

URTeC 1619821

## Rheological and Chemical Properties of Alaska Heavy Oils

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This paper was prepared for presentation at the Unconventional Resources Technology Conference held in Denver, Colorado, USA, 12-14 August 2013.

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### Summary

The goal of this project was to improve recovery of Alaskan North Slope (ANS) heavy oil resources in the Ugnu formation by improving our understanding of the formation's vertical and lateral heterogeneities via fluid and rock characterization. Although the reserves of heavy oil on the North Slope of Alaska are enormous (estimates are up to 10 billion barrels in place), difficult technical and economic hurdles must be overcome to produce them. The Ugnu formation contains the most viscous, biodegraded oils and standard production methods are ineffective.

Heavy oils are viscoelastic fluids. Thus, it is critical that we understand the properties of the heavy oils we are trying to produce before the geophysical model and modeling plan can be completed. The Ugnu oils (including more than 18 oil, oil/sand, oil/water, and oil/sand/water mixtures) exhibited non-Newtonian characteristics, including shear thinning and a non-zero shear modulus. The complex viscosity of the dead oils has been found to be as high as 7,000 Pa·s and a shear modulus at -10°C above 10,000 Pa (and frequency dependent). A complete set of "live" oil rheology experiments were completed. A large range of temperatures (-10 to 60°C) and pressures (15 to 2000 psi) were controlled and viscosity measured in novel high-pressure rheology setup.

Saturate-Aromatic-Resin-Asphaltene (SARA) fractions have been measured on site and by an outside laboratory. The SARA technique has large experimental variation when used to measure heavy oils. Asphaltene content varied from 3 to 9% in the same sample measured by CSM and an outside laboratory. A large number of experiments have been completed, including molecular beam mass spectroscopy (MBMS), optical and scanning electron microscopy, and other techniques not reported here. Chemistry signatures from the MBMS and SARA have been correlated with the viscosity of the heavy oils.

#### Technical Contributions:

1. Live oil viscosity measurements completed on Alaska heavy oils
2. Detailed chemical characterization can lead to correlation between chemistry and viscosity of heavy oils

## Introduction

The production of unconventional oil/bitumen has grown continuously in recent years. Estimates of more than 80 % of the total world oil reserves are heavy oil, extra-heavy oil, and bitumen [1-3]. Enormous Alaskan heavy oil reserves are of significant interest for the US economy. Difficult technical, economic, and environmental aspects are involved in producing the Alaskan heavy oil due to high viscosity, high asphaltene and heteroatom content, low reservoir temperatures, deep permafrost line, and relatively shallow burial depth.

Among Alaskan oil formations, the Ugnu formation on the North Slope contains 7 to 10 billion barrels of oil in place, which is the most viscous (viscosity up to 1000 Pa·s), biodegraded (relatively high amount of N, S, O, heavy metals, and asphaltenes), and, hence, the heaviest (specific gravity of 7 to 12 °API) [4,5]. The Ugnu formation is quite cold with temperature of 45 to 65°F and shallow with 2400 to 3000 ft depth and 1300 psi reservoir pressure. Unconsolidated sands of the Ugnu formation create potential problems of sand control, handling and disposal. Thus, standard production methods will be ineffective and an enhanced oil recovery (EOR) technology will be required. Various non-traditional and more expensive methods can be applied for Ugnu oil extraction, such as cold heavy oil production with sand (CHOPS), steam assisted gravity drainage (SAGD), and other EOR methods. Therefore, in order to simulate the real situation in the process of heavy oil production, accurate chemical and thermophysical properties of oil fluids (dead and live oil, oil/water/sand mixtures) are required for the development of efficient oil production and transportation on the North Slope. For example, high temperature transport properties are extremely important for future development of thermal oil recovery, which may be an efficient production scheme in the arctic environment; or, detailed knowledge of heavy oil constituents could potentially provide ways of predicting oil properties from its chemical composition and vice versa, and lead to discover more efficient surfactants, catalysts, processing conditions for upgrading, refining, and environmental protection.

In this work, we present viscosity measurements for Ugnu oil fluids (including more than 18 oil, oil/sand, oil/water, and oil/sand/water mixtures) across a wide range of pressures and temperatures, analysis of components in heavy oils using pyrolysis molecular beam mass spectrometry (MBMS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and nuclear magnetic resonance (NMR). We attempt to make an improvement in heavy oil chemical-physical property correlations based on the resulted data.

## Methods

**Materials.** Two heavy oil samples from the Ugnu formation (S pad, Milne Point field) donated by BP were studied: MPS-37 (specific gravity of 11.4°API and water content of 3.15 wt%) and MPS-41 (specific gravity of 12.9°API and water content of 0.64 wt%) collected and separated from sand in January 2009 and August 2011, respectively. The densities were measured by an Anton Paar DMA 4500 density meter. The water content was measured with a Mettler Toledo V20 volumetric Karl Fisher titrator. In addition to these two samples, ten MPS-37 heavy oil samples taken in September 2008 from one production well and named by the day of production (D#1, D#2, etc.) were analyzed to study the variability of produced oil. The latter samples may contain residual sand.

In order to correctly reproduce oil + sand mixtures, sand was separated from Ugnu oil sands (donated by BP) obtained from the produced Ugnu oil after recovery. Goo Gone, a commercial cleaner, was applied to remove residual oil. Rinsing the clean sands in ethanol and drying completed the cleaning process. The particle diameter measurements (Figure 1) were performed using an Olympus IX81 Motorized Inverted Microscope (sand grains suspended in mineral oil) and an FEI Quanta

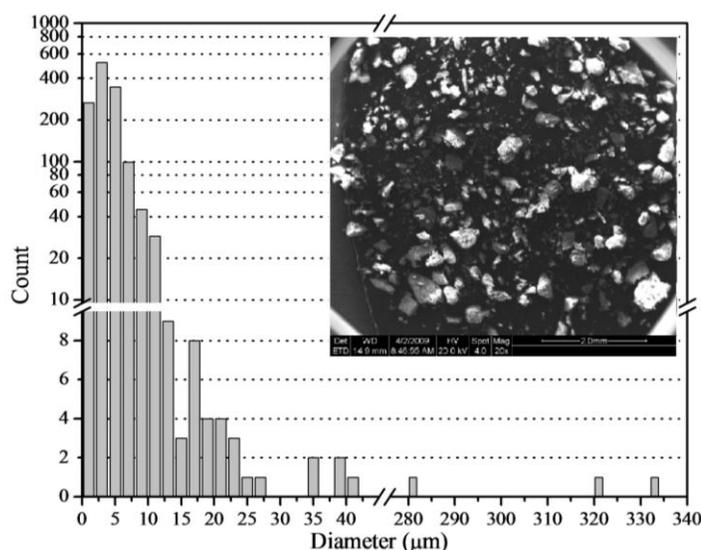


Figure 1. Size distribution of Ugnu sand grains from optical microscopy and electron microscopy (insert)

600 environmental scanning electron microscope (high vacuum mode). Despite of the different state of sand (wet and dry), there is no difference between the results of diameter distribution by these methods. The particle-number and mass averaged diameters are 5  $\mu\text{m}$  (standard deviation of 15  $\mu\text{m}$ ) and 41  $\mu\text{m}$  (standard deviation of 114  $\mu\text{m}$ ). The Princeton Gamma-Tech Prism energy dispersive X-Ray spectrometer (EDX) tested the elemental composition of the Ugnu sand in parallel with the electron microscopy: the clean sand grains consist of almost pure silica ( $\text{SiO}_2$ ) with a trace amount of alumina ( $\text{Al}_2\text{O}_3$ ). Hence, the Ugnu sand will be considered as pure silica in this work.

Oil/water/sand mixtures were prepared using either a VIRTIS mechanical homogenizer for 2 hours at  $\sim 200$  rpm at room temperature (for ambient pressure measurements) or in a Parr Instruments 4560 Mini Stirred Reactor for 30 min at  $\sim 1000$  rpm at room temperature (for high pressure measurements). No visual phase separation was observed during preparation procedures.

**Rheology.** Rheological measurements for Ugnu oil samples were carried out using an AR-G2 rheometer (TA Instruments, New Castle, DE) using two different setups. For ambient pressure experiments, a Peltier parallel plate geometry (40 mm diameter, 1 mm gap) designed to work in a wide temperature range from  $-40^\circ\text{C}$  to  $200^\circ\text{C}$  with a temperature accuracy of  $0.1^\circ\text{C}$  was applied. A solvent trap was used to minimize the loss of volatiles and evaporation. For high-pressure measurements, a unique high-pressure rheology setup rated for pressures from ambient to 2000 psi and temperatures from  $-10^\circ\text{C}$  to  $150^\circ\text{C}$  was constructed. A schematic of the high-pressure setup is shown in Figure 2 and detailed in three very recent publications [6-8]. The design uses a high-pressure Couette system with a magnetically driven concentric cylinders geometry (1 mm gap), a stand-alone high-pressure vessel for mixing/saturation, and a high-pressure syringe pump connecting the two vessels.

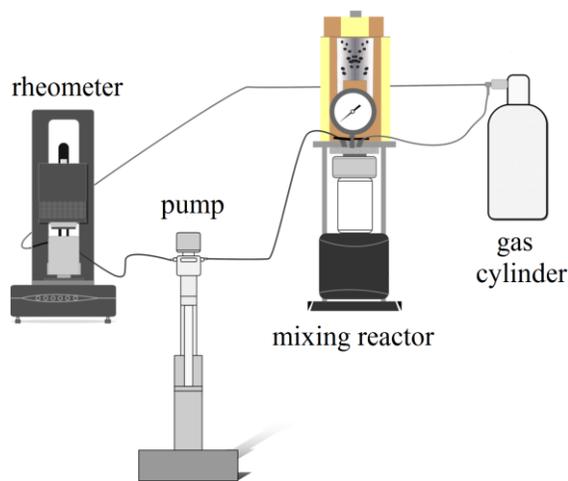


Figure 2. Schematic of the high pressure rheometer system, adapted from [8]

A series of isothermal small amplitude oscillatory (frequency sweep) and/or steady state flow tests were conducted at selected temperatures from  $-10^\circ\text{C}$  to  $60^\circ\text{C}$ , and back to  $20^\circ\text{C}$  (to check for repeatability) in both setups. A stress sweep test was utilized first to determine the linear viscoelastic range. The storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) are then measured over the frequency range of 0.1–100 Hz. Steady state flow tests were performed at a shear rate range from  $0.01\text{ s}^{-1}$  to either  $500\text{ s}^{-1}$  or the shear rate before significant viscous shear heating of the sample starts. The uncertainty of viscosity and modulus measurements was estimated to be better than  $\pm 10\%$ . The repeatability of the rheological measurements was better than 1 %.

**VSARA analysis.** The volatile fraction was obtained by passing nitrogen for 24 h. The asphaltene fraction was determined by precipitation using isooctane. Saturate, aromatic, and resin fractions were further determined using open column liquid chromatography. The procedure is described in detail in [9]. The SARA composition of Ugnu oil samples was then correlated with their viscosity.

**Molecular beam mass spectroscopy.** The type of chemical groups in nine MPS-37 D# Ugnu oil samples was evaluated using molecular beam mass spectrometry (MBMS). A temperature profiling was carried out to facilitate the analysis of such complex chemical mixtures. Ugnu oil samples were placed in a crucible and inserted in a quartz tube with 720 mL/min  $\text{N}_2$  carrier gas. The tube can be heated up to  $750^\circ\text{C}$  using a LabVIEW program controlled tubular furnace. The volatiles generated at any time were then introduced into the custom-built  $10^{-8}$  Torr MBMS analysis chamber, through a pressure reducing nickel nozzle and skimmer via ultrasonic expansion to generate a molecular beam. The MBMS system has an Axial Molecular Beam Ionizer, a  $3/4''$  quadrupole mass filter (1-500 amu mass range), and an analogue conversion dynode multiplier (ABB Inc., Extrel Quadrupole Mass Spectrometry Division, Core Mass Spectrometers). The electron impact energy was 70 eV and the ion flight time in the quadrupole was set to be 10  $\mu\text{s}$ . The resolution is about 2,000 at 400 amu using full width at half maximum peak height. The spectra were reprocessed by subtracting the background spectrum.

Chemical components' mass variables from the MBMS analysis were used as predictor variables (X matrix) and correlated with viscosities (Y matrix) using partial least squares regression analysis (PLSRA) with full cross validation in Unscrambler 9.8 (CAMO Inc). For the X variables, each sample MS data set was the integration of each 500 mass peak over time during the entire heating and cooling process (about 1,200 spectra). Masses were chosen to best represent the molecular information as well as the prediction model. The model was validated by full cross validation, which calculates predicted viscosity of one sample using the data set of rest samples, and all the sample viscosities are repeated this way. The coefficients of determination are a measure of the goodness of fit for the model by comparing predicted viscosities against measured viscosities.

**FT-IR spectroscopy.** The infrared spectra of heavy oils were taken on a Perkin Elmer ATR accessory added in an FTIR instrument (Thermo Fisher Inc.) on top of a thallium bromide (KRS-5) internal reflectance element. The spectra were collected at room temperature from  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ , averaged by 1000 scans at a resolution of  $4\text{ cm}^{-1}$ . A deuterated triglycine sulphate (DTGS) detector was used. Before and after each experiment, the ATR crystal and the holder were wiped clean immediately using acetone to remove the heavy oil, and air dried.

**NMR spectroscopy.** High resolution single pulse excitation (SPE)  $^1\text{H}$  NMR and proton decoupled  $^{13}\text{C}$  NMR experiments were performed on an ECA 500 MHz NMR spectrometer (JEOL Ltd.). Deuterated methylene chloride lock solvent (99.9% purity, Cambridge Isotope Laboratories) was used as a solvent for heavy oil. To separate overlapped structural groups in 1-D broadband NMR spectra, 2-D gradient enhanced double filtered quantum coherence homonuclear shift correlation spectroscopy (DQF-COSY), 2-D C,H-heteronuclear shift correlation spectroscopy (HETCOR), and multi-pulse distortion less enhanced by polarization transfer (DEPT) experiments were performed.

## Results

**Rheology.** The measured complex viscosities (oscillatory test) for two subsamples of MPS-37 heavy oil taken from a single, master container in batches on 22 June 2009 and 08 January 2010, agree well with one another (Figure 3). Since the biggest differences are about 15% at high frequency at  $-10$  and  $60^\circ\text{C}$ , no aging occurs to the heavy oil preserved during at least its half-a-year stay. On the other hand, various samples from different locations and production days have viscosities differing by several times due to difference in chemical composition (Figure 4).

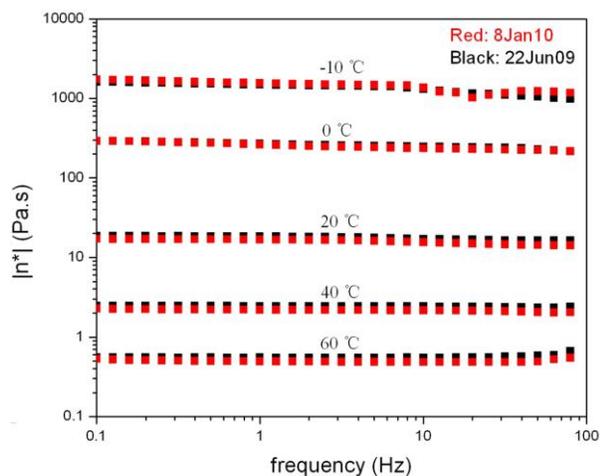


Figure 3. Complex viscosity of MPS-37 as a function of frequency, temperature, and aging

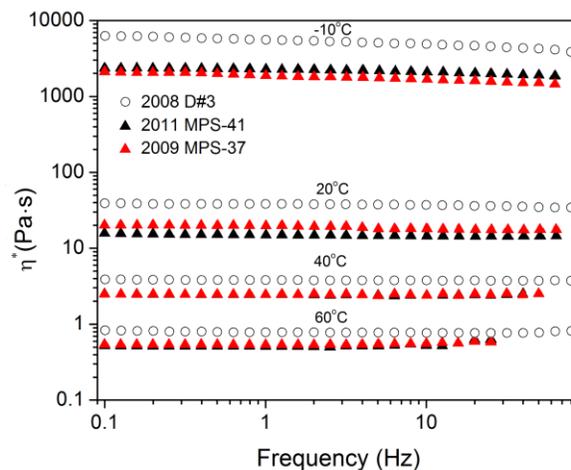


Figure 4. Complex viscosity of various Ugnu oil samples

It is evident from Figures 3-4 that the oils showed Newtonian behavior at temperatures above  $0^\circ\text{C}$ , i.e., no frequency dependence is observed. At lower temperatures, the viscosity slowly decreases with increasing frequency (shear rate), indicating minor shear-thinning behavior. This behavior might be a result of interaction of oil components with ice formed at  $0^\circ\text{C}$  and below.

The complex viscosity of the oils also exhibits a strong dependence on temperature. This behavior is also seen in all ten production day samples (Figure 5). The viscosity versus inverse temperature plot shows a very slight systematic concave behavior, due to secondary interactions in this complex heterogeneous oil. However, to a first approximation and to compare with other values in the literature, a linear correlation between the logarithm of the viscosity and the inverse temperature can be quantified by an Arrhenius type relationship,  $\eta^* = A \cdot \exp(-E_{\text{vis}}/RT)$ , where  $E_{\text{vis}}$  is the activation energy of viscosity, a measure of interaction between components in a fluid. The  $E_{\text{vis}}$  values of the oils ranged from  $85 \text{ kJ}\cdot\text{mol}^{-1}$  to  $92 \text{ kJ}\cdot\text{mol}^{-1}$ . This result agrees well with a previous work by Hinkle et al. [10] providing  $E_{\text{vis}}$  values of  $73 \text{ kJ}\cdot\text{mol}^{-1}$  to  $120 \text{ kJ}\cdot\text{mol}^{-1}$  for a range of heavy oils possessing a large variation in physical properties from a much larger geographical distribution. The higher activation energies of viscosity for heavy oils compared to lighter oils and simple mixtures may be related to higher molecular weight components (e.g., asphaltenes, resins), hydrogen bonding, or other molecular interactions.

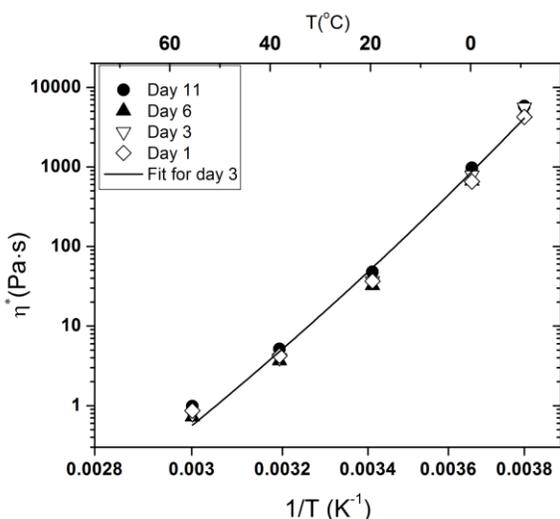


Figure 5. Temperature dependence of complex viscosity of MPS-37 D# samples, adapted from [11]

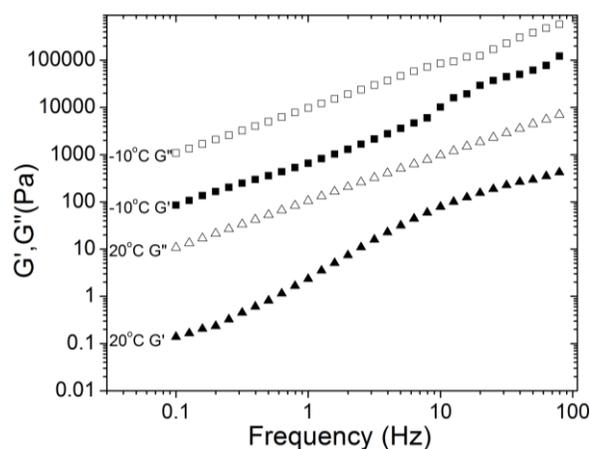


Figure 6. Storage and loss moduli for MPS-41

In parallel to the complex viscosity measurements, storage and loss moduli ( $G'$  and  $G''$ ) were determined (Figure 6). The oils exhibit a certain degree of viscoelasticity diminishing with temperature. However, even at the lowest studied temperature ( $-10^\circ\text{C}$ ), the loss modulus is higher than the storage ones, indicating that the viscoelastic response of the fluid is dominated by the liquid-like contribution. No gel point has been reached for any of the studied sample.

Although the ten MPS-37 D# samples were collected over a two week period, the difference in viscosity reaches two times at the same temperature. The samples have water content ranging from 1 wt% to more than 15 wt%, which can contribute to such a difference (Figure 7, nine samples are reported in the figure). Although the dependence on water content is not regular, the trend is still traceable, i.e. viscosity increases with increasing water content. However, other factors should be also considered: different chemical composition of the matrix oil, different amount of residual sand, etc. In order to separate the influence of sand, water, and their interaction, rheological measurements for a set of 18 oil/sand/water samples with water content varying from 3.5 to 15 wt% and sand content from 0 to 50 wt% were carried out.

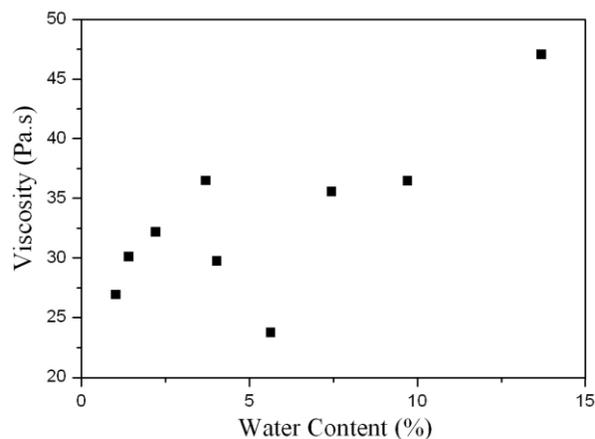


Figure 7. Viscosity vs water content for MPS-37 D# samples at  $20^\circ\text{C}$

Since all 18 oil/sand/water samples exhibit shear thinning behavior, the frequency dependent data ( $\eta^*$  vs.  $f$ ) were treated using a power law Ostwald model,  $\eta^* = Kf^{-m}$ , where  $K$  is the consistency coefficient (i.e. complex viscosity at 1 Hz),  $m$  is the shear thinning degree. If the fluid is Newtonian,  $m = 0$ ; the more shear thinning the fluid is, the greater  $m$  is observed. The power law was successfully applied to all 18 samples. The results are shown in Figure 8 and 9. The regression coefficient was more than 0.99 in all cases.

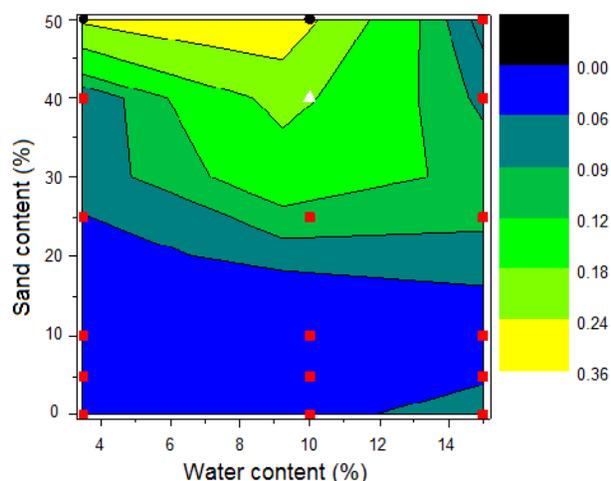


Figure 8. Contour of shear thinning degree  $m$  as a function of sand and water contents at 20°C for MPS-37

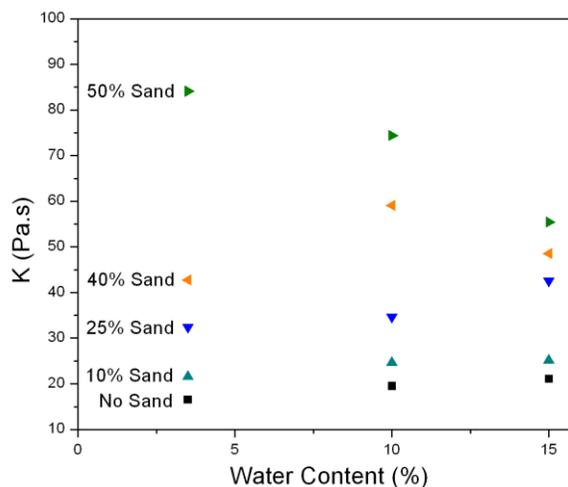


Figure 9. Consistency coefficient  $K$  as a function of sand and water contents at 20°C for MPS-37

The samples' viscosities show obviously high positive dependence on sand content, with the strength of the dependence decreasing as the water content increases, because water acts like a kind of lubricant between sand and oil, thus the resistance caused by sand is lowered by adding water. The influence of water on the oil viscosity is weak and variable: in the absence of sand, the viscosity of water-in-oil emulsion increases with water content; in the presence of sand, two opposite factors compete – water-wettability of sand and lubrication ability of water. The shear thinning degree also changes with water and sand content but in a complicated way. At low to middle sand contents (0 – 25 wt%), the shear thinning degree either increases or keeps on the same low level with water content. At higher sand contents, the shear thinning degree increases with water content at first, but then decreases dramatically. On the other hand, the dependence of  $m$  on sand content is simpler: it does not change a lot as the sand content increases from 0 to 25 wt%, and then increases dramatically from 25 to 50 wt%, except for the case of 15 wt% water content, where the shear thinning degree does not change a lot with the sand content. A hypothesis is that once frequency rises, different components may respond at different rates. Such a difference could decrease intermolecular interactions and forces, and finally drop the viscosity.

To provide data for simulating realistic behavior of Ugnu oil in situ, viscosity of MPS-41 saturated with methane was measured at temperature from 0°C to 60°C and pressure from 15 psi to 1800 psi (Figure 10). Under all saturated conditions, the oil behaves as a Newtonian fluid. Both temperature and pressure have a drastic impact on the Ugnu oil viscosity. The pressure effect consists of two contributions: oil matrix compression (2-time increase in viscosity from  $p_{\text{atm}}$  to  $\approx 1600$  psi) and methane dissolution (40-time decrease in viscosity from 0 to 100 % saturation at  $p \approx 1600$  psi). Hence, methane serves as an efficient thinning agent. The magnitude of the viscosity drop with temperature is the same as for dead oil samples – 3 orders of magnitude from 0°C to 60°C. Moreover, when all isopleths (iso-compositional curves) for Ugnu oil are plotted in a single viscosity vs  $T$  graph, they appear to follow a single master curve with appropriate shifts along the  $T$ -axis ( $\Delta T_{\text{shift}}$  depends on the saturation pressure of an isopleth).

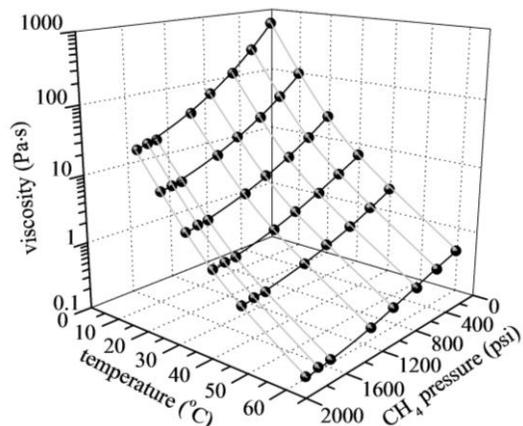


Figure 10.  $p, T$ -dependence of methane saturated Ugnu oil: black lines, isotherms; grey lines, isopleths (constant liquid concentration), adapted from [8]

Based on the above observations, a two-variable pressure-temperature correlation based on Antoine-type temperature equation, the Henry-law solubility equation, and pressure dependent shift  $\Delta T_{\text{shift}}$  (6 fitting parameters altogether) was developed for “live” Ugnu oil and fit the experimental data in Figure 10. The results of the fit are shown in Figure 11. The average relative deviation of the fit is 2.4 %. The average enthalpy of solution of methane in the Ugnu oil was estimated to be  $-2.0 \pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$ , which is in agreement with literature data [12]. More details about the developed  $p,T$ -correlation can be found elsewhere [8].

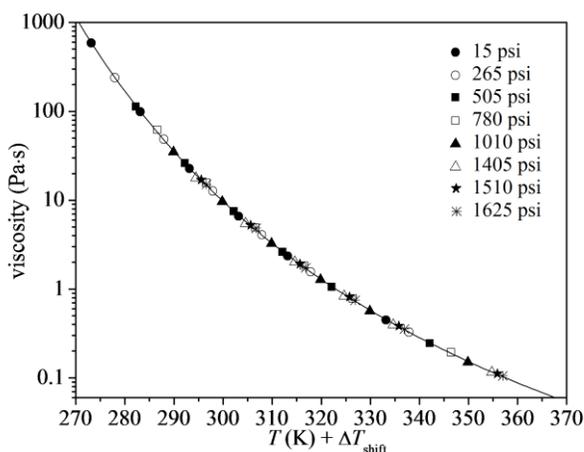


Figure 11. Temperature dependence of viscosity of Ugnu oil with isopleths shifted by  $\Delta T_{\text{shift}}$  (dependent on saturation pressure and determined from the  $p,T$ -correlation) along  $T$ -axis, adapted from [8]

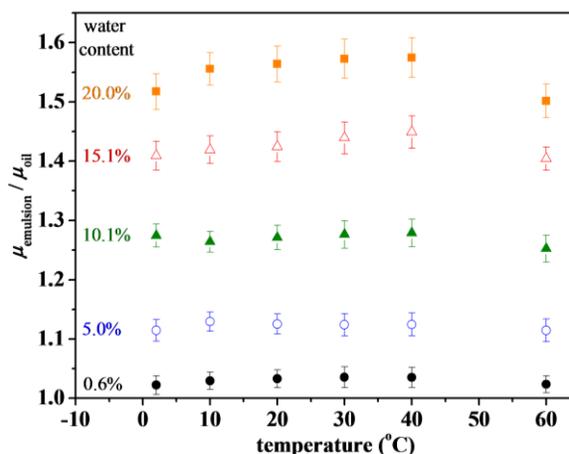


Figure 12. Temperature dependence of relative viscosity of “live” Ugnu oil + water emulsions at different mass fractions of water at pressure  $p_{\text{ref}}=1520 \text{ psi}$ , adapted from [8]

The viscosity for methane saturated Ugnu oil + water emulsions with 0.6 wt% to 20.0 wt% of water (water-in-oil type) at different temperatures from 2°C to 60°C was measured (Figure 12). These emulsions exhibit a Newtonian behavior. The relative viscosity (relative to viscosity of pure oil) of the emulsions increases linearly with increasing water concentration and remains constant with increasing temperature up to 40°C. The deviation at higher temperatures may be attributed to some of the water phase separating. Although possible in the timescale of days, hydrate formation at temperatures below 13°C (thermodynamic hydrate formation temperature at 1500 psi [13]) did not interfere with the rheological measurements for the emulsions.

*Chemical analysis.* It has been established that besides SARA composition it is important to determine the amount of volatiles that are lost during passing nitrogen through the sample for drying (up to 40 wt% for MPS-37 samples). Hence, the SARA composition should not be normalized to the corresponding “dry” sample, but rather VSARA composition should be reported. The repeatability of VSARA measurements were determined to be better than 5%. Parallel measurements for the same oil sample were made in our laboratory and in a commercial lab. The result comparison revealed the following: the total amount of small molecules (saturates + aromatics) and the total of heavy fractions (resins + asphaltenes) are similar, but separation of saturates from aromatics, and resins from asphaltene gives the relative deviations up to 30%. There are several potential sources of such data variation: (1) commercial labs usually normalize SARA composition to 100%, while SARA total fraction from our lab includes volatiles; (2) different solvents are used (iso-octane or heptane for saturates, benzene or toluene for aromatics).

VSARA fraction percentages vary greatly among the ten different oil samples from the same well (MPS-37 D#), which represents the heterogeneity of reservoir fluid chemical composition: volatiles – from 7 to 37 wt% (including water ranging from 1 to 14 wt%), saturates – from 20 to 35 wt%, aromatics – from 22 to 36 wt%, resins – from 8 to 20 wt%, and asphaltenes – from 6 to 13 wt%. Numerous publications exist trying to correlate viscosity with asphaltene and/or asphaltene + resin concentration in heavy oils [10, 14]. Figure 13 shows our attempt to find any correlation of this kind for Ugnu oil. However, it is obvious that no such correlation can be established mainly due to large variation in other parameters, such as water content and volatiles, which generally effect heavy oil viscosity in opposite directions (Figure 14): water increases viscosity of oils due to formation of emulsion as it was observed for live Ugnu oil (Figure 12); volatiles normally decrease oil viscosity, since the fraction consisting of rather small molecules serves as a diluent media for heavier molecules.

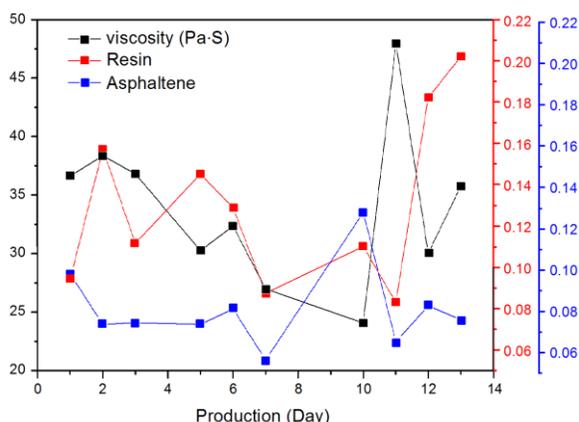


Figure 13. Viscosity versus asphaltene and resin fractions for MPS-37 D# samples

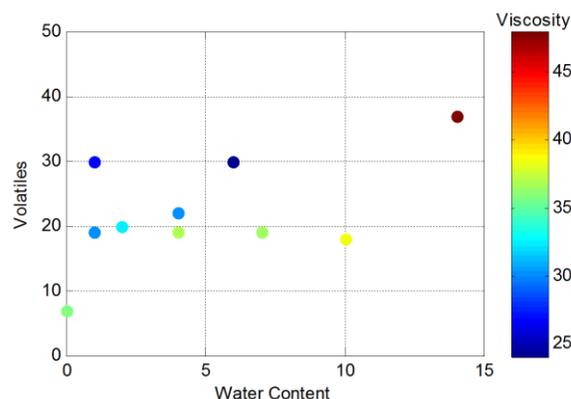


Figure 14. Viscosity versus volatiles and water fractions for MPS-37 D# samples

Further chemical analyses (FT-IR, NMR, and MBMS) have been conducted on nine MPS-37 D# Ugnu samples, since the amount of the 10<sup>th</sup> sample was not enough for this study. In general, FT-IR spectra of the samples (Figure 15) are similar in peak shape and peak locations. The FT-IR for samples dried overnight in air showed no change in peak locations or intensity. The spectral analysis showed the presence of the following possible functional groups and organic classes existing in the heavy oil: water, alkyl chains, phenyl rings, polycyclic and metalloporphyrin fragments, amino, hydroxyl, carboxyl, carbonyl, sulfide, and sulfinyl/sulfonyl groups.

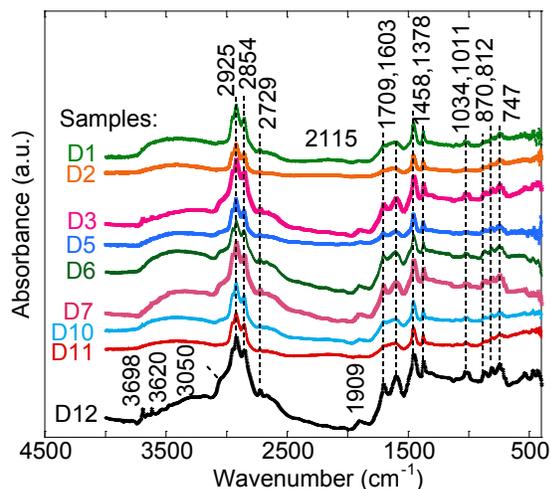


Figure 15. ATR-FT-IR spectra of nine MPS-37 D# samples, adapted from [11]

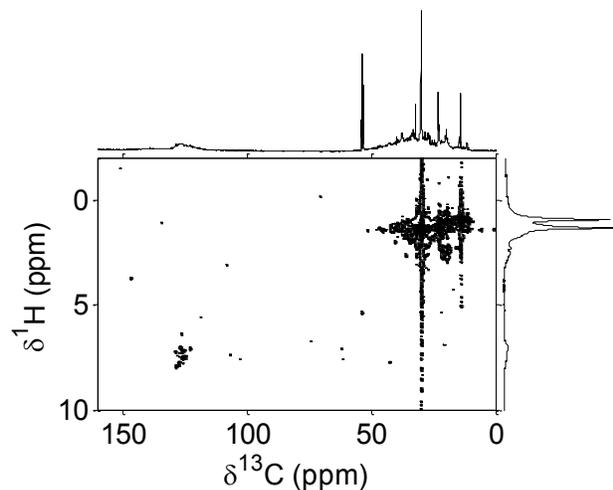


Figure 16. <sup>13</sup>C-<sup>1</sup>H HETCOR NMR of MPS-37 D#3 heavy oil sample, adapted from [11]

Due to the overlapping of thousands of compound peaks, 2D <sup>1</sup>H-<sup>1</sup>H COSY, <sup>13</sup>C-<sup>1</sup>H HETCOR, and DEPT (J-coupling values of 135, 140, and 145 Hz) NMR spectra were used to improve the proton and carbon chemical shift assignments. Figure 16 shows an example of <sup>13</sup>C-<sup>1</sup>H HETCOR NMR spectra. The assignment for the <sup>1</sup>H and <sup>13</sup>C chemical shift peaks was performed by comparing the chemical shifts with reference spectra. It is consistent with the FT-IR that saturated and non-saturated, branched and normal alkyl and aromatic groups exist in the heavy oil. However, the absence of peaks in the certain regions of <sup>1</sup>H and <sup>13</sup>C projections rules out many compounds although they are reasonably possible from the FT-IR spectra assignments, such as pyridine-type molecules, alkynes, alcohols, carbonyl/carboxyl, nitrile, nitro, amino groups, etc. These compounds might exist in the heavy oils, but probably do not have a large enough concentration above the NMR detection limit.

Each pyrolysis MBMS analysis consists of several hundred scans of 500 atomic mass units (amu) collected over a heating profile taking 10 min. Due to the small window of the detector and the way of desorption method, higher mass or boiling point molecules such as asphaltenes are out of detection, which is the limitation of this MBMS instrument. After heating up to 750 °C, up to 10 wt% of ash and flocculent residuals were left in the crucible after the experiment, which are minerals, bitumens that have higher pyrolysis and vaporization temperatures, or coking products. Nevertheless, the fast, reliable, and myriad mass spectra still give valuable chemical information.

All the oils showed similar MBMS spectra. Figure 17 shows chromatograms for the most abundant ions for MPS-37 D#3 sample. Depending on the water content in the sample, the low temperature region of the chromatogram can be complicated by the presence of water clusters. On the other hand, high temperature spectra can include products from pyrolysis, consequently, that region was excluded from the analysis. With the assistance of FT-IR and NMR, a set of possible molecules deduced by MBMS spectra for vaporized heavy oil molecules was compiled based on the probability based matching (PBM) method. The set includes normal and branched alkanes, alkenes, alkadienes, alicyclic and aromatic compounds, phenyl sulfides and disulfides, thianthrene, phenanthrene.

Figures 18-19 show the result of PLSR analysis using the collected MBMS masses to predict the correlation between the heavy oil compounds and the viscosities as discussed above. Only the evaporated components detected by the MBMS can be used as the basis, which potentially introduces error due to not including the residual fractions. The viscosity values are in a small range, but correlate with significant mass variants selected from the ion masses for the set of identified molecules. This indicates the potential for time resolved pyrolysis MBMS (with/or without FT-IR) to be a more reliable and faster predictor of heavy oil viscosity than SARA. The root mean square error (RMSE) for the validation is 3.0 for the sample data and 5.0 for the predicted value. More details about the PLSRA and the set of molecular species in the heavy oil can be found in our previous publication [11].

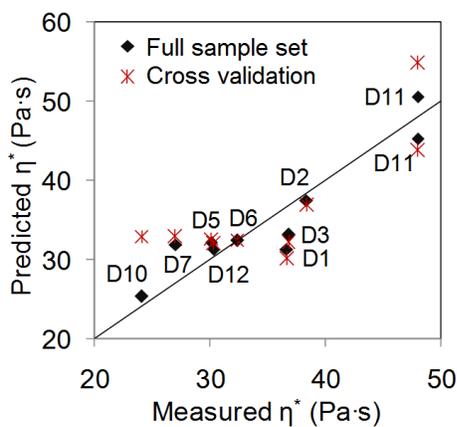


Figure 18. Measured viscosity of nine MPS-37 D# samples (D#11 was measured twice) at 20°C and 1 Hz versus PLSRA model predicted viscosity values, adapted from [11]

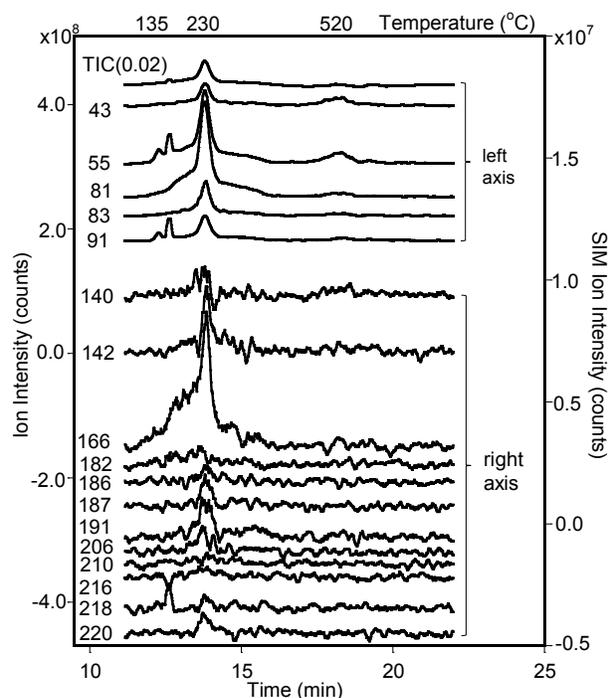


Figure 17. Total ion chromatograph (TIC) and selected ion masses (SIM) for Ugnu heavy oil MPS-37 D#3, adapted from [11]

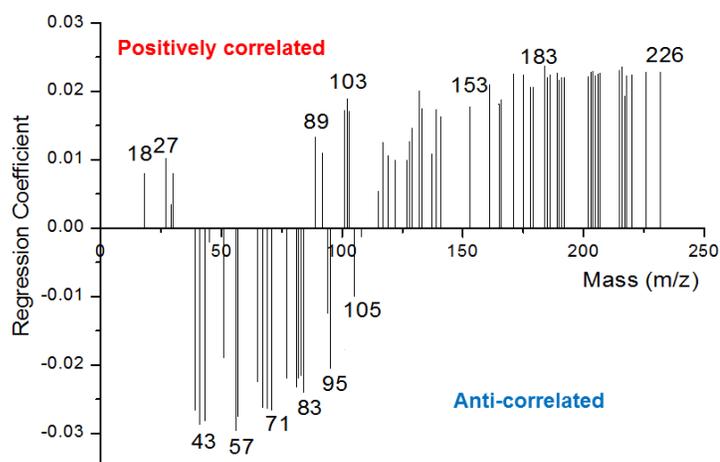


Figure 19. Correlation coefficient of MBMS variables with viscosities from PLSRA, adapted from [11]

Masses with a positive regression coefficient are positively correlated with viscosity on the first principle component (77% sample data validated), which corresponds to water, alkylbenzene, thianthrene, etc. Masses with negative regression coefficient are anti-correlated on the viscosity values, which corresponds to the saturated and unsaturated aliphatic components in the heavy oil. The conclusion about the influence of water on oil viscosity is consistent with the direct rheological observations shown above.

## Conclusions

The presented research provided a deeper insight into a large variety of factors influencing transport properties of Alaskan heavy oil, which is crucial for development and optimization of production schemes in the north environment.

## Acknowledgements

The authors greatly appreciate financial support provided by the U.S. Department of Energy, DE-NT-0005663, and collaboration between CSM and Earthworks, and the Department of Geophysics at the University of Houston. BP is thanked for providing the heavy oil samples.

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