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Role of water and fine solids in onset of coke formation during bitumen cracking

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ABSTRACT

The aim of this study was to examine the effect of water and fine solids on coke formation during thermal cracking of a residue fraction from vacuum distillation (Athabasca vacuum tower bottoms) and Athabasca bitumen froth. Experiments were conducted in a batch reactor with 0–33.3 wt.% water at 410 °C for up to 80 min to measure the time of onset of coke formation, total coke yield as a function of time, and conversion of vacuum residue. Removal of fine solids significantly shortened the onset time of coke formation, but the addition of water had no significant impact on onset time. The yield of cracked products, as determined by simulated distillation, was insensitive to the presence of water and fine solids. Based on the findings from this study, it was concluded that residual fine solids have a beneficial effect on thermal upgrading as they delayed the onset of coke formation, while water has little impact within the tested concentration range of 0–33 wt.% water.

1. Introduction

Water has attracted significant interest as a reaction medium for high-pressure conversion of heavy oils and bitumens [1–5]. The heaviest fractions of heavy oil and bitumen, in the vacuum residue range, have little solubility in aqueous phases at high pressure [4,6], but the lighter fractions are miscible with aqueous phases above the critical pressure of water, and at temperatures in excess of 400 °C. This behavior has led to proposed thermal processing of water–bitumen mixtures to extract converted products into the aqueous phase, leaving the unconverted vacuum residue as an insoluble phase for alternate disposition, for example, to generate steam for in situ recovery [2]. One attractive aspect of processing water-heavy oil blends is that such mixtures are ubiquitous in production, either as water in oil emulsions stabilized by asphaltene and surface active components, or in bitumen froth from water-based oil sands extraction, a water-in-oil emulsion stabilized by fine mineral solids [7]. In either case, direct processing of oil/water mixtures offers the opportunity to eliminate process steps.

A number of studies have examined the benefits of adding significant amounts of water to bitumen during processing, summarized in Table 1. The effects of adding water were generally beneficial, with reduced viscosity, reduced yield of coke, and enhanced conversion being claimed in a majority of cases. The role of water is claimed to include chemical interaction in free radical processes, as a solvent to extract components into an aqueous phase, and as a solvent to dilute and swell heavy components, such as asphaltenes.

All of these experimental conditions used large amounts of water, in the range from 44 to 80 wt.%, which is much higher than typical heavy oil emulsions and bitumen froths. From a reaction point of view, the conditions suggested by these experiments require holding very large volumes of fluid at high reaction pressures, over 20 MPa, for long residence times. Such conditions face significant barriers in materials of construction and reactor cost.

When water and bitumen are blended and subjected to thermal reaction, the phase behavior can be very important. Water solubility in bitumen increases significantly with temperature, although no data are available at temperatures of interest for thermal cracking, i.e., over 400 °C [6,13]. The available data suggest that the heavy hydrocarbon phase can accommodate over 20 wt.% water at 350 °C [13]. Depending on the water concentration and the total pressure, an initial emulsion could give a single hydrocarbon phase with dissolved water, or two phases comprising a dense oil rich phase and a less-dense aqueous phase. As the pressure increases at a given temperature, the density of the aqueous phase will increase from steam-like at low pressure to solvent-like above the critical pressure of water (22 MPa). A higher-density aqueous phase will tend to extract more components from the oil.

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Table 1
Summary of literature on thermal cracking of bitumen or vacuum residue with water.

Author(s)	Feed	Water:oil (wt.)	Temp. (°C)	Pressure (MPa)	Reaction time	Effect of water
Berkowitz and Dunn [8]	Heavy oil	Undisclosed	300–450	4–21	25 s–10 min	Reduced coke yield, lower viscosity
Cheng et al. [9]	Vacuum residue	2:1–4:1	380–420	25–27	1 h	Reduced coke yield, increased conversion
Gregoli et al. [10]	Bitumen	1:4–2:3 of brine[a]	380–490	23–25	0.25–2.5 h	Lower viscosity, increased conversion
He at al. [11]	Bitumen	1:1–2:1	374–400	23–28	20–40 min	Lower viscosity, increased conversion
Morimoto et al. [1,3]	Bitumen	2:1	420–450	27–30	0.5–2 h	Reduced coke yield, increased conversion
Vilcáez et al. [4]	Bitumen	>2.5:1	340–440	13–27	0–2 h	Reduced coke yield
Watanabe et al. [5]	Bitumen	2:1	450	NA[a]	0–30 min	Faster coke formation
Zhao et al. [12]	Vacuum residue	0.8:1–4:1	380–460	23–27	1 h	Increased conversion, reduced metals and nitrogen in product

[a] Pressure not given, water density to 200 kg/m^3.

The fine minerals that are typical of Athabasca bitumen from the hot water extraction process can also have an effect on coke formation [14]. Coke formation can be delayed by the presence of the minerals from bitumen froth, and addition of specific minerals such as kaolinite can suppress coke formation [15]. In the presence of high concentrations of water the wettability of such fine minerals may be altered, changing the interactions with the bitumen or heavy oil components during coke formation.

Direct thermal upgrading of water-bearing streams, such as heavy oil emulsions and bitumen froths, may be of interest if the resulting flowsheet is simplified by eliminating process steps, and if the presence of water has a beneficial impact. Previous studies of upgrading in water have focused mainly on high pressures, well over 22 MPa, in order to gain the benefits of a denser, more solvent like aqueous phase. In this study, we investigated the use of lower pressures that would be expected with emulsions and froths in the range of 0–33.3 wt.% water. Emulsions and froths from Athabasca that also contain fine solids are difficult to use in controlled studies because the content of water cannot easily be reduced without altering the oil components. The approach used here was to study thermal cracking of Athabasca vacuum tower bottoms at 410 °C with controlled amounts of water and fine solids in order to understand the impact on the onset of coke formation, the yield of coke, and on the conversion of vacuum residue components. An actual sample of bitumen froth was then used for comparison at a fixed water content.

2. Experimental

2.1. Chemicals and materials

Two types of feed material were used in these experiments, Athabasca vacuum tower bottoms (VTB) and Athabasca bitumen froth. Both samples were provided by Syncrude Canada Ltd. Solvents were obtained from Fisher Scientific (Mississauga, ON), and compressed ultra-high purity nitrogen from Praxair (Fort Saskatchewan, AB). Milli-Q quality water was used which was prepared using equipment from Millipore.

In order to determine the initial solids content in the feed, 3 g of vacuum tower bottoms was diluted with 150 mL of toluene and mixed for 3 h, then vacuum filtered with 0.22 μm filter paper. The filter paper was washed and dried to determine the weight of fine solids. All analyses were repeated 3 times. CHNS analysis was performed by a VARIOMICRO Elemental Analyzer.

In order to determine the mineral composition in the feed, approximately 50 g of vacuum tower bottoms were diluted with 500 mL of toluene and mixed for 3 h, then centrifuged at 30,000 RCF for 20 min. The supernatant was removed and the sediments were diluted with toluene and centrifuged again. This process was repeated until the supernatant was clear. The sediment collected was dried in an oven to evaporate the remaining solvent. The solids remaining were subject to quantitative X-ray diffraction analysis to obtain mineral composition.

In order to determine water content in the bitumen froth, Dean–Stark analysis was completed on a sample of froth. A large sample of approximately 60 g was used to minimize the effect of sampling errors. The water content was determined to be 10 wt.%. The solid content was determined by the centrifuge procedure described above, and was found to average 3.3 wt.% from 3 replicate measurements. The solids collected were analyzed for mineral composition as well as elemental analysis.

2.2. Microreactor experiments

In order to investigate coke formation and conversion of vacuum residue, a batch microreactor fabricated from Swagelok tubing was used with water contents in the range 0–33 wt.% water. For each experiment, approximately 3 g of feed was placed into a 15 mL stainless-steel microreactor. Milli-Q water was added as required to obtain the desired concentration. The microreactor was leak-tested with nitrogen, then purged three times to remove air and filled with nitrogen. The microreactor was then immersed in a heated sand bath and agitated for the desired reaction time. A reactor temperature of 410 °C was selected for these experiments, to give slow enough onset of coke formation to enable good experimental repeatability. Reactor temperature and heating rates were verified by inserting a thermocouple into the reactor. Reaction times in this study are reported from the time of introduction into the sand bath, to the time of removal. From the moment the reactor was immersed in the sand bath, the reactor reached 350 °C in 100 s and 400 °C in 267 s. The reactor reached the final stable temperature of 410 °C in approximately 10 min. Upon removal from sand bath, the temperature dropped to below 350 °C in 220 s.

After the reactor was removed from the sand bath, it was allowed to cool for at least 12 h, then the gas was vented in a fume hood and the liquid and solid products were extracted using toluene for analysis. Filter solids in the reactor product were determined by vacuum filtration using 0.22 μm filter paper. The weight of the mineral is assumed to be constant during reaction and from this, total coke yield was calculated as:

$$\%\text{Coke Yield} = \frac{\text{Mass of Solids on Filter Paper} - \text{Mass of Initial Solids}}{\text{Mass of Feed} - \text{Mass of Initial Solids}} \quad (1)$$

The ASTM D-5307 method was used to measure the simulated distillation curves of the feeds and product liquids. Conversion was calculated using the following equation:

$$\text{Conversion} = \frac{m_{\text{feed},524+} - m_{\text{product},524+}}{m_{\text{feed},524+}} \quad (2)$$

where m is the mass of material in the reactor.