Viscosity Reduction and Upgrading of Athabasca Oilsands Bitumen by Natural Zeolite Cracking

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Abstract—Oilsands bitumen is an extremely important source of energy for North America. However, due to the presence of large molecules such as asphaltenes, the density and viscosity of the bitumen recovered from these sands are much higher than those of conventional crude oil. As a result the extracted bitumen has to be diluted with expensive solvents, or thermochemically upgraded in large, capital-intensive conventional upgrading facilities prior to pipeline transport. This study demonstrates that globally abundant natural zeolites such as clinoptilolite from Saint Clouds, New Mexico and Ca-chabazite from Bowie, Arizona can be used as very effective reagents for cracking and visbreaking of oilsands bitumen. Natural zeolite cracked oilsands bitumen products are highly recoverable (up to ~ 83%) using light hydrocarbons such as pentane, which indicates substantial conversion of heavier fractions to lighter components. The resultant liquid products are much less viscous, and have lighter product distribution compared to those produced from pure thermal treatment. These natural minerals impart similar effect on industrially extracted Athabasca bitumen.

Keywords—Natural Zeolites, Oilsands Bitumen, Cracking, Viscosity Reduction, Upgrading.

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I. INTRODUCTION

NATURAL, synthesized or acidified minerals, particularly clays, have been found to effectively break heavy petroleum fractions such as gas oil [1], but the application of natural zeolites (NZs) as cracking catalysts/reagents for oilsands bitumen is a novel approach [2]. Canada's oilsands bitumen, the majority of which is in Alberta, represents 15% of the proven global crude oil resources, [3] and is an extremely valuable source of energy for North America. However, the density, viscosity, and residue fraction of the bitumen recovered from these sands are much higher than those of typical crude oil due to the presence of large molecules such as asphaltenes. Our previous studies showed that NZs such as clinoptilolite from Saint Clouds, New Mexico and Ca-chabazite from Bowie, Arizona can be acidified and developed as more effective reagents for cracking of oilsands bitumen than standard petroleum cracking agent, zeolite Y [2,4]. Low-cost NZs, particularly clinoptilolites, are found in large natural deposits and can be used as very inexpensive cracking agents [5]. NZ-cracked products are almost entirely recoverable using light hydrocarbons, which indicates substantial conversion of heavier fractions to lighter components [4]. This study investigates the reduction in heavy fractions and viscosity of bitumen by untreated NZ catalyzed cracking of raw oilsands and industrially extracted Athabasca bitumen. We have quantified the effects of different catalyst loadings and reaction temperatures on the extent of cracking and viscosity reduction, and compared the results with the baseline data for raw and thermally cracked feed materials.

II. EXPERIMENTAL PROCEDURE

A. Materials

Clinoptilolite (SC) and sedimentary Ca-chabazite (CC) were obtained from Saint Clouds, New Mexico and Bowie, Arizona respectively. The samples were ground to <44 μm particles.

Raw Athabasca oilsands and industrially produced Athabasca bitumen were obtained from the Syncrude facility at Mildred Lake near Fort McMurray, Alberta, Canada.

B. Cracking Reaction and Extraction

A large custom-designed, continuously stirred stainless steel autoclave of approximately 1000 cm³ capacity was used to conduct the catalytic cracking of unextracted bitumen in oilsands. For each reaction, the autoclave was loaded with 500 g of oilsands and a specified amount of NZ (0-5 wt.% of oilsands), purged with helium at >1400 kPa pressure and leak tested, and then subjected to a specified reaction temperature in a heating furnace for 1 hour. The reactor was then immediately quenched in cold water, allowed to reach thermal equilibrium, degasified, and stripped of the light oil fractions by re-heating to 150 ˚C and collecting the condensate in a cold trap. The liquid products were extracted from 80 g of the reacted mixture using a Soxhlet apparatus for 6-8 hours with pentane as the solvent, and then dried at 40 ˚C prior to re-adding the condensate fractions to the products. The liquid products were also toluene-extracted from another 80 g of the reacted mixture following the same procedure and then drying at 110 ˚C prior to re-adding the condensate fractions.

Stainless steel micro-batch reactors (~14 cm³ capacity) were used for cracking reactions of industrially produced Athabasca bitumen. Reactors were loaded with approximately 3 g of bitumen and specified amounts of NZ, purged and leak tested in a similar manner, and then subjected to a mild cracking temperature in a fluidized sand bath maintained at 400 ℃. The reactor was quenched in cold water to stop the reaction 40 minutes after reaching thermal equilibrium. The liquid products were separated from the solid catalyst by repeated centrifuge separation and toluene extraction, and then dried under vacuum at a temperature slightly higher than the equivalent atmospheric boiling point of toluene (~115 °C).

C. Asphaltenes and Coke Measurement

The C_5-asphaltenes contents were determined by re-extracting the pentane-extracted depleted sands with toluene in a Soxhlet extractor, drying (at 110 °C) and weighing the depleted sands extract. To measure the amount of coke make, the depleted sands were stripped of any remaining toluene by drying at ~250 °C for 2 hours under helium flow. The dried depleted sands were then weighed, and placed in a high temperature muffle furnace at 850 °C for 5 hours, in presence of air, to combust the remaining organic solids. The amount of coke was determined from the weight difference of the depleted sands before and after combustion.

D. Saturates, Aromatics, Resins and Asphaltenes (SARA) fractionation

SARA fractions were determined by clay-gel adsorption column chromatography (ASTM D2007M), the detailed method and apparatus for which are described elsewhere [6]. About 4 g of toluene-extracted bitumen samples were stripped of the asphaltenes content by pentane extraction (solvent to bitumen ratio>40:1) then placed in an ultrasonic bath for 45 minutes, settled overnight and filtered. The asphaltenes were dried at 110 °C for at least 3 hours, and pentane was removed from the remaining liquid by Rotavap. The saturates, aromatics and resins fractions were then separated by successive chromatographic extractions using pentane, toluene following a 50:50 pentane-toluene mixture, and methanol following a 60:40 methanol:methylene chloride charge, respectively. The extracted fractions were dried at 110 °C in an oven to evaporate remaining solvents prior to weighing.

E. Viscosity Measurement

Viscosities were measured by a Brookfield DV-E chamber and spindle viscometer at least at three different temperatures. The 2-3 mL of toluene-extracted bitumen samples were allowed to reach thermal equilibrium prior to each measurement. The two parameters of the ASTM equation, namely a_1 and a_2 [7], were determined from fitting of experimental data, and the resulting viscosity values were converted to an equivalent 50 °C value if no reading were found at this temperature. Where, μ is the viscosity measured at temperature T (K), and a_1 and a_2 are constants determined from data fitting, the ASTM equation is:

$$\ln[\ln(\mu)] = a_1 + a_2 \ln(T) \qquad (1)$$

III. RESULTS

A. Characterization of Feed Oilsands

The maltenes, defined as the pentane-extracted liquid plus the re-added light condensate fraction, and asphaltenes contents of the raw toluene-extracted bitumen of the feed oilsands are 76.7 wt.% and 19.5 wt.% of the bitumen respectively (Table I).

B. Cracking and Product Recovery

Our results indicate that at 300 ˚C, SC and CC catalyzed cracking reactions produce higher yields (up to 83%) of maltenes compared to thermal cracking under the same

TABLE I
COMPOSITION OF RAW BITUMEN EXTRACTED FROM FEED OILSANDS

Fraction	Weight %
Maltenes	76.7
C_5-asphaltenes	19.5
Toluene-insoluble organic solids	3.8

conditions (Fig. 1). This temperature is significantly lower than the typical visbreaking temperature of bitumen (≥400 ˚C) [8], or pyrolysis temperature of large hydrocarbon molecules [9]. The limited thermal cracking observed at this temperature can possibly be due to higher wall temperatures, or the matrix effect of the clay materials present in the oilsands. At 300 ˚C, the reactions were dependent on catalyst loading with the higher maltenes yields at 5% loading.
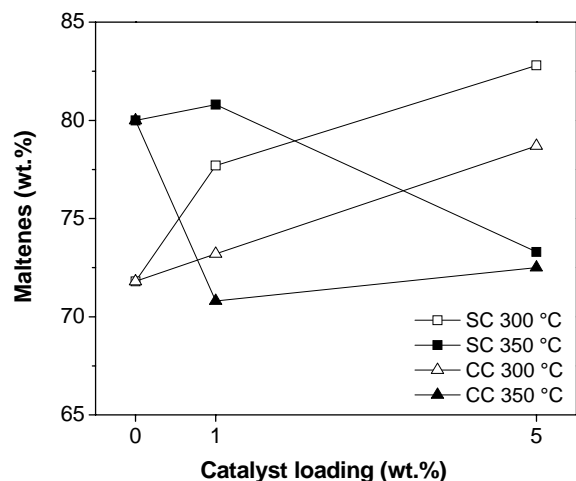
Fig. 1 Maltenes fraction (pentane extractables) generated by the cracking reactions as a function of catalyst loading (0% loading refers to thermal cracking)

Based on the asphaltene conversion results (Fig. 2), the maltenes yield at 300 ˚C correlates very well to the catalytic conversion of the asphaltene fraction in bitumen. Both the SC and CC catalyzed reactions at 300 ˚C yield significantly higher maltenes with increased loading (Fig. 1), which is consistent with the reduced asphaltenes fraction (Fig. 2). Clearly, increased amounts of catalysts cause higher conversion of the heavy asphaltenes into desirable maltenes fraction.
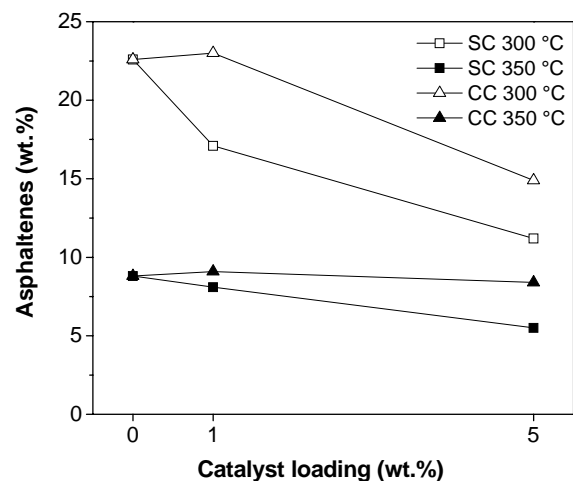
Fig. 2 C_5-asphaltenes fraction from the cracking reactions as a function of catalyst loading (0% loading refers to thermal cracking)

At 300 ˚C, high maltenes and low asphaltenes contents also corresponded to low gas (4.5-5.6 wt.%) and coke (0.4-0.8 wt.%) make by the NZ catalyzed cracking reactions (Figs. 3

and 4). Interestingly, both thermal cracking and 1% CC reactions at 300 ˚C result in higher asphaltenes content (22.6% and 23%) compared to the raw bitumen (19.5%). This is due to the concentration of the asphaltenes fraction in remaining bitumen following conversion into gas and coke, which can be up to ~11 wt. % of the feed. Another possible explanation is dismutation of the resins fraction, typically observed in visbreaking operations at mild thermal conditions, which increases the asphaltenes content in bitumen [8].
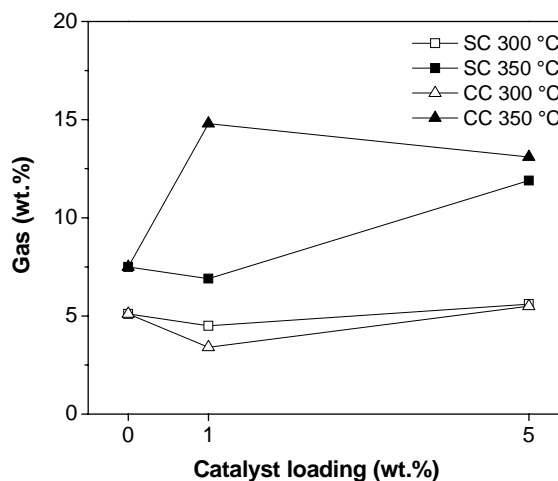

Fig. 3 Gas production from the cracking reactions as a function of catalyst loading (0% loading refers to thermal cracking)
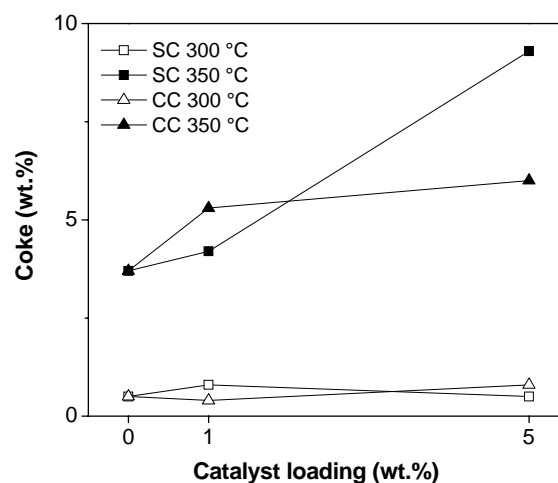

Fig. 4 Coke make from the cracking reactions as a function of catalyst loading (0% loading refers to thermal cracking)

Catalyzed reactions at higher temperature (350 ˚C) further decreased the asphaltenes content (Fig. 2) while producing much higher amounts of gas (Fig. 3) and coke (Fig. 4),

resulting in less maltenes (Fig. 1). The increased gas make could be due to gradual exhaustion of crackable components and overcracking of feeds as observed in other catalytic cracking processes [10].

Importantly, the catalyzed reactions at 300 ˚C reduced the asphatenes fraction close to the amount present in bitumen generated by thermal cracking at 350 ˚C. The catalyzed reactions at 300 ˚C also produced comparable or higher amounts of maltenes than that generated by thermal cracking at 350 ˚C, and much less gas and coke. From an industrial perspective, these translate into significant reduction of the operating temperature and cost, while maintaining higher yield and selectivity of maltenes.

C. Distribution and Quality of Toluene-Extracted Bitumen

The results from SARA fractionation of toluene-extracted bitumen samples generally show that the NZ catalyzed reactions reduce the asphaltenes and resins fractions and increase the concentrations of saturates and aromatics, as compared to the analogous thermal cracking reactions (Fig. 5). Saturates and monoaromatics are precursors to producing usable gasoline and derived products [11]. The reduction in asphaltenes is more pronounced at 350 ˚C. It should be noted that similar to the C_5-asphaltenes measurements by extraction, there is a general increase in the asphaltenes content in some of the samples compared to extracted raw bitumen. Again, this is due to the concentration of the asphaltenes fraction in remaining bitumen following conversion of bitumen into gas and coke (up to ~11 wt.% of the feed). Both SARA and the extraction analysis show the same general trend of asphaltenes reduction by NZ catalyzed cracking. However, SARA fractions are measured by column chromatography on liquid samples which makes the asphaltenes content (Fig. 5) uncomparable to the C_5-asphaltenes contents determined by toluene extraction on the pentane-extracted oilsands (Fig.2). SARA fractions are based only on a %-total of the toluene extracted liquid product while C_5-ashpalenes are based on a wt.% of the overall reaction.
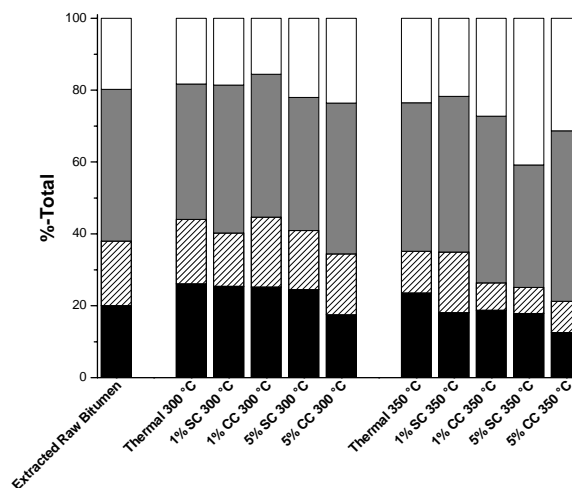

Fig. 5 SARA fractionation of bitumen derived from thermal and NZ catalyzed cracking reactions (legends: ☐ saturates, ■ aromatics, ▨ resins, and ■ asphaltenes)

Results show that catalytic cracking of oilsands bitumen, even at the low temperature of 300 ˚C, can decrease the viscosity of the toluene-extracted bitumen significantly compared to analogous thermally cracked samples (Fig. 6). This reduction in viscosity is strongly dependent on catalyst loading, and somewhat correlated to the reduction in asphaltenes content. At 350 ˚C, an increase in SC loading from 1-5% resulted in significant decrease in viscosity (10310-1525 cP) (Fig. 6) and also correlates to the decrease in the asphaltenes content (8.1%-5.5%) (Fig. 2). The same trend is observed for 1-5% CC catalyzed samples at 300 ˚C. However, for 1% SC loading at 300 ˚C, despite a decrease in the asphaltenes content, the viscosity of the sample was higher compared to the thermally cracked sample (Fig.6). With the increase in SC loading to 5%, both the asphaltenes content and the viscosity of the sample decreased to a great extent as expected.

The viscosity measurements were not affected by shear thinning/thickening properties of bitumen (Fig. 7) and time effects which are detected by significant change in values with shear rate and time [12]. Viscosity measurements, however, can be impacted by the lighter components generated from cracking of maltenes fraction, which may then act as diluents, reducing the viscosity values but not the heavy fraction of bitumen.
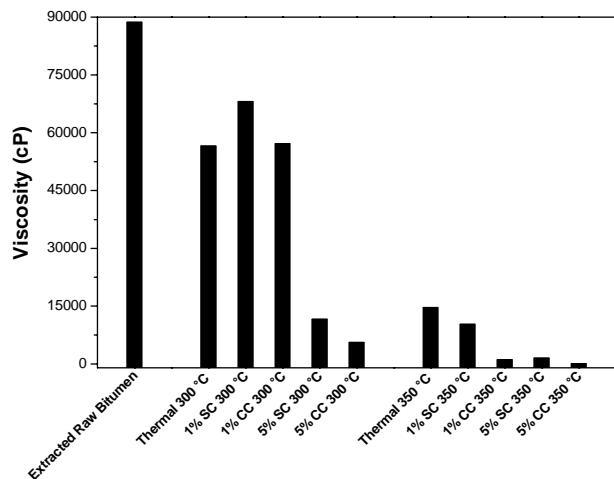
Fig. 6 Viscosities of bitumen samples produced from thermal and catalytic cracking reactions, measured at 50 ˚C
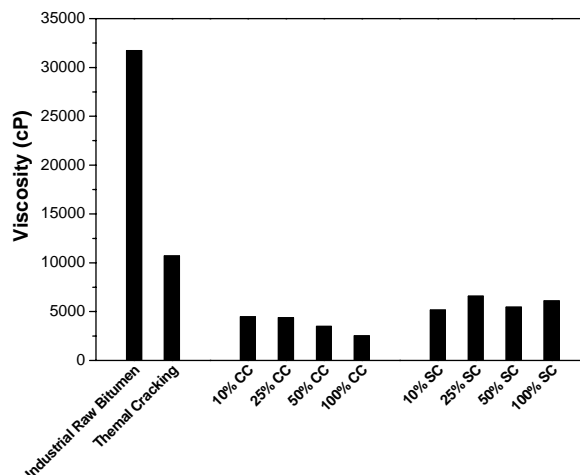

Fig. 8 Viscosity of industrially-extracted Athabasca bitumen after thermal or NZ catalyzed cracking, measured at 50 ˚C
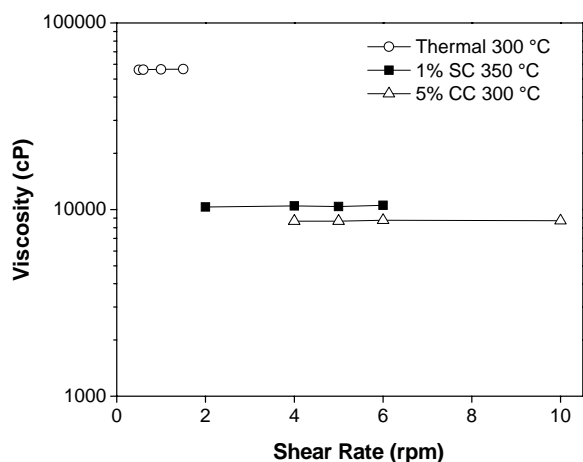

Fig. 7 Dependence of viscosities of bitumen samples on shear rate (viscosities are measured at 50 ˚C)

Catalyzed cracking of industrially-extracted raw Athabasca bitumen by NZs produces a similar effect on viscosity of the samples. Reactions using 10 wt.% loading of the catalysts (based on bitumen weight) reduced the viscosity of bitumen to approximately 14-16% (using CC) and 16-20% (using SC) of the viscosity of the raw feed (Fig. 8). These measured viscosities are also significantly lower ($\leq$55%) than those of thermally cracked bitumen. For both catalysts, increasing the loading beyond 10 wt.% does not significantly impact viscosity reduction.

D. Accuracy of Experimental Measurements

The standard deviations (SDs) of the experimental measurements of the products were 1.1, 2.1, 1.1 and 0.9 wt.% on maltenes, asphaltenes, gas and coke make respectively. The maximum SDs of the viscosity and SARA fractionation were found to be 3.0 cP% and 3.7 wt.% respectively, based on repeated measurements conducted on multiple samples.

IV. CONCLUSION

This study demonstrates that NZs are very effective agents for oilsands bitumen cracking and upgrading at temperatures as low as 300 °C, well below the typical thermal cracking temperature for bitumen. These natural minerals can effectively convert the asphaltenes fraction into substantially lighter components, producing bitumen samples with a high maltenes yield and rich in desired saturates and aromatics. The reactions also result in less coking and considerably less viscous products. Similar cracking effects are observed on industrially-extracted Athabasca bitumen.

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