PROCESSABILITY AND THERMAL BEHAVIOUR OF ATHABASCA BITUMEN WITH VARYING ASPHALTENES CONCENTRATION

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ABSTRACT

The coking propensity and thermal hydrocracking of extra heavy Athabasca bitumen vacuum bottoms fractions obtained by a short path distillation were investigated using hot-stage microscopy and microautoclave. The microscopy results indicated that the initial boiling point of the feedstocks (ranging from +525°C to +675°C) and asphaltene content (varying from 32 to 56wt%) did not significantly affect the mesophase induction period. However, the coke yield obtained at different severities using a microautoclave correlated with the asphaltene content and the molecular weight of the feedstocks.

INTRODUCTION

The production of synthetic crude oil from Athabasca bitumen in Alberta is increasing from the current 450 K bbl/day to approximately 1.2 MM bbl/day by the year 2005. The main upgrading technologies presently used to convert the vast reserves of oil sands bitumen to SCO are delayed coking at Suncor Energy Inc. and fluid coking at Syncrude Canada Ltd. Both plants process atmospheric bottoms. Recently, Suncor Energy Inc. has installed a vacuum tower and Syncrude Canada Ltd. will soon install a vacuum tower to process vacuum bottoms.

Upgrading by a coking process results in the production of volatile liquids, gases and coke. Heavier and larger molecules present in the vacuum bottoms would have a greater tendency to form macroscopic particles of solid coke by free radical polymerization reactions in the absence of hydrogen and catalyst. Even in a hydrogen addition process semisolid sediment, sometimes referred to as "incompletely polymerized coke," is formed.[1] According to Wiehe[2] heptane insoluble asphaltenes are the main culprit in coke formation. These asphaltenes, under coking temperatures, are first converted to pseudocomponents called "asphaltenes cores" the concentration of which may exceed the solubility limit in the reaction medium. Once these asphaltene cores are produced, phase separation takes place which leads to irreversible polymerization forming solid coke.

Changing the cut point of the feedstocks from atmospheric to vacuum bottoms will affect their chemical composition which in turn will alter the chemistry of the process. It is well known that the ratio of resins to asphaltenes is an important factor in keeping asphaltenes in solution and thus preventing phase separation.[3]

The present work addresses how the changes in the feedstocks as a result of removing lighter boiling point materials by distillation would affect the upgrading of Athabasca bitumen during thermal processing.

EXPERIMENTAL

Athabasca bitumen atmospheric bottoms (+343°C) was distillated using the automated ASTM D1160 procedure to produce vacuum residue (+525°C) to be used as feed to a short path distillation unit (Leybold-Heraeus model KDL4-P). The system pressure and the temperature of the evaporator were adjusted to produce the desired distillate cuts. The yields and some properties of the residue fractions (+525°C, +575°C, +625°C, and +675°C) are shown in Table 1. Thermal hydrocracking experiments were performed in duplicate in a semi-batch 18-mL microautoclave for 30 min with 13.9 MPa hydrogen pressure and 3.0 L/min (STP) hydrogen flow rate. The reaction temperature and residence time were kept constant at 440°C and 32 min respectively. The product distribution is shown in Fig. 1. In this work, coke is defined as methylene chloride insolubles, asphaltenes as pentane insolubles, and maltenes as pentane soluble fractions.

The coking propensities of these fractions were determined using hot-stage microscopy. The detailed experimental procedures can be found elsewhere.[4] Briefly, the experiments were conducted at a pressure of 750 psi at 440°C in the presence of nitrogen and hydrogen gases in order to determine the differences in mesophase induction period, mesophase size and growth rate as a function of gas used. The heating rate used was 11°C/min and the flow rate of the gas was kept at 35 mL/min. Photomicrographs were taken at regular intervals to illustrate the mesophase growth rate and optical texture. The long axis of each photo is 300μm.

RESULTS AND DISCUSSIONS

The bitumen upgrading chemistry is significantly influenced by the composition of the feedstocks. The understanding of the chemical transformation is difficult because of the complex nature of the resid. One way to simplify this complexity is by fractionating the resid into narrow distillate cuts and solubility classes. Some of the properties of the distillation residues from Athabasca bitumen are shown in Table 1. The data in this table show that as the distillate cuts increased, the molecular weight, MCR, asphaltenes, sulphur, nitrogen and the metals also increased. On other hand, there is only a small change in the aromaticity of the fractions as a function of boiling point.

The product distribution from the autoclave experiments is shown in Fig. 1. In this figure the coke yield is based on the weight percent of the feed processed. In general the coke, asphaltenes, and gas yield increased with increasing boiling point of the feedstocks. Since the asphaltenes are the major component of the residues, their conversion was

plotted as a function of boiling point. The asphaltenes conversion {defined as [wt% asphaltenes (in)-wt% asphaltenes (out)] /wt% asphaltenes (in)} is shown in Fig. 2. This figure shows that asphaltenes conversion increases as boiling point increases. Obviously, some of the asphaltenes is converted to coke (Fig. 3) but some liquid products can also be obtained from asphaltenes decomposition. Production of liquid from asphaltenes is in agreement with the findings of Speight,[5] which showed that the thermal decomposition of asphaltenes from Athabasca bitumen produced not only 40wt% coke but also produced a high yield of volatile products.

The coking propensity of the residues was also studied using hot-stage microscopy.[6] The induction period, which is the period of time before the coke precursors (mesophase) are observed, is known to depend on the composition of the feedstock and most importantly on the concentration of asphaltenes.[2] As shown in Table 1, the C_5 asphaltenes content of the residues increased from approximately 32wt% to 56wt% (although not shown there is a corresponding decrease in the maltenes fraction). Mesophase induction period as a function of boiling point is shown in Fig. 4. The results indicate that within the experimental error, the induction period for the boiling point fractions remained relatively constant under either hydrogen or nitrogen atmospheres. Although the asphaltenes content of the fractions increased, no shortening of the mesophase induction period was observed. The maltenes, although present at a relatively low concentration in the highest boiling point fraction, still have the ability to peptize asphaltenes thus keeping them in the solution and prolonging the induction period.

Another important observation worth noting is the size and the optical texture of mesophase. Under hydrogen atmosphere, large mesophase were formed in all fractions. The ultimate result was the development of bulk mesophase having large domains and vacuoles (Fig. 5). Under nitrogen atmosphere, the size of mesophase remained small and the optical texture was fine-grained.[7]

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Table 1. Properties of Athabasca bitumen distillate residues

	ASTM (D1160)	Distact Distillation*		
Cut point	+525 °C	+575 °C	+625 °C	+675 °C
Yield, wt%	50.8	75.6	67.6	62.2
Mw, Dalton (VPO)	862	1890	2010	2565
MCR, wt%	26.7	31.8	34.0	36.0
Asphaltene, C_5, wt%	32.7	41.5	48.7	56.2
Aromaticity, fa	0.41	0.38	0.40	0.40
Sulphur, wt%	6.53	6.83	6.91	7.20
Fe, ppm	994	989	1088	1217
V, ppm	364	462	471	509
Ni, ppm	148	183	186	209

* The yield of distillate residues are based on +525°C feed

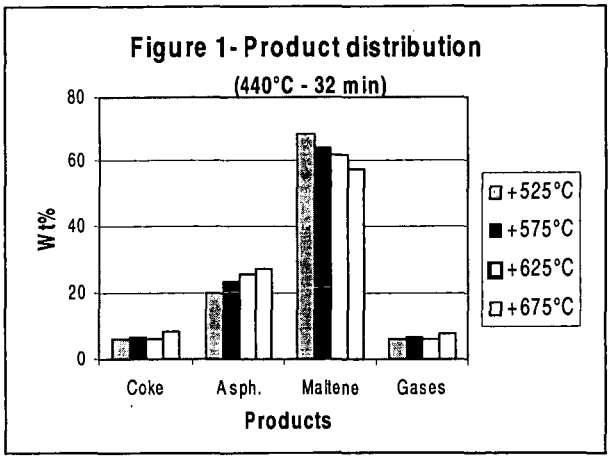
Figure 1- Product distribution
(440°C - 32 min)
80
60
40
20
0
Wt%
+525°C
+575°C
+625°C
+675°C
Coke
Asph.
Maltene
Gases
Products

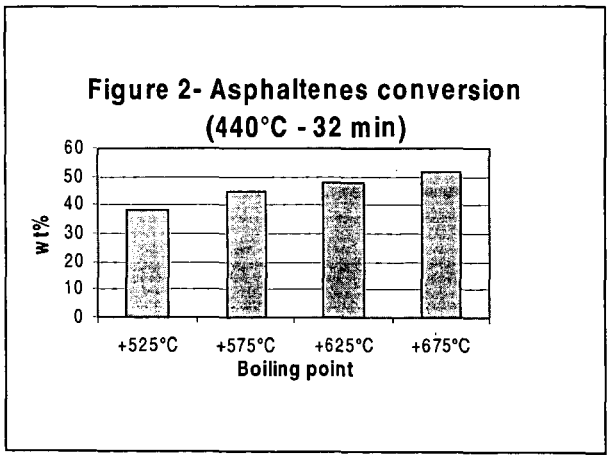
Figure 2- Asphaltenes conversion
(440°C - 32 min)
60
50
40
30
20
10
0
wt%
+525°C
+575°C
+625°C
+675°C
Boiling point

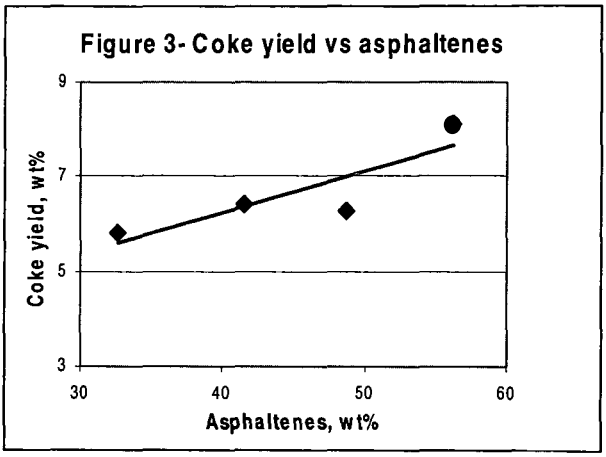
Figure 3- Coke yield vs asphaltenes
Coke yield, wt%
9
7
5
3
30
40
50
60
Asphaltenes, wt%

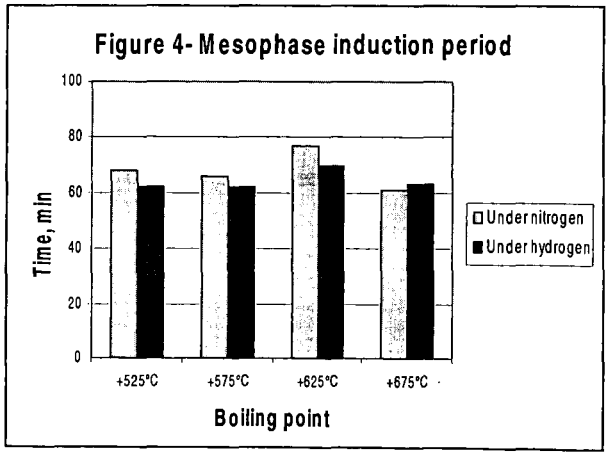
Figure 4- Mesophase induction period
Time, min
100
80
60
40
20
0
+525°C
+575°C
+625°C
+675°C
Boiling point
Under nitrogen
Under hydrogen
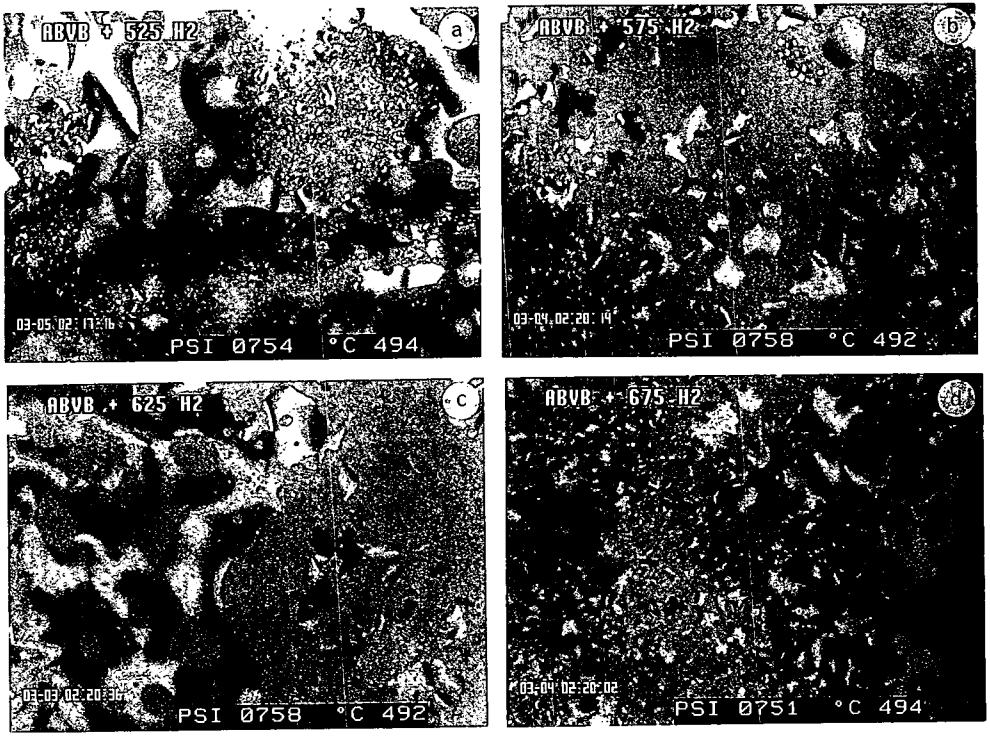
Figure 5 - Mesophase formation under hydrogen