

## SOLVING A HYDTROTREATER FEED FILTER FOULING PROBLEM

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### ABSTRACT

Feed filters were installed in Syncrude hydrotreater units to protect the catalyst beds from plugging by fine solids in the feed. Severe filter fouling occurred after a process flow sheet change. The root cause of fouling was revealed through a step-by-step scientific investigation. It was first confirmed that the fouling problem was related to a process flow sheet change that introduced a heavy vacuum gas oil (HVGO) stream into the coker combined gas oil (KCGO) stream prior to filtration. Characterization of the foulant and the feed indicated that the fouling reactions are likely oxidative polymerization. Iron naphthenate or naphthenic acid in the HVGO stream could act as a catalyst for such a reaction. A bench-scale oxidation test was carried out to compare the oxygen uptake rates and the C<sub>7</sub>-insoluble contents after oxidation in KCGO, KCGO+HVGO, KCGO+iron naphthenate and KCGO+naphthenic acid streams. While the oxygen uptake kinetics for these samples were similar, the C<sub>7</sub>-insoluble contents for KCGO+HVGO and KCGO+iron naphthenate increased significantly after oxidation compared to the base case of KCGO. No significant increase of the C<sub>7</sub>-insoluble content was observed for KCGO+naphthenic acid, indicating that it was the iron naphthenate that catalyzed the fouling reactions. Iron naphthenate was a corrosion product in the HVGO stream, which could be eliminated by preventing corrosion in the vacuum distillation unit. The filter fouling problem indeed disappeared after the installation of corrosion-resistant equipment. This paper is the modified version of a former publication: X.A. Wu, K.H. Chung, 2007, Hydrotreater feed filter fouling and its remedy, *Energy Fuels* Vol. 21, pp. 1212-1216.

### INTRODUCTION

As the supply of light crude oils dwindle worldwide, heavy crude oils including bitumen extracted from Athabasca oil sands in Canada are becoming important refinery feedstock. Athabasca bitumen produced by mining and water-based extraction processes usually contains trace amounts of fine solids, posing a challenge for refiners and upgraders. Feed filters are often installed in hydrotreater units to protect the downstream catalyst beds from plugging. At Syncrude (a major oilsands bitumen producer and upgrader), severe fouling occurred in the hydrotreater feed filter (see Fig.1) after a process flow sheet change (refer to Fig.2). Note that buildup of normal filter cakes that

are readily removed by backwashing is not considered filter fouling. The fouling incident at Syncrude required frequent dismantlement of the filter units and manual cleaning of the filter elements, which created safety, cost and environmental issues.

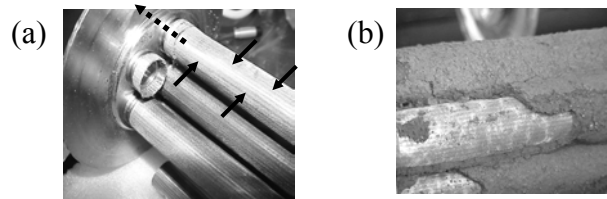


Fig. 1 Clean (a) and fouled (b) 25 µm mesh filters on a hydrotreater feed stream. The arrows in (a) indicate the direction of flow in filtration mode. Solids laying down on the mesh surface can be backwashed by reversing the direction of oil flow. Thick and sticky foulant in (b), however, cannot be removed by backwashing.

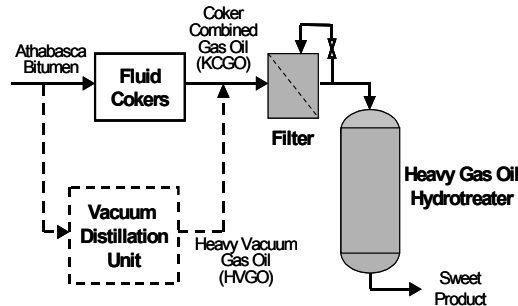


Fig.2 Simplified flow diagram of Syncrude bitumen upgrading plant. Dashed lines represent the process flow sheet change in late 1999. KCGO includes coker light and heavy gas oils.

### INVESTIGATION AND RESULTS

The first step of the investigation was to confirm the proximate cause of fouling, *i.e.* blending a small heavy vacuum gas oil (HVGO) stream into the main coker combined gas oil (KCGO) stream prior to filtration as part of the process flow sheet change, which essentially added the vacuum distillation unit (VDU) to the existing process. The experimental setup was a filtration simulation device

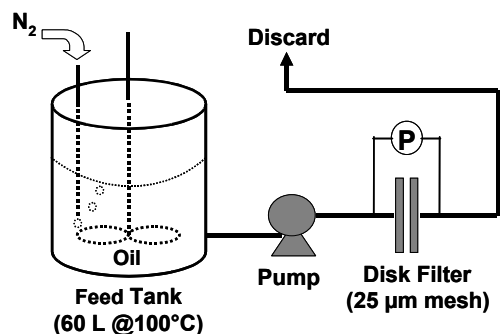


Fig. 3 Diagram of a filtration simulation device.

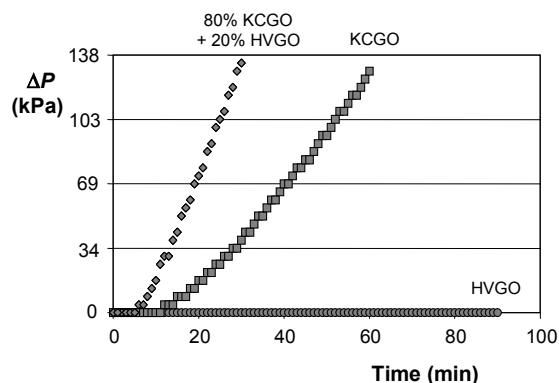


Fig. 4 Pressure drop buildup curves for simulated filtration of KCGO (squares), HVGO (circles) and their mixture (diamonds).

constructed and operated by researchers at University of British Columbia (see Fig.3). It was found that the  $\Delta P$  buildup across the test filter is faster for 80% KCGO/ 20% HVGO mixed stream (typical plant mixing ratio) than for either KCGO or HVGO stream alone (see Fig.4). It should be noted that the simulated filter did not have a backwashing capability and the  $\Delta P$  buildup curve, affected by both the concentration of backwashable solids, e.g. clays and coke, and the concentration of non-backwashable foulant, was not an ideal indicator for filter fouling. However, since the former was a well-controlled parameter, i.e. the 80% KCGO /20% HVGO feed contained 80% of the backwashable solids of the 100% KCGO feed, the results in Fig.4 did indicate that KCGO/HVGO mixed stream causes faster fouling of the filter than KCGO alone. The cause of this phenomenon will be discussed later.

The second step of the investigation was to characterize the foulant and the filter feed. The results showed that the foulant is compositionally close to the polar fraction of the feed, especially for the concentration of pyrrolic nitrogen species determined using x-ray photoelectron spectroscopy (XPS) technique (see Fig.5). Higher oxygen content and molecular weight (790 vs. 260) for foulant as compared to the polar fraction of the feed suggest that the fouling precursors, e.g. polar pyrrolic species, undergo oxidative polymerization in the presence of trace amounts of

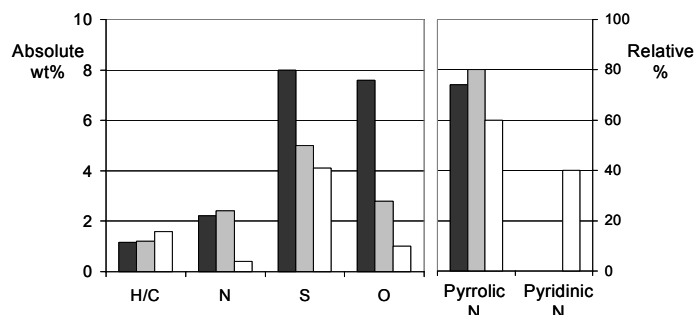


Fig. 5 Elemental compositions of the chloroform-soluble fraction of the foulant (black), the polar fraction of the filter feed (gray) and the whole feed (white). The left chart was based on bulk elemental analysis and the right chart was based on XPS analysis.

molecular oxygen ( $O_2$ ) leaked into the system (Frankenfeld, 1983a; Speight, 1998). These precursors are primarily present in the KCGO instead of the HVGO. Detailed analytical data of the oil streams and the foulant can be found elsewhere (Yui and Chung, 2001; Xu, et al., 2005; Woods, et al., 2007).

The third step of the investigation was to understand the role of HVGO in the fouling. HVGO and KCGO are fully compatible, thus no phase separation occurs after mixing. HVGO could be the  $O_2$  carrier (Vadekar, 2002). This hypothesis was refuted after dissolved oxygen measurement in a sealed HVGO sample (Wu and Chung, 2006). HVGO contained relatively high concentrations of naphthenic acid (TAN: 4 mg KOH/g) and iron naphthenate (Fe: 2-10 mg/L) when filter fouling occurred. The latter was a corrosion product from the VDU installed during the flow sheet change. Both could act as catalysts in fouling reactions (Frankenfeld, Taylor and Brinkman, 1983; Denisov and Emanuel, 1960). A bench-scale oxidation apparatus was built to identify the true fouling catalyst (see Fig.6). Gas oil samples such as KCGO, KCGO/16% HVGO, KCGO/39 ppm ferric naphthenate and KCGO/3%

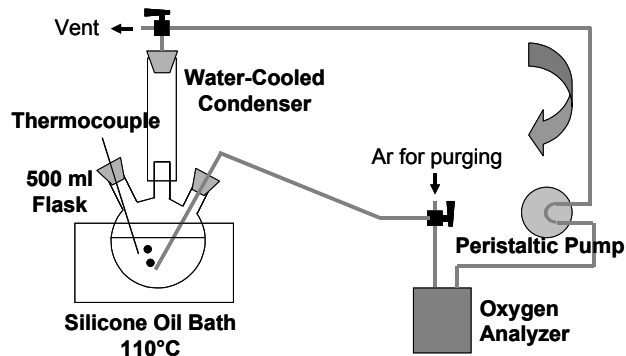


Fig. 6 Bench-scale setup for mild oxidation test on gas oils. The flask and the condenser were purged with argon during heating. Air trapped in the tubing between two 3-way valves (next to arrows) was introduced after the temperature reached the set point. The initial oxygen concentration in the system was about 1/10 of the atmosphere.

naphthenic acid were mildly oxidized at 110°C until 95% of the initial oxygen in the apparatus had been consumed. For the small sample volume, it is difficult to exact fouling deposits directly. Instead, the C<sub>7</sub>-insoluble content in the oxidized oil was used as a benchmark to compare their fouling propensities. For KCGO/HVGO and KCGO/ferric naphthenate, their C<sub>7</sub>-insoluble contents increased significantly after oxidation compared to the base case of KCGO (see Fig.7). No significant increase of the C<sub>7</sub>-insoluble content was observed for KCGO/naphthenic acid. As a conclusion, the root cause of the filter fouling has been identified as oxidative polymerization of certain polar species, likely pyrroles, in the KCGO stream, catalyzed by a corrosion product, iron naphthenate, in the HVGO stream.

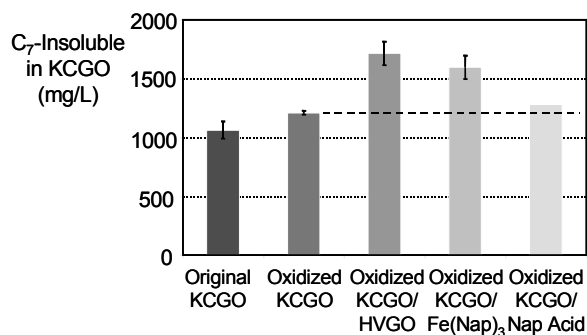


Fig. 7 C<sub>7</sub>-insoluble concentrations in original KCGO, oxidized KCGO, oxidized KCGO/16% HVGO, oxidized KCGO/39 ppm ferric naphthenate and oxidized KCGO/3% naphthenic acid. C<sub>7</sub>-insolubles were extracted from the test oils by mixing them with n-heptane at 1:40 ratio. Oxidized KCGO serves as the base case, shown by a dashed line.

Molecular oxygen apparently played an important role in the oxidative fouling. However, the aforementioned bench-scale oxidation test showed similar O<sub>2</sub> uptake rates for different oil mixtures even though their fouling propensities represented by the C<sub>7</sub>-insoluble contents were markedly different. Even more puzzling are the filtration test results in Fig. 4 showing different fouling rates for various feeds, all bubbled with N<sub>2</sub> and presumably O<sub>2</sub>-free. In one literature study (Mochida, Sakanishi and Fujitsu, 1986), it was found that iron does not enhance the oxidation but strongly increase the amount of fouling deposits. In other studies (Denisov and Emanuel, 1960; Pickard and Jones, 1997), iron was found to catalyze the decomposition of hydroperoxide, an intermediate product of oil oxidation, and the polymerization of the resulting free radicals. Hence, it is possible that the intermediate oxidation products, e.g. hydroperoxide, had been generated in the KCGO prior to the tests and the addition of iron naphthenate simply enhanced the formation of fouling deposits.

## REMEDIES AND CONCLUSION

Based on the aforementioned root cause of fouling, we had several options to eliminate the filter fouling: allowing

the HVGO to bypass the filter, use of anti-oxidants, identifying and fixing air leaks on the KCGO stream or its storage tanks and eliminating iron naphthenate from the HVGO. The first one might shift the fouling downstream and was not implemented. Use of anti-oxidants could cause unpredictable side effects. Finding and fixing air leaks was costly without any guarantee of success since as low as 0.5-5 ppm of O<sub>2</sub> in oils could cause serious fouling (Vadekar, 2002). Meanwhile, the VDU was scheduled to upgrade its pipes to prevent corrosion one year after this investigation. Iron naphthenate was expected to disappear from the HVGO stream after the material upgrade. Knowing the root cause of the filter fouling gave us enough confidence to wait for a year without trying any unnecessary or potentially harmful fixes. The hydrotreater feed filter fouling indeed disappeared shortly after the installation of corrosion-resistant pipes in the VDU.

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