

ATHABASCA BITUMEN UPGRADING WITH ULTRADISPERSED CATALYSTS AT CONDITIONS NEAR TO IN-RESERVOIR OPERATION

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Introduction

Existing upgrading technologies must be improved in order to increase exploitation oil from oil sand reserves in Canada since only 10 % of the total oil in place is available using current methods.¹ Typically, high temperatures and pressures²⁻³ are required to treat bitumen and heavy oils since the higher the hydrocarbon molecular weight the lower the hydrogen/carbon ratio.⁴ This type of upgrading has been achieved in modern refineries via hydrocracking processes. However, the conventional operating conditions for refining processes are far from those found in-situ during production operation. From the previous, one can say that the demand for conversion of heavy oils and bitumen at moderate operation conditions that can match in-reservoir conditions, are linked to the development of more efficient upgrading technologies in which current hydrocracking processes and catalysts must be improved.

Dispersed catalysts have been studied for heavy oil and bitumen processing as a substitute of supported catalysts since the contact between reactants (oils and hydrogen) can be maximized on the high surface area of the small catalytic particles.⁵⁻⁶ It is believed that deactivation problems due to coke poisoning would be reduced because of the higher rates of reaction while maintaining catalytic activity high. Also finely divide catalysts may travel along with the feedstock to be treated, so that reaction times can be longer than conventionally used.¹ Ultradispersed catalysts obtained from water in oil emulsions containing transition metals are able to catalyze such reactions.⁷ Because this is a novel development there is a great deal of research to be produced in this area. This work concerns to the evaluation of ultradispersed catalytic formulations for the hydrocracking of Athabasca bitumen at moderate operating conditions that maybe suitable for in-situ upgrading.

Experimental

Preparation of catalytic emulsions. UD catalysts containing Ni, W and Mo were obtained by emulsification of Athabasca bitumen (main properties in Table 1) with aqueous solutions of transition metal salts: a) nickel acetate, 98% Aldrich; b) ammonium metatungstate, 88% Aldrich; and c) ammonium heptamolybdate, 99% Stream Chemicals, respectively. The amount of metallic precursors was added to obtain 1000 ppmw of metal with respect to the bitumen in the following ratios: Ni/metals_(atomic) = 0.3 and Mo/W_(atomic) = 3. The emulsification procedure involves the mixture of the organic component with the aqueous solutions under high mixing speed. A surfactant, to promote emulsification, was formulated in house to produce a hydrophilic-lipophilic

balance, *HLB* = 8 by combining the commercial surfactants SPAN 80, Sigma; and TWEEN-80TM, Sigma-Aldrich (0.65/0.35 wt/wt). Two different types of catalytic emulsions were prepared, as follows: a) *Fresh*: used immediately after preparation with a maximum amount of water of 5 wt%; and b) *Dry*: A sample prepared as fresh catalytic emulsion is then maintained during 8 hours under low stirring (200 rpm) and at a temperature of 40 °C to evaporate the water down to 0.5 wt%.

Experimental Set-up and procedure. A batch autoclave reactor with 100 ml of capacity was isothermally operated for all the upgrading experiments. For every experiment about 30 g of feedstock is placed into the reactor, hydrogen is fed while the temperature is raised to the desired value and maintained for a fixed period. All the experiments were performed at a total pressure of 3.45 MPa. After reaction the unit is allowed to cool down, gases and liquids samples are properly collected and analyzed in order to perform mass balance and conversions calculations.

Results from simulated distillation are used to determine the fraction of residue 545°C⁺ for both feed and products which are then used to calculate conversion, as follows:

$$\text{Conv}_{545^{\circ}\text{C}^{+}} = \frac{545^{\circ}\text{C}^{+}_{\text{feed}} - 545^{\circ}\text{C}^{+}_{\text{product}} - \text{coke}}{545^{\circ}\text{C}^{+}_{\text{feed}}} \times 100 \quad (1)$$

Two different sets of experiments were performed. The first set was designed to evaluate the extent of reactivity of Athabasca bitumen whether catalyst was used or not and also to investigate their reproducibility, these evaluations were carried out at 380 °C, and a reaction time of 8 hours for both fresh and dry emulsions. The second set comprised the study of the effect of parameters on both conversion and product quality when operating closer to in-reservoir conditions.

Samples characterization. Feedstock and products were characterized as follows: Viscosity was evaluated at 40 °C using a Brookfield viscometer model DV-II+ Pro. Water content was determined by the Karl Fisher titration method on a Mettler Toledo DL-32. High temperature simulated distillation (HTSD) to determine petroleum cuts was performed according to ASTM D7169-2005.⁸ Coke was defined as the insoluble matter in 2g of sample contacted with 100 ml of CHCl₃. Microcarbon residue was determined using a method developed in-house.⁹ Elemental analyses were carried out in LECO (H and C) and Antek 9000 (N and S) equipments.

Table 1. Athabasca Bitumen Composition

Property	
Viscosity, μ , @ 40 °C (cP)	7680
API Gravity (°API)	9.5±0.15
Microcarbon residue (wt%)	12.0
H/C (mass ratio)	0.1271±0.0001
Sulphur (wt%)	4.25
Distillation cuts (wt%)	
Naphtha: IBP-213°C	2.76 ±0.29
Distillates: 213-343 °C	14.89±0.81
VGO: 343-545 °C	34.68±1.81
Residue: > 545 °C	47.95±1.57

Results and Discussion

Effect of catalyst. The results obtained in the first stage of this evaluation are presented in Tables 2 and 3. Table 2 includes for both feedstock and products the mass of the fraction 545°C⁺ and its conversion, while the amount of coke produced during reaction, microcarbon residue (MCR) as well as the sulphur content is presented in Table 3. This set of results compares a) effect of catalyst (1 vs. 2 or 4); b) effect of water in the emulsion (2 or 3 vs. 4); and c) reproducibility (2 vs. 3). In all cases, when catalyst was used the extent of conversion of the residue fraction was improved. However, when comparing the dry emulsion (exp 4) to the fresh emulsion (exp 2 or 3) the result was a higher improvement on the conversion. This outcome may be due to the fact that not only light hydrocarbon gases are released during reaction but also that the water contained in the fresh emulsion evaporates and consequently produces a lower hydrogen partial pressure in the reactor available for interaction with the bitumen molecules. However, a detrimental effect of water on the activity of the catalyst cannot be completely ruled out. On the other hand, a high reproducibility for these experiments was observed (experiment 2 vs. 3).

Table 2. Conversion of Residue (Athabasca Bitumen) at 380 °C and 8 h of Reaction Time (3.45 MPa of Total Pressure)

Experiment	Catalyst	Conv 545°C ⁺ , wt%
Feedstock	-	-
1	No (Blank experiment)	39
2	Fresh – 4.4 wt% water	45
3	Fresh – 4.3 wt% water	44
4	Dry – 0.3 wt% water	56

Table 3. Product Quality from Athabasca Bitumen Upgrading at 380 °C and 8 h of Reaction Time

Experiment	Catalyst	Coke, wt%	MCR, wt%	S, wt%
Feedstock	-	0.0	12.3	4.0
1	No (Blank experiment)	7.6	15.6	3.2
2	Fresh – 4.4 wt% water	1.4	14.7	3.4
3	Fresh – 4.3 wt% water	1.3	14.5	3.3
4	Dry – 0.3 wt% water	0.2	11.1	2.5

Coke (insolubles in CHCl₃) was observed for all products of reaction but it was significantly decreased from almost 8 wt% (blank) down to 1.4 wt% and 0.2 wt% when using fresh or dry catalyst, respectively. This result indicates that the active phases included as UD catalysts are favoring the hydrogenation reactions thus inhibiting the formation of massive coking usually present with thermal processing of heavy hydrocarbons.^{6,10} Another improvement, as a result of catalyst use, was the reduction in sulphur content which showed a similar trend as already discussed for both fresh and dry catalysts. In the case of MCR, it increased from 12 wt% in the feed to about 16 wt% for the blank experiment. This result is in agreement with the values of coke encountered here, since it has been mentioned that the MCR value can be used as a direct measurement of the potentiality for coke formation.⁹ Also, an improvement in the MCR value for the dry emulsion was observed.

Effect of pressure, temperature and reaction time. The effect of hydrogen partial pressure on the residue conversion of Athabasca bitumen evaluated at 350 °C and 30 h of reaction time is presented in Figure 1a. The partial pressure was estimated as the average of the gas composition at initial and final operating conditions while assuming the ideal gas EOS. At these conditions, the partial pressure of hydrogen had a minor effect on conversion which would become an advantage when employing these catalysts at the low pressures available in the Athabasca reservoir. It is important to mention that typical values for processing these feedstocks are usually higher than 1500 psi.⁴ Figure 1b shows a plot of the evolution of the conversion of the residue fraction (545°C⁺) as a function of reaction time for temperatures 320 – 380 °C. As expected the conversion increased with both temperature and reaction time. It was also noticed that at high severity (380 °C) for reaction times longer than 8 hours, the effect of this parameter on conversion becomes less significant, suggesting that a pseudo equilibrium conversion is almost reached. Similar results, when studying the conversion of heavy hydrocarbon feedstocks, have been already reported elsewhere.¹¹

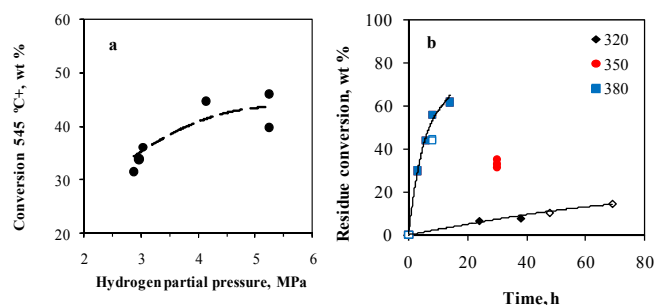


Figure 1. Conversion of Athabasca residue fraction as a function of a) hydrogen partial pressure at 350 °C and 30 h, and (b) temperature and reaction time at 3.45 MPa in the presence of ultradispersed catalytic emulsions. Closed symbols: dry emulsion, open symbols: fresh emulsion.

Product quality. Viscosity, sulphur content, API gravity, and solids (or precipitate) content are important parameters when testing the quality of upgraded products. These parameters will determine the market value of such a product. While viscosity is tied to transport-phenomena problems, sulphur is an undesirable element from an environmental point of view. On the other hand, API gravity indicates the amount of heavy components in the oil, and solids content product of the hydroprocessing reaction should be kept to a minimum in order to avoid product instability and increased solid deposition when further processing. Figure 3 shows a summary of the quality improvement in terms of viscosity, sulphur, and API gravity for the Athabasca bitumen after processed with ultradispersed catalysts under hydrogen atmosphere. In all cases the higher the conversion the better the quality as a result of the upgrading achieved. As expected, the viscosity steadily decreased while the API gravity and the sulphur removal increased. For moderate operation conditions such as 350 °C and 30 h, the residue conversion was observed around 35 wt% will produce a synthetic oil close to 150 cP

(measured at 40 °C), sulphur removal of 30 wt% with an API gravity of 14 °API.

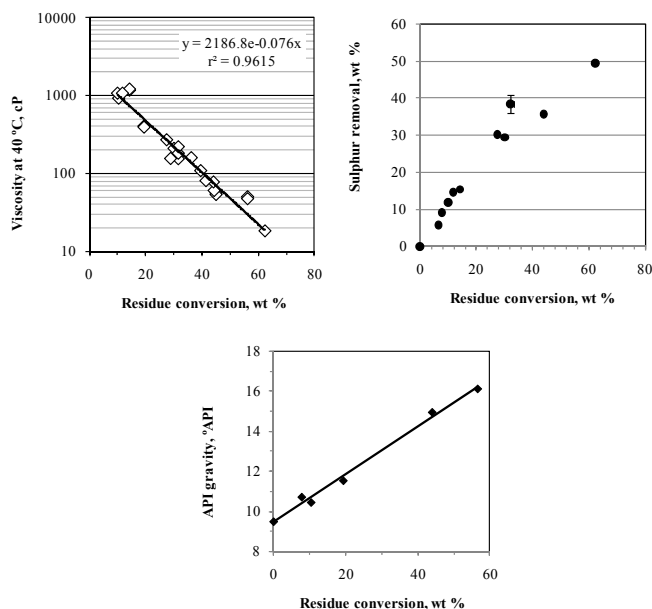


Figure 3. Viscosity, sulphur content, and API gravity as a function of the residue conversion during the upgrading of Athabasca bitumen with ultradispersed catalysts.

The production of solids (coke) as a function of severity is depicted in Figure 4 where micrographs at 40x magnification from the observation of a drop of liquid product are presented, along with their corresponding coke amount for both blank and catalytic experiments. As expected the heterogeneity of the sample increases with reaction time in concurrence with the coke production, as can be seen for catalytic experiments. It is important to remark though that the addition of catalyst remarkably reduced the production of coke as evidenced when comparing the pictures for both samples, blank and catalytic, after reaction for 8h, whose amount of coke were found to be 7.58 and 0.15 wt%, respectively. The theoretical maximum amount of solids from catalyst addition is assumed to be 0.15 wt%. The production of high amounts of coke is undesirable because it involves a great deal of operating problems “downstream” when further treatment is required. Thus, the results here described represent an important advantage for using UD catalysts since it is possible to process the heavy feed for long reaction times without generating an “unstable” product.

Conclusions

Ultra-dispersed catalysts delivered into the reaction medium in the form of water-in-oil catalytic emulsions of transition metals successfully enhanced the upgrading of Athabasca bitumen when operating at lower temperatures and pressures than those used for typical upgrading applications. The upgrading at moderate conditions near to in-reservoir operation may produce synthetic upgraded oil with 150 cP of viscosity and 14 °API. Main advantages by using UD catalysts are: reduction of viscosity, sulphur removal, and reduction of micro-carbon residue (potential coke production). These

results are very encouraging for continuing systematic work in this research area.

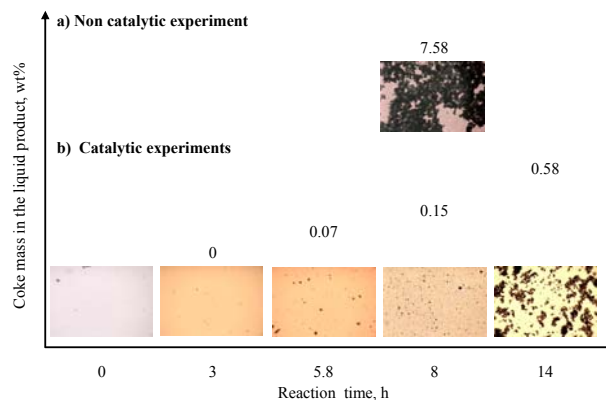


Figure 4. Micrographs (40x) for liquids products from the hydrocracking of Athabasca bitumen at 380 °C and at a total pressure of 3.45 MPa obtained for catalytic and non-catalytic experiments.

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