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Bitumen and Heavy Oil Rheological Properties: Reconciliation with Viscosity Measurements

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Complex viscosity and phase-angle measurements for Athabasca bitumen and Maya crude oil were performed with a rotational rheometer using parallel plates and a double gap cylinder in the oscillatory mode over the temperature range of (200 to 410) K. A large range of shearing conditions were applied (frequency of oscillations, shear strain, or stress), and up to three orders of magnitude of variations in measured viscosity values for individual samples at a fixed temperature were obtained. Athabasca bitumen and Maya crude oil were found to be solid-like materials up to (260 to 280) K and (230 to 240) K, respectively. Athabasca bitumen is a non-Newtonian shear-thinning fluid up to (310 to 315) K, whereas Maya crude is a shear-thinning fluid up to (280 to 285) K. Both are Newtonian at higher temperatures. Maya crude oil was also found to possess thixotropic behavior. Athabasca bitumen reveals the thermal irreversibility of complex viscosity, if it is heated above 360 K. These rheological behaviors are attributed to the multiphase behavior of these materials over the temperature range of interest, and these results can be used to reconcile the large differences in reported viscosity values for bitumen and heavy oil obtained with diverse viscometers where shear rate and other variables are not controlled. Additional artifacts introduced during measurements are also addressed. Sample variation due to geographical location, depth of formation, and production and postproduction processing can also result in up to three orders of magnitude of differences between the measured "viscosity" of bitumen when the measurement method and temperature are fixed. The flow properties of bitumen and heavy oil are expected to be strong functions of sample source and the hydrodynamics prevailing in situ or in processes at temperatures where non-Newtonian behaviors prevail.

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1. Introduction

Bitumen and heavy oil have become mainstream energy resources.[1] Accurate thermochemical and transport properties for these materials are key inputs for the oil industry. For example, viscosity is of crucial importance for production, transport, and refining operations. Since bitumen and heavy oils are complex multicomponent fluids and multiphase over a broad range of temperatures,[2] three main issues must be taken into account when reporting, interpreting, and using viscosity data: (1) sample identity (origin or geographical location, elevation or depth of formation, sample pretreatment history); (2) experimental conditions (measurement method, temperature, shear conditions, sample history during measurements); and (3) applicability, restrictions, and errors of certain experimental methods and techniques when applied to such complex fluids.

Chemical and phase composition, degree of dispersion, and the strength of intermolecular and interparticle interactions are the main characteristics, from an internal point of view, that are responsible for rheological behavior of heavy oils and bitumen. Without insight into the structure of these fluids, observed rheological behavior can be misinterpreted or attributed to experimental error or other extraneous factors. The large deviation in reported viscosity values for Athabasca bitumen in the literature is well-known.[3,4] More than 20 sets of viscosity data for bitumen from the Athabasca area have been reported.[5−29] It was shown[30] that the viscosity of heavy oils and bitumen is strongly influenced by properties of asphaltenes, which appear to be colloidally dispersed in maltenes. The unusual properties of bitumen, for example, extremely high viscosity and non-Newtonian rheological behavior, are typically attributed to asphaltene association.[30,31] Because of their complex phase behavior, particularly at low temperatures, such hydrocarbon resources can in principle exhibit shear thinning (or thickening), thixotropy, and so forth.[32] If a fluid is a shear-thinning (thickening) fluid, its viscosity decreases (increases) with increasing shear rate. Thixotropic fluids show a reversible decrease (increase) in viscosity with time at a constant shear rate, depending on the shear history of the fluid, reaching an equilibrium viscosity value during a finite period of time. In spite of such likelihood of complex rheological behavior, the reported viscosity values were obtained using diverse measurement techniques, many of which presume Newtonian sample behavior as a basis for measurement. Differences among reported viscosity values reach two to three orders of magnitude at fixed temperature, but generally, the slope of the temperature dependence of viscosity, $\eta = \eta(T)$ is the same in most cases. This level of apparent measurement uncertainty is significant and is reflected in prediction errors for heavy oil viscosity

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Table 1. SARA Analysis for Athabasca Bitumen and Maya Crude Oil Samples

sample	saturates	aromatics	resins	C5 asphaltenes
	Mass Fraction			
Athabasca bitumen	0.161	0.485	0.168	0.186
Maya crude oil	0.316	0.425	0.102	0.157

Table 2. Elemental Composition of Athabasca Bitumen and Maya Crude Oil Samples

element	Athabasca bitumen	Maya crude oil
	Mass Fraction	
C	0.832	0.845
H	0.097	0.113
N	0.004	0.003
S	0.053	0.033
O	0.017	0.012
	Metal Analysis/mg·kg^{-1}	
Al	492	1.0
Ba	6.4	< 0.1
K	77	1
Ca	163	29
Cr	2.8	0.8
Fe	762	4.0
Mg	65	0.7
Mn	30	< 0.1
Mo	12	3.0
Na	91	112
Ni	93	56
Si	355	80
Ti	24	0.4
V	247	263
Zn	4.4	1.6

commonly exceeding one to two orders of magnitude even for specialized correlations (ASTM D341-03, API procedure 11A4.2). Such uncertainties present challenges to producers targeting pipeline specifications for fluids and pipeline designers. For example, Enbridge Pipelines, Inc., having one of the largest crude oil and petroleum product pipeline systems, limits kinematic viscosities to 350 cSt at 285 K.[33] For an oil with a density of 1000 kg·m^{-3}, this corresponds to a maximum dynamic viscosity of 0.350 Pa·s. Hence, reliable viscosity data and predictions for heavy oils and bitumen are required.

In this contribution, factors affecting the apparent viscosity of Athabasca bitumen and Maya heavy oil are examined experimentally in the (200 to 410) K temperature range. Resource and sample preparation variability and the impact of measurement methods themselves are key lines of inquiry.

2. Experimental Section

2.1. Materials. Athabasca bitumen (Alberta, Canada) was obtained from Syncrude Canada Ltd. The sample was characterized as a coker feed obtained from mined bitumen subjected to stream warm-water extraction, naphtha dilution, and naphtha recovery by distillation between (523 and 623) K. Some volatile constituents present initially are lost during sample preparation. Maya crude oil (a commercial-blend heavy oil from Mexico) was supplied by the Mexican Petroleum Institute. Both samples were stored in closed vessels in a refrigerator prior to use.

The SARA (saturates, aromatics, resins, and asphaltenes) analysis results for both samples (Table 1) were obtained according to ASTM D2007 for saturates, aromatics, and resins and ASTM D3279 for pentane (C5) asphaltenes. Elemental compositions for all samples are given in Table 2: the carbon, hydrogen, and nitrogen contents were determined using ASTM D5291 on a LECO CHN-1000 analyzer; the sulfur content was obtained using ASTM D1552 on a LECO SC-432 sulfur analyzer; the analysis on oxygen was performed using a PE 2400 series II analyzer. Metal analyses were performed according to ASTM D5600 using an Anton Paar Multiwave-3000 microwave sample preparation system coupled with a Perkin-Elmer Sciex Elan DRC-II inductively coupled plasma quadrupole mass spectrometer. All analyses were performed at the National Centre for Upgrading Technology (NCUT), Devon, Canada. For detailed information concerning the applicable concentration ranges, analysis methods precision, repeatability, and reproducibility of these analyses readers are referred elsewhere.[34]

2.2. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) of bitumen and heavy oil samples was performed using a TG-DSC 111 thermoanalyzer (Setaram, France). The initial masses of the aliquots were from (15 to 30) mg. Isothermal TGA curves of the samples were obtained in a dry helium stream. The mass loss of the samples due to the evaporation of light components as a function of the time was recorded.

2.3. Rheological Measurements. Rheological experiments were carried out in the oscillatory mode using a controlled stress/strain Bohlin Gemini HR nano rheometer (Malvern Instruments Limited, U.K.). The following measuring configurations were used: (1) a double gap 24/27 mm concentric cylinder with a Peltier assembly using the principle of the Peltier heat pump, allowing measurements from (253 to 453) K with stability of ± 0.2 K; and (2) parallel plates (25 mm and 40 mm diameter) with an extended temperature cell (ETC) using a forced gas system to heat and cool the sample. The ETC can also be fitted with a low temperature extension (LTE): cooling with cold vapors from liquid nitrogen, if measurements below ambient temperatures are required. The ETC in these two complementary configurations (with and without LTE) covers the temperature range from (123 to 823) K with stability better than ± 0.2 K.

The sample temperature in the ETC is measured with a thermocouple (calibrated to ITS 90 using a PT100 resistance thermometer) inserted into the middle of the lower plate. A thermocouple was also used in the Peltier cylinder and calibrated in the same way. The uncertainty in temperature measurements in both cases is estimated to be less than 0.2 K. If a simple exponential (Arrhenius-type) temperature dependence of viscosity is assumed, the uncertainty in the temperature of ± 0.2 K was estimated to contribute (2 to 3) % to the uncertainty in viscosity. A possible contribution of temperature gradients arising in the ETC when LTE is used is described below in Section 3.1.

All experiments were conducted under a nitrogen atmosphere to avoid sample oxidation. The gap between the parallel plates was between (500 and 1000) μm depending on the range of viscosity values studied. For measurements obtained with the double gap cylinder, the gap was fixed at the default value of 150 μm. The experimental conditions and the operating parameter values for the rheological experiments were validated by measuring the viscosity of the Cannon certified viscosity standards N2700000SP, N74B, N1400B, and N115B (from Cannon Instrument Company, U.S.A.) and PRA standard oils #12 and U3600 (from Paint Research Association, U.K.). The agreement with the recommended data in the certified temperature range (244 to 349) K was within 5 % for the double gap cylinder in the Peltier assembly and for the parallel plates in the ETC without cooling and within 10 % for the parallel plates in the ETC with nitrogen cooling. These values can be taken as the uncertainty of viscosity measurements for Newtonian

Table 3. Validation of Viscosity Measurements Using a Bohlin Gemini HR Nano Rheometer in Two Configurations[a,b]

	T	η_{stand}	η_{meas}/Pa·s		$100\,(\eta_{\text{meas}} - \eta_{\text{stand}})/\eta_{\text{stand}}$	
standard	K	Pa·s	DGC-PA	PP-ETC	DGC-PA	PP-ETC
PRA standard oil #12	293.2	1.449	1.425	1.419[c]	−1.7	−2.1
	298.2	0.972	0.961	0.997[c]	−1.1	2.6
PRA standard oil U3600	293.2	15.33	15.31	15.80[c]	−0.1	3.1
	296.2	11.63	11.55	11.94[c]	−0.7	2.7
	298.2	9.705	9.623	9.936[c]	−0.8	2.4
	303.2	6.287	6.203	6.343[c]	−1.3	0.9
Cannon certified viscosity standard N2700000SP	325.2	604.9		582.1[c]		−3.8
	331.2	397.6		391.1[c]		−1.6
	337.2	267.3		259.0[c]		−3.1
	343.2	183.1		180.4[c]		−1.5
	349.2	128.1		124.0[c]		−3.2
Cannon certified viscosity standard N74B	273.2	3.502	3.383	3.551[d]	−3.4	1.4
Cannon certified viscosity standard N1400B	260.2	168.9	169.6	174.4[d]	0.4	3.3
	262.2	135.2	137.2	142.9[d]	1.5	5.7
Cannon certified viscosity standard N115B	244.3	140.2		146.9[d]		4.8
	247.0	94.10		96.65[d]		2.7
	249.8	64.45		69.73[d]		8.2
	255.4	31.93	32.41	33.64[d]	1.5	5.4
	260.9	17.00	16.84	17.44[d]	−0.9	2.6
	266.5	9.575	9.496	10.16[d]	−0.8	6.1

[a] DGC-PA is the double gap cylinder in a Peltier assembly; PP-ETC are the parallel plates in an ETC; η_{stand} is the reference viscosity value; η_{meas} is the actual measured viscosity value. [b] Oscillation experiments at 1 Hz frequency. Gaps between plates of 25 mm diameter in the PP-ETC configuration: 750 μm for PRA standard oil #12 and PRA standard oil U3600, 700 μm for Cannon certified viscosity standards N74B, N115B, and N1400B, and 1000 μm for Cannon certified viscosity standard N2700000SP. Test shear strain range used: (1 to 50) % for PRA standard oil #12 and PRA standard oil U3600, (0.1 to 50) % for Cannon certified viscosity standards N74B, N115B, and N1400B, and (0.3 to 1) % for Cannon certified viscosity standard N2700000SP. [c] Measured in the ETC without nitrogen cooling. [d] Measured in the ETC with nitrogen cooling.

samples without thixotropic behavior. The results of the verification including the operation parameters are summarized in Table 3.

Two measuring techniques were applied: (1) temperature sweep measurements with the cooling and heating rates of 3 $K \cdot min^{-1}$ at constant frequency and constant shear stress or constant shear strain; and (2) isothermal measurements at constant frequency and constant shear stress or constant shear strain (see details in the Section 3.2). The frequency of the oscillation was varied between (0.1 and 10) Hz (or between 0.63 s^{-1} and 63 s^{-1} in terms of angular frequency, ω). The largest scatter for complex viscosity and phase angle values was realized at the highest frequencies.

3. Results and Discussion

3.1. Experimental Artifacts in Rheological Measurements. Significant effort was expended to avoid introducing artifacts into the rheological measurements. These can arise mainly from two sources: the rheometer itself may introduce artifacts due to local cooling or heating, or/and samples can degrade or vaporize over the course of an experiment, impacting the evaluation of thermal history effects.

Local Cooling Effects. Operation of the ETC with the LTE unit required special precautions for avoiding local cooling effects introduced by the cold nitrogen vapor. In a Bohlin Gemini HR nano rheometer, a strong flow of cold nitrogen enters the measurement chamber from only one side. This cold nitrogen comes into direct contact with the edge of the parallel plates with the sample facing the flow, leading to a temperature gradient in the sample, especially when the rheometer is operated in the oscillatory mode. The temperature of the sample is recorded at the center of the lower plate, whereas viscosity is measured as an average value throughout the plate. Thus, the actual value of viscosity at the recorded temperature might be significantly lower than the measured one because of the impact of local cooling as reported in Figure 1 for experiments with PRA standard oil #12, a Newtonian fluid, and Maya crude oil. The Peltier cylinder and the ETC without LTE (i.e., without nitrogen cooling) provide viscosity values for PRA standard oil #12 at 293.15 K (Figure 1b), that are in good agreement within (2 to 3) % with the certified value −1.449 Pa·s at 293.15 K. Below this temperature, the ETC requires the LTE with nitrogen cooling. According to the manufacturer, cold nitrogen at a gauge pressure of 20 kPa should be used for rheological measurements in the ETC/LTE at isothermal conditions. From Figure 1, the resulting viscosity values are higher than those obtained with the Peltier cylinder, up to 50 % for PRA standard oil #12 and up to 25 times for Maya crude oil. Reduction of the nitrogen pressure to 15 kPa gauge, the lowest pressure, at which the device can operate in a steady way, allows us to reduce the temperature gradient and, hence, to obtain viscosity values closer to those obtained using the Peltier cylinder. Application of larger plates for the ETC/LTE also improves the results slightly, as shown for Maya crude oil (Figure 1c).

Thermal gradient effects also arose with the use of the ETC/LTE parallel plates, when examining the thixotropic behavior of Maya crude oil. At 278.15 K the viscosity dependence on shear strain found using the ETC/LTE parallel plates over a range of shear strains was significant (9 times!), whereas the variation was only 15 % with the Peltier cylinder in the same shear strain range. This artifact makes it appear as if the experiments are performed outside of a linear visco-elastic region.

Clearly, parallel plates with an ETC without cooling provide reliable viscosity data. Parallel plates with an ETC with nitrogen cooling can give satisfactory quality of viscosity data (within 10 %) provided that the rheological response of samples is simple (not complicated by thixotropy as in the Maya crude oil case) and the flow of cold nitrogen vapor is controlled to the minimum required to maintain a specific temperature. If parallel plates with an ETC and nitrogen cooling are used, result validation should be performed using an independent measurement method (e.g., double gap cylinder).

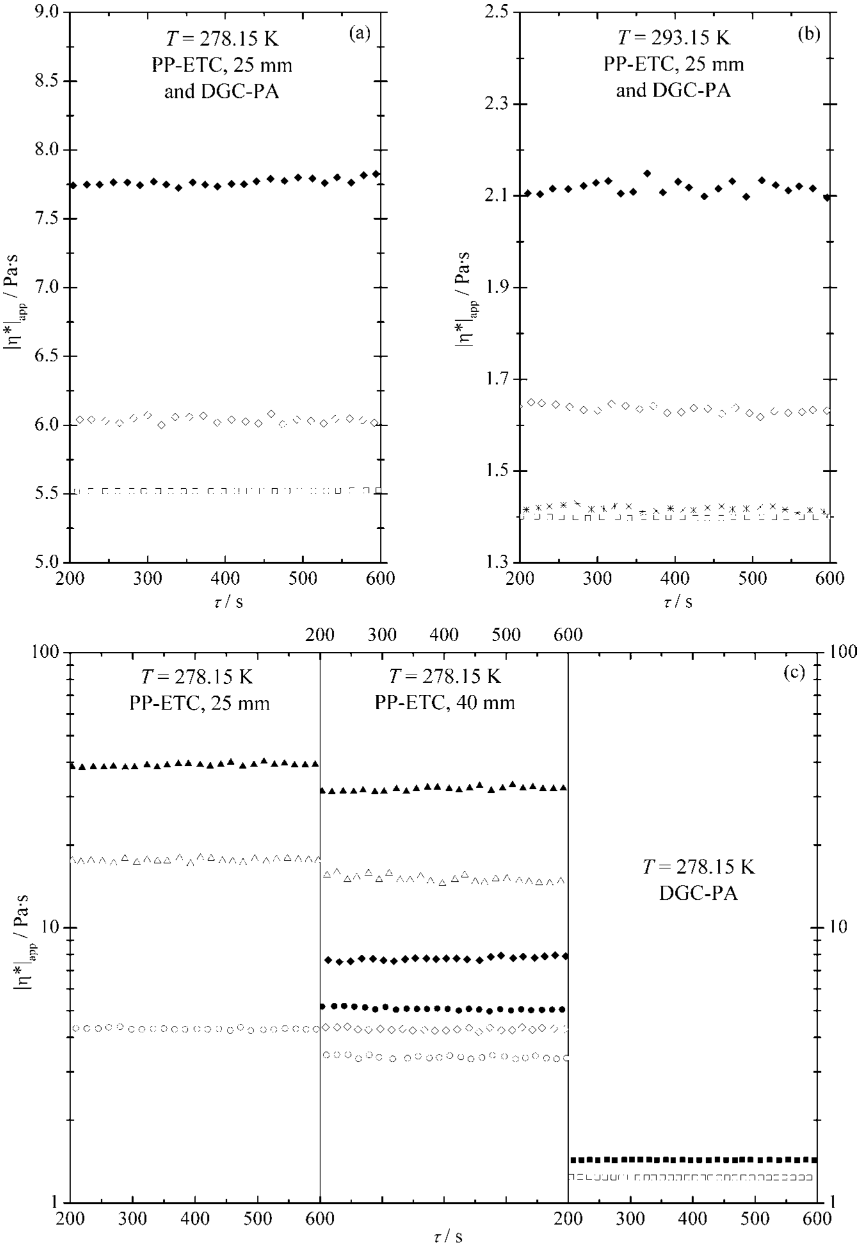

Figure 1. Variation of apparent complex viscosity ($|\eta^*|_{app}$) for PRA standard oil #12 at $T = 278.15$ K (a) and at $T = 293.15$ K (b) and for Maya crude oil at $T = 278.15$ K (c) depending on experimental technique ($\omega = 6.3\ s^{-1}$). DGC-PA is the double gap cylinder, Peltier assembly: ■, from 0.1 % to 5 % strain; □, 100 % strain. PP-ETC is the parallel plates, ETC (750 μm gap): ▲, 20 kPa of N_2, 0.3 % strain; △, 15 kPa of N_2, 0.3 % strain; ◆, 20 kPa of N_2, 30 % strain; ◇, 15 kPa of N_2, 30 % strain; ●, 20 kPa of N_2, 100 % strain; ○, 15 kPa of N_2, 100 % strain; *, without cooling, 30 % strain.

Sample Degradation. TGA results revealed noticeable mass loss for Maya crude oil: 5.8 % during the first hour of exposure at 323 K and 1.9 % during the first hour of exposure at 293 K. The evaporation of light components at ambient and higher temperatures precludes use of the ETC for rheological measurements under these conditions. For example, at 323 K, viscosity values increase continuously with time in the ETC, up to 10 times within 4 h. Hence, the Peltier system with a double-gap cylinder was used for Maya crude down to 258 K (the low temperature limit for the Peltier double gap cylinder is 253 K). At lower temperatures the ETC/LTE was employed with as low pressure of cold nitrogen vapors as possible to maintain temperatures under study. Athabasca bitumen shows insignificant mass loss during TGA measurements in the temperature range of interest: 0.067 % during the first hour of exposure at 323 K and 0.21 % during the first hour of exposure at 363 K. Such a low mass loss permitted use of the ETC for the whole temperature interval from (233 to 363) K. Since the mass loss comprises 2.1 % per hour at 413 K, the results of viscosity measurements for Athabasca bitumen at temperatures higher than 363 K are influenced by evaporation processes.

3.2. Variation of Viscosity with Experimental Conditions. Athabasca Bitumen. Viscosity and phase-angle measurements for Athabasca bitumen (Figure 2) were obtained on heating and cooling between (233 and 363) K at different oscillation frequencies at constant shear strain of 0.3 % (Table S1 of the Supporting Information). Rheological measurements from (233 to 310) K were carried out in the ETC/LTE using the lowest possible pressure of cold nitrogen and at $T > 300$ K, in the ETC without cooling. Viscosity and phase angle values for the bitumen obtained using these two configurations agree with one another within 5 % and 1 %, respectively, in the overlap region, (300 to 310) K; that is, the effect of local cooling in the ETC/LTE is insignificant for highly viscous Athabasca bitumen. Both

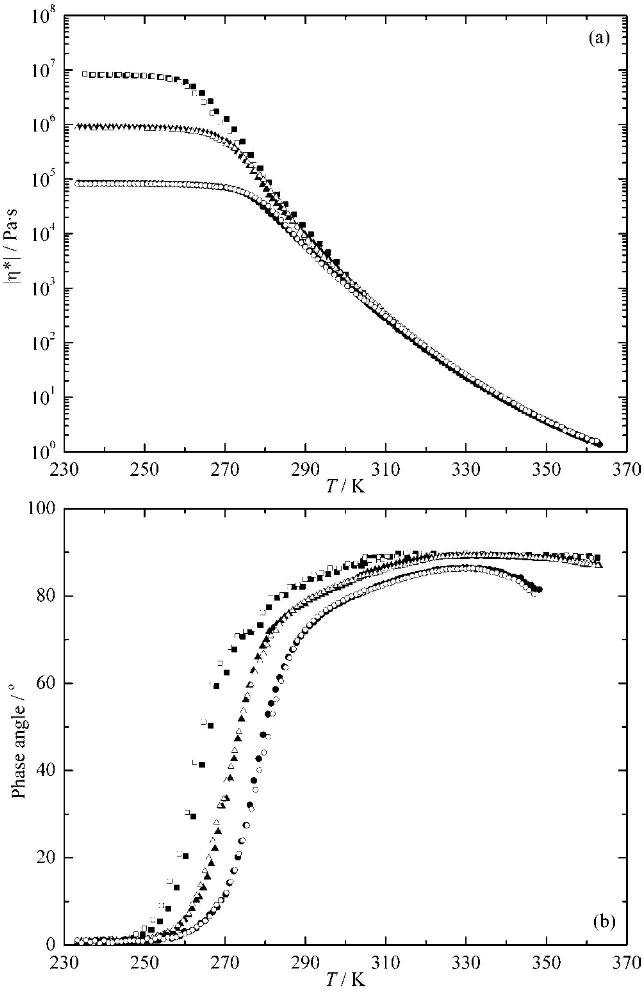

Figure 2. Frequency and temperature dependence of complex viscosity (a) and phase angle (b) for Athabasca bitumen (3 K·min^{-1}, 0.3 % strain, 1000 μm gap): ■, cooling, $\omega = 0.63$ s^{-1}; □, heating, $\omega = 0.63$ s^{-1}; ▲, cooling, $\omega = 6.3$ s^{-1}; △, heating, $\omega = 6.3$ s^{-1}; ●, cooling, $\omega = 63$ s^{-1}; ○, heating, $\omega = 63$ s^{-1}.

sets of viscosity data are reported in Figure 2a and are indistinguishable.

In the temperature interval studied, the complex viscosity of Athabasca bitumen was found to be reversible with temperature variation when other shearing conditions were maintained constant. However, a frequency dependence is evident which provides evidence for non-Newtonian shear-thinning behavior, discussed in detail below, while the complex viscosity of Athabasca bitumen is independent of the applied shear stress (shear amplitude) (Figure 3). Higher temperature measurements, up to 413 K, revealed irreversibility of complex viscosity upon heating and cooling (Figure 4, two heating−cooling cycles). This behavior may arise from two possible underlying processes: (1) evaporation of light components (see Section 3.1), and (2) irreversible (or slowly reversing) phase transitions in asphaltenes. For example, from DSC measurements,[2,35,36] the melting behavior of asphaltenes includes an irreversible transition; the first DSC scans are always more complicated than subsequent ones, which typically show only one broad endothermic transition. Since viscosity measurements are fast (3 K·min^{-1}) and not more than 10 min were spent at 413 K, evaporation should give only a minor contribution to the irreversibility of viscosity compared with the influence of an irreversible phase transition in asphaltenes. Additional experiments are still needed to clarify this matter.

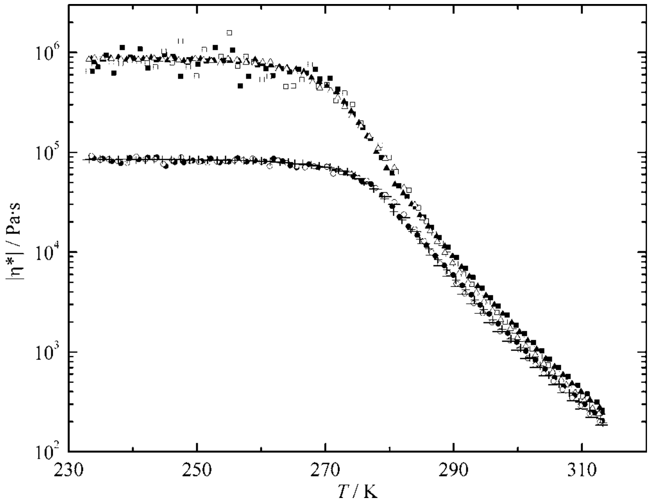

Figure 3. Shear stress dependence of viscosity for Athabasca bitumen (3 K·min^{-1}, 1000 μm gap, σ is the shear stress): ■, cooling, $\omega = 6.3$ s^{-1}, $\sigma = 50$ Pa; □, heating, $\omega = 6.3$ s^{-1}, $\sigma = 50$ Pa; ▲, cooling, $\omega = 6.3$ s^{-1}, $\sigma = 500$ Pa; △, heating, $\omega = 6.3$ s^{-1}, $\sigma = 500$ Pa; ●, cooling, $\omega = 63$ s^{-1}, $\sigma = 200$ Pa; ○, heating, $\omega = 63$ s^{-1}, $\sigma = 200$ Pa; +, cooling, $\omega = 63$ s^{-1}, $\sigma = 2000$ Pa; −, heating, $\omega = 63$ s^{-1}, $\sigma = 2000$ Pa.

Maya Crude Oil. Since a large amount of sample (10 mL) is used with the double-gap cylinder of the Peltier system, temperature sweep experiments could not give reliable viscosity values because of the thermal inertia of materials on heating and cooling. Therefore, complex viscosity and phase angle measurements for Maya crude oil were measured from (203 to 298) K isothermally with a step of 5 K (or 2.5 K in the temperature range where the viscosity gradient is high). In contrast to Athabasca bitumen, the results of the measurements are strongly influenced by the thermal prehistory of the Maya crude sample as well as experimental conditions. The isothermal equilibration time before an experiment is crucial for reaching constant viscosity values for Maya crude (Figure 5). Since the measuring system is closed and there is no evaporation of light components, this behavior could be explained by low rates of formation of contacts between molecules and molecular aggregates in the oil, and enough time should be given for the material to form an equilibrium interparticle network. The complex viscosity of Maya crude oil also exhibits a noticeable dependence on shear strain applied after reaching equilibrium (Figure 6). Low shear strain (depending on temperature) gives constant time-independent viscosity values, whereas higher strain results in a continuous decrease in complex viscosity with time, which is characteristic of thixotropy. At lower temperatures, smaller strains reveal thixotropy, and it is of larger magnitude than that at higher temperatures; for example, compare Figure 6, parts a and b. This behavior is consistent with the earlier comment on kinetics of the interparticle network formation. Low strain does not influence the stability of the well-formed network, but higher strain breaks networks down. At higher temperatures, some weak bonds are broken thermally, reducing the impact of thixotropy compared with lower temperatures.

Taking into account these two observations, the following experimental conditions were chosen for measurements of viscosity of Maya crude oil: (1) samples were maintained at each temperature until constant equilibrium viscosity values were reached, and (2) all measurements were carried out at shear strain low enough not to provoke thixotropy but high enough to provide good accuracy for rheological measurements. The latter point is important since low shear strain, especially at

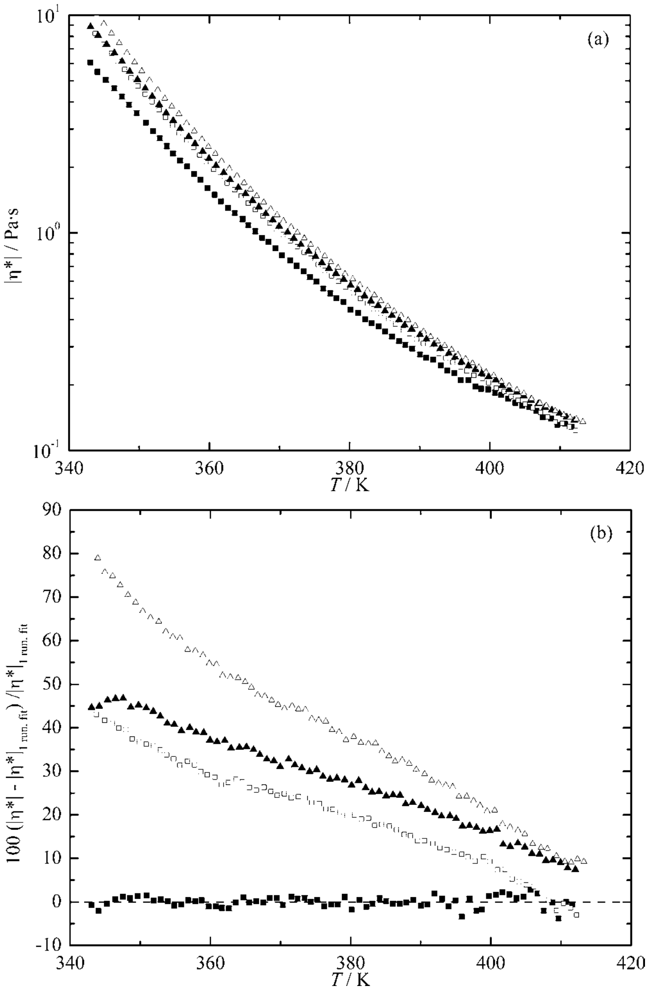

Figure 4. Impact of thermal history on the high-temperature viscosity of Athabasca bitumen (3 K·min^{-1}, 500 μm gap, $\omega = 6.3$ s^{-1}, 5 Pa shear stress), successive experiments; (a) complex viscosities, (b) percentage deviation of complex viscosities ($|\eta^*|$) from smoothed temperature dependence of viscosity observed in the first heating run ($|\eta^*|_{1\text{run,fit}}$): ■, heating 1; □, cooling 1; ▲, heating 2; △, cooling 2.

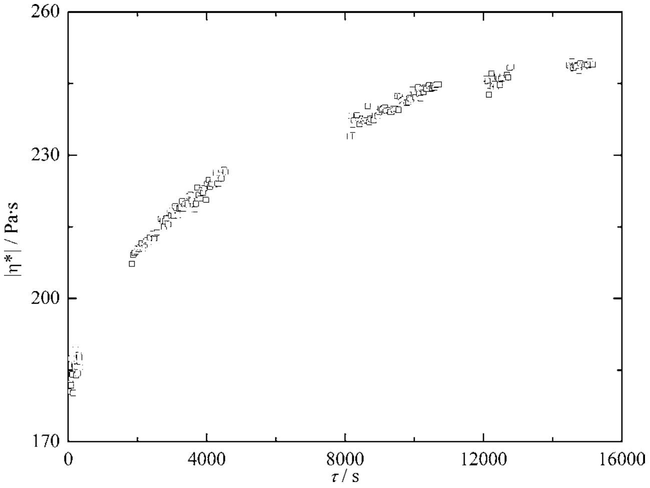

Figure 5. Time dependence of viscosity for Maya crude oil upon equilibration after reaching a stable temperature $T = 260.65$ K (double-gap cylinder, Peltier assembly, $\omega = 0.63$ s^{-1}, 0.1 % strain).

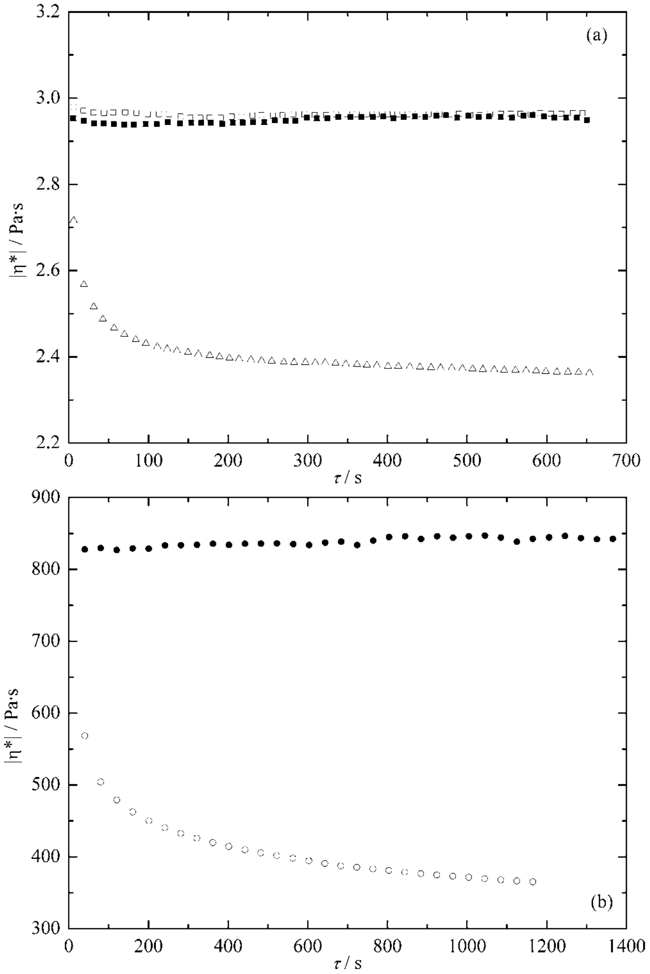

Figure 6. Time dependence of viscosity for Maya crude oil at (a) $T = 273.15$ K and $\omega = 6.3$ s^{-1}; (b) $T = 258.15$ K and $\omega = 0.63$ s^{-1} (double-gap cylinder, Peltier assembly): ■, 1 % strain; □, 2 % strain; △, 100 %; ●, 0.2 % strain; ●, 5 % strain.

high temperatures, is generated by stress, which could be close to or below the detection limit of the rheometer, causing significant scatter in the viscosity data. The complex viscosity and phase-angle results for Maya crude oil are presented in Figure 7 and in Table S2 of the Supporting Information. Results obtained using parallel plates with the ETC/LTE and a double-gap cylinder with the Peltier assembly agree within 7 % at $T = 258.15$ K, where the two methods overlap. Finally, along with Athabasca bitumen, the viscosity of Maya crude oil exhibits a frequency dependence.

Non-Newtonian Behavior. Both Maya crude oil and Athabasca bitumen exhibit non-Newtonian shear-thinning behavior; that is, viscosity decreases with increasing oscillation frequency (Figures 2 and 7). The greatest impact (more than two orders of magnitude) is observed at low temperatures where the complex viscosity has a plateau (temperature-independent viscosity): below (260 to 280) K for Athabasca bitumen and below (230 to 240) K for Maya crude. On the basis of our previous study of the phase behavior of Maya crude,[2] the low-temperature plateau for complex viscosity can be attributed to a solid-continuous phase state. The solid-to-liquid maltene transition for Maya crude begins at approximately 170 K (from calorimetric measurements[2]), while the phase angle rises from 0° at (220 to 230) K (Figure 7b). A similar phase angle rise for Athabasca bitumen occurs at (250 to 260) K (Figure 2b). For the phase angle to rise, about 35 % liquid on a volume basis must be present.[2] Complex viscosity only begins to decrease, once sufficient liquid is present for the fluid to flow, as is clear from a comparison between Figure 2, parts a and b, for Athabasca bitumen and Figure 7, parts a and b, for Maya crude.

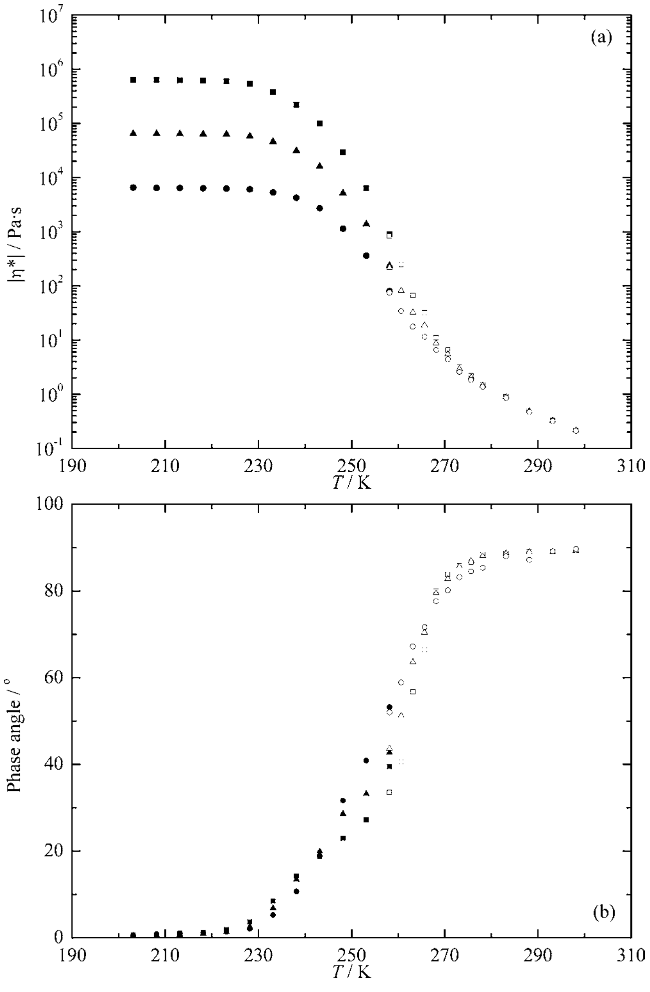

Figure 7. Frequency and temperature dependence of complex viscosity (a) and phase angle (b) for Maya crude oil (for strain see text, DGC-PA is the double-gap cylinder, Peltier assembly, and PP-ETC is the parallel plates, ETC): □, DGC-PA, $\omega = 0.63\ \mathrm{s}^{-1}$; △, DGC-PA, $\omega = 6.3\ \mathrm{s}^{-1}$; ○, DGC-PA, $\omega = 63\ \mathrm{s}^{-1}$; ■, PP-ETC, $\omega = 0.63\ \mathrm{s}^{-1}$; ▲, PP-ETC, $\omega = 6.3\ \mathrm{s}^{-1}$; ●, PP-ETC, $\omega = 63\ \mathrm{s}^{-1}$.

At a phase angle of 45°, there is approximately 50 % liquid, and at 90° (at the upper plateau of phase angle), a minimum of 65 % liquid must be present.[2] At higher temperatures, Athabasca bitumen and Maya crude continue to behave as non-Newtonian shear-thinning fluids, but the impact of frequency on viscosity values diminishes with increasing temperature. Maya crude becomes Newtonian at (280 to 285) K; that is, viscosity becomes independent of frequency, whereas Athabasca bitumen exhibits moderate non-Newtonian character up to (310 to 315) K.

The rheological measurements in this work demonstrate that heavy oils and bitumen are non-Newtonian fluids at low temperatures. Their complex viscosities are sensitive to experimental conditions and may possess a temperature dependence, a frequency dependence, a dependence on thermal prehistory, and a time dependence (thixotropy). Variations of two orders of magnitude in complex viscosity values are observed at low temperatures (less than ≈ 270 K for Athabasca bitumen and less than ≈ 240 K for Maya crude oil). Clearly, details of rheological measurements and sample history are important factors explaining the large reported variations for bitumen and heavy oil "viscosity" data.

3.3. Comparison of Rheological Results for Athabasca Bitumen with Literature Data. The present results and literature values for the viscosity of Athabasca bitumen are presented in Figure 8. Differences between reported values range up to three orders of magnitude at fixed temperature. Variation is greatest at low temperatures and diminishes as temperature is increased.

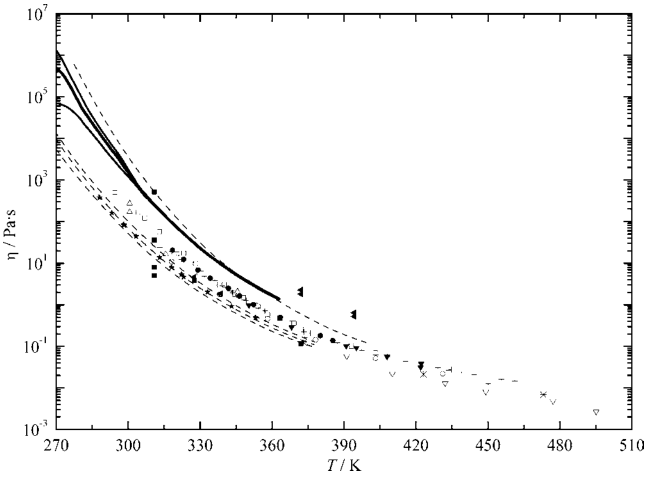

Figure 8. Viscosity variation for Athabasca bitumen with temperature: solid lines, PPR, $\omega = 0.63\ \mathrm{s}^{-1}$, $6.3\ \mathrm{s}^{-1}$, and $63\ \mathrm{s}^{-1}$ (this work); dashed lines, from different locations, CapV, γ' n/s (ref 5); left-pointing solid triangle, method n/s, γ' n/s (ref 6); ■, from different locations, method n/s; γ' n/s (ref 7); ○, CCV, γ' from $13\ \mathrm{s}^{-1}$ to $2300\ \mathrm{s}^{-1}$ (ref 8); ▽, RBV, γ' from $14\ \mathrm{s}^{-1}$ to $225\ \mathrm{s}^{-1}$ (refs 9, 10); ▼, CCV, γ' from $12\ \mathrm{s}^{-1}$ to $1400\ \mathrm{s}^{-1}$ (refs 9, 10); □, CCV, γ' n/s (refs 11, 12); +, CCV, γ' n/s (ref 13); △, MS, $\gamma' = 1\ \mathrm{s}^{-1}$ (ref 14); *, CapV, γ' n/s (ref 15); ●, CCV, γ' n/s (ref 16); ★, CCV, $\gamma' = 460\ \mathrm{s}^{-1}$ (ref 17). Abbreviations and symbols: PPR, parallel plate rheometer; CapV, capillary viscometer; CCV, concentric cylinder viscometer; RBV, rolling ball viscometer; MS, mechanical spectrometer; n/s, not stated; γ', shear rate; ω, angular frequency (equivalent to shear rate).

Details of Experiment. The viscosity data for Athabasca bitumen reported in Figure 8 were obtained using diverse viscometers including capillary flow, rotating cylinder, cone and plate, and rolling ball viscometers. Each measurement method is characterized by a range of shear conditions that can differ from sample to sample and among methods. For example, in the case of rotational viscometers the steady shear mode was used for all measurements reported in the literature.[8−14,16,17] In this study, oscillatory rheometry was performed. According to the Cox−Merz rule,[37] the complex viscosity $|\eta^*(\omega)|$ in an oscillatory experiment (where ω is the angular frequency, $\omega = 2\pi f$) is equivalent to the steady-shear viscosity $\omega(\gamma')$ (where γ' is the shear rate) provided that $\omega = \gamma'$. Therefore, we can compare "oscillatory" viscosity values with "steady-shear" ones provided that we have information on the shear rate/frequency applied. As bitumen and heavy oils are shear-thinning fluids over a wide temperature range, "viscosity" has meaning only if the shear condition is clearly defined. For example, from Figures 2a and 3 only oscillatory frequency (or shear rate) has an influence on the viscosity of Athabasca bitumen. Many publications do not report the values of shear rate applied in their steady-shear measurements. Even if these parameters are given (Figure 8), they are essentially different for low and high temperatures (e.g., refs 8−10). Below 310 K, viscosity values obtained in this work approach the average of the previously reported range for viscosity data as long as a higher angular frequency is used. Thus, differences in shear rates can explain the discrepancies among viscosity values due to non-Newtonian behavior of Athabasca bitumen at least up to 310 K. Thermal irreversibility of viscosity for Athabasca bitumen, if heated above 360 K, may arise because of slowly reversing or irreversible phase transitions in asphaltenes and/or evaporation of light components (Section 3.2). Consequently, a thermal

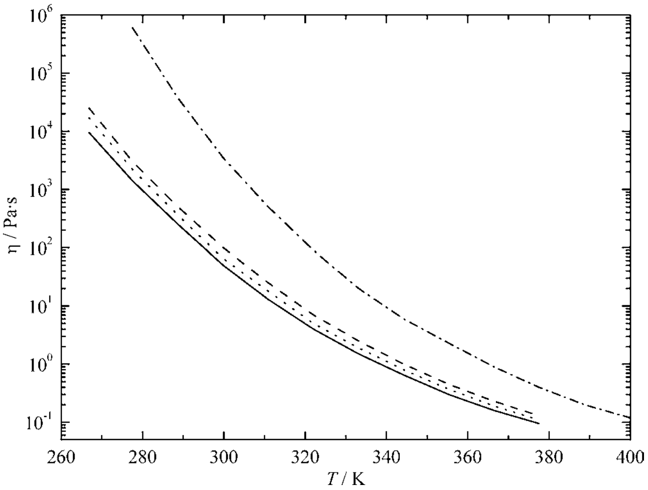

Figure 9. Impact of source location and elevation on the viscosity for Athabasca bitumen. Measurements from Ward and Clark[5] (measurement method: capillary viscometry; recovery method: benzene-based extraction standardized for all samples; Bitumount # 1 to # 4 differ by 180 m elevation): solid line, Bitumount # 1; dashed line, Bitumount # 2, 3, and Ells River; dotted line, Bitumount # 4; dash-dotted line, Abasand.

history of Athabasca bitumen before and during viscosity measurements is important, since this can also lead to additional viscosity variation. In this work, viscosity was measured below 360 K, and so the influence of thermal history during experiments was avoided. The absence of thermal history information (e.g., order of measurements) in refs 5−13, 15, and 16 creates ambiguity in data interpretation even under conditions where bitumen exhibits Newtonian behavior, and in principle all measurement methods should yield equivalent results.

Geographic Location and Depth within a Reservoir. Ward and Clark[5] found that bitumen from Abasand has a viscosity of up to three orders of magnitude higher than bitumen from more northern locations in the Athabasca region (Figure 9). The variation with depth within a reservoir is less pronounced (less than one order of magnitude) but still appreciable, and viscosity has a tendency to increase with depth. Ward and Clark[5] extracted all of their samples using the same procedure and employed the same viscosity measurement technique (capillary viscometry) for all samples. One may be tempted to conclude that the differences identified are solely attributable to sample source, but the prevailing shear rate in the capillary is a function of the "viscosity". At low temperatures, the samples are not Newtonian, so differences among samples, though real, become exaggerated. Erno et al.,[38] who used a cone and plate viscometer for viscosity experiments at 298 K at (1 to 10) s^{-1} shear rates, also found an increase of viscosity of heavy oils with depth within a well for different locations in Alberta, Canada.

Most publications do not include detailed information on bitumen origin, which restricts our ability to correlate viscosity with geographical origin and with elevation within a reservoir. A supplier but not the exact deposit and/or elevation is typically provided (e.g., Great Canadian Oil Sands Ltd.,[11−14] Syncrude Canada Ltd.,[8,17] Shell Canada Ltd. (one of the bitumen samples from ref 7), Abasand Oil Ltd.,[5] Research Council of Alberta,[6,21] etc.). Samples could be obtained directly from one location or could be blends from different deposits leased by the supplier. For example, the bitumen sample studied in this work could be a mixture or an individual sample from Mildred Lake, Aurora, and/or North Mine deposits: the main operation areas of Syncrude Canada Ltd. located between Abasand and Bitumount.

Production and Postproduction Treatment Procedure. From a chemical and structural point of view, bitumen in a deposit and materials produced from it are not identical; that is, different production procedures yield bitumen with differing properties. This variation strongly depends on the production and postproduction treatments.

Two methods are applied for producing bitumen from oil sands at the industrial scale: in situ and mining processing schemes. In both, additional components are normally used for injection into wells or extraction from mined sands: water (or steam) or solvent. Hence, samples studied in this work or by other authors have undergone one of these two production procedures. In general, each additive has a well-known influence on viscosity. For example, the viscosity of bitumen usually increases when small amounts of water are added (up to 10 % to 40 %), while further addition reduces viscosity.[3,39] Solvent addition decreases viscosity.[3] From a practical perspective, variations in the postproduction procedure can change fluid properties significantly. For example, if high temperature distillation is used in a naphtha-based production method,[7] light ends present in the bitumen are removed along with the naphtha. This increases the viscosity. At the same time, residual naphtha reduces viscosity.

Among the data from Figure 8, a mining + water and naphtha addition production procedure was used in refs 6 and 17 and this work. A solvent-based one was applied to samples in refs 5 and 11−16. On the basis of the information given in the references, solvent and water residues may be present in some cases.[6,14,15,17] There is no apparent trend in the viscosity values for bitumen exposed to these different production procedures. No extraction process was applied in refs 8−10 since the bitumen sample was obtained as it oozed from the mined tar sand[8] or by centrifugation through filter pads.[9,10] According to the study of Henry and Fuhr,[40] where oil-sand samples were obtained by ultracentrifuging without adding any solvent, the Athabasca bitumen adhering to the sand grains was asphaltene deficient relative to the supernatant bitumen, but the latter contained more light components, which are usually lost during the solvent extraction procedure. They found that the viscosity of ultracentrifuged bitumen was the lowest and that of bitumen recovered by solvent extraction was the highest. Consequently, it is not surprising that the viscosity for the samples obtained without adding solvent[8−10] fall below most of the data sets presented in Figure 8. Since the bitumen sample studied in this work was exposed to distillation at high temperatures between (523 and 623) K (removal of naphtha) following warm-water extraction, it is not surprising that its viscosity is higher than that of other samples treated under milder conditions, at 423 K[11−13,16] or at 308 K.[14]

4. Conclusions

Maya heavy oil and Athabasca bitumen are shear-thinning fluids over temperature ranges of industrial interest for production, storage, and transport. Complex viscosity must be associated with a specified shear condition for reported viscosity values to have meaning. Up to three orders of magnitude of variation in reported viscosity values for Athabasca bitumen can be attributed to the impact of shear as an uncontrolled variable in viscosity measurements. At elevated temperatures, bitumen and heavy oil approach Newtonian rheological behavior. Sample origin, production method, and postproduction treatments can also account for up to three orders of magnitude variation in measured viscosity values. By contrast, thermal and shearing history plays a secondary role: Variations, if present, fall within one order of magnitude; however, the effect of thixotropy for such complex fluids should be taken into consideration. A clear understanding of the variables affecting the rheological properties of bitumen and heavy oil is of crucial importance for selecting or optimizing flow regimes for their production and transport. Results reported here are expected to reduce the technical uncertainty related to the design and development of heavy oil and bitumen production and transport processes and to allow practitioners to discriminate real from phantom variables present in their own measurements and in the literature.

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Supporting Information Available:

Tables S1 and S2 summarize complex viscosity data for Athabasca bitumen and Maya crude oil. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) *Alberta's Energy Reserves 2007 and Supply/Demand Outlook 2008−2016*; ERCB Document # ST98-2008; Energy Resources Conservation Board: Calgary, Canada, 2008.

(2) Fulem, M.; Becerra, M.; Hasan, MD. A.; Zhao, B.; Shaw, J. M. Phase behaviour of Maya crude oil based on calorimetry and rheometry. *Fluid Phase Equilib.* **2008**, *272*, 32–41.

(3) Robinson, D. B., Ed. *The thermodynamic and transport properties of bitumens and heavy oils*; AOSTRA Technical Report; Alberta Oil Sands Technology and Research Authority: Edmonton, Canada, 1984.

(4) Seyer, F. A.; Gyte, G. W. Viscosity. In *AOSTRA Technical Handbook on Oil Sands, Bitumens and Heavy Oils*; Hepler, L. G., Hsi, C., Eds.; AOSTRA Technical Publication: Edmonton, Canada, 1989; pp 155−184.

(5) Ward, S. H.; Clark, K. A. *Determination of the viscosities and specific gravities of the oils in samples of Athabasca bituminous sand*; Report 57; Research Council of Alberta: Edmonton, Canada, 1950.

(6) Charbonnier, R. P.; Draper, R. G.; Harper, W. H.; Yates, A. *Analyses and characteristics of oil samples from Alberta*; Information Circular IC 232; Canada Department of Energy Mines and Resources, Mine Branch: Ottawa, Canada, 1969; pp 182−184.

(7) Camp, F. W., Ed. *The Tar Sands of Alberta, Canada*, 2nd ed.; Cameron Engineers Inc.: Denver, CO, 1974; p 23.

(8) Flock, D. L.; Boogmans, T. *A laboratory investigation of steam solvent extraction of heavy oils and bitumen for in-situ application*; Final Report on AOSTRA Research Agreement 8; Alberta Research Council: Edmonton, Canada, March 1978 (cited in ref 3).

(9) Briggs, J. P. *Summary of viscosity measurement data obtained during February and March 1978*; Alberta Research Council: Edmonton, Canada, April 1978 (cited in ref 3).

(10) Briggs, J. P. *The measurement of bitumen viscosity at shear rates, temperatures and pressures which approximate to reservoir conditions*; Alberta Research Council: Edmonton, Canada, June 1978 (cited in ref 3).

(11) Jacobs, F. A.; Donnelly, J. K.; Stanislav, J.; Svrcek, W. Y. Viscosity of gas-saturated bitumen. *J. Can. Pet. Technol.* **1980**, *19* (4), 46–50.

(12) Khan, M. A. B.; Mehrotra, A. K.; Svrcek, W. Y. Viscosity models for gas-free Athabasca bitumen. *J. Can. Pet. Technol.* **1984**, *23* (3), 47–53.

(13) Svrcek, W. Y.; Donnelly, J. K.; Stanislav, J. *Measurement, correlation and prediction of oil sand hydrocarbons*; Final Report on AOSTRA Research Agreement 13; Alberta Research Council: Edmonton, Canada, June 1979 (cited in ref 3).

(14) Dealy, J. M. Rheological properties of oil sand bitumens. *Can. J. Chem. Eng.* **1979**, *57*, 677–683.

(15) Robinson, D. B.; Sim, S.-K.; Chen, C.-J. *The behavior of bitumen mixtures during in-situ recovery*; Final Report on AOSTRA Agreement 184; Alberta Research Council: Edmonton, Canada, July 1983 (cited in ref 3).

(16) Mehrotra, A. K.; Svrcek, W. Y. Viscosity, density and gas solubility data for oil sand bitumen. Part I: Athabasca bitumen saturated with CO and C_2H_6. *AOSTRA J. Res.* **1985**, *1*, 263–268.

(17) Schramm, L. L.; Kwak, J. C. T. The rheological properties of an Athabasca bitumen and some bituminous mixtures and dispersions. *J. Can. Pet. Technol.* **1988**, *27* (1), 26–35.

(18) Fu, B. C. H. *An evaluation of mechanisms and criteria for solvent extraction of bitumen from Athabasca oil sand*; M.Sc. Thesis, University of Toronto, Department of Chemical Engineering and Applied Chemistry, Toronto, Canada, 1978.

(19) Patel, M. S. *Determination of viscosities of oils from Mannville formation oil sand*; Research Council of Alberta: Edmonton, Canada, October 1973 (cited in ref 3).

(20) Smolek, K. *Viscometric investigation of bitumen from Athabasca oil sands at subcracking temperatures and elevated pressures*; Alberta Research Council: Edmonton, Canada, May 1976 (cited in ref 3).

(21) Mehrotra, A. K.; Svrcek, W. Y. Viscosity of compressed Athabasca bitumen. *Can. J. Chem. Eng.* **1986**, *64*, 844–847.

(22) Bowman, C. W. Molecular and interfacial properties of Athabasca tar sands. In *Proceedings of the 7th World Petroleum Congress, Mexico City*; Vol. 3; Elsevier: New York, 1967; pp 583−604.

(23) Closmann, P. J.; Seba, R. D. Laboratory test on heavy oil recovery by steam injection. *Soc. Pet. Eng. J.* **1983**, *23*, 417–426.

(24) Nagra, S. S.; Armstrong, D. A.; Adam, F. C. Test for radiation fluidization of Athabasca tar sands. *Energy Process./Can.* **1978**, *71*, 58–64.

(25) Bunger, J. W.; Thomas, K. P.; Dorrence, S. M. Compound types and properties of Utah and Athabasca tar sand bitumens. *Fuel* **1979**, *58*, 183–195.

(26) Fu, B. C. H.; Phillips, C. R. New technique for determination of diffusivities of volatile hydrocarbons in semi-solid bitumen. *Fuel* **1979**, *58*, 557–560.

(27) Rubinstein, I.; Strausz, O. P. Physical properties of conventional and biodegraded oils. *Am. Chem. Soc., Div. Fuel Chem. Prepr. Pap.* **1977**, *22* (3), 20–25.

(28) Baughman, G. L., Ed. *Synthetic Fuels Data Handbook*, 2nd ed.; Cameron Engineers Inc.: Denver, CO, 1978; p 274.

(29) Smith, N. A. C.; Smith, H. M.; Blade, O. C.; Garton, E. L. *The Bureau of Mines routine method for the analysis of crude petroleum, Part I: The analytical method*; Bulletin 490; U.S. Bureau of Mines: Washington DC, 1951.

(30) Lin, M.-S.; Chaffin, J. M.; Davison, R. R.; Glover, C. J.; Bullin, J. A. A new suspension viscosity model and its application to asphaltene association thermodynamics and structures. In *Structures and Dynamics of Asphaltenes*; Mullins, O. C., Sheu, E. Y., Eds.; Plenum Press: New York, 1998; pp 267−302.

(31) Luo, P.; Gu, Y. Effects of asphaltene content on the heavy oil viscosity at different temperatures. *Fuel* **2007**, *86*, 1069–1078.

(32) Barnes, H. A.; Hutton, J. F.; Walters, K. *An Introduction to Rheology*; Elsevier Inc.: San Diego, CA, 1989.

(33) Crude oil characteristics; Enbridge Pipelines Inc.: http://www.enbridge.com/pipelines/about/operatingPipeline/crude-oil.php.

(34) Zhao, B.; Shaw, J. M. Composition and size distribution of coherent nanostructures in Athabasca bitumen and Maya crude oil. *Energy Fuels* **2007**, *21*, 2795–2804.

(35) Zhang, Y.; Takanohashi, T.; Sato, S.; Saito, I.; Tanaka, R. Observation of glass transition in asphaltenes. *Energy Fuels* **2004**, *18*, 283–284.

(36) Zhang, Y.; Takanohashi, T.; Shishido, T.; Sato, S.; Saito, I.; Tanaka, R. Estimating the interaction energy of asphaltene aggregates with aromatic solvents. *Energy Fuels* **2005**, *19*, 1023–1028.

(37) Cox, W. P.; Merz, E. H. Correlation of dynamic and steady flow viscosities. *J. Polym. Sci.* **1958**, *28*, 619–622.

(38) Erno, B. P.; Chriest, J. R.; Wilson, R. C. Depth-related oil viscosity variation in Canadian heavy oil reservoirs. *J. Can. Pet. Technol.* **1991**, *30* (3), 38–41.

(39) Steinborn, R.; Flock, D. L. The rheology of heavy crude oils and their emulsions. *J. Can. Pet. Technol.* **1983**, *22* (5), 38–52.

(40) Henry, D.; Fuhr, B. Preparation of bitumen from oil sand by ultracentrifugation. *Fuel* **1992**, *71*, 1515–1518.

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