Challenges in Processing Bitumens and Heavy Oils

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Introduction

The volume of oil in place in the various deposits of oil sand in Alberta is estimated at 1.7 trillion barrels, of which 174 billion barrels is recoverable using existing technology. Currently the level of production has reached one million barrels per day, and is expected to increase to about three million barrels per day by 2015. Oil sand crudes are expected to represent more than 75% of the crude produced in Western Canada[1]. Physical and chemical characteristics of bitumens and heavy oils are significantly different from those of conventional crudes. Pipeline transportation to refineries and conversion of these heavy materials to transportation fuels present both challenges and opportunities that are addressed in this paper.

Pipeline transportation

Bitumens are viscous and must be diluted with a lighter hydrocarbon stream to meet the specifications required for shipping in pipelines, i.e., viscosity 350 cSt (11ºC), gravity 19 ºAPI, etc[2]. Thermal processing could reduce the viscosity of the bitumen crudes and thus reduce the diluent requirement but would produce less-stable fuels[2]. Shortages of local diluents and compatibility between diluents and bitumen are important concerns of the Canadian oil sands industry. The properties of typical bitumen are given in Table 1. These feedstocks are characterized by high viscosity, high gravity, high asphaltene contents, high aromaticity, and high total acid number (TAN). Various synthetic crudes make up the majority of the bitumen-derived crudes on the market today. Currently about 400,000 bbl/d of bitumen produced by SAGD technique is shipped to market without having been upgraded and this volume is expected to increase. The bitumen must be diluted with a lighter hydrocarbon stream to meet the specifications for shipping in pipelines. The diluted bitumen, dilbit, normally contains 25–30 vol% diluent or condensate and 70–75 vol% bitumen. Bitumen may also be blended with sweet synthetic crude to produce SynBits, which typically contain 50 vol% synthetic crude and 50 vol% bitumen[1].

Compatibility concerns

When blending bitumen with diluent or synthetic crude to produce pipelineable crude, the blended components must be compatible to prevent asphaltene precipitation. The solubility parameters, solubility blending number (S_{BN}) and insolubility number (I_N) were measured using an oil compatibility model developed by Wiehe[3,4]. For a mixture of oils, the criterion can be stated as follows:

Compatibility criterion: $S_{BNmix} > I_{Nmax}$

where S_{BN} is the solubility blending number and I_N is insolubility number. Tables 2 and 3 show the compatibility characteristics of natural gas condensates (NGC) and synthetic crude with Athabasca bitumen at different dilution ratios. In order to meet the oil compatibility criterion for the blends i.e., $S_{BNmix} > 28$, the maximum volume blending ratio for NGC and Athabasca bitumen is 70/30 and for synthetic crude with Athabasca bitumen is 85/15. Consequently, both NGC and synthetic crude produce compatible mixtures, but synthetic sweet crude is more compatible with Athabasca bitumen.

Upgrading and fouling propensity

To convert Athabasca bitumen to higher-quality feedstocks that can be processed in refineries, there must be significant reductions in boiling point, viscosity, density, molecular weight, and aromaticity. Both H-addition and carbon rejection processes can convert large molecules to lower-molecular-weight species, mainly through cleavage of C-C bonds. Other important reactions in the primary upgrading processes beside cleavage of C-C bonds, include chain fragmentation, radical hydrogen transfer and electron transfer reactions, hydrogen shuttling, ring hydrogenation /dehydrogenation, ring growth, ring opening, and formation of olefins/diolefins. The upgrading chemistry of heavy oils, investigation the major reaction paths leading to products, and the correlation between the chemical composition of extra heavy oil fractions and their processability under thermal conditions were reported earlier[5]. It was shown for four different Athabasca bitumen fractions (from supercritical fluid extraction) that, while bigger molecules are converted to smaller ones, under thermal conditions molecules become more aromatic (Figure 1). Athabasca bitumen contains large amounts of resins and aromatics and as such is very stable and has low fouling propensity[6]. In a separate study Athabasca bitumen was subjected to visbreaking to yield up 20 wt% pitch conversion. The fouling propensities of the distillates were measured using an Alcor fouling rig. As shown in Figure 2, the fouling propensity of the distillates increased as the severity of the process increased. These data are consistent with the increased aromaticity (compared to the aromaticity of the feedstocks) of the liquid products as the reaction severity is increased.

Effect of contaminants in bitumen processing

Besides sulfur, nitrogen, clay minerals, and chlorides, bitumen contains organic acids (naphthenic acids) that may cause naphthenic acid corrosion in processing equipment. Reports and data on refinery corrosion due to the presence of naphthenic acids in oil sands processing are limited and the issue is a matter of controversy. To investigate the effect of thermal treatment on naphthenic acid conversion, vacuum gas oil from Athabasca bitumen was subjected to temperatures between 300-400°C in an autoclave. It was shown that the TAN did not change significantly until the reaction temperature reached 350°C (Figure 3). These experiments were carried out in a flow of nitrogen to ensure that any water produced as a result of condensation reactions was removed and collected in a condenser. The quantities of organic phase collected in the condenser in runs at 350°C and 400°C were about 3 wt% and 6 wt% respectively and TAN content was high (>5.0 mg KOH/g oil). Further analysis of the reactor content and the condenser products by FT-ICR mass spectrometry revealed that the condenser products contained naphthenic acids with much lower carbon numbers (lower boiling points) than those that remained in the reactor[7] (Energy & Fuels 2008 in press). It was concluded that most likely these lower molecular weight and lower boiling naphthenic acids are the ones that cause corrosion in vacuum distillation towers.

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Table 1 Characteristics of Athabasca Bitumen

Viscosity (cP)	>100,000
Gravity (ºAPI)	7-15
Asphaltene (wt%)	17
Aromaticity	0.33
TAN (mgKOH/g oil)	3-4

Table 2 Compatibility of NGC with Athabasca Bitumen

	Solubility S_{BN}	Insolubility I_N
NGC	5.2	0
AB feed	85.5	28.3
NGC (v%)	AB feed	S_{BNmix}
0	100	85.5
5	95	81.5
15	85	73.5
25	75	65.4
30	70	59.5
40	60	53.4
50	50	45.3
60	40	37.3
70	30	29.3

Table 3 Compatibility of Synthetic with Athabasca Bitumen

	Solubility S_{BN}	Insolubility I_N
Synthetic	18.8	0
AB feed	85.5	28.3
NGC (v%)	AB feed	S_{BNmix}
0	100	85.5
5	95	82.2
20	80	72.2
30	70	65.5
40	60	58.8
50	50	52.2
65	35	42.2
70	30	38.8
85	15	28.1

Figure 1 - Effect of thermal hydrocracking on aromaticity of polyaromatic fractions of Athabasca bitumen

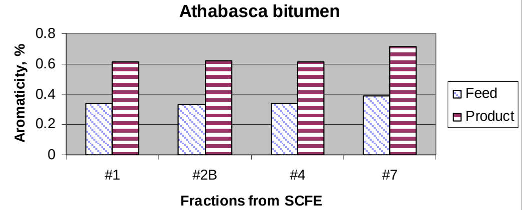

Figure 2- Fouling propensity of visbroken products from Athabasca bitumen

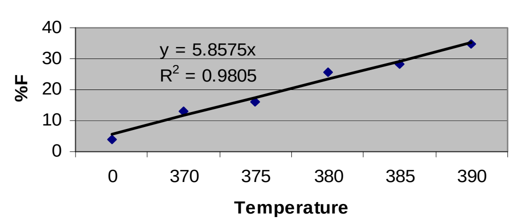

Figure 3- Effect of temperature on TAN conversion