Visbreaking oilsands derived bitumen in the temperature range 340-400 °C

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Abstract

The low temperature visbreaking of Canadian oilsands derived bitumen was investigated. The aim was to determine the extent to which the fluidity of the bitumen can be improved by less severe thermal conversion than normally employed industrially, while at the same time maintaining a high liquid yield. Most of the experimental work was conducted in the temperature range 340-400 °C, although some data was also obtained at lower temperatures. It was possible to limit gas and coke formation and obtain a 96-97 wt% liquid yield, while decreasing the bitumen viscosity from around 100 to 1 Pa·s (measured at 40 °C). More remarkable was that viscosities of around 3 Pa·s could be obtained by just heating the bitumen to either 360, or 380 °C and then cooling it down. The most plausible explanation for the rapid decrease in viscosity during low temperature visbreaking was that there was a decrease in the effective volume fraction of the colloidal fraction. The viscosity change over time at constant temperature was complex, with at least one local minimum and maximum being observed. This aspect of the behavior could not yet be fully explained. Overall it was found that the bitumen was reactive and that its thermal conversion behavior over the temperature range studied was comparable to that of a young crude oil, not a residuum.

Keywords: Oilsands bitumen, visbreaking, thermal cracking, viscosity, Field Upgrading, asphaltenes.

1. INTRODUCTION

One of the main production hurdles during recovery and transportation of bitumen from the Canadian oilsands deposits in Northern Alberta is low fluidity. The viscosity of bitumens from the Cold Lake and Athabasca deposits are in the range 10^4 to 10^5 mPa·s (cP) at 25 °C,(1) and the viscosity is an order of magnitude higher at the North American pipeline specification temperature of 7.5 °C. The viscosity specification is maximum 0.33 Pa·s at a maximum density of 940 kg·m^{-3} (350 cSt and 19 °API).(2) In order to get the bitumen to market, the fluidity of the bitumen must be improved. Two strategies are predominantly employed. The first strategy is to dilute the bitumen with 25-35 % naphtha range material, thereby reducing the viscosity of the mixture.(2) The second strategy is to convert the bitumen to some degree in order to reduce its viscosity. This paper deals with the latter strategy, namely, to reduce bitumen viscosity by conversion.

One of the technologies that can be used to reduce the viscosity of heavy oils is visbreaking. Visbreaking is one of the oldest refining technologies. Visbreaking involves the mild thermal cracking of the heavy oil to produce a lower viscosity fuel oil as major product and lighter boiling materials as minor products. Conversion of material in the vacuum residue boiling range (>550 °C) is of the order 6-12 % depending on the severity of operation and typical operating conditions are 430-500 °C and ~1 MPa.(3)(4)(5) The maximum operating severity in turn depends on the stability of the feed material, with a more aromatic feed resulting in better stability.(6)

An application that is of interest for oilsands bitumen production is the use of visbreaking technology for Field Upgrading. A Field Upgrader is a small conversion facility that can be constructed at the point of bitumen recovery, so that the bitumen can be upgraded to a transportable and marketable product in the field. Not only does it avoid the cost associated with a large centralized Upgrader facility, but it also avoids the problems associated with transporting bitumen from the different points of recovery to a centralized Upgrader facility, as is currently the practice. In order to make visbreaking suitable for Field Upgrading, there are some constraints to be considered. One particularly important constraint is the more limited utility infrastructure. When this constraint is applied to visbreaking, it implies that one would ideally want to:

(a) Operate visbreaking at low temperature to reduce the cost associated with the fired heater.
(b) Minimize the gas yield during visbreaking to reduce the off-gas treatment requirements.
(c) Reduce oil viscosity to a level where fluidity is sufficient for undiluted pipeline transport.
(d) Reduce the density to improve economics and make oil acceptable for pipeline transport.
(e) Produce a stable product for pipeline transport that will not cause gumming or precipitation.

A historic report on the upgrading of oilsands bitumen by Ball(7) caught our attention. It was reported that a fresh sample of oilsands bitumen from the Athabasca region was subjected to a temperature of 360 °C for 32 minutes. This resulted in a product with an order of magnitude lower viscosity, lower density and conversion resulted in "[n]o fixed carbon and virtually no free gases". Directionally this was what was required for visbreaking in a Field Upgrader.

In this study the visbreaking of oilsands bitumen was investigated in the temperature range 340-400 °C, which falls outside the normal operating temperature range for visbreaking processes. As a first step the observations by Ball(7) were confirmed. This was followed by a systematic evaluation of the relationship between temperature, reaction time and the fluidity of the products obtained by the visbreaking of oilsands bitumen at these lower temperatures.

2. EXPERIMENTAL

2.1 Materials

The investigation was performed using bitumen from the Cold Lake region in Alberta, Canada. The fresh oilsands derived bitumen was characterized before use (Table 1). Since the work was performed over an extended period of time, material was taken from more than one feed drum. The uncertainties in analyses are indicated as one sample standard deviation. Ranges represent the outcome of analyses of different bitumen samples.

Methylene chloride (99.9 % CH_2Cl_2) that was employed as solvent to remove residual products from the reactors after reaction, was commercially obtained from Fischer Scientific. Nitrogen (99.999 % N_2) that was employed to provide an inert atmosphere and pressurize the reactors for visbreaking, was obtained in cylinders from Praxair. Asphaltene precipitation was performed with *n*-pentane (98 %) supplied by Sigma Aldrich and that contained >99.5 % pentanes (C_5H_{12}).

2.2 Equipment and procedure

The visbreaking of oilsands derived bitumen was conducted in a semi-batch reactor (Figure 1) held at constant pressure and temperature. The reactor was constructed from 316 stainless steel Swakelok tubing and fittings. The reactor body was made from ½ inch tubing (12.7 mm outside diameter, 10.7 mm inside diameter) with a length of 100 mm, excluding fittings. The pressure was controlled by a back pressure regulator. The temperature inside the semi-batch reactor was measured and controlled by submerging the reactor into a fluidized sand bath heater, which was maintained at an appropriate temperature by controlled electric heating. All temperatures reported are internal reactor temperatures.

During a typical experiment 8 g Cold Lake bitumen was placed into the reactor. The reactor was then closed, purged with nitrogen and leak tested. The back pressure regulator was set to 4 MPa, which means that the reactor pressure was maintained at 4 MPa. The reactor was then submerged in the preheated fluidized sand bath. At the end of the reaction, the reactor was removed from the fluidized sand bath and allowed to cool down before the pressure was released and the reactor was opened. The reaction product was removed from the reactor by dissolving it in methylene chloride in a ratio of approximately 1:40. The solids were then separated from the product by vacuum filtration using a 0.22 μm filter and the solids were dried and weighed. The methylene chloride was removed from the liquid filtrate under reduced pressure (60 kPa absolute) at 30 °C in a rotary evaporator over a period of 30 min. Samples were left overnight at ambient conditions in a fume hood to allow evaporation of any residual methylene chloride that may have remained. During all steps the masses were noted. Material balance closure was within 97-103 wt% for the reported experiments. Experiments were conducted in triplicate or better and results are reported as an average (x) with one sample standard deviation (s).

Due to the importance of the temperature history in this work, a typical heat-up and cool-down temperature profile of the semi-batch reactor filled with bitumen is provided for the highest temperature operation (Figure 2). The profiles for three runs are provided to give an indication of the repeatability of the heat-up and cool-down temperature profiles. The start-of-run time is defined as the time when the internal temperature in the reactor reached its set point value. The set point temperature for all experiments was reached within 6 min. A conversion time of 0 min is when the bitumen is just heated up to the set point temperature and once the start-of-run is reached, it is immediately cooled down (Figure 2). Conversion times exclude the heat-up and cool-down times.

2.3 Analyses

Viscosities were determined with a RheolabQC rheometer from Anton Paar using a C-CC17/QC-LTC measuring cup. The viscosity determinations were performed at a constant shear rate of 10 s^{-1}. Densities were determined using an Anton Paar DMA 4500M density meter. Refractive indexes were determined relative to air using the sodium D-line (589 nm). The measurements were performed with an Anton Paar Abbemat 200. The micro carbon residue (MCR) values were determined by thermogravimetric analysis (TGA) using a Mettler Toledo TGA/DSC1 LF FRS2 MX5. The MCR values were obtained by heating the samples in alumina crucibles at a constant rate of 10 $°C\cdot min^{-1}$ from 25 to 600 °C under an inert atmosphere. The ash content was determined by continuing the heating from 600 to 900 °C under airflow. Penetration values were determined using a Humboldt model ML 1200 penetrometer.

3. RESULTS

3.1 Confirming historic observations

The simplest way to confirm the historic observations that the oilsands bitumen was readily converted at mild conditions was to repeat the work of Ball.(7) This was done, albeit with a different source of oilsands derived bitumen. Instead of 4-6 °API (1030-1045 kg·m^{-3}) Athabasca bitumen that was heated to 360 °C for 32 min,(7) 7 °API (1022 kg·m^{-3}) Cold Lake bitumen was heated to 360 °C for 30 minutes and the converted product was characterized (Table 2).

The historical data was qualitatively corroborated. With the exception of density, all other properties exhibited analogous changes to that reported by Ball.(7) The experimental results indicated that there was no decrease in density after thermal treatment of the bitumen. It was further found that the change in the distillation profile was less pronounced, but that the relative decrease in kinematic viscosity was more. Instead of a softening point, a penetration test was performed and it confirmed that the thermally treated bitumen was "softer".

The outcome of this evaluation (Table 2) provided sufficient justification to embark on a more extensive evaluation of the thermal conversion at temperatures of 400 °C and below.

3.2 Product yields

Previous work(8) on the mild thermal cracking of oilsands bitumen at 400 °C was expanded to cover conversion times ranging from 0 to 120 min. The product yields at different conversion times are given (Table 3). In the reaction period 0 to 60 min there was a slight decrease in liquid yield from 98 to 95 wt% over time, with a corresponding increase in gas and solids yield. At 90 min there was a step change in the liquid yield, which decreased from 95 to 88 wt%. The solids yield was constant from 0 to 20 min and increased monotonously from 30 min onwards.

The visbreaking experiments were repeated at lower temperatures, but the conversion times were extended to allow sufficient reaction time for a meaningful increase in solids formation. Since the step change in yield profile occurred between 60 and 90 min conversion time, the equivalent conversion time to 90 min at 400 °C was calculated. It was known from visbreaking literature that the time required for constant conversion doubled with every 15 °C decrease in visbreaking temperature.(3) The time (t) versus temperature (T) relationship could be simply expressed as (Eq. 1):

$$\ln\frac{t_2}{t_1} = \frac{T_1 - T_2}{15}.\ln(2) \qquad \text{... (1)}$$

Thus, according to Eq. 1, in order to achieve the same conversion as 90 min at 400°C, it was necessary to extend the reaction time to ~230 min at 380 °C, ~570 min at 360 °C and ~1440 min at 340 °C.

The product yields obtained at different conversion times for bitumen visbreaking at 380 °C are given (Table 4). There was a slight decrease in liquid yield with conversion time, but with the liquid yield remaining at 96 wt%, the gas and solids yields remained low. A noticeable increase in the gas yield between 60 and 120 min and then in the solids yield between 120 and 232 min were observed. However, the yield profile at 232 min and 380 °C was meaningfully different from that at 90 min and 400 °C.

The yield profile from bitumen visbreaking at 360 °C and different conversion times (Table 5) looked quite similar to that of visbreaking at 380 °C. There was also a slight decrease in liquid yield with conversion time and the liquid yield decreased only to 96 wt%. The gas yield started increasing between 240 and 577 min, but the solids yield remained low.

The same pattern of yield versus conversion time as observed at 360 °C, was found when the conversion was performed at 340 °C. The yields at different conversion times during bitumen visbreaking at 340 °C are given (Table 6). The liquid yield decreased to 97 wt% after 1440 min conversion time, when a small increase in gas and solids yields became apparent.

3.3 Viscosity

The viscosity of the products obtained by visbreaking in the temperature range 340 to 400 °C was measured at different conversion times (Table 7). Instead of a monotonous decrease in viscosity with increasing conversion time, the viscosity first decreased, then increased and then decreased again. This relationship between viscosity and conversion time behavior was observed at all of the visbreaking temperatures evaluated, but occurred at different conversion times.

The conversion time was adjusted using Eq.1 to be equivalent to the conversion time at 400 °C and the viscosity versus time profiles were compared (Figure 3). The comparison highlighted two aspects. First, it showed that the profiles of viscosity versus time for visbreaking in the range 340-400 °C were similar, but that the magnitude differed meaningfully. Second, it showed that the local minima and maxima of viscosity that were observed during visbreaking occurred at shorter adjusted time (based on Eq.1) as the visbreaking temperature was decreased.

One of the more surprizing results was the extent of viscosity reduction at short contact time. The viscosity could be reduced by an order of magnitude by just heating the bitumen to some temperatures and then cooling it down, as shown in the heating up and cooling down temperature profile (Figure 2). For example, by heating the bitumen to 360 °C and then cooling it down, the viscosity measured at 40 °C was decreased from 92 ± 3.6 to 3.5 ± 0.04 Pa·s (Table 7).

It was reasoned that even at 0 min conversion time, the bitumen was exposed to a temperature profile during the heating up period. Meaningful viscosity reduction may have taken place at even lower temperatures. A series of experiments was performed at 0 min conversion time to cover a wider temperature range (Figure 4). It revealed that there was at least one additional local viscosity minimum at 320 °C and even at the lowest temperature tested, 260 °C, there was a decrease in viscosity of the product compared to that of the bitumen feed.

There was a concern that the work up procedure, which involved addition and removal of methylene chloride, may have affected the viscosity values. The impact of the procedure on the absolute viscosity value of bitumen was evaluated (Table 8). It was found that the bitumen viscosity was increased by around 15 % after the addition and removal of methylene chloride.

The bitumen feed viscosity at 40 °C that should therefore be used for comparison with the data of thermally treated bitumen is 106 ± 3.2 Pa·s and not 92 ± 3.6 Pa·s. A further implication is that the actual absolute viscosity values for the thermally treated bitumen may be somewhat lower.

The addition of methylene chloride is necessary for product recovery and filtration. Filtration is one of the most time consuming steps in the work up procedure. Furthermore, it was found that the nature of the solids produced at different time-temperature combinations was different and that filtering in some instances became especially arduous. The impact of avoiding the filtration step was evaluated (Table 8). The results confirmed that filtration and the use of a solvent was necessary. When the thermally converted bitumen was solvent treated, but not filtered, the viscosity of the unfiltered product was around 55 % higher.

Lastly is should be pointed out that the viscosity reduction that was achieved by visbreaking was permanent. Samples that were stored in closed containers for further analysis did not exhibit a measurable increase in viscosity over a period of one year.

3.4 Density

The density of the bitumen was not meaningfully changed by low temperature thermal conversion (Table 9). This implies that the kinematic viscosity followed the same viscosity trends that were reported in the previous section. If there was any change in density, then the only statistically meaningful change was the minor increase of density from 1007 ± 1 to 1012 ± 2 $kg \cdot m^{-3}$ observed after thermal conversion at 400 °C for 120 min.

4. DISCUSSION

4.1 Ease of thermal conversion

The historic observations by Ball(7) were for the most part corroborated (Table 2). The only aspect of the historic work that was not confirmed was the decrease in product density. In our work it was found that bitumen was readily converted at temperatures in the range 340-400 °C. The viscosity of oilsands derived bitumen could be decreased from 92 to 3 Pa·s by just heating to either 360, or 380 °C (Figure 4). At longer conversion times the viscosity could be reduced by two orders of magnitude while maintaining a liquid yield of 96-97 wt%. It was clear that oilsands derived bitumen was considerably more reactive than was predicted from the visbreaking of conventional heavy oil fractions.

A more detailed review of the older literature revealed various investigations remarking on the reactivity of bitumen from the Canadian oilsands.

Speight(9) summarized the literature on the thermal conversion of oilsands derived bitumen that was published before 1973, which included some studies on the thermal conversion of bitumen at lower than conventional visbreaking temperatures. The consensus was that bitumen was readily converted at lower temperatures. Furthermore, the oilsands asphaltenes fraction, which is usually erroneously considered the most difficult to upgrade, was reported to be heat-sensitive, with thermal decomposition taking place at >150 °C.(10) Thermal conversion of Athabasca asphaltenes at 200 °C and 1.5 h in an open system produced a gas yield of 1.7 wt% and the remaining product had a 4.5 % selectivity to pentane soluble oil with higher H:C ratio than the remaining asphaltenes.(11) Hydrogen disproportionation increased with increasing temperature and at 400 °C the gas yield was 18.5 wt% and none of the remaining product was pentane soluble.(11)

Lee, et al.(12) found a decrease in asphaltenes content from 12 to 9 %, a corresponding increase in maltenes and no coke formation after low temperature thermal cracking. Although information about the experimental conditions was incomplete, it formed part of a larger project on low temperature oxidation and the likely conditions were 200 °C for 24 h as described in a related paper.(13) These results supported the asphaltenes conversion data of Moschopedis, et al.(11)

Egloff and Morrell(14) investigated the thermal conversion of Athabasca bitumen at 400 °C and 0.6 MPa. It was observed that: “The Alberta tar lends itself particularly to cracking at low temperature and pressure ...". However, in this study the bitumen was allowed to react over an extended period of time to induce coking.

Henderson and Weber(15) evaluated the low temperature upgrading of Athabasca bitumen in relation to six conventional crude oils. The results are of particular interest and are repeated for ease of reference (Table 10). Although long conversion times were employed, meaningful upgrading was achieved. Viscosity was decreased by two orders of magnitude at ~370 °C, the density was decreased and amount of material in the residue boiling fraction was decreased without significant gas yield. These results provided direct support of the earlier observations by Ball.(7)

Erdman and Dickie(16) compared the thermal conversion of Athabasca bitumen with that of other heavy oils with densities in the range 940 to 1030 kg·m^{-3}. Thermal conversion was conducted at 350 °C for 24 hours in a batch reactor. It was found that the "... Athabasca tar oil is quite heat-sensitive ...", with the viscosity at 38 °C (100 °F) being decreased from 34 to 0.2 Pa·s. The only heavy oil that was more heat-sensitive was the oil from Rozel Point, which was classified as being "recent" in terms of geological age, i.e. a young crude oil.

It was pointed out that the bitumen should not be considered a residuum, but a "young or virgin oil that nature has not subjected to the pressure and heat that ordinary oil-field oils have suffered."(7) A similar observation was made a decade later, when it was reported that oilsands derived bitumen exhibited thermal conversion behavior that was typical of a young crude oil.(17) These conclusions were prompted by the reactivity of the oilsands derived bitumen and does not reflect on the geological age of the Canadian oilsands deposits, which are estimated to date from the lower Cretaceous period.(18) The oilsands bitumen is also considered a severely biodegraded oil.(1)

Our work supports the contention that for conversion purposes Canadian oilsands derived bitumen should be viewed as a young oil and not as a residuum.

4.2 Coke formation

Thermal conversion leads to hydrogen disproportionation that over time leads to the formation of a solid carbonaceous phase that is commonly referred to as coke. Based on the experimental evidence provided in literature, hydrogen disproportionation starts below 200 °C.(11)(12) This implies that temperature alone cannot be used during the thermal conversion of oilsands derived bitumen to avoid hydrogen disproportionation and that coke formation cannot be prevented even at low temperatures. However, this is only the chemical description of the coke formation and in bitumen the process also depends on the physical changes taking place.

There is an induction period during thermal conversion during which no coke is formed. The onset of coke formation is associated with the partitioning of the liquid phase into two, with the new phase (mesophase) consisting of molecules lean in transferable hydrogen, which can readily form coke as hydrogen disproportionation proceeds.(19)(20)

When solid materials are present in the bitumen, as was the case in the present study, the solids are associated with organics that are not easily removed.(21) The mineral matter content of 0.9 wt% determined by ashing (Table 1) is consequently lower than the solids content of 1.1 to 1.4 wt% determined by filtration (Tables 3 to 6). The methylene chloride insoluble organic material associated with the mineral matter was by calculation between 0.2 and 0.5 wt% of the bitumen. The amount varied with the extent and temperature of thermal conversion, which affected the solubility of this material in methylene chloride. The solids can also act as nucleation sites for mesophase formation and by doing so the presence of solids affects the apparent length of the induction period before the onset of coking, as well as the size of the coke, which depends on the ability of the mesophase to coalesce.(22)(23) The coke formed during continued thermal conversion changes in nature and size. These changes are reflected in the general rheological behavior,(19) as well as the ease of filtration.(24) Both impacts were observed in the present study.

Although thermodynamics describes the driving force for the development of a mesophase, it does not describe the kinetics or local mass transport phenomena that may affect the formation and size of a mesophase.(23) Hence, the temperature history, viscosity and agitation may all affect the induction time before the onset of observable coking. Coke formation, beyond the possible association of coke with mineral matter, was not observed at 340 and 360 °C (Tables 5 and 6). There was a possible onset of coke formation between 120 and 232 min at 380 °C (Table 4) and at around 30 min at 400 °C (Table 3).

4.3 Viscosity change during low temperature visbreaking

The viscosity versus conversion time and temperature behavior was complex (Table 7). The magnitude of the viscosity change in relation to the visbreaking severity made it unlikely that the observed decrease in viscosity was due to a decrease in average molecular mass caused by thermal cracking. Only a minor change in distillation profile was observed after low temperature visbreaking (Table 2), while the viscosity decreased by two orders of magnitude.

In addition to the viscosity changes due to visbreaking it was also important to account for the changes that could have been caused by the experimental protocol (Table 8). An overview of the viscosity behavior of oilsands bitumen pointed to two factors that could explain these observations. A decrease in viscosity could result from the addition of a small amount of dissolved gas or light materials, or the converse if such material is removed.(25) The 15 % increase in viscosity that was observed after adding and removing methylene chloride as solvent (Table 8), could therefore have been caused by the associated removal of a small amount of lighter material. An increase in viscosity could result from the presence of some emulsified water droplets or particulate matter.(25) The higher viscosity observed before filtration (Table 8), was therefore consistent with the literature.

The same procedure was applied for all samples and the consistent bias introduced by the use of methylene chloride as solvent did not invalidate the results. Even though the actual viscosity values may have been lower than that reported, it would not have changed the directionality of the increase or decrease in viscosity. Similarly, all products were filtered to determine the solids yields (Tables 3 to 6) and even if some solids passed through the filter, only a higher viscosity would result. The experimental protocol could therefore not explain the orders of magnitude decrease in viscosity that was found after low temperature visbreaking.

A comprehensive review of the various physical and chemical factors that affect bitumen viscosity was written by Lesueur.(26) Three parameters were identified as governing bitumen viscosity:

(a) Maltenes viscosity. If one considers the bitumen as a colloidal solution, then the maltenes viscosity is the viscosity of the continuous phase in the absence of any colloids or particulates. In the absence of molecular assemblies, colloids or separate liquid and/or solid phases, the viscosity of the bitumen is simply governed by the maltenes viscosity. Only the maltenes viscosity is influenced by molecular mass.

(b) Asphaltenes, or aggregate content. The asphaltenes are present as aggregates rather than being molecularly dissolved. Strictly speaking it is better to refer to the aggregate content, because not all aggregates are asphaltenes and vice versa. In fact, was reported that feed viscosity was poorly correlated with asphaltenes content,(27) which suggests that the aggregate content should not be equated with the asphaltenes content. Also, to avoid confusion about terminology, aggregates in this context refers to associated molecules in any size range from a few nanometers to aggregates that are visible by light microscopy. The aggregates have a maximum packing density in the bitumen and the minimum volume fraction occupied by the aggregates at their maximum packing density is denoted by Φ_m. When the aggregates are solvated, the molecules at the boundary layer are hydrodynamically part of the aggregates and not the continuous phase. Likewise, the aggregates may trap molecules within the aggregate structure, increasing the volume of the aggregates. The effective volume fraction of the aggregates in the bitumen, Φ_{eff}, is therefore larger than the volume of the aggregates at maximum packing density, i.e. $\Phi_{eff} > \Phi_m$. The viscosity of the bitumen (μ) is increased relative to the vanishing-shear viscosity of the maltenes ($\mu_{0,malt}$) following Roscoe's law (Eq.2):(28)

$$\frac{\mu}{\mu_{0,\mathrm{malt}}} = \left(1 - \Phi_{\mathrm{eff}}\right)^{-2.5} \qquad \text{... (2)}$$

Roscoe's law (Eq.2) is not valid for concentrated dispersions and the limiting criterion for its validity is $\Phi_{eff} < 0.6$.(28) Beyond this value, aggregate packing becomes structured. For a specific mass fraction of aggregates in the bitumen, x_a, the relationship between the effective volume fraction of the aggregates in the bitumen (Φ_{eff}) is related to its solvation parameter, κ, and it is given by Eq. 3:(26)(28)

$$\Phi_{eff} = \kappa \cdot x_a \qquad \text{... (3)}$$

(c) Solvation parameter. The ratio between the solvation parameter (κ) and minimum volume fraction of the aggregates (Φ_m) is called the solvation constant (κ/Φ_m). According to Lesueur(26) the solvation constant at 60 °C of bitumens with 7 to 25 wt% asphaltenes, as determined by *n*-heptane precipitation, is usually in the range 3 to 8, with a typical value of 5.5. It is speculated that a narrower range of values for the solvation parameter may be obtained if the aggregate content, rather than the asphaltenes content were employed, while at the same time acknowledging that it is experimentally easier to determine a value for the asphaltenes content.

It is unlikely that a decrease in the maltenes viscosity was the major contributing factor to the decrease in bitumen viscosity after low temperature visbreaking. As mentioned before, the boiling point distribution did not change much and the extent of thermal cracking was minor. The density also remained constant (Table 9). There was some conversion of the bitumen that caused changes in the nature of the thermally treated bitumen, but it would not explain the orders of magnitude change in the viscosity of the maltenes ($\mu_{0,malt}$), which would require significant thermal cracking.

The implication is that the decrease in viscosity was mainly due to a decrease in the hydrodynamic bulk of the aggregates, or differently put, there was a decrease in the effective volume fraction that was occupied by the colloidal aggregate fraction. No direct experimental proof of the existence of aggregates or colloids was sought or provided in this work. Nevertheless, a disaggregation of clustered asphaltenes and other aggregating species, the release of trapped material and/or a potential decrease in the boundary layer volume around the aggregates could all potentially explain the marked decrease in viscosity. These are physical processes, or processes involving weak chemical interactions. Hence, it is conceivable that low temperature and low contact time conversion could disrupt such physical and weak chemical interactions.

The addition of aromatic solvents improves the solubility of asphaltenes and aggregates in heavy oils at ambient conditions,(29) and also under visbreaking conditions.(6) This does not imply that aggregates are disaggregated, or that aggregated species become a molecular solution on dilution with appropriate solvents. The aggregates are not precipitates either. The onset of precipitation is determined by the solubility parameter of the mixture.(29) Adding and removing a solvent had little impact on the bitumen viscosity (Table 8). Hence, it is unlikely that the decrease in bitumen viscosity on dilution affects the microstructure of the bitumen, because removal of the solvent causes the bitumen to revert to its original viscosity. However, after low temperature visbreaking the viscosity decreased by two orders of magnitude and the viscosity change was permanent. These dramatic changes were possible even though the extent of conversion was limited (e.g. Table 2). These observation support the postulate that the decrease in viscosity during low temperature visbreaking is caused by a decrease in the effective volume fraction (Φ_{eff}) of the aggregating species.

If this interpretation is correct, the high viscosity of bitumen is not due to asphaltenes per se, as can also be noted from the results of Brauch et al.(27) The high viscosity is predominantly due to the solvation of aggregating species, only some of which can be precipitated as asphaltenes. Low temperature thermal conversion reduces the value of the solvation parameter (κ), which is a measure of the hydrodynamic bulk of the strongly solvated species, and/or the fraction of the bitumen that is aggregated (x_{a}). The relative contribution of each was not resolved by this study.

The interpretation of viscosity reduction in terms of a decrease in the effective volume fraction of strongly solvated species would also help to explain the failure of the conventional crude oil visbreaking time-temperature relationship (Eq.1) to predict the low temperature visbreaking performance of oilsands bitumen. The viscosity decrease was not due to a decrease in bulk oil viscosity and therefore the decrease in viscosity was not governed by the cracking of vacuum residue material to lighter products. This can also be illustrated by comparison with results from conventional crude oil residue visbreaking. In a study that evaluated the visbreaking performance of 47 different residues in a commercial visbreaker-soaker operated at 450 °C (residence time not reported) found that the average ratio of product viscosity to feed viscosity was 0.131.(27) In comparison, with oil sands bitumen a ratio of product viscosity to feed viscosity of 0.013 could be obtained after only 10 min at 360 °C (Table 7).

Kinetic descriptions that relate viscosity changes during low temperature oilsands visbreaking to thermal cracking, such as the work by Shu and Venkatesan,(30) predictably obtained low rate constants, slow conversion rates and long residence time requirements for viscosity reduction. The orders of magnitude decrease in oilsands bitumen viscosity was observed at short contact time and low temperature in this work (Tables 2 and 7) and in work by others,(7)(9)(10)(11)(12)(14)(15)(16)(17) is therefore not related to cracking conversion.

Based on the aforementioned observations it is concluded that low temperature thermal conversion resulted mainly in the conversion of weakly bonded and/or associated material so that the effective volume fraction of such material in the bitumen was reduced. The nature of these chemical changes was not elucidated and it provides scope for further study.

5. CONCLUSIONS

The experimental investigation of the thermal conversion of Canadian oilsands derived bitumen and subsequent interpretation of the results revealed the following:

(a) It was possible to limit gas and coke formation and obtain a 96-97 wt% liquid yield at a product viscosity of ~1 Pa·s at 40 °C.
(b) Coke formation was not observed during thermal conversion at 400 °C up to 30 min, 380 °C up to 120 min and over the complete time-range studied at 360 and 340 °C, which was 577 and 1440 min respectively.

(c) In conventional crude oil visbreaking, a fixed temperature versus inverse time relationship describes the extent of conversion. This relationship failed to predict low temperature visbreaking performance with oilsands bitumen as feed, which required less conversion time for a given operating temperature to achieve the same level of viscosity decrease.

(d) It is possible to obtain a two orders of magnitude viscosity decrease from ~100 to ~1 Pa·s at 40 °C by visbreaking at 340 to 400 °C. More remarkable is that viscosities of 3.0 ± 0.08 and 3.5 ± 0.04 Pa·s at 40 °C could be obtained by just heating the bitumen to 380 and 360 °C and then cooling down the bitumen immediately.

(e) The viscosity behavior was interpreted based on literature. The most plausible explanation for the rapid decrease in viscosity during low temperature visbreaking, was a decrease in the effective volume fraction (Φ_{eff}) that was occupied by the colloidal fraction. A decrease in Φ_{eff} could result from disaggregation, the release of colloidally trapped material and a decrease in colloidal boundary, which are all due to physical processes, or weak chemical interactions.

(f) In addition to the marked decrease in viscosity, the change in bitumen viscosity over time for any given conversion temperature was found to be complex. At least one local viscosity minimum and maximum was observed at intermediate conversion time. This behavior could not yet be fully explained and remains a topic for future investigation.

(g) The reactivity of the oilsands bitumen to thermal conversion is comparable to that of a young crude oil, which has not been subjected to high temperature and pressure over geological time. This is not a new observation, but our experimental observations are supported by literature over a long period going back to 1926.(7)(9)(10)(11)(12)(14)(15)(16)(17) The implication is that the oilsands bitumen should not be treated like a residuum, despite its distillation profile suggesting so.

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References

(1) Strausz, O. P.; Lown, E. M. *The chemistry of Alberta oil sands, bitumens and heavy oils*; Alberta Energy Research Institute: Calgary, AB, 2003.

(2) De Klerk, A.; Gray, M. R.; Zerpa, N. Unconventional oil and gas: Oilsands. In *Future energy. Improved, sustainable and clean options for our planet*, 2ed; Letcher, T. M. Ed.; Elsevier: Amsterdam, 2014, p. 95-116.

(3) Leprince, P. Visbreaking of residues. In *Petroleum Refining Vol.3 Conversion Processes*; Leprince, P. Ed.; Editions Technip: Paris, 2001, p.365-379.

(4) Gary, J. H.; Handwerk, G. E.; Kaiser, M. J. *Petroleum refining. Technology and economics*, 5ed; CRC Press: Boca Raton, FL, 2007, p. 97-120.

(5) Joshi, J. B.; Pandit, A. B.; Kataria, K. L.; Kulkarni, R. P.; Sawarkar, A. N.; Tandon, D.; Ram, Y.; Kumar, M. M. Petroleum residue upgrading via visbreaking: A review. *Ind. Eng. Chem. Res.* **2008**, *47*, 8960-8988.

(6) Stratiev, D.; Kirilov, K.; Belchev, Z.; Petkov, P. How do feedstocks affect visbreaker operations? *Hydrocarb. Process.* **2008**, *87* (6), 105-112.

(7) Ball, M. W. Development of the Athabaska oil sands. *Can. Inst. Min. Metall.* **1941**, *44*, 58-91.

(8) Wang, L.; Yang, S.; Prasad, V.; De Klerk, A. Visbreaking oil sands bitumen at 400 °C. *Prepr. Pap.-Am. Chem. Soc., Div. Energy Fuels* **2013**, *58* (2), 635-637.

(9) Speight, J. G. Thermal cracking of Athabasca bitumen. In *Bitumens, asphalts and tar sands*; Chilingarian, G. V., Yen, T. F. Eds.; Elsevier: Amsterdam, 1978, p. 123-154.

(10) Speight, J. G.; Moschopedis, S. E. The influence of crude oil composition on the nature of the upgrading process: Athabasca bitumen. In *The future of heavy crude and tar sands*; Meyer, R. F., Steele, C. T., Olson, J. C. Eds.; McGraw-Hill: New York, 1981, p. 603-611.

(11) Moschopedis, S. E.; Parkash, S.; Speight, J. G. Thermal decomposition of asphaltenes. *Fuel* **1978**, *57*, 431-434.

(12) Lee, D. G.; Noureldin, N. A.; Mourits, F. M. The effect of low temperature oxidation on the chemical and physical properties of maltenes and asphaltenes derived from heavy oil. *Prepr. Pap.-Am. Chem. Soc., Div. Petrol. Chem.* **1987**, *32* (4), 853-856.

(13) Lee, D. G.; Noureldin, N. A. Effect of water on the low-temperature oxidation of heavy oil. *Energy Fuels* **1989**, *3*, 713-715.

(14) Egloff, G.; Morrell, J. C. The cracking of bitumen from Canadian Alberta tar sands. *Trans. Am. Inst. Chem. Eng.* **1926**, *18*, 347-363.

(15) Henderson, J. H.; Weber, L. Physical upgrading of heavy crude oils by the application of heat. *J. Can. Petrol. Technol.* **1965**, *4* (4), 206-212.

(16) Erdman, J. G.; Dickie, J. P. Mild thermal alteration of asphaltic crude oils. *Prepr. Pap.-Am. Chem. Soc., Div. Petrol. Chem.* **1964**, *9*, B69-B79.

(17) McNab, J. G.; Smith, P. V. Jr; Betts, R. L. The evolution of petroleum. *Ind. Eng. Chem.* **1952**, *44*, 2556-2563.

(18) Masliyah, J. H.; Czarnecki, J.; Xu, Z. *Handbook on theory and practice of bitumen recovery from Athabasca oil sands. Volume I: Theoretical basis*; Kingsley Knowledge Publishing: Canada, 2011.

(19) Rand, B. The pitch-mesophase-coke transformation as studied by thermal analytical and rheological techniques. *ACS Symp. Ser.* **1986**, *303*, 45-61.

(20) Wiehe, I. A. A phase-separation kinetic model for coke formation. *Ind. Eng. Chem. Res.* **1993**, *32*, 2447-2454.

(21) Kotlyar L. S.; Sparks, B. D.; Woods, J. R.; Raymond, S.; Le Page, Y.; Shelfantook, W. Distribution and types of solids associated with bitumen. *Pet. Sci. Technol.* **1998**, *16*, 1-19.

(22) Sanaie, N.; Watkinson, A. P.; Bowen, B. D.; Smith, K. J. Effect of minerals on coke precursor formation. *Fuel* **2001**, *80*, 1111-1119.

(23) Rahmani, S.; McCaffrey, W. C.; Elliott, J. A. W.; Gray, M. R. Liquid-phase behavior during the cracking of asphaltenes. *Ind. Eng. Chem. Res.* **2003**, *42*, 4101-4108.

(24) Pasternack, D. S. Low-ash asphalt and coke from Athabasca oil-sands oil. *Athabasca Oil Sands, Research Council of Alberta Information Series* **1963**, *45*, 207-229.

(25) Seyer, F. A.; Gyte, C. W. Viscosity. In *AOSTRA technical handbook on oil sands, bitumens and heavy oils*; Hepler, L. G., Hsi, C. Eds.; Alberta Oil Sands Technical and Research Authority: Edmonton, AB, 1989, p. 153-201.

(26) Lesueur, D. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Adv. Colloid Interface Sci.* **2009**, *145*, 42-82.

(27) Brauch, R.; Fainberg, V.; Kalchouck, H.; Hetsroni, G. Correlations between properties of various feedstocks and products of visbreaking. *Fuel Sci. Technol. Int.* **1996**, *14* (6), 753-765.

(28) Storm, D. A.; Barresi,R. J.; Sheu, E. Y. Rheological study of Ratawi vacuum residue in the 298-673 K temperature range. *Energy Fuels* **1995**, *9*, 168-176.

(29) Wang, J. X.; Buckley, J. S. Asphaltene stability in crude oil and aromatic solvents - the influence of oil composition. *Energy Fuels* **2003**, *17*, 1445-1451.

(30) Shu, W. R.; Venkatesan, V. N. Kinetics of thermal visbreaking of a Cold Lake bitumen. *J. Can. Petrol. Technol.* **1984**, *23* (2), 60-64.

Table 1. Characterization of Cold Lake bitumen.

Property	Cold Lake bitumen
Density at 30 °C (kg·m^{-3})	1013.2 ± 1.0
Viscosity at 40 °C (Pa·s)	92 ± 3.6
Viscosity at 60 °C (Pa·s)	9.2 ± 3.6 to 9.7 ± 0.3
Asphaltene content (wt %) [a]	13.4 ± 1.0 to 18.6 ± 1.2
Microcarbon residue (wt %)	15.0 ± 0.7 to 17.8 ± 0.5
Mineral matter (wt %)	0.9 ± 0.1
Elemental analysis (wt %)	
C	82.6 ± 0.1 to 82.9 ± 0.1
H	10.1 ± 0.01 to 10.3 ± 0.1
N	0.6 ± 0.002 to 0.6 ± 0.1
S	4.7 ± 0.1 to 4.9 ± 0.03

[a] Asphaltene content determined by precipitation with *n*-pentane.

Table 2. Thermal conversion of Cold Lake bitumen at 360 °C for 30 min in a closed batch reactor and comparison with literature data.

Property	Literature values(7) [a]		Experimental data	
	Feed	Product	Feed	Product
Density at 16 °C (kg/m^3)	1000 [b]	928 [b]	1022 ± 1.0	1023 ± 1.5
Kinematic viscosity at 65 °C (cSt)	6045	225	6150 ± 200	96 ± 12
Refractive index at 25 °C	-	-	1.5814 ± 0.0018	1.5868 ± 0.0003
Softening point (°C)	28	-15	-	-
Penetration, 0.01 s with 100 g (mm)	-	-	2.0 ± 0.46	3.4 ± 0.23
Distillation profile (°C)				
IBP	260	71	243 [c]	268 [c]
T10	379	254	365	358
T20	446	332	417	406
T30	-	-	465	449
T40	-	-	516	498
T50	-	-	576	555
T60			642	628
Yield of products (wt %)				
gas	0	~0 [d]	0	0.7 ± 0.6
liquids	100	~100 [d]	99.1	97.5 ± 0.4
solids	0	~0 [d]	0.9	1.8 ± 0.3

[a] Units converted from original data reported in °F, °API and Saybolt Furfurol units.

[b] Typical density decrease observed, but it was determined on an 8-10 °API bitumen.

[c] T0.5 value from simulated distillation by the ASTM D7169 standard test method.

[d] Only a qualitative description was provided.

Table 3. Yields during visbreaking of bitumen in a semi-batch reactor at 400 °C, 4 MPa and different conversion times.

Conversion time (min)	Liquid (wt %) [a]		Gas (wt %) [a]		Solids (wt %) [a]	
	x	s	x	s	x	s
0	98	0.18	0.91	0.19	1.2	0.004
10	97	0.38	2.1	0.38	1.2	0.003
20	96	0.35	2.9	0.35	1.2	0.004
30	96	0.51	2.5	0.50	1.4	0.004
60	95	0.79	3.0	0.38	1.7	0.44
90	88	3.3	9.3	3.1	2.6	0.32
120	90	0.94	4.9	0.20	5.6	1.1

[a] Average (x) and sample standard deviation (s) of experiments in triplicate.

Table 4. Yields during visbreaking of bitumen in a semi-batch reactor at 380 °C, 4 MPa and different conversion times.

Conversion time (min)	Liquid (wt %) [a]		Gas (wt %) [a]		Solids (wt %) [a]	
	x	s	x	s	x	s
0	97	0.50	1.5	0.57	1.4	0.08
10	98	0.14	1.0	0.14	1.3	0.003
20	97	0.006	1.7	0.003	1.2	0.002
30	97	0.29	1.8	0.29	1.1	0.002
60	97	0.07	1.7	0.07	1.3	0.07
120	96	0.20	2.4	0.25	1.3	0.07
232	96	0.32	2.5	0.14	1.5	0.19

[a] Average (x) and sample standard deviation (s) of experiments in triplicate.

Table 5. Yields during visbreaking of bitumen in a semi-batch reactor at 360 °C, 4 MPa and different conversion times.

Conversion time (min)	Liquid (wt %) [a]		Gas (wt %) [a]		Solids (wt %) [a]	
	x	s	x	s	x	s
0	98	0.50	0.8	0.26	1.4	0.29
10	98	0.55	1.0	0.49	1.2	0.07
20	98	0.33	0.9	0.4	1.2	0.07
30	97	0.33	1.5	0.32	1.2	0.07
60	97	0.54	1.5	0.47	1.2	0.07
240	97	0.07	1.5	0.07	1.3	0.0009
577	96	0.43	2.7	0.36	1.3	0.07

[a] Average (x) and sample standard deviation (s) of experiments in triplicate.

Table 6. Yields during visbreaking of bitumen in a semi-batch reactor at 340 °C, 4 MPa and different conversion times.

Conversion time (min)	Liquid (wt %) [a]		Gas (wt %) [a]		Solids (wt %) [a]	
	x	s	x	s	x	s
0	99	0.006	0.3	0.001	1.2	0.005
60	98	0.002	0.6	0.0008	1.2	0.002
120	98	0.19	0.8	0.19	1.2	0.002
240	98	0.45	0.9	0.50	1.2	0.003
480	98	0.13	0.3	0.07	1.3	0.08
1440	97	0.33	1.2	0.40	1.4	0.06

[a] Average (x) and sample standard deviation (s) of experiments in triplicate.

Table 7. Viscosity of products from bitumen visbreaking in a semi-batch reactor at the conversion times and temperatures indicated.

Conversion time (min)	Viscosity at 40 °C (Pa·s) [a]							
	400 °C		380 °C		360 °C		340 °C	
	x	s	x	s	x	s	x	s
0	36	0.32	3.0	0.076	3.5	0.039	39	1.4
10	14	0.20	2.8	0.035	1.2	0.080	- [b]	- [b]
20	7.5	0.11	1.5	0.046	0.89	0.037	- [b]	- [b]
30	0.71	0.046	1.3	0.034	0.60	0.036	- [b]	- [b]
60	0.76	0.064	1.5	0.008	0.31	0.007	35	0.31
90	5.6	0.22	- [b]	- [b]	- [b]	- [b]	- [b]	- [b]
120	0.68	0.074	2.6	0.072	- [b]	- [b]	19	0.042
240	- [b]	- [b]	0.20 [c]	0.004	1.0	0.034	2.3	0.023
480	- [b]	- [b]	- [b]	- [b]	- [b]	- [b]	5.1	0.20
577	- [b]	- [b]	- [b]	- [b]	0.68	0.031	- [b]	- [b]
1440	- [b]	- [b]	- [b]	- [b]	- [b]	- [b]	3.1	0.19

[a] Average (x) and sample standard deviation (s) of experiments in triplicate.

[b] No visbreaking experiments were performed at these conditions.

[c] Conversion time 232 min.

Table 8. Evaluation of the impact of experimental procedure on absolute viscosity values.

Description	Viscosity at 40 °C (Pa.s) [a]	
	x	s
Impact of methylene chloride washing		
bitumen feed	92	3.6
bitumen after washing and drying	106	3.2
change in viscosity	15%	
Impact of solids removal by filtration		
340 °C, 1 h visbroken filtered bitumen	35	0.31
340 °C, 1 h visbroken unfiltered bitumen	54	0.21
change in viscosity	55%	

[a] Average (x) and sample standard deviation (s) of experiments in triplicate.

Table 9. Density of products from bitumen visbreaking in a semi-batch reactor at the conversion times and temperatures indicated.

Description	Density at 40 °C (kg·m^{-3}) [a]	
	x	s
Bitumen feed	1007	1.0
Visbreaking at 400 °C for 120 min	1012	1.8
Visbreaking at 380 °C for 232 min	1007	4.5
Visbreaking at 360 °C for 577 min	1008	0.4
Visbreaking at 340 °C for 1440 min	1008	0.9

[a] Average (x) and sample standard deviation (s).

Table 10. Low temperature thermal conversion of Athabasca bitumen and oilsands reported by Henderson and Weber.(15)

Temperature (°C)	Conversion time (min)	Yield (wt %)			Viscosity at 66 °C (Pa·s)	Density at 16 °C (kg·m^{-3})
		gas	gas oil	residue [a]		
			Athabasca bitumen			
Feed	-		19.1	80.9	5.2	1022
371	171	1.7	24.0	74.3	0.33	1009
371	585	3.1	31.8	65.1	0.09	1002
366	1178	3.7	34.8	61.5	0.08	981
310	11625	2.3	28.0	69.7	0.24	1004
263	66505	0.8	20.9	78.3	1.3	1014
			Athabasca oilsands			
371	240		29.1	70.9	0.54	1015
371	600		39.3	60.7	0.07	996
371	1440		44.6	55.4	0.04	994
319	6025		27.8	72.2	0.34	1003
277	30592		19.7	80.3	1.5	1013

[a] Material with true boiling point >400 °C (>427 °F at 5 mm Hg).

Figure 1. Semi-batch reactor used for visbreaking studies.

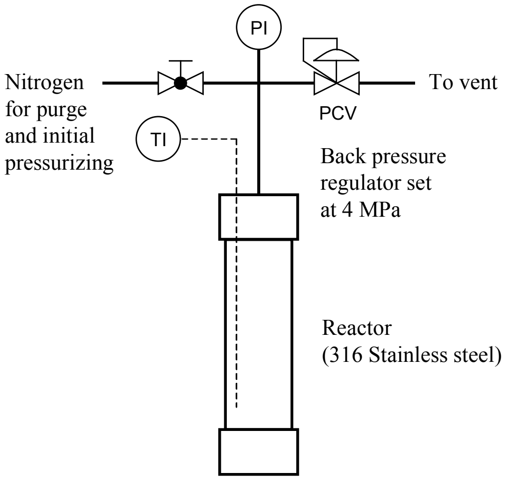

Figure 2. Internal temperature versus time profile of the semi-batch reactor filled with bitumen.

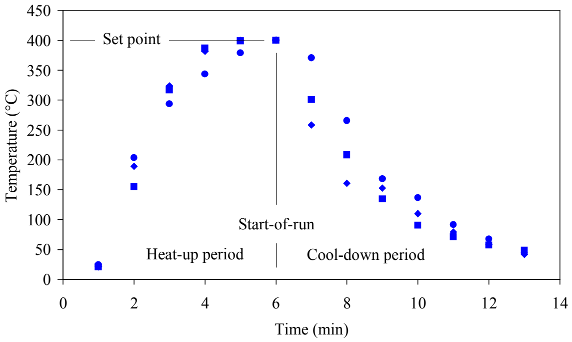

Figure 3. Viscosity versus time profile for visbreaking bitumen at 400 °C (■), 380 °C (♦), 360 °C (●) and 340 °C (▲).

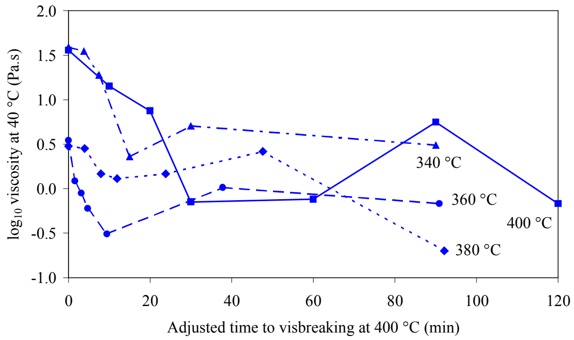

Figure 4. Viscosity from bitumen visbreaking in a semi-batch reactor at 0 min conversion time.