



Research article

Investigation of corrosion and fouling in syngas cooler tubes

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ABSTRACT

A promising way of upgrading bitumen is de-asphalting with the subsequent partial oxidation of asphaltene. Sulfur, metals (V, Ni), and other minerals concentrated in the asphaltene are subjected to reactions at elevated temperatures in both oxidizing and reducing atmospheres. Upon the cooling of the raw syngas, some of the particulate and condensable material deposit surfaces and ages.

This paper discusses the subsequent deposition of layers on syngas cooler tubes. The deposit consists of a corrosion layer of FeS, a condensation layer of Ni₃S₂, and subsequent fouling layers composed of V₂O₃ and Ni₃S₂. Firstly, the base metal is corroded by the H₂S electrochemical attack with the simultaneous Ni₃S₂ condensation on the cold surface. With the increasing fouling thickness of the Ni₃S₂ layer, the surface temperature at the process side increases, causing the condensation process to come to a gradual stop. Then infusible nanometer size V₂O₃ particles with Ni₃S₂ are deposited upon this sticky and rough surface, forming an extremely thick composite fouling layer. A high resolution inspection of this layer shows three sub-layers with distinct morphologies: (i) a fully molten liquid dense layer of Ni₃S₂ with V₂O₃ particles soaked below solidified into the smooth surface, (ii) very fine-grained (average particle size of 140 nm) spherical V₂O₃ particles embedded within a melting Ni₃S₂ sheet along with scale, where the spaces between the V₂O₃ particles are filled with Ni₃S₂, and (iii) a fire side sub-layer consisting primarily of spherical V₂O₃ particles wrapped by the condensed Ni₃S₂ glue and keeping the original morphology of the particles in the syngas. The paper discusses the mechanism in detail.

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1. Introduction

The gasification process converts carbonaceous feed stocks into synthesis gas that can be used for power generation or as chemical feed stock [1]. Under high temperature and pressure conditions, carbonaceous materials in the feed react with oxygen, steam, and CO₂, and produce H₂ and CO, while some of the minerals form a molten slag. Nowadays, the increased demands for oil products necessitate taking deeper cuts in refining crude, leaving a residue: asphaltene high in vanadium and nickel [2]. The increasing refining operation has created an interest in using this byproduct – asphaltene [3] as a fuel for steam generators producing steam and electricity. However, the high content of sulfur (6–7 wt.%) and the presence of high concentrations of hetero-atoms and metals in the asphaltene create many problems for traditional utilization. Even though some portion of the asphaltene is used essentially as glue for paving roads, most asphaltene is considered refinery waste, which makes it more attractive as a gasification feedstock. This feedstock has a substantial viscosity at elevated temperatures and an ash content of approximately 0.3%, mainly consisting vanadium and nickel compounds.

The gasification of the feedstock occurs by partial oxidation using pure oxygen. The process pressure is 6.5 MPa, and the produced syngas has a temperature exceeding 1300 °C. The syngas passes through a syngas cooler for recovering sensible heat with the boiler feed water to produce steam at a pressure of 7.7 MPa. The syngas cooler is of the fire-tube type, having multiple coils spiraled upwards while submerged in a water bath. The tubes have a number of size reductions to maintain a velocity, so as to ensure that soot and ash particles are conveyed through the coils with manageable fouling and acceptable erosion/corrosion. The syngas side skin temperature ranges from the steam saturation temperature of 296 °C to theoretically 600 °C. Conversion of the asphaltene results in a reducing atmosphere with CO and H₂ as the dominant gas phases, with H₂O and H₂S components in a volume of 7.5% (as estimated) and 1.6%, respectively. The high concentration of H₂O and H₂S make the syngas considerably corrosive. The volatile species, such as sodium, potassium, chlorine, fluorine and sulfur, pass through the gasifier with the syngas.

At present, a great amount of research has been conducted on the corrosion and fouling in the coal and biomass gasification process [4–8]. However, while the ash composition of coal and biomass is generally Ca, Fe, Si, Al, K, Na, and Mg, the ash from asphaltene is much finer and mainly consists of vanadium and nickel. The large compositional difference between these two ash compositions may lead to different and unpredictable slagging/fouling problems because the transformation of V and Ni

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is quite different from the general ash behavior at high temperatures. V exhibits triple valences V^{3+} , V^{4+} , and V^{5+} at different atmospheres at high temperatures [9]. V_2O_3 is stable under a reducing atmosphere, and transforms into V_2O_5 in an oxidizing atmosphere. Meanwhile, Ni exists in a wide range of oxidation states as Ni, Ni^{2+} , and Ni^{3+} in a high temperature range. The fate of V and Ni in the thermal conversion calculation of coal was investigated by Frandsen et al. [10]. In standard reducing conditions, solid V_2O_3 is present at temperatures lower than 1477 °C and NiS is formed at 772 °C and present below 1427 °C. Even though very little information is available for corrosion and fouling resulting from asphaltene gasification, specifically in commercial gasifiers under pressurized, reducing conditions where sample probes cannot readily be inserted into the syngas coolers. The operating pressure, long residence time, and complex chemistry of the system make bench-scale testing useful for better understanding. Further, thermodynamic calculations are very difficult, especially without knowing the actual mineral species forming in the gasifier.

Therefore, to gain a better current understanding of the corrosion and fouling, ascertaining the mechanism of the formation of those layers is critical to combat the unstoppable growth of the fouling layer in the real syngas cooler. For this purpose, several 1 m long pieces were cut from a single long coil at different locations in a commercial syngas cooler. These samples were then analyzed with an electron microprobe, a scanning electron microscope, an X-ray diffraction unit, and a reflective light microscopy to illustrate the effect of temperature and fluid flow on the deposit chemistry.

2. Experimental

2.1. Sample preparation

The 1 m coil sections were reduced further in size and set in epoxy and hardener to stabilize the deposit. These set samples were cross-sectioned into slices with a 10 mm height and finely ground and polished using standard reflective light polishing procedures, then cut into small dices at 3 O'clock direction (extrados) and 9 O'clock direction (intrados), as shown in Fig. 1. We then analyzed a large number of coil sections at different distances from the inlet to determine how change in temperature through the coil affects the deposit character – morphology and chemistry. Most of the results in this paper concentrate on the typical sections that undergo the most serious corrosion and fouling.

2.2. Characterization of the deposit in syngas cooler

2.2.1. Chemical characterization

The research team prepared the ashes into fused beads for X-ray fluorescence (XRF) analysis using a Katanax™ fuser with a platinum crucible and pan. The fused beads were analyzed with a Bruker S4 Explorer XRF equipped with a wavelength dispersive spectrometer (WDS). We employed calibration standards based on certified reference materials for elemental quantification.

2.2.2. Physical characterization

The morphological and structural features of the deposits were examined by field emission scanning electron microscopy (FE-SEM, JEOL 6301F). The researchers determined the crystalline components of deposits by X-ray diffraction. We analyzed the samples in a PANalytical B.V.-X'Pert Pro multi-purpose X-ray diffractometer (40 mA, 40 kV, $Co\ K\alpha$). The X-ray patterns were recorded in the scan range $2\theta = 10\text{--}90^\circ$.

3. Results

3.1. SEM and EDX mapping

Fig. 2(a) shows the back-scatter image with different contrasts. The brighter area represents the higher atomic number. Fig. 2(b) is the EDX mapping image. The dark blue band on the left side represents base metal, while the light blue band represents the corrosion layer of (Fe_xS_y). The large spalling between them occurs due to a substantially different thermal expansion coefficient from the matrix or due to the formation of an interfacial product, which may possess a different crystal structure with a distinct density change. The first deposition layer (Ni_3S_2), colored in green, lies next to the corrosion layer. The researchers observed no spalling, boundary, and transition zone between them. On the right hand side, we observed the thickest layer, V_2O_3 , red in color. At the same time, some green lines (Ni_3S_2) are interspersed in this layer and highly probable to be the binding agent for this thick layer.

Table 1 shows the major mineral distribution estimated by EDX, and the thickness of each layer. It can be seen that the thickness of the first (Fe_xS_y) and second (Ni_3S_2) layer are comparable while the last layer (V_2O_3) is far thicker than the other two. Moreover, due to the high concentration of H_2S and H_2O in the syngas (in total 10 vol.%), the formation of the FeS layer is inevitable with the long operation time. The formation

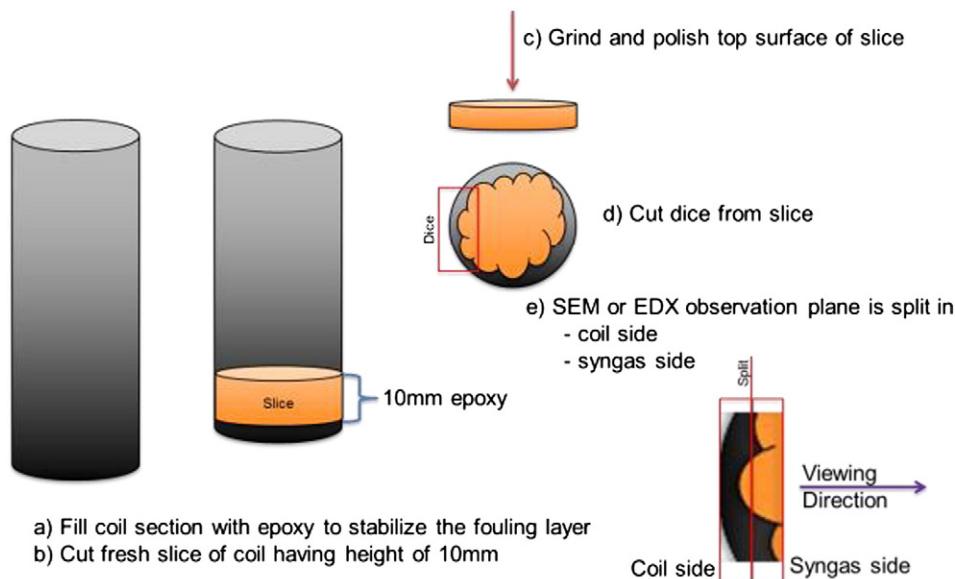


Fig. 1. Sample preparation procedure.

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