for the Canadian oil & gas industry mostly due to its economic advantages.⁵

Although research works have been performed to develop suitable and applicable technologies for partially upgrading the oilsands bitumen, not much information is available regarding the corrosion challenges to construct the partial upgrader. Based on the upgrading results in literature,⁶⁻⁸ thermal cracking at 440 °C can produce liquid products whose properties meet the pipeline transportation requirements. Therefore, we conducted corrosion assessments at 440 °C in our previous studies to evaluate the corrosion performance of commonly used reactor constructional materials including UNS K02700, UNS K91560, and UNS S31603 under the environment of bitumen partial upgrading (BPU).^{15, 16} Stainless steel (UNS S31603) exhibited superior corrosion resistance to carbon steel (UNS K02700) and low-alloyed steel (UNS K91560) under the investigated conditions. In this paper, the corrosion susceptibility of UNS S31603 was assessed under the thermal cracking BPU environments at 360 °C and 400 °C, and the corrosion mechanisms were explored based on characterization results.

EXPERIMENTAL PROCEDURE

Sample Preparation

The testing samples are rectangular coupons with the dimensions of 20 mm long × 10 mm wide × 3 mm thick. A hole with the diameter of 2 mm was drilled near the top of coupon to facilitate the mounting on a sample holder. These coupons were cut from a commercial UNS S31603 plate, with the bulk composition listed in Table 1. The coupons were polished using a series of sand papers (120 grit, 240 grit, 400 grit and 600 grit), during which process distilled water was used to remove the contaminations introduced during samples machining. The prepared coupons were then submerged in ethanol and further cleaned with the assistance of ultrasound for 10 min, followed by drying using compressed air. Each clean coupon was stamped with an ID. The samples were weighed using a 6-digit microbalance, and their dimensions were accurately measured using a digital caliper (precision of 0.01 mm). Prior to the corrosion tests, the samples were put in a vacuum desiccator for storage.

Table 1
Chemical Composition of UNS S31603 (wt%, Balance Fe)

C	Mn	P	S	Si	Cr	Mo	Ni	N
0.02	1.1	0.0285	0.001	0.02	16.4	2.8	13	0.1

Corrosion Performance Evaluation

The corrosion tests were conducted under thermal cracking of bitumen at two temperatures: 360 °C and 400 °C. At each temperature, four cyclic tests were run on the same set of corrosion testing coupons. In a typical run, raw bitumen was first heated to 80 °C, at which temperature it starts to flow. The warm bitumen was poured in a 500 mL autoclave reactor. The coupons were hung on a two-level sample holder made of UNS N06625 using Ni-Cr wires (Figure 1). Note that the sample holder and the Ni-Cr wires were pre-oxidized to avoid potential galvanic effect. The coupons on the top level will be exposed to the gas phase in the reactor, and those on the bottom level to the liquid phase. A blank test without the addition of coupon samples was conducted to determine the maximum liquid level.

The sample holder loaded with coupons was placed in the reactor. The reactor was sealed for leaking test. When the leaking test was passed, the air inside the reactor was removed by repeatedly vacuuming and nitrogen purging the reactor for three times. 1 atm nitrogen gas was charged into the reactor (reading of pressure gauge: 0), and the reactor was heated to the designated temperature and held for 2 hours. Afterward, the heater was turned off and the reactor was quickly cooled by a fan. The gas products were collected for analysis when the temperature inside the reactor dropped to room temperature. After opening the reactor, the sample holder with coupons was moved to the desiccator for storage, and the reactor was cleaned for next use after the collection of upgrading products was completed. Same operations were repeated for another three times at the same thermal cracking temperature. The coupons after 4 cycles of BPU tests were carefully removed from the sample holder for corrosion rate measurements and characterization.