Investigation of the fluid behavior of asphaltenes and toluene-insolubles by high temperature ^{1}H NMR and rheometry and their application to visbreaking

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ABSTRACT

The fluid behavior of asphaltenes at elevated temperatures impacts on coke formation in a number of hydrocarbon conversion processes, including visbreaking and delayed coking. In this study, the asphaltenes from a number of sources, namely a vacuum residue, a petroleum source rock (Kimmeridge Clay) bitumen obtained by hydrous pyrolysis, and bitumen products from a sub-bituminous coal and pine wood obtained by thermolytic solvent extraction using tetralin, have been characterized using high temperature ^{1}H NMR and the results correlated with those from small-amplitude oscillatory shear rheometry. Further for comparison, the coke (toluene-insolubles) obtained from visbreaking the vacuum residue was also characterized. All the asphaltenes became completely fluid by 300 °C with the hydrogen being completely mobile with coke formation, identified as a solid phase, not occurring to a significant extent until 450 °C. Extremely good agreement was obtained between high temperature ^{1}H NMR and rheometry results, which confirmed that the asphaltenes were highly fluid from 300 °C and initial signs of resolidification being observed at temperatures of around 450 °C. During softening, extremely good correlations between fluid hydrogen and phase angle were obtained as the asphaltenes softened. The toluene-insolubles however did contain some fluid material and, thus, it cannot be regarded as strictly solid coke but, clearly, with increasing temperature, the fluid material did convert to coke. Under actual process conditions, this fluid material could be responsible for coke adhering to reactor surfaces.

1. INTRODUCTION

Asphaltenes are operationally defined as toluene-soluble, n-heptane insoluble material and are extremely heterogeneous and complex mixtures of species comprising heteroatoms (N, O, S), relatively small condensed aromatic nuclei, aliphatic chains and naphthenic rings, as well as metals such as V, Ni and Fe.[1] They have been the topic of intense structural investigation and to represent their complex nature, average molecular structures have been proposed, an example for Athabasca vacuum residue by Sheremata et al.[2] using a Monte Carlo construction method is shown in Figure 1. A wide range of techniques have been used to characterize the chemical composition of asphaltenes,[3,4] including ^{1}H and ^{13}C nuclear magnetic resonance (NMR), size-exclusion chromatography (SEC), mass spectrometry and Fourier transform infrared spectroscopy (FTIR). Disassociated petroleum asphaltenes are characterized by number average molecular masses of *ca*. 1500−2500[5] but contain fewer heteroatoms than asphaltenes from sources, such as biomass and coal liquefaction products. Solubility is thus covered by a combination of molecular mass, polarity and the degree of condensation of aromatic nuclei, the latter two parameters controlling the extent of inter-molecular association.[6] The more polar asphaltenes obtained from coal and biomass generally have lower molecular mass ranges. The H donor ability, the chemical structure and sulfur content of the asphaltenes have been identified as factors that contribute to the formation of coke. The H donor ability of asphaltenes is lower than their H acceptor ability, which is considered to be responsible for the combination of radical species during thermal conversion that leads to coke formation.[7] Chiaberge et al.[3] found that asphaltenes treated at 400 °C tend to aromatize to form structures that can be considered as coke precursors.

To understand their thermal and softening behavior, studies on asphaltenes have also been carried out using thermal gravimetric analysis (TGA) and rheometry.[8−10] Trejo et al.[8] used TGA to study the weight loss of asphaltenes as a function of temperature, and found that approximately 45 wt % of the asphaltenes mass was lost over the temperature range 300−500 °C. A small weight loss occurred at around 370 °C which was considered to result from the elimination of alkyl groups located in peripheral sites, and the maximum weight loss occurred at 430 °C, with the asphaltenes converting into coke, gases, oils and resins. Above 450 °C, condensation reactions dominated and the asphaltenes converted into coke. They also found that slower heating rates (4 °C/min) produced more coke and less liquids and gases than faster heating rates (16 °C/min). Regarding softening, Asprino et al.[9] studied the fluid properties of asphaltenes at 310−530 °C using an apparatus that allowed the calculation of the surface tension of the melted asphaltenes. The surface tension was then used to calculate the viscosity of the liquid bridge of asphaltenes during elongation. The viscosity of the asphaltenes decreased with temperature and it was found to be in the range of 9−18 Pa.s at 312−358 °C, whereas the viscosity increased above 400 °C due to compositional changes in the asphaltenes induced by thermal reactions. Thermogravimetric analysis also showed that asphaltenes were the main contributor to coke formation during thermal cracking of atmospheric distillation residues.[10]

A powerful technique that can monitor in situ the development of fluidity at temperatures up to around 500 °C is high temperature ^{1}H NMR, also defined as proton magnetic resonance thermal analysis (PMRTA). There is a vast amount of published literature related to the use of this technique combined with small-amplitude oscillatory shear (SAOS) rheometry to study fluidity development in coals during carbonization.[11−16] High temperature ^{1}H NMR monitors the fluid and rigid components in the sample, whereby the spectrum peak at a particular temperature is deconvoluted into a Lorentzian distribution function and a Gaussian distribution function. The area of the Lorentzian peak provides the fraction of fluid phase and its width at half-height is inversely proportional to the spin-spin relaxation time (T_{2L}), which is a measure of the changes in the mobility of the fluid phase. This technique can also be used to monitor the evolution of the solid and liquid phases in the asphaltenes at high temperatures, and hence, elucidate in situ the role of these compounds on coke formation.[17,18] High temperature SAOS rheometry is a technique that measures the linear viscoelastic properties of the sample as a function of temperature and has been used in the past in combination with high temperature ^{1}H NMR to elucidate the effect of carbonaceous additives in coking blends used in the carbonization process.[19,20] In this manner, the aim of this study is to investigate the fluidity development in asphaltenes during pyrolysis through the combined use of high temperature ^{1}H NMR and high temperature SAOS rheometry to provide a more detailed understanding of fluidity development with respect to softening and then conversion to coke at temperatures above 400 °C.

Visbreaking which is an important thermal cracking process used to convert petroleum vacuum residue into lighter distillate fuels[21] is used as a conversion process to demonstrate the applicability of the approach. There is the simultaneous formation of unwanted pyrolytic coke, which is known to comprise condensed large ring polyaromatic hydrocarbons with low hydrogen to carbon ratios. Coke formation results in the fouling of reactor and causes pipeline blockages, which ultimately leads to shut down of the visbreaker unit for maintenance.[22,23] Wiehe[21] postulated the process of coke formation to be a result of polymerization and condensation reactions from light to heavy aromatic fractions in the order: aromatics → resins → asphaltenes

→ coke. Goncalves et al.[10] also found that asphaltenes produce coke when they are thermally stressed at high temperatures, whereas Wiehe[21,24] showed that asphaltenes directly convert to coke without an induction period, although the formation of coke was inhibited by the presence of n-heptane solubles. Indeed, feeds with initial high resins and asphaltenes contents generally had higher tendencies to form coke than paraffinic feeds under same operating conditions.[25,26] Other authors[27–29] believe that when the concentration of asphaltenes exceeds their solubility limit, the asphaltenes create a new phase referred to as 'coke precursor' that separates out from the oil phase. However, Kok and Karacan[30] did not find a good correlation between coke yield and the amount of asphaltenes in the crude oil. Here, ^{1}H NMR and rheometry were used to follow coke formation in-situ from vacuum residue asphaltenes to compare with the results from laboratory visbreaking experiments. Further, the toluene-insolubles obtained from the laboratory experiments have also been characterized by ^{1}H NMR and comparisons drawn with those from the hydrous pyrolysis products.

2. EXPERIMENTAL SECTION

2.1. Vacuum residue and visbreaking

A vacuum residue derived from an Urals crude oil was used in this study. The maltene fraction was separated into aliphatics, aromatics and resins by silica/alumina column chromatography using a 5 mL burette. This involved adsorption of the maltene (30 mg) onto silica gel which was placed above a silica/alumina column, followed by elution with 15 mL of n-hexane for the aliphatics, 15 mL of n-hexane/dichloromethane (60:40 volume/volume) mixture for the aromatics and 15 mL of dichloromethane/methanol (50:50 volume/volume) mixture for the resins. Laboratory-scale visbreaking of the vacuum residue was conducted by heating approximately 2 g of the sample under nitrogen atmosphere at 410 °C for 60 minutes in a stainless steel mini reactor immersed in a temperature controlled fluidized sand bath pre-heated to 410 °C.[31] The amount of distilled water added to the reactor was approximately 1 wt% of the sample mass. After pyrolysis, the reactor was removed from the sand bath and allowed to cool to ambient temperature. Then, the reactor contents were recovered and refluxed overnight in toluene, followed by filtration to separate toluene insoluble (coke) from toluene soluble (oil). The toluene-soluble oil was rotary evaporated so as to contain a minimal amount of toluene. The asphaltenes fraction was separated from the maltene fraction by adding 40-fold excess of n-heptane to the toluene soluble present in minimal amount of toluene, and the mixture was stirred for 30 minutes with a magnetic stirrer. The mixture was then transferred to centrifuge tubes and centrifuged for 5 minutes at 2500 revolutions per minute to remove the n-heptane insoluble asphaltenes from suspension before decanting off the n-heptane solution. The process was repeated 5 times with the asphaltenes re-dissolved in 1.0 mL of dichloromethane each time until a clear n-heptane solution was obtained.

2.2. Other samples

Asphaltenes from Kimmeridge Clay source rock, a sub-bituminous coal (Illinois No 6) and pine wood bitumens were used for comparison purposes. The Kimmeridge Clay source rock bitumen was generated using hydrous pyrolysis at 310 °C for 7 hours as previously described.[32] The bitumens from the sub-bituminous coal and pine wood were obtained using liquefied solvent extraction at 410 °C for 1 hour using tetralin as solvent. The asphaltenes from the Kimmeridge Clay source rock, sub-bituminous coal and pine wood bitumens were isolated by the addition of 700 mL of n-heptane to about 2.5 g of bitumen previously dissolved in 7 mL of dichloromethane.

The mixture was then stirred using a magnetic stirrer for 30 minutes and left overnight in the fume cupboard for the n-heptane insoluble asphaltenes suspension to precipitate out of solution. The n-heptane solution was decanted off and the process was repeated 5 times until a clear n-heptane solution was obtained. The isolation method used for the source rock, coal and pine wood asphaltenes was different to that used for the vacuum residue asphaltenes due to the larger amount of sample used.

2.3. Nuclear magnetic resonance (NMR)

A Doty 200 MHz ^{1}H NMR probe was used in conjunction with a Bruker MSL300 instrument to determine fluidity development in the coke and asphaltenes obtained after visbreaking and the asphaltenes from Kimmeridge Clay source rock bitumen. A flow of 25 L/min of dry nitrogen was used to transfer heat to the sample and to remove the volatiles that escape from the ceramic sample container. Below the sample region, a flow of 60 L/min of dry air prevented the temperature rising above 50 °C to protect the electrical components. In addition, air was blown at 20 L/min into the region between the top bell Dewar enclosing the sample region and the outer side of the probe to prevent the temperature exceeding 110 °C. The sample temperature was monitored using a thermocouple in direct contact with the sample container. The solid echo pulse sequence (90°−τ−90°) was used to acquire the data. A pulse length of 3.50 μs was maintained throughout the test. Approximately 140−150 mg of sample (<53 μm) was packed lightly into a boron nitride container, and 100 scans were accumulated using a recycle delay of 0.3 seconds. The asphaltenes derived from the vacuum residue, Kimmeridge Clay source rock bitumen, sub-bituminous coal and pine wood were analyzed using a slow heating rate (3 °C/min) from 50 °C to 410 °C. The cokes derived from these samples with the exception of the source rock bitumen were also analyzed using the same conditions. The spectra were acquired at increments of 25 °C and were deconvoluted into Gaussian and Lorentzian distribution functions. The area of the Lorentzian peak multiplied by 100 and divided by the total area of the NMR signal represents the concentration of fluid H in the sample and the width of the Lorentzian peak at half-height is inversely proportional to the mobility of the fluid phase (T_{2L}). In addition, the asphaltenes and coke from the vacuum residue were heated from room temperature to 410 °C at approximately 70 °C/min and then held at that temperature for 20 minutes. The spectra were acquired at intervals of 1 minute and were deconvoluted into Gaussian and Lorentzian distribution functions. As an example, Figure 2 shows the deconvoluted ^{1}H NMR spectra of the composite toluene insoluble coke sample from visbreaking acquired at 410 °C after 0, 10 and 20 minutes. These spectra show that the liquid component (Lorentzian peak) reduces with time and the solid component increases (Gaussian peak). This deconvolution procedure has previously been used to monitor the softening, maximum fluidity and resolidification stages of coal during carbonization.[13]

2.4. Small-amplitude oscillatory shear (SAOS) rheometry

Rheological measurements were performed in a Rheometrics RDA-III high-torque controlled-strain rheometer. A TA AR-2000 rheometer with smooth parallel plates was also used to characterize the asphaltenes from coal and wood and to validate the results obtained with the RDA-III rheometer. The TA rheometer is best suited for measuring the viscosity of asphaltenes since it possesses a lower torque measuring range (0.05–200 μN.m) than that for the Rheometrics instrument (100–10^7 μN.m). For this purpose, identical sample preparation and analysis conditions were employed in both instruments. The asphaltenes (1.0 g) from the vacuum residue, source rock bitumen, sub-bituminous coal and pine wood were compacted under 5 tons of pressure in a 25 mm die to form disks with thickness of approximately 2.6 mm. The test involved placing the sample disk between two 25 mm parallel plates which had serrated surfaces to reduce slippage. The sample was heated from room temperature to 500 °C at a rate of 3 °C/min. The furnace surrounding the sample was purged with a constant flow of nitrogen to transfer heat to the sample and remove volatiles. The sample temperature was monitored using a thermocouple inside the furnace. A continuous sinusoidal varying strain with amplitude of 0.1% and frequency of 1 Hz (6.28 rad/s) was applied to the sample from the bottom plate throughout the heating period. The stress response on the top plate was measured to obtain the complex viscosity (η^*) and phase angle (δ) as a function of temperature. The complex viscosity decreases as the material becomes more liquid-like in character whereas the phase angle varies between 0° for an ideal elastic or rigid material and 90° for an ideal viscous or fluid material.[33]

3. RESULTS AND DISCUSSION

3.1. High temperature ^{1}H NMR of asphaltenes

The high temperature ^{1}H NMR results for the asphaltenes when heated from 50 °C to 410 °C at 3 °C/min are presented in Figure 3. All the asphaltenes soften with temperature and become completely fluid by 300 °C, although differences are evident in their softening behavior. Further heating of the asphaltenes to 410 °C failed to produce any measurable quantity of coke, as indicated by the absence of any measurable amount of rigid H. The high fluidity in the asphaltenes (100%) was accompanied by high mobility or relatively low viscosity as indicated by the relatively long T_{2L}values of ~200 μs. Kopsch[34] reported that the glass transition temperatures of asphaltenes derived from vacuum residues were around 294 °C, which matches the temperature for the minimum in mobility within experimental error for the vacuum residue investigated here. However, this may be a coincidence as the glass transition temperature may vary depending on the measuring technique, the heating rate used and the sample pre-treatment.[35]

The differences in the concentration and mobility of the fluid phase for the different asphaltenes are probably related to differences in their chemical/physical characteristics. Regarding the asphaltenes from Kimmeridge Clay source rock bitumen, there is a gradual increase in the amount of fluid material from room temperature up to 250 °C, and the asphaltenes are completely fluid from 250 °C up to the final temperature (410 °C). The mobility of the fluid phase as measured by T_{2L} is fairly constant up to 100 °C, and then starts to increase from 50 μs to approximately 190 μs at 300 °C. Compared to the vacuum residue, the asphaltenes from the source rock bitumen become completely fluid at a lower temperature (250 cf. 275 °C) with the increase in fluidity with temperature being more gradual. Furthermore, the apparent mobility of the fluid phase for the asphaltenes from the source rock bitumen reaches a maximum at higher temperatures (300 °C cf. 225 °C) and it is slightly lower (T_{2L} of 190 μs cf. 210 μs) than in the case for the asphaltenes from the vacuum residue. However, other factors, particularly difference in free radical concentration could account for these relatively small differences in T_{2L}.

The trends for the percentage of fluid H as a function of temperature for the asphaltenes from the sub-bituminous coal and pine wood extracts are fairly similar to those from the asphaltenes derived from the vacuum residue and Kimmeridge Clay source rock bitumen. The mobility of the fluid phase in the asphaltenes derived from pine wood presents a similar trend to those of the asphaltenes from the vacuum residue and Kimmeridge Clay source rock bitumen. However, the fluid component of the asphaltenes obtained from the sub-bituminous coal shows an abnormal decrease in mobility at intermediate temperatures (150−200 °C). These results suggest that the initial material that softens is highly mobile but this is followed by generation of extremely viscous fluid material as the temperature increases. Eventually, the mobility increases with further softening and achieves similar mobility values (T_{2L}~180 μs) to the other samples once complete softening has occurred.

3.2. High temperature rheometry of asphaltenes

The tests were carried out in the Rheometrics RDA-III rheometer using the same heating rate of 3 °C/min as in the ^{1}H NMR tests in order to compare the results from both techniques. It is important to mention that the definition of a fluid from a rheological standpoint differs from the concept of a fluid defined by NMR. A rheological fluid is defined here as a system composed of gas and liquid phases that undergo thermally-induced physical and chemical transformations and affect the viscoelastic properties of the whole sample mas. For instance, an increase in the amount and/or mobility of the rheological fluid material during softening will cause a decrease in complex viscosity or increase in phase angle. On the other hand, the fluid material defined by NMR only considers the hydrogenated mobile entities at the molecular level, i.e. fluid H. Despite these differences, an increase in the percentage of fluid H in coal during carbonization has been found to be associated with a decrease in complex viscosity (or increase in phase angle) and viceversa.[12]

The viscoelastic properties of the asphaltenes obtained from the vacuum residue, Kimmeridge Clay source rock bitumen, the sub-bituminous coal and pine wood are presented in Figure 4. As expected, the results show that the phase angle (δ) increases when the complex viscosity (η^*) decreases. The scattering of the data over the temperature range of 200−450 °C results from the limitations of the rheometer, which cannot analyze materials that develop complex viscosity values below 1000 Pa.s and asphaltenes can reach complex viscosity values of around 10 Pa.s at these temperatures.[9] However, differences are evident in the temperatures at which the various asphaltenes soften and resolidify, which reflect their different chemical compositions. The asphaltenes from the source rock bitumen develop similar viscoelastic behavior to those from the vacuum residue although they soften at lower temperatures (180 °C cf. 230 °C). Qualitatively, the fact that asphaltenes from the source rock bitumen soften at lower temperatures than those from the vacuum residue corroborates the results obtained through high temperature ^{1}H NMR (Figure 3). The resolidification of the asphaltenes due to condensation reactions starts at around 450 °C, which is comparable to the resolidification temperature of the asphaltenes from the vacuum residue. The asphaltenes from the coal and pine wood develop minima in complex viscosity that fall below 1000 Pa.s indicating that the asphaltenes from these carbonaceous materials also develop high fluidity. However, the asphaltenes from coal soften at lower temperatures (170 °C) than the other asphaltenes (~200 °C) whereas the asphaltenes from pine wood seem to be less fluid (i.e. higher viscosity) than the other asphaltenes in the temperature range 250−450 °C.

Figure 5 shows that there is linear relationship between the phase angle and the percentage of fluid H during softening of the asphaltenes derived from the vacuum residue, Kimmeridge Clay source rock bitumen and pine wood. The asphaltenes from the sub-bituminous coal are not included in this plot since the softening process in the rheometer occurs too rapidly to obtain representative data. This correlation indicates that the viscoelastic behavior during softening is controlled by the amount of fluid H in the asphaltenes. The gradient values for the asphaltenes from source rock bitumen and pine wood are fairly similar (1.2−1.5) despite the expected higher content of oxygenated structures in pine wood asphaltenes as a result of the higher oxygen content in the parent material.

The asphaltenes from the sub-bituminous coal and pine wood were also analyzed in a TA AR-2000 rheometer with smooth parallel plates to validate the results obtained in the Rheometrics RDA-III instrument. Figure 6 proves that these asphaltenes are also highly fluid and confirms that the scattered data presented in Figure 4 are due to the limitations of the instrument when analyzing materials that develop complex viscosity values <1000 Pa.s. The viscoelastic behavior of the sub-bituminous coal asphaltenes is fairly similar in both rheometers. However, the different viscoelastic behavior observed with the asphaltenes from pine wood could be due to changes in the chemical structure during storage and/or due to the use of different types of parallel plates (i.e. with smooth and serrated surfaces). The minimum complex viscosity of the asphaltenes from pine wood determined using the TA rheometer is 40 Pa.s, which is comparable to the viscosity values reported by Asprino et al.[9] for Athabasca vacuum residue (10 Pa.s).

3.3. Asphaltenes from vacuum residue visbreaking

The compositions of the vacuum residue before and after visbreaking of the vacuum residue at 410 °C for 60 minutes are listed in Table 1. The asphaltenes content increased considerably

(19%) during visbreaking, largely at the expense of the maltenes and resins. Simultaneously, there was an increase in toluene-insolubles (coke) from 0.1 to 2.4% w/w. The aliphatics content did not change during visbreaking (~21 wt%). The fact that the aromatics and resins fractions are responsible for the increase in toluene-insolubles and asphaltenes is in agreement with the mechanism of coke formation proposed by Wiehe.[21]

Figure 7 shows the changes in percentage of fluid H and mobility of the fluid phase as a function of time at 410 °C for the asphaltenes derived from visbreaking the vacuum residue. The asphaltenes remain completely fluid after 20 minutes, although the mobility decreases with time, which could be related to the formation of higher molecular mass species by condensation reactions, the mobility is still appreciable (T_{2L} of 120 μs). This finding is consistent with induction period of over 30 minutes being required at 410 °C for the onset of coke formation[31] for this particular vacuum residue. Asphaltenes do aromatize when thermally treated at 400 °C for 3 hours,[3] and thus, agree with the results from Schabron et al.[23] who found that coke yield is greatly affected by changes in residence time when treating petroleum residue. For example, in contrast to the results here (Figure 7), asphaltenes from other vacuum residues have previously been found to form coke immediately at a high rate without any induction period.[24]

3.4. Toluene-insolubles from vacuum residue visbreaking

The high temperature ^{1}H NMR results for the toluene insolubles when heated from 50 °C to 410 °C at 3 °C/min are presented in Figure 8. Coke softens between 100 °C and 200 °C, but higher temperatures do not increase significantly the amount of fluid material in the sample (~40%). Furthermore, the mobility of the fluid phase in the cokes obtained from the vacuum residue and pine wood does not change throughout the temperature range studied. However, the mobility of the fluid phase in the toluene-insolubles from the sub-bituminous coal increases sharply from 50 μs to more than 150 μs at 200 °C and remains at those levels up to 300 °C, but the amount of fluid H is negligible (<5%).

Figure 9 shows the changes in percentage of fluid H and mobility of the fluid phase as a function of time at 410 °C for the toluene-insolubles coke from visbreaking the vacuum residue. Initially, the coke generated 44% mobile hydrogen with modest mobility (T_{2L} of 66 μs). Afterwards, there is a gradual reduction of the fluid phase with time and this decrease in fluidity is considered to be a transformation phase from a highly viscous and sticky fluid (corresponding to sponge coke) to a more solid component (shot coke). Therefore, it is likely that the initial coke formed in visbreaking with a high proportion of viscous fluid material could be responsible for its ability to case fouling by adhering to metal surfaces.

4. CONCLUSIONS

Consistent agreement was obtained for the non-isothermal studies on the asphaltenes between high temperature ^{1}H NMR and rheometry, which confirmed that the asphaltenes were highly fluid from 300 °C. This produced extremely good correlations between fluid hydrogen and phase angle as the asphaltenes softened. Signs of resolidification were observed at temperatures of around 450 °C and indicate that the conversion of asphaltenes into toluene-insoluble coke is minimal over a wide temperature range (~150 °C). This behavior has also been observed in asphaltenes from the Kimmeridge Clay source rock bitumen, and the tetralin extracts of the sub-bituminous coal and pine wood, suggesting that these findings will apply to asphaltenes from many other hydrocarbon sources.

High temperature ^{1}H NMR tests on the toluene insolubles coke showed that at 410 °C they contain a significant amount of fluid hydrogen (~43%). This fluid H originates from a highly viscous liquid, and thus, the toluene insoluble material is not a completely solid coke as referred to by many investigators. The subsequent decrease in fluidity with time is considered to be a transformation of a highly viscous and sticky fluid or sponge coke to a more solid component or shot coke in the case of visbreaking.

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Notes

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ABBREVIATIONS

NMR, nuclear magnetic resonance; SEC, size-exclusion chromatography; FTIR, Fourier transform infrared spectroscopy; SAOS, small-amplitude oscillatory shear; TGA, thermal gravimetric analysis.

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Table 1. Composition of the vacuum residue feed before and after visbreaking at 410 °C for 60 minutes.

	Coke (wt %)	Asphaltenes (wt %)	Maltene (wt %)	Aliphatics (wt %)	Aromatics (wt %)	Resins (wt %)
Initial feed	0.1	6.5	93.4	20.0	30.6	36.8
After visbreaking	2.4	25.6	72.0	22.2	15.2	20.0

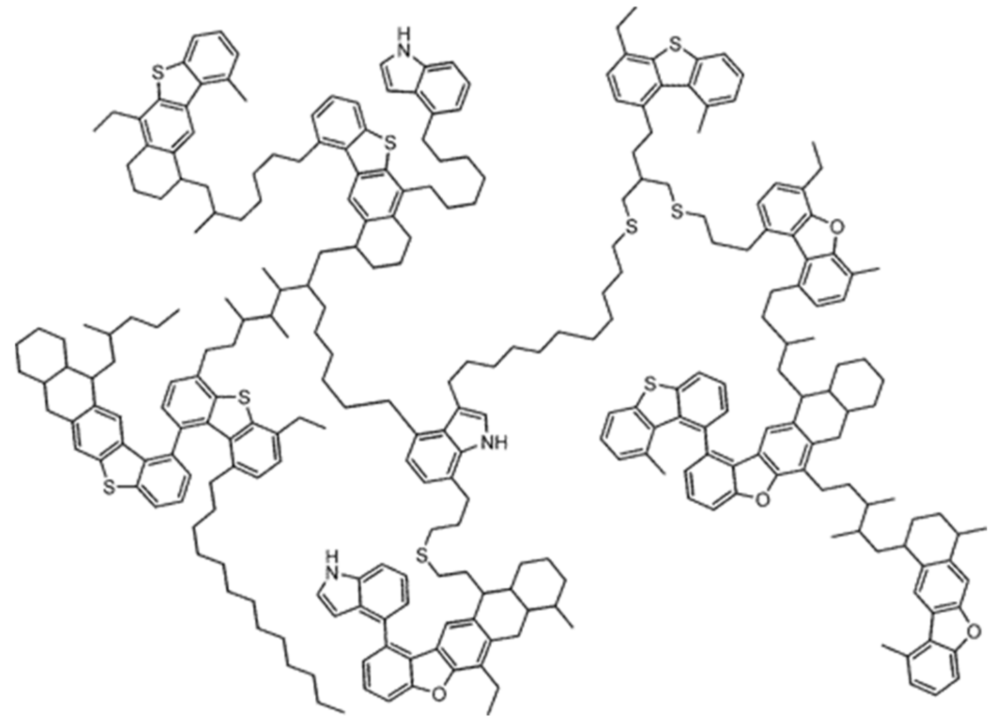

Figure 1. Possible asphaltenes structure for Athabasca vacuum residue proposed by Sheremata et al.[2]

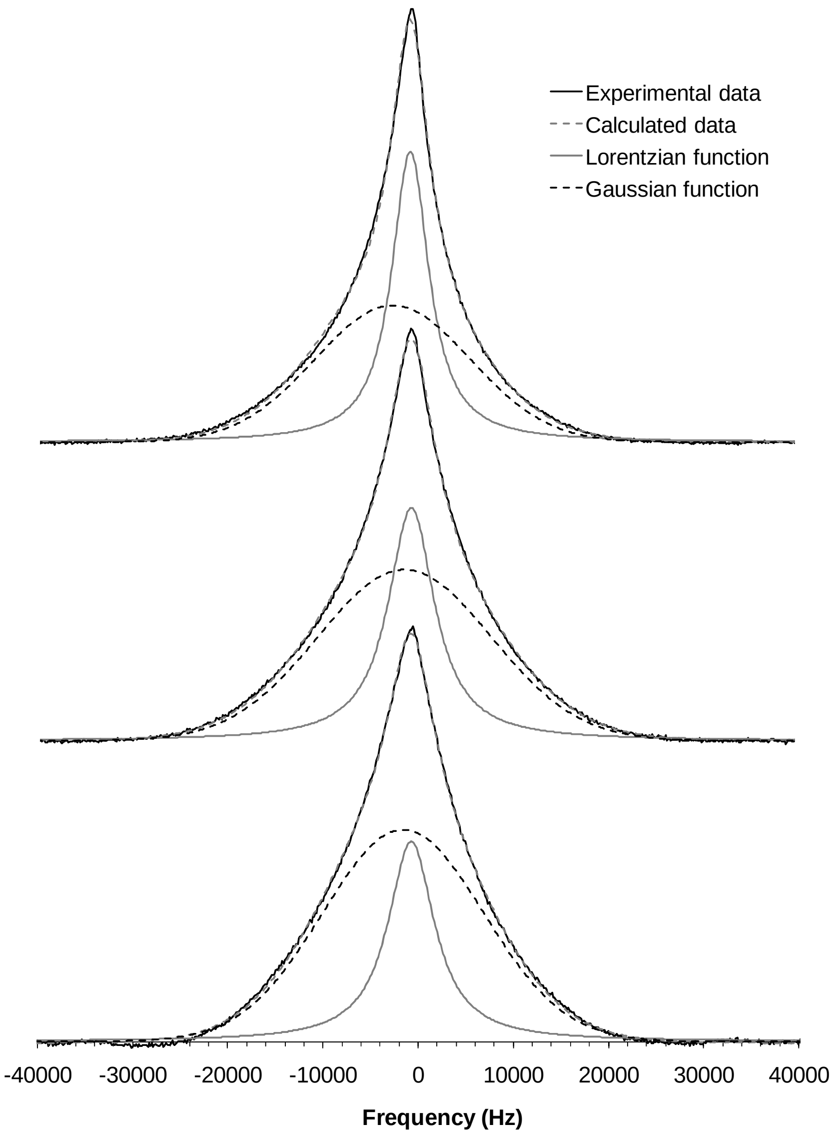

Figure 2. ^{1}H NMR spectra of the toluene-insolubles (coke) obtained from visbreaking the vacuum residue after 0 minutes (top), 10 minutes (middle) and 20 minutes (bottom) at 410 °C.

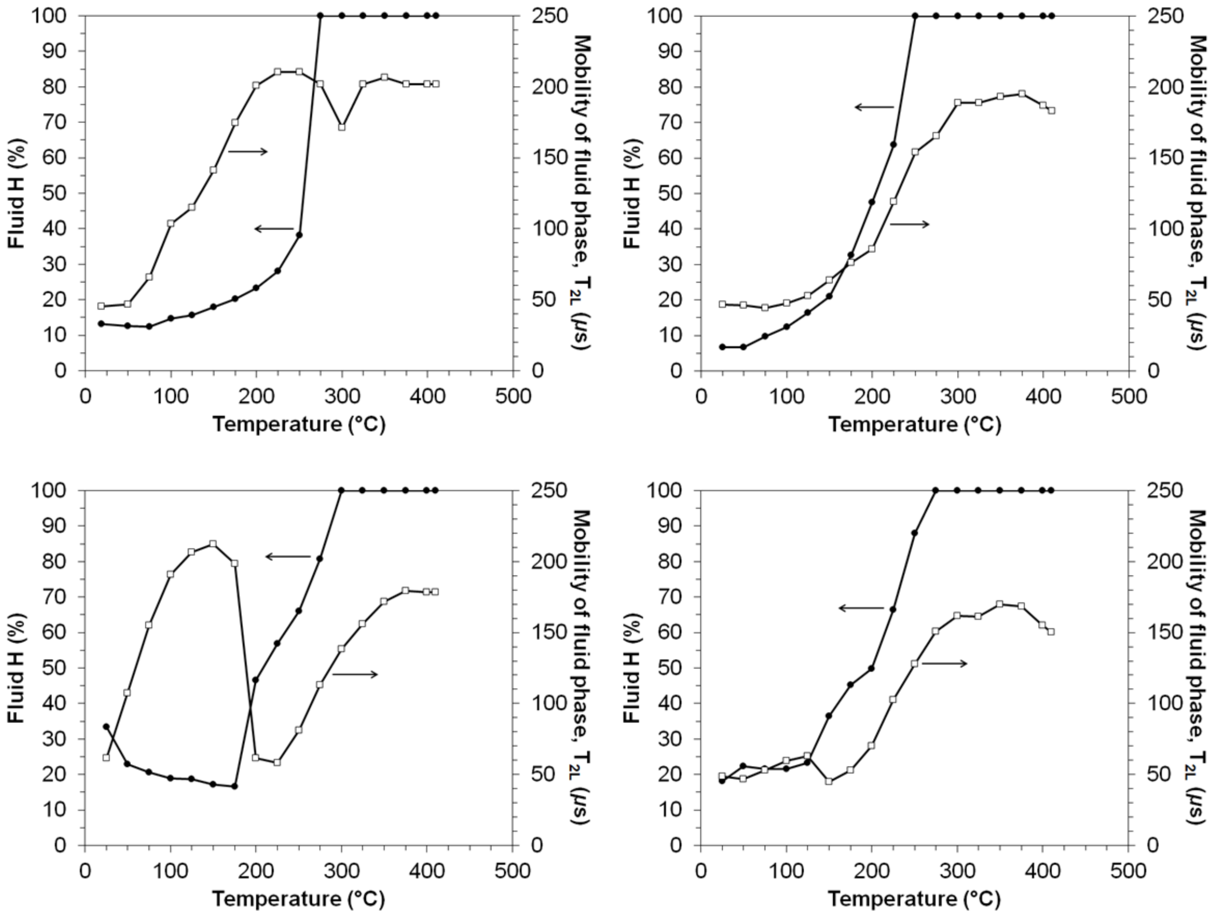

Figure 3. Percentage of fluid H and the T_{2L} of the fluid hydrogen as a function of temperature using a heating rate of 3 °C/min for the asphaltenes obtained from visbreaking the vacuum residue (top, left), the Kimmeridge Clay source rock (top, right), sub−bituminous coal (bottom, left) and pine wood (bottom, right) bitumens.

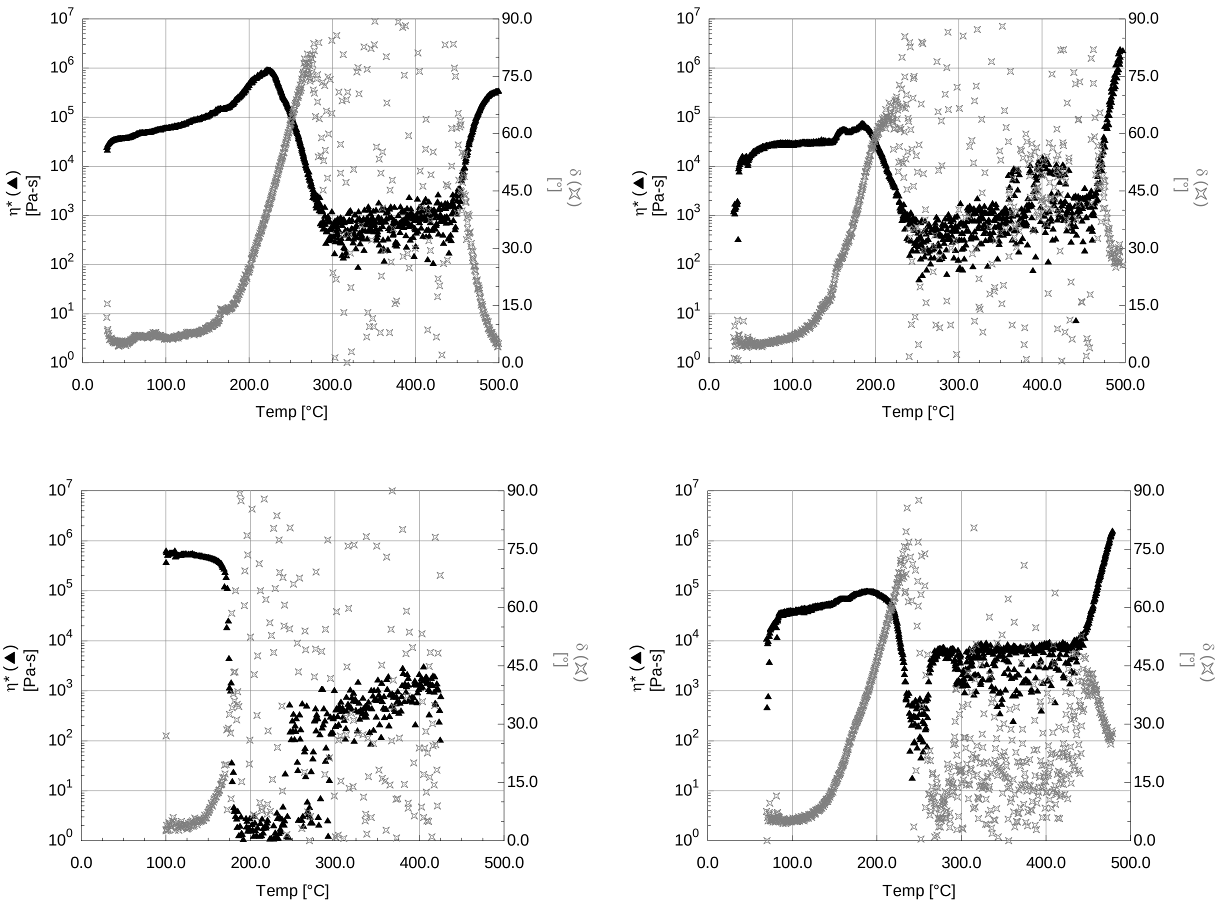

Figure 4. Complex viscosity (η^*) and phase angle (δ) as a function of temperature using a heating rate of 3 °C/min for the asphaltenes obtained from the vacuum residue (top, left), the Kimmeridge Clay source rock (top, right), sub–bituminous coal (bottom, left) and pine wood (bottom, right) bitumens.

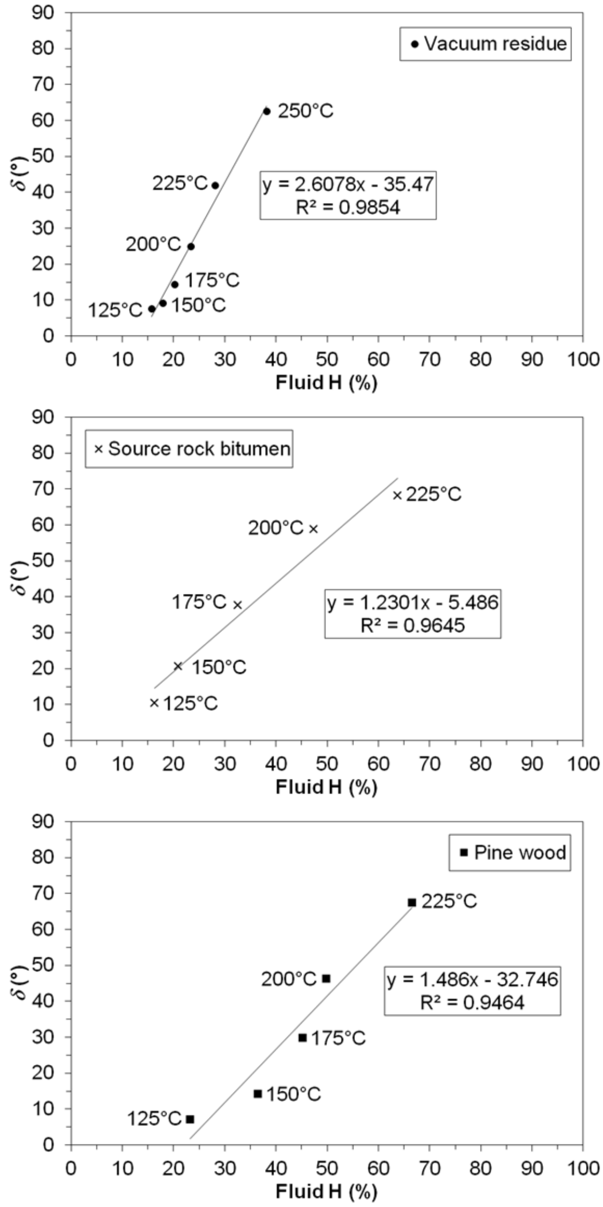

Figure 5. Correlation between phase angle (δ) and percentage of fluid H during softening of the asphaltenes obtained from visbreaking the vacuum residue (top), the Kimmeridge Clay source rock bitumen (middle) and the pine wood tetralin extract (bottom).

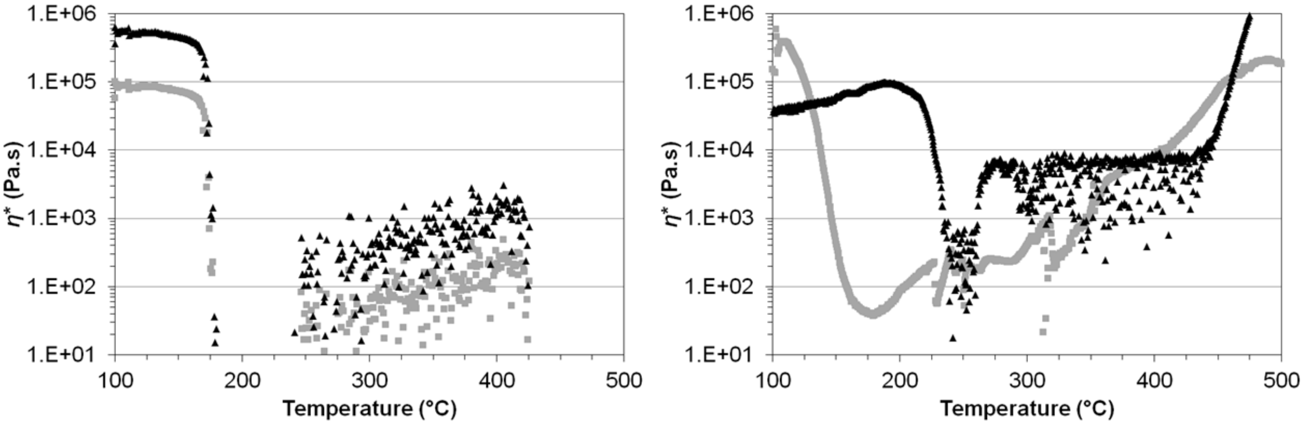

Figure 6. Complex viscosity (η*) as a function of temperature for the asphaltenes obtained from the tetralin extracts of the sub–bituminous coal (left) and pine wood (right) using the RDA-III rheometer (black symbol) and the TA AR-2000 rheometer (grey symbol).

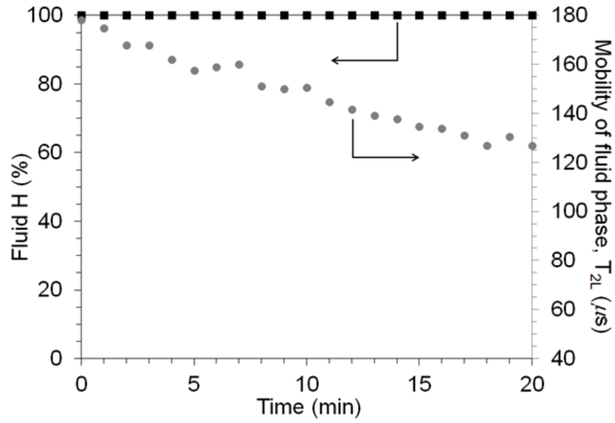

Figure 7. Percentage of fluid H and the T_{2L} of the fluid hydrogen as a function of time at 410 °C for the asphaltenes obtained from visbreaking the vacuum residue.

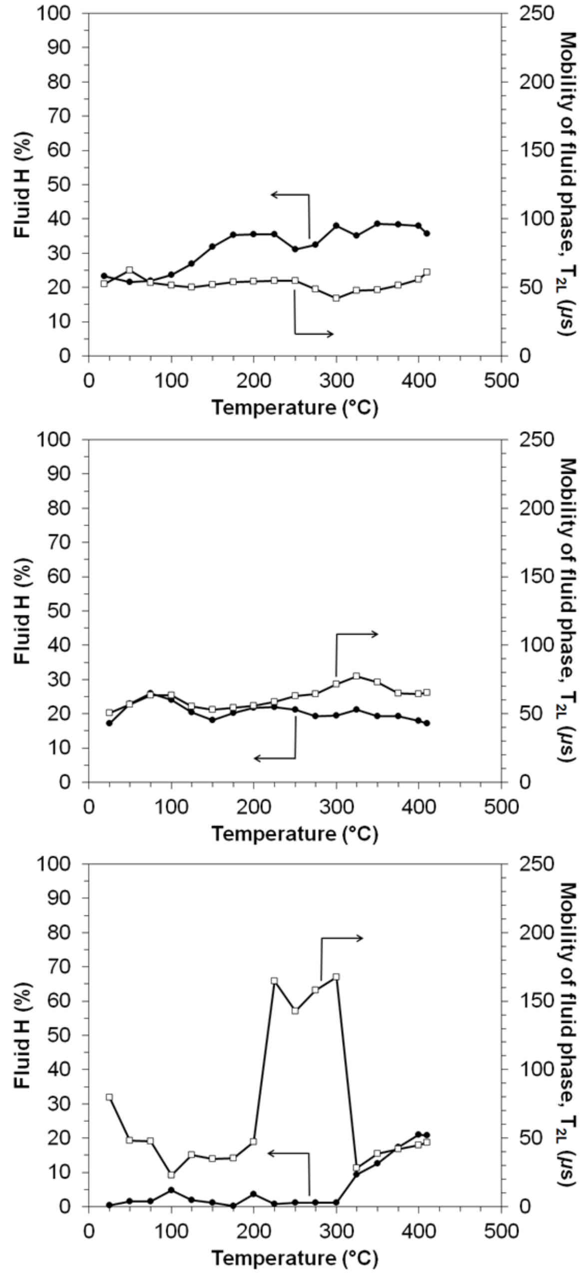

Figure 8. Percentage fluid H and the T_{2L} of the mobile phase as a function of temperature with a heating rate of 3 °C/min for the toluene-insolubles obtained from visbreaking the vacuum residue (top) and bitumen extracts from the sub–bituminous coal (middle) and pine wood (bottom).

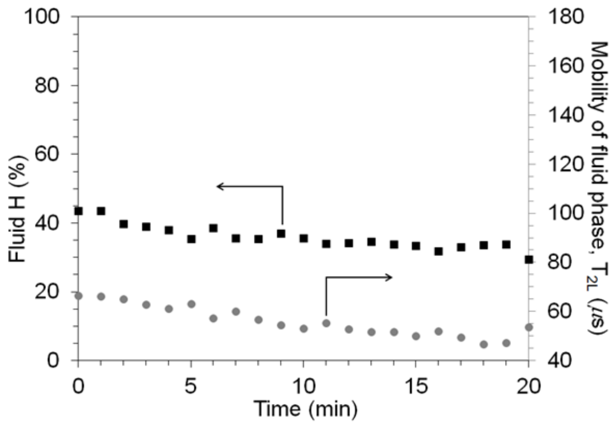

Figure 9. Percentage of fluid H and the T_{2L} of the fluid hydrogen as a function of time at 410 °C for the toluene-insolubles obtained from visbreaking the vacuum residue.