Correlating the Chemical and Physical Properties of a Set of Heavy Oils from around the World

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Abstract

Variations in the viscosity and other physical properties of heavy oils are poorly understood. The viscosities measured for different heavy oils can vary by orders of magnitude even at the same API gravity, which is the standard metric for lighter oils. Heavy oils are viscoelastic materials, and the shear modulus and the viscosity are coupled. Understanding what controls heavy oil viscosity will provide insight into what controls heavy oil shear modulus. Therefore, using rheology, ultrasonic measurements and molecular beam mass spectroscopy (MBMS) the physical and chemical properties of seven heavy oils from around the globe are explored. The viscoelastic nature of the oils is quantified as a function of temperature. Overall, the heavy oil samples show little correlation between the viscosity or shear modulus and the API gravity, separate resin content or separate asphaltene content as measured from SARA analysis. However, the total resin plus asphaltene content collapses the viscosity and modulus values to provide empirical relations between these quantities. Also, a partial least squares regression analysis provides tight correlations for the chemical signatures from the MBMS. The rapid and quantitative nature of the MBMS make it an attractive substitute for the inconsistencies endemic to SARA analysis.

Keywords: heavy oil, viscosity, MBMS

1. Introduction

Heavy oil has recently become an important resource as conventional oil reservoirs have limited production and oil prices rise. More than 6 trillion barrels of oil in place have been attributed to the world's heaviest hydrocarbons [1]. Therefore, heavy oil reserves account for more than three times the amount of combined world reserves of conventional oil and gas. Of particular interest are the large heavy oil deposits of Canada and Venezuela, which together may account for about 55-65% of the known <20 degree API (American Petroleum Institute) oil deposits in the world [1].

Heavy oils cover a large range of API gravities, from 22 degrees for the lightest heavy oils to less than 10 degrees for extra-heavy oils. This wide range of values means that heavy oils vary greatly in their physical properties. Thus, extensive research is required before the properties of heavy oil can be properly understood. Several prevailing issues are seen repeatedly in various fields around the world including how to make measurements on unconsolidated sandstone cores, production of sand with oil and its effect on the formation, exsolution gas drive of heavy oil, understanding the controls on the viscosity and other physical properties of heavy oils, and monitoring of steam recovery processes. Simply, the high viscosity of heavy oils limits its extraction by traditional methods.

Two important distinctions must be made between API gravity and viscosity. First, viscosity determines how well oil will flow while density more closely relates to the yield from the distillation. Additionally, temperature and paraffin content have a large effect on viscosity values while API density is relatively unaffected by these parameters [1]. Heavy oils usually begin as lighter oils (30 to 40 degrees API) which were then altered, often by biodegradation.

Argillier et al. (2001) conducted a rheological study of several heavy oils and concluded that the asphaltene content was a controlling factor for viscosity [2]. Their data indicate that when the asphaltenes passed a critical weight fraction (around 10%), viscosity increased dramatically. They speculate that the long asphaltene chains begin to conglomerate and tangle. In contrast, increased resin content actually decreased viscosity. However, a recent analysis by Hossain et al. (2005) found no strong viscosity correlation with asphaltene content [3]. Since viscosity is correlated with shear modulus for heavy oils, it partly controls our seismic velocities. The influence of asphaltenes and resins will be examined more thoroughly this work.

Previous reports identify variations in asphaltenes content as the primary determinant for the large spread of viscosities observed in heavy oils [2, 4, 5]. If asphaltene concentration determines heavy oil viscosity, it should also directly relate to the heavy oil shear modulus. Here, a comprehensive suite of measurements on seven heavy oil samples from around the world address the chemical and physical properties of heavy oils in the context of the solubility classifications, such as asphaltenes and resins. A rapid screening technique for alternative hydrocarbons is needed to be more rapid, reliable and meaningful than the traditional Saturate-Aromatic-Resin-Asphaltine (SARA) analysis [6]. Pyrolysis-Molecular Beam Mass Spectrometry (Pyrolysis-MBMS) has been shown to be a method that can rapidly generate large data sets of chemical information on complex substances [7-10]. Pyrolysis-MBMS can be optimized to crack and volatilize the entire sample in a few minutes leading to chemical information much more rapidly than Nuclear Magnetic Resonance (NMR) or SARA analysis. Furthermore, as the entire sample is introduced into the MBMS, the chemical information can be correlated with bulk properties of the original oil. When the MBMS is correlated with the signature of a particular species or class of molecules, in this case ashpaltenes, it becomes a very powerful predictive tool. Rheometric, ultrasonic and MBMS measurements will lead to a predictive tool correlating chemical signatures to the viscosity and shear modulus of heavy oils.

2. Experimental

2.1 Heavy Oil Samples

Heavy oil is defined by the US Department of Energy as having API gravities that fall between 10.0 degrees and 22.3 degrees [11]. Extra-heavy oils are defined as having API gravities less than 10.0 degrees API. Heavy oils are classified as such using API gravity rather than viscosity values. API gravity can be expressed in the following way:

$$API = \frac{141.5}{\rho_f} - 131.5\,, \qquad \textbf{(1-1)}$$

where ρ_f is the specific gravity of the fluid at 0.1 MPa and 15.6 C.

Heavy crude oils are often characterized geochemically using a process called SARA fractionation. The crude oil can be separated into four components based on solubility classes. These four components are saturates, aromatics, resins, and asphaltenes. Heavy oils tend to be rich in the high molecular weight components, which are resins and asphaltenes. Unfortunately, there are numerous issues that render the SARA fractionation problematic [6]. Procedures used within testing laboratories vary widely. Normally, resins are the fraction soluble in pentane but insoluble in propane. Asphaltenes dissolve in solvents such as carbon disulfide, but various laboratories precipitate the material in different light alkanes. Some use pentane, others use heptane, still others use iso-octane. The molecular weight of these fluids used has been shown to have a major influence on the results [6]. In addition, the techniques used to wash and filter the precipitants also varies significantly. To reduce some of these variabilities, all of our analyses were performed at a single commercial laboratory. Still, variations in reported values of resins or asphaltenes for any single oil can easily vary by 10 percent.

Seven heavy oil samples are investigated here: three samples from Canada, one sample from Venezuela, one Alaskan sample (Ugnu), one Utah sample (Asphalt Ridge), and one west Texas sample (Uvalde). SARA analysis was performed for all of the samples by Humble Geochemical (Table 1). The fluid densities were determined by dividing mass by volume of the heavy oils. The Canadian, Venezuelan, and Alaskan heavy oil was donated from various companies. The Utah and Texas samples came from rocks collected at the outcrop and the oil was extracted. All of the samples were dead oils, or gas-free.

2.2 Rheology

Low frequency viscosity and shear modulus measurements were collected in a range from 0.01 to 100 Hz on a TA Instruments AR-G2 rheometer (New Castle, DE). A small amount of heavy oil (~1.5 mL) is loaded between a Peltier plate and a 40 mm aluminum plate. A sample gap of 1 mm was used for all measurements. Isothermal experiments at temperatures from 0 to 80^{o}C (±0.1^{o}C) were completed. A sinusoidal torsional stress over the frequency range of 0.1 to 100 Hz is applied to the sample and the resulting sinusoidal strain is measured. The shear modulus (G') is the ratio of the stress in phase with the strain to the strain magnitude and the loss modulus (G'') is the ratio of the stress 90 degrees out of phase with strain to the strain magnitude [12, 13]. The complex viscosity is also recorded during a stress sweep measurement. Amplitude sweeps (i.e., a measurement of the moduli as a function of stress at a constant frequency) were recorded for each sample to verify that the sample is in the linear viscoelastic region for the stress sweep measurements.

2.3 Ultrasonic measurements

High frequency shear modulus measurements were collected in a range of 0.5 to 1 MHz using a standard ultrasonic pulse technique. Compressional and shear wave velocities of the material are determined from the travel time of an ultrasonic pulse through the heavy oil. Once the velocities are determined, they can be related to shear and bulk modulus using the following equations:

$$V_s = \sqrt{\frac{G'}{\rho}},$$

$$V_p = \sqrt{\frac{K + 4/3G'}{\rho}},$$

where V_s = shear wave velocity, V_p = compressional velocity, ρ = fluid density, K = Bulk Modulus, and G' =shear (or storage) modulus. It is difficult to differentiate between noise and the shear wave signal above about 20^oC. For this reason, the shear data collected resides in a temperature range between -25 and 20^oC.

2.4 Molecular Beam Mass Spectroscopy (MBMS)

Pyrolysis of the heavy oil samples was carried out to study their chemical composition and correlate chemical information with SARA analysis. A molecular beam mass spectrometer (MBMS) was used to detect chemical species since it allowed direct and real time sampling from the pyrolysis system. All reactions were carried out under atmospheric pressure in a quartz tube reactor. All samples (≅30 mg) were contained in a quartz holder, or "boat", and inserted into flowing, preheated helium carrier gas. The carrier gas, 10 L/min, was introduced through the end of a reactor consisting of a quartz tube with 2.5 cm inner diameter. The reactor was heated by using an electric furnace set at 550°C and coupled to a MBMS for product detection [14, 15]. The residence time of the pyrolysis vapors in the reactor pyrolysis zone was estimated to be about 100 ms, which is short enough to minimize secondary cracking reactions at this temperature. Total pyrolysis time was three minutes. The short timeframe indicates the rapid nature of this method and the potential for screening large number of samples. Vapors exiting the reactor flow through the sampling orifice of the MBMS with subsequent formation of the molecular beam, which provides rapid sample quenching and inhibits condensation and aerosol formation. The MBMS provides universal detection of all sampled products and the molecular beam sampling ensures that representative products from the original molecules are detected [15, 16].

In this work, a mass range of 50-350 amu and ionization energy of 25 eV was used. The pyrolysis-MBMS method of sample analysis is rapid (2-10 min) and can generate data from 100 samples per day depending on analytical conditions. A detailed description of techniques and methodologies is given in previous work [14, 15, 17]. The pyrolysis-MBMS results were used as a basis of multiple predictor variables for least squares regression analysis to build predictive model for geophysical properties of heavy oils such as SARA. Software package used was Unscrambler [18-20]. The partial least squares regression analysis can be viewed as a two-stage procedure. First, the model is constructed using training samples, for which the predictor and predicted variables are known or measured. Next, the model is validated by comparing the predictions against reference values for samples that were not used for model building. After the model is validated, it is used for the prediction of the response variable for unknown samples [18-20]. Detailed description of the analysis is out of scope for this work and only pertinent results will be reported.

3. Results

3.1 Rheology

The measured values of complex viscosity, shear modulus, and loss modulus as collected on the G2 rheometer provide insight into the changing viscoelastic nature of heavy oils as a function of temperature and chemical makeup. As expected, complex viscosity shows a strong dependence on temperature. Viscosity increases orders of magnitude as the temperature is decreased linearly for the Canada 1 heavy oil (Figure 1). The Canada 1 heavy oil is representative of the basic rheological response of the seven oils examined. Also, the viscosity decreases with increasing frequency (i.e., shear thinning) for temperatures below 40°C. At higher temperatures the Canada 1 heavy oil behaves like a Newtonian fluid, i.e., no frequency dependence. Overall, the shear thinning response of the heavy oils is more pronounced at high frequencies and low temperatures.

Since the storage and loss moduli (G' and G'', respectively) are directly related to the complex viscosity, the heavy oil samples exhibit strong dependence on temperature and frequency (Figure 2). The Canada 1 heavy oil again serves as a typical example of the seven oils studied. The moduli increase with both decreasing temperature and increasing frequency. At all temperatures and frequencies examined, the loss modulus is larger than the storage modulus. The larger G'' indicates the viscoelastic response of the fluid is dominated by the liquid-like (or out of phase) contribution to the stress. The coupling of the viscosity and the moduli is further probed using ultrasonic measurements in the next section.

The temperature dependence of all seven heavy oils is clearly demonstrated in an Arrhenius type plot (Figure 3). A linear correlation between the logarithm of the viscosity and inverse temperature is quantified by an Arrhenius type relationship [21], $\eta^* = e^{-E_{vis}/RT}$. The range of viscosity activation energies (E_{vis}) covers 73 kJ/mol (Canada 3 heavy oil) to 120 kJ/mol for (Texas heavy oil). The viscosity activation energy of a fluid can be related to the fluid's heat of vaporization [21] and will be investigated in future work.

The dependence of the viscosity of lighter, conventional crude oils strongly correlates with the API gravity. However, the viscosity of these heavy oils is not dependent on fluid density (Figure 4). Therefore, the next logical step is to correlate the viscosity of the heavy oils to their chemical make up. One chemical control suggested in the literature is asphaltenes content [2, 4, 5]. In order to test this possibility, viscosities for each sample (at 20^{o}C and 1 Hz) were plotted as a function of asphaltenes content (Figure 5). The choice of 20^{o}C and 1 Hz is arbitrary, but the trends seen under this condition hold at other temperatures and frequencies. No apparent correlation between viscosity and asphaltenes is evident. Since asphaltenes do not correlate strongly with viscosity, viscosity was then plotted with respect to resins content (Figure 6). A linear relationship between the logarithm of the viscosity and resin content is possible, but there is one far outlying point. The extremely high viscosity of the Uvalde, Texas heavy oil sample, does not scale with resin content in the same way as the other six oils.

Since the viscosity seems dependent on the resin and asphaltene content, the correlation between the sum of these two heavier chemical components and viscosity may lead to a more definitive relationship. A linear relationship between the log of the complex viscosity and the total resin plus asphaltene content encompasses all seven oils (Figure 7). The empirical relationship represented by the solid line in Figure 7 is $\log(\eta^{*}) = 1.63e^{14.6(wt\%A+R)}$, where wt%A+R is combined weight percent of asphaltenes and resins. The R^2 value for the relationship between viscosity and combined asphaltenes and resins content for the oil samples was 0.95 (Figure 7). The correlation for asphaltenes plus resins is much better than the relationships for asphaltenes or resins alone. Since there is a definitive correlation between viscosity and combined asphaltenes and resins content, the shear modulus from ultrasonic measurements should also depend on combined resins and asphaltenes content.

3.2 Ultrasonic

The correlation of the ultrasonic data with the various chemical components of the SARA analysis is analogous to the rheological studies in the previous section. In general, the shear modulus measured for these oils ranges from 0.2 to 0.9 GPa at $-7^{o}C$. Additionally, the measured shear modulus of the Canada 1 heavy oil increases by six times as the temperature is decreased $30^{o}C$, which is analogous to Figure 1 from the rheology section. Reproducible measurements were not obtained for two samples, Canada 2 and Canada 3 and thus are missing from this discussion. Again, the property of interest, shear modulus in this case, was plotted as a function of API gravity, resin content and asphaltene content with little or no correlation between the measured heavy oils. For brevity, these plots are omitted but are available [22]. However, a power law correlation is observed for these heavy oils when correlated with the total resin plus asphaltene content (Figure 8). The empirical power law relationship for these heavy oils is $Shear Modulus = 0.98x^{0.67}$ where x is the combined weight percent of asphaltenes and resins. The R^2 for this relationship is 0.94.

3.3 MBMS

The chemical analysis of the heavy oils using MBMS provides new insight and convenience beyond the traditional SARA fractionation analysis. An average spectrum from the pyrolysis of selected heavy oil samples, Alaska, Canadian 1, and Texas heavy oils, respectively, provides the raw chemical information from this experiment (Figure 9a, b, c). The short timeframe of typical product evolution as shown in the inserts of Figure 9a, b, c indicates the rapid nature of this method and the potential for screening large number of heavy oil samples for characterization. Simply, the average spectra are very complex and very difficult to identify chemical similarities between the different heavy oils. However, common products for the three heavy oils are found at m/z 57, 71, 85 (saturated alkene fragment ions), m/z 95, 109, 123 and137 (two double bond species), m/z 68, 82, 96, 110, 124, 138, 152, 166 and 180 (one triple bonded fragment ions), m/z 56, 70, 84, 98 and 112 (alkene species) with a systematic 14 amu growth for each group of species. While these similarities between the spectra are observable, there are still differences in other portions of the spectra when comparing different oils. We used these MBMS multivariate data as predictor variables to build a predictive model for SARA properties. If geo-chemical properties can be predicted by running a large number of samples in a short period time using pyrolysis-MBMS, it would be very powerful and convenient characterization tool for heavy oils.

In Figure 10, the result of partial least squares regression using pyrolysis-MBMS to predict one of SARA properties, asphaltenes is shown. Only five samples out of seven samples were used for this analysis as those five samples had duplicates. The correlation coefficient is 0.93. It is notable that with a limited number of samples, it was possible to have a decent predictive model for one of the SARA components from the rapid pyrolysis-MBMS data. In Figure 11, mass variables which were positively and negatively correlated with asphaltenes are shown. Detailed studies of the masses are needed for a more complete understanding of the chemical characteristics of asphaltenes. This analysis proves the rapid screening capability of pyrolysis-MBMS, which could be used for building predictive models for heavy oils in the near future.

4. Conclusions

Heavy oils are viscoelastic materials. The parameters that control heavy oil viscosity will also control heavy oil shear modulus. Chemistry was shown to be essential to understanding variations in viscosity and shear modulus. Previously, the viscosity of heavy oils was often correlated with asphaltenes weight content alone. However, almost all of the published papers studied a single heavy oil sample where saturates, aromatics, and resins contents were constant while asphaltenes content varied [2, 5, 23, 24]. In this work, various naturally occurring heavy oil samples were studied and indicate that viscosity depends on the combined asphaltenes and resin concentration.

In the petroleum industry, viscosity mapping of heavy oil fields is currently based on API gravity measurements. As was demonstrated in this work, and has been reported by other researchers [4], there is no good correlation between API gravity and viscosity for heavy oil. Combined resins and asphaltenes content could be used to better map viscosity variations across heavy oil fields. Combined asphaltenes and resins could also be helpful for predicting shear modulus variations in heavy oil fields.

In addition, pyrolysis-MBMS techniques were demonstrated as a tool for rapid characterization of heavy oil. An empirical relationship was established between MBMS measurements and one of available heavy oil geo-chemical measurements, asphaltenes. Results suggest that the MBMS may provide a more consistent compositional analysis than SARA fractionation. In addition, with more complete calibration to establish more robust relationships, a model using MBMS data could be developed to predict viscosity and shear modulus for heavy oils for which no data is available is possible. In closing, the merging of field measurements with the extracted fluid properties is the subject of current research with the objective of identifying more efficient and effective methods for economic extraction of the abundant heavy oil resource.

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Table 1. Properties of seven heavy oils

Sample Name	Saturate (wt%)	Aromatic (wt%)	Resin (wt%)	Asphaltene (wt%)	Density (g/cc)	API Gravity
Alaska	23	22	35	18	0.997	10.4
Canada 1	18	33	30	20	1.014	8.09
Canada 2	18	27	27	15	0.991	11.3
Canada 3	15	23	19	10	1.003	9.56
Texas	4	17	37	43	1.119	-5.00
Utah	19	14	46	20	1.000	10.0
Venezuela	19	32	29	18	1.013	8.05

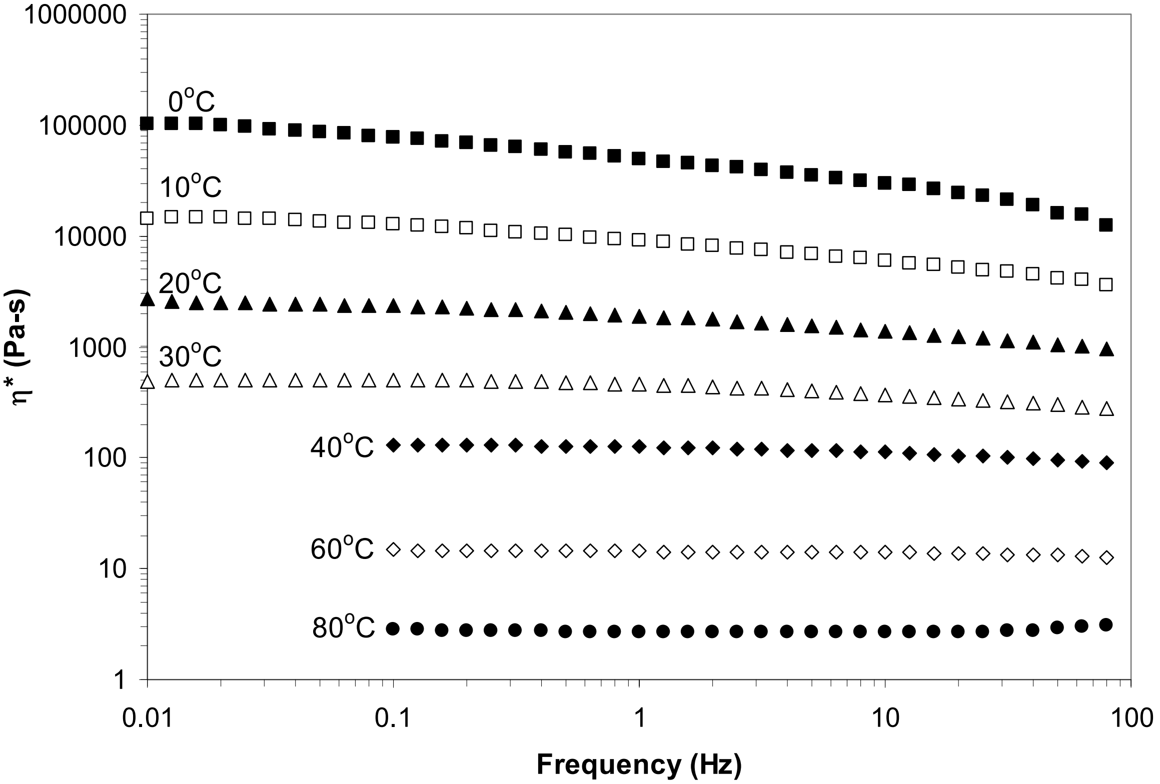

Figure 1. Complex viscosity as a function of frequency at various temperatures for Alaska heavy oil.

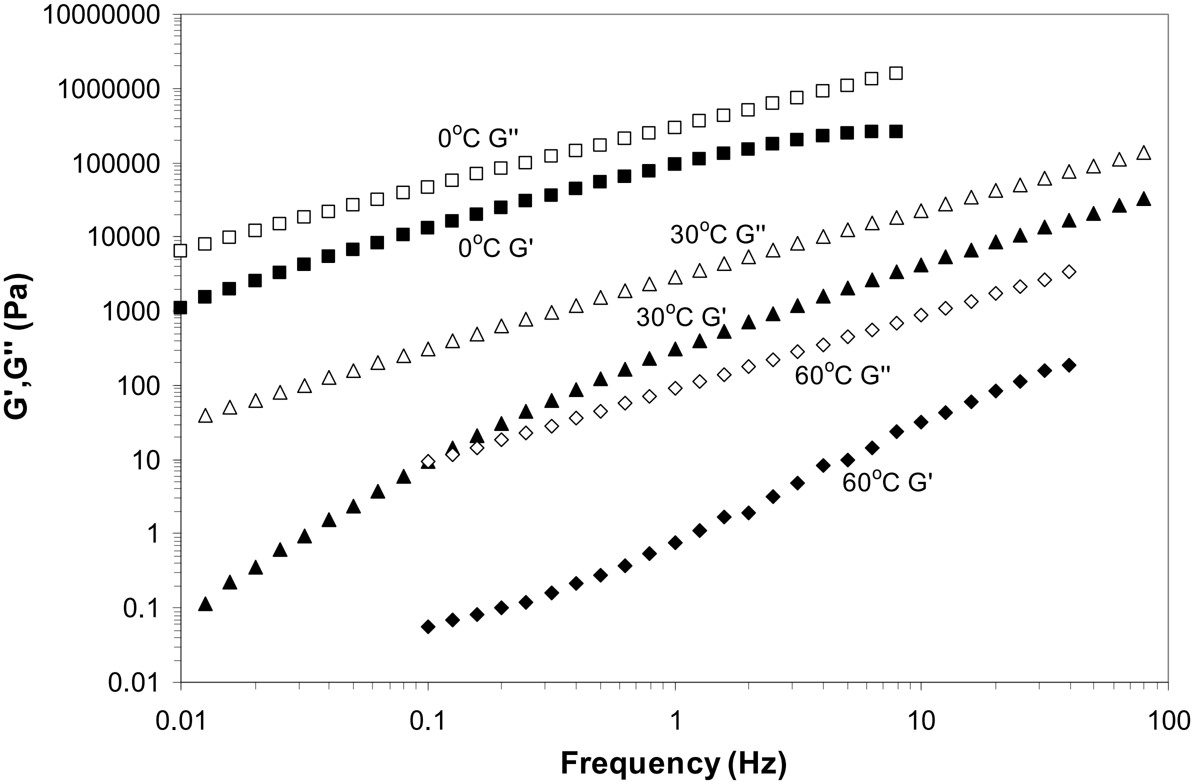

Figure 2. Storage modulus (G') and loss modulus (G'') measured as a function of temperature and frequency for Alaska heavy oil.

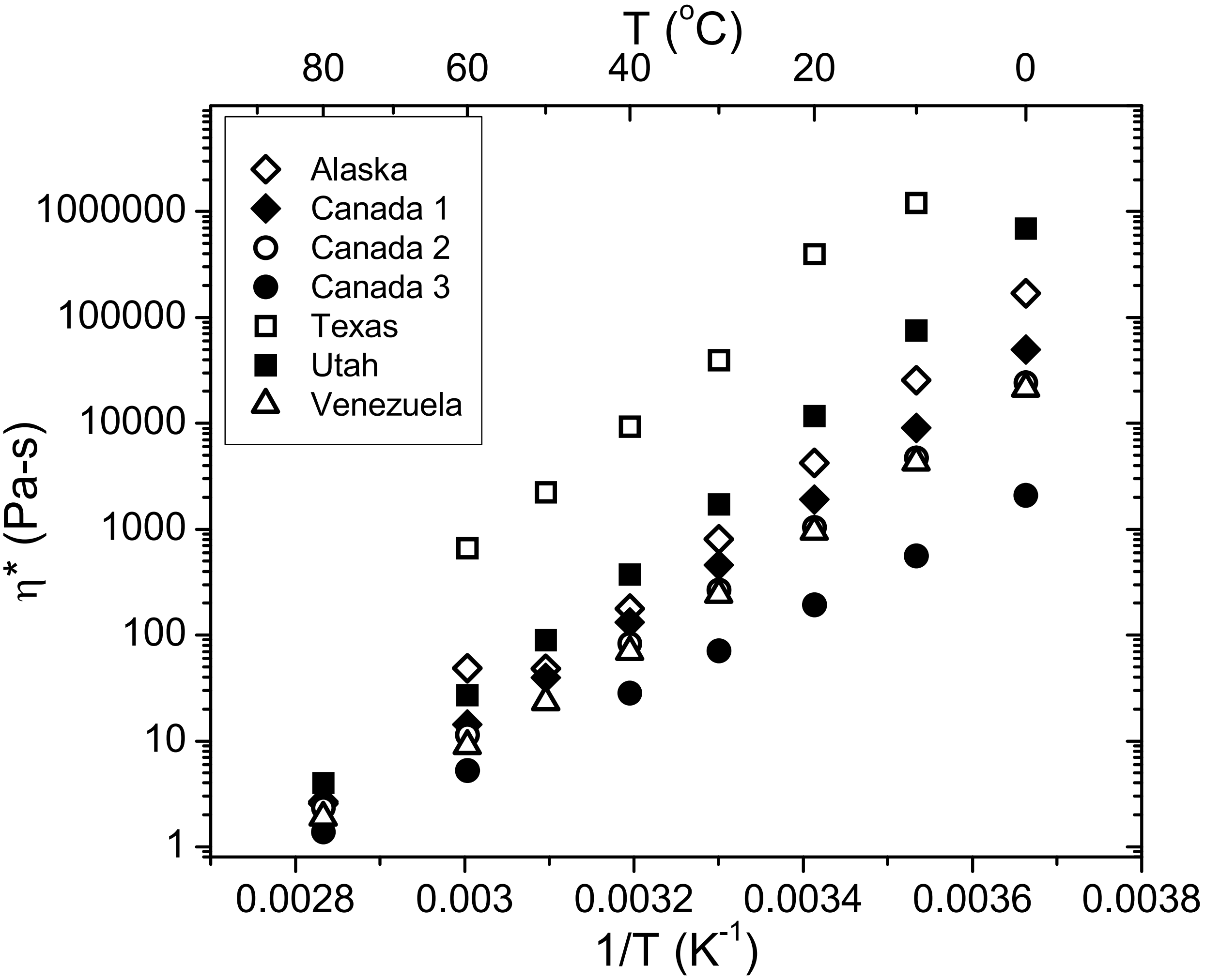

Figure 3. Arrhenius plot of complex viscosity as a function of inverse temperature (all data at 1 Hz).

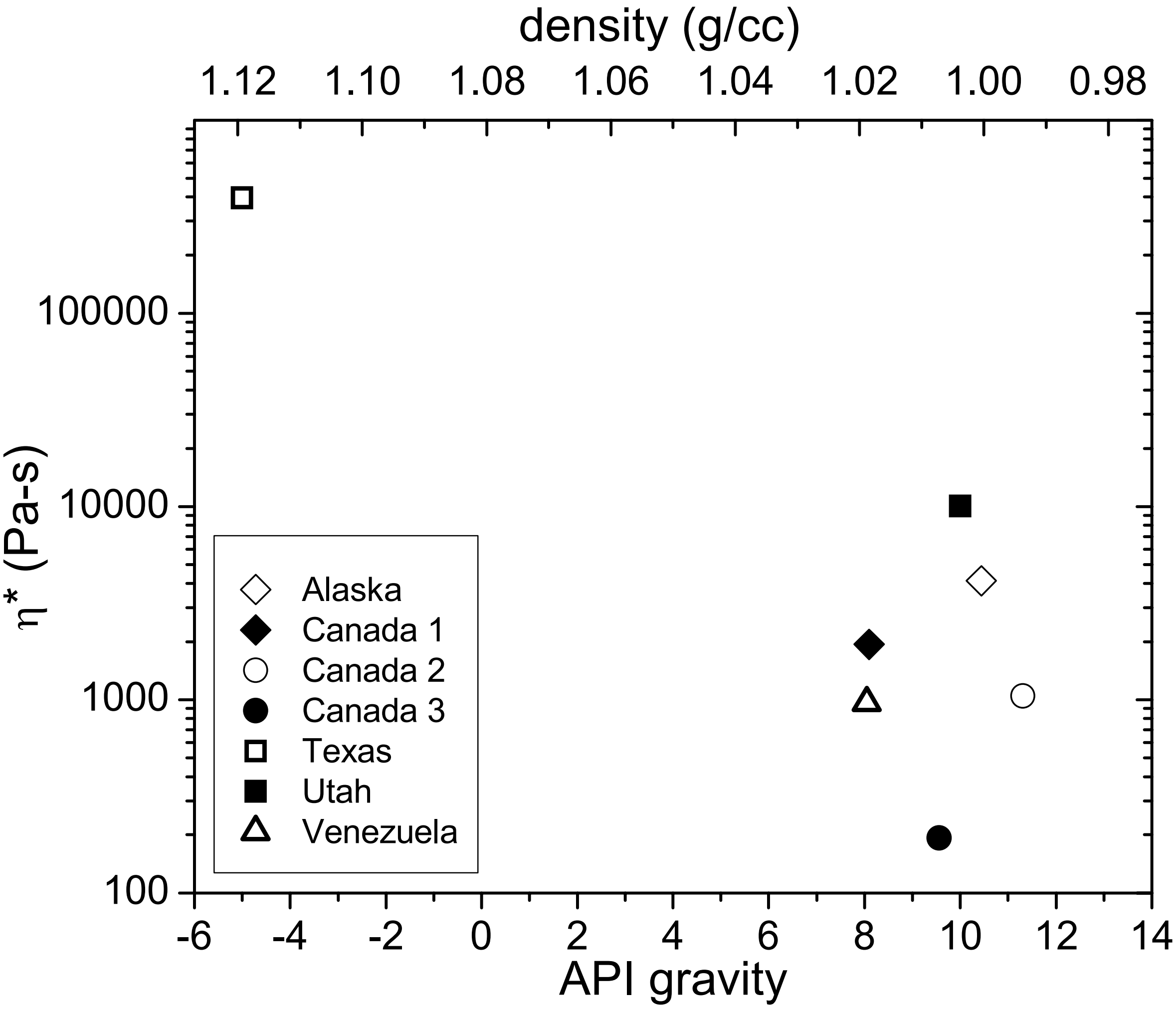

Figure 4. Complex viscosity as a function of API gravity for seven heavy oils (all data at T=20^{o}C, 1 Hz).

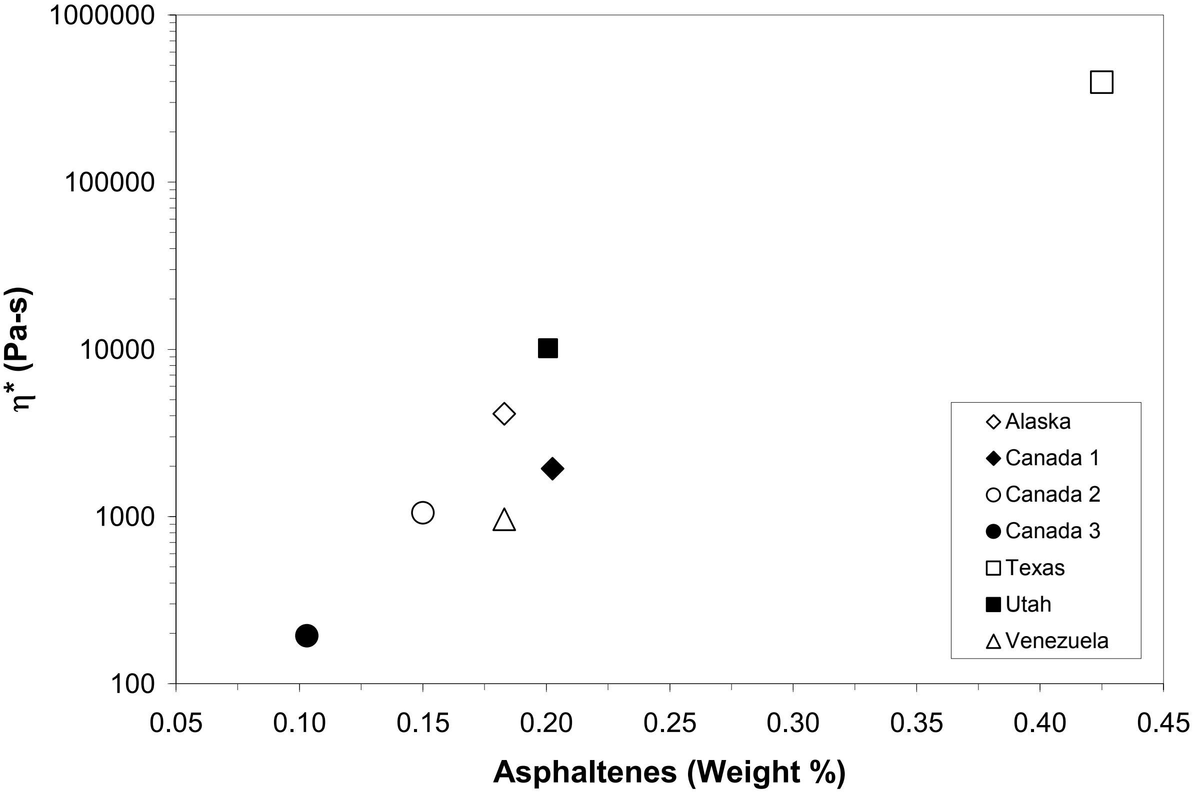

Figure 5. Complex viscosity as a function of resins content for seven different heavy oil samples (all data at T=20^{o}C, 1 Hz)

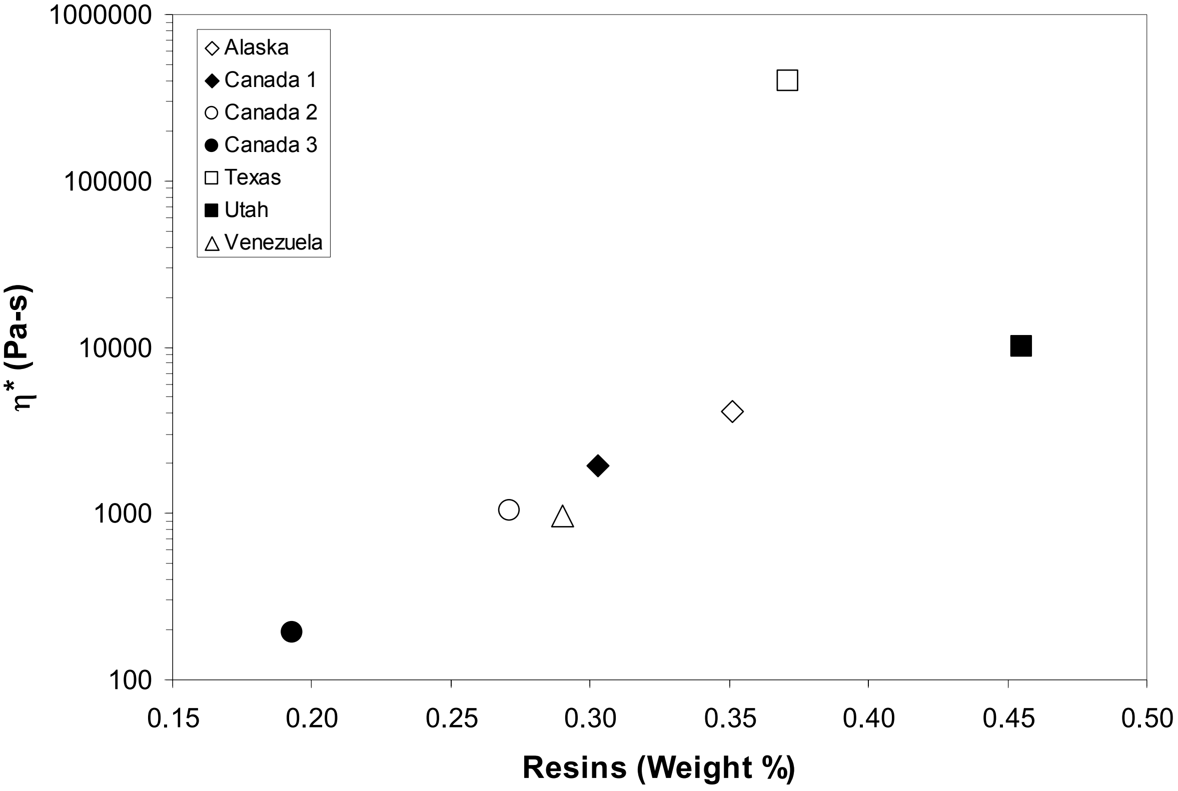

Figure 6. Complex viscosity as a function of asphaltenes content for seven different heavy oil samples (all data at T=20°C, 1 Hz).

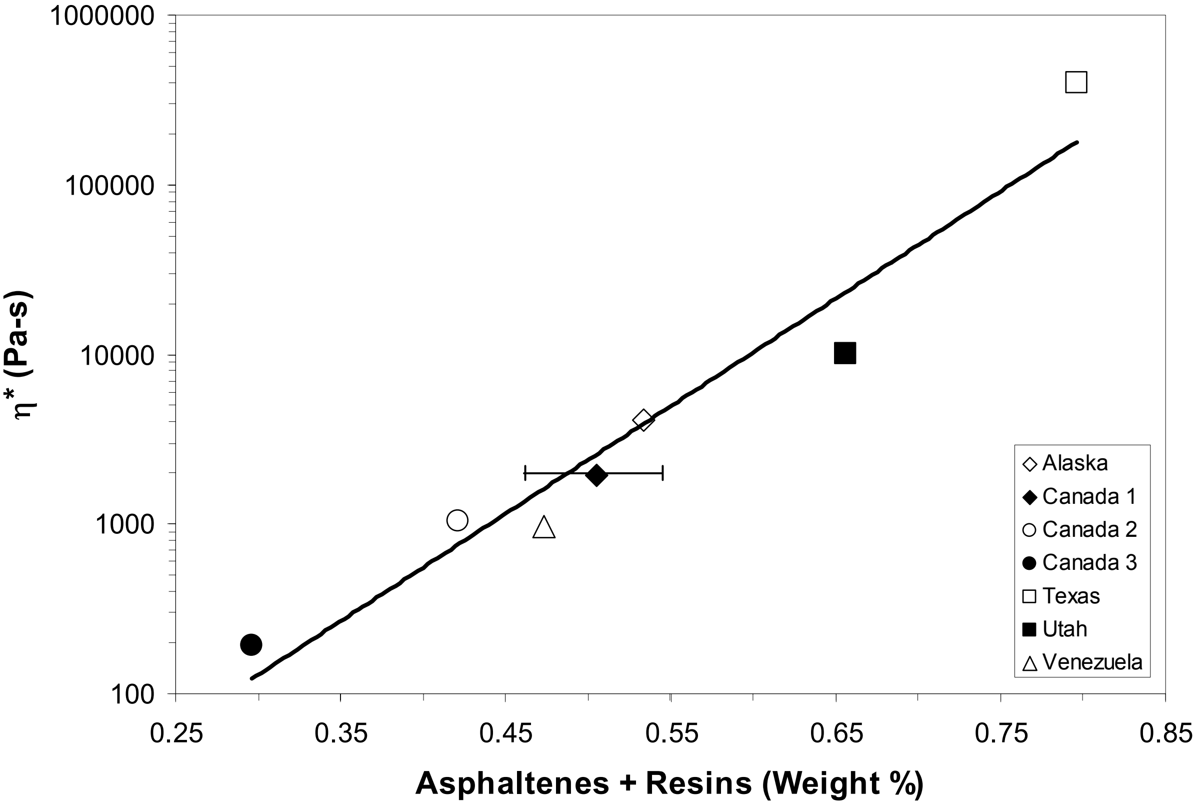

Figure 7. Complex viscosity as a function of combined resins and asphaltenes content for seven different heavy oil samples (all data at T=20°C, 1 Hz). The error in the total resin + asphltenes is somewhat lower, since underestimates in resin contents is usually compensated in asphaltene values, and vise versa.

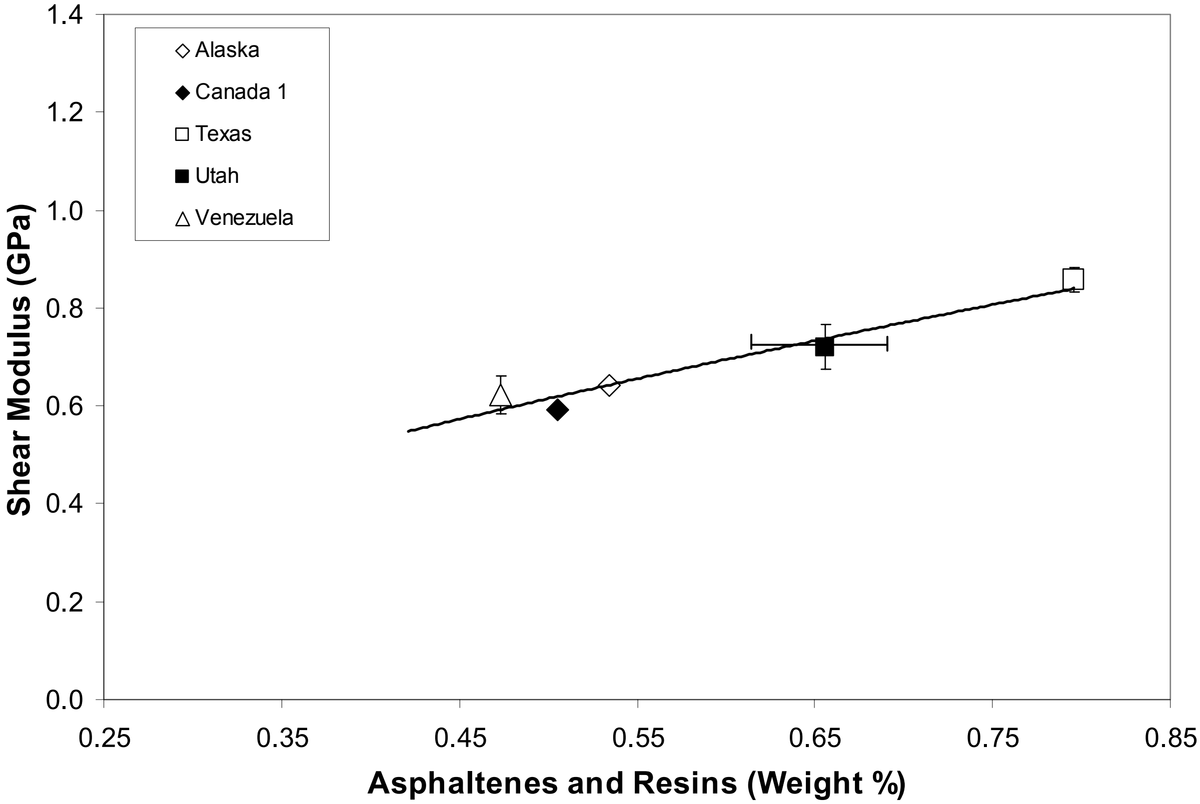

Figure 8. Ultrasonic shear modulus as a function of combined resins and asphaltenes content. (T = -10°C)

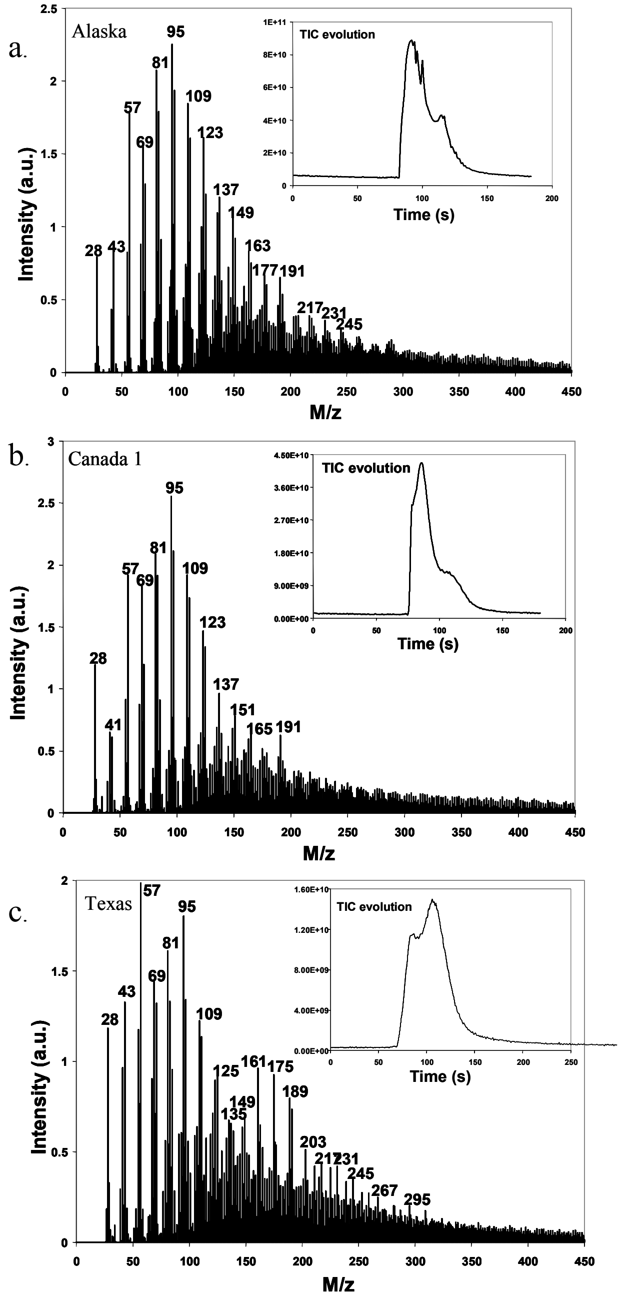

Figure 9. Average spectra of products (with background correction) detected by MBMS resulting from the pyrolysis of Alaska (a.), Canada 1 (b.) and Texas (c.) heavy oil at 550°C with residence time ≈ 0.1s.

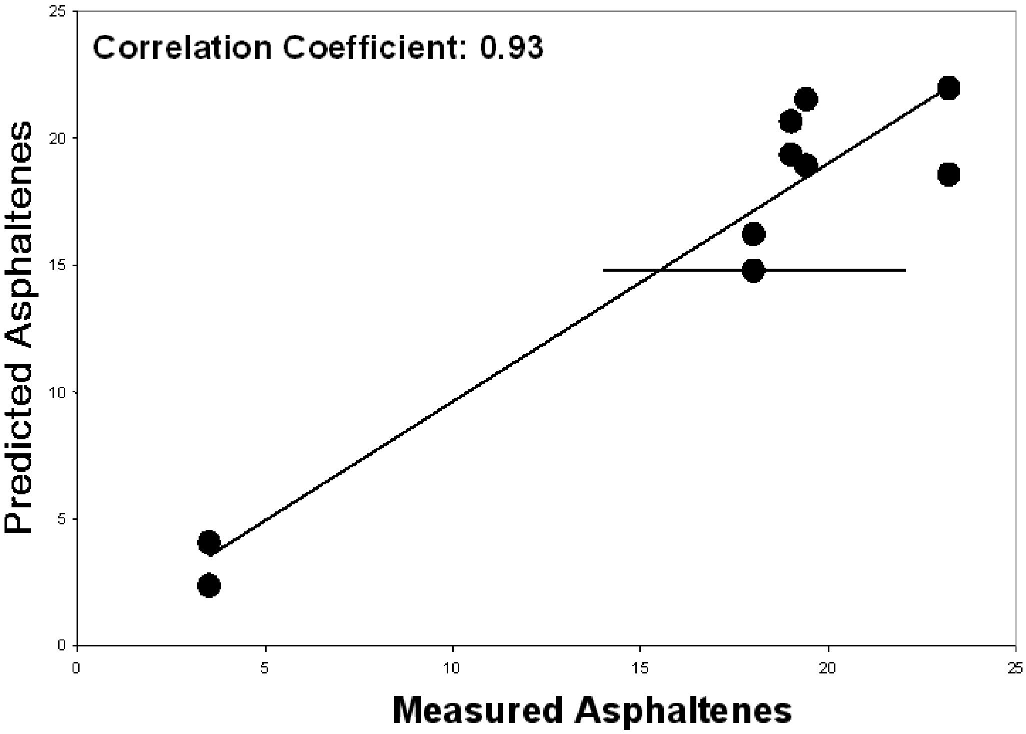

Figure 10. Measured value versus prediction for asphaltenes using pyrolysis-MBMS data as predictor variables.

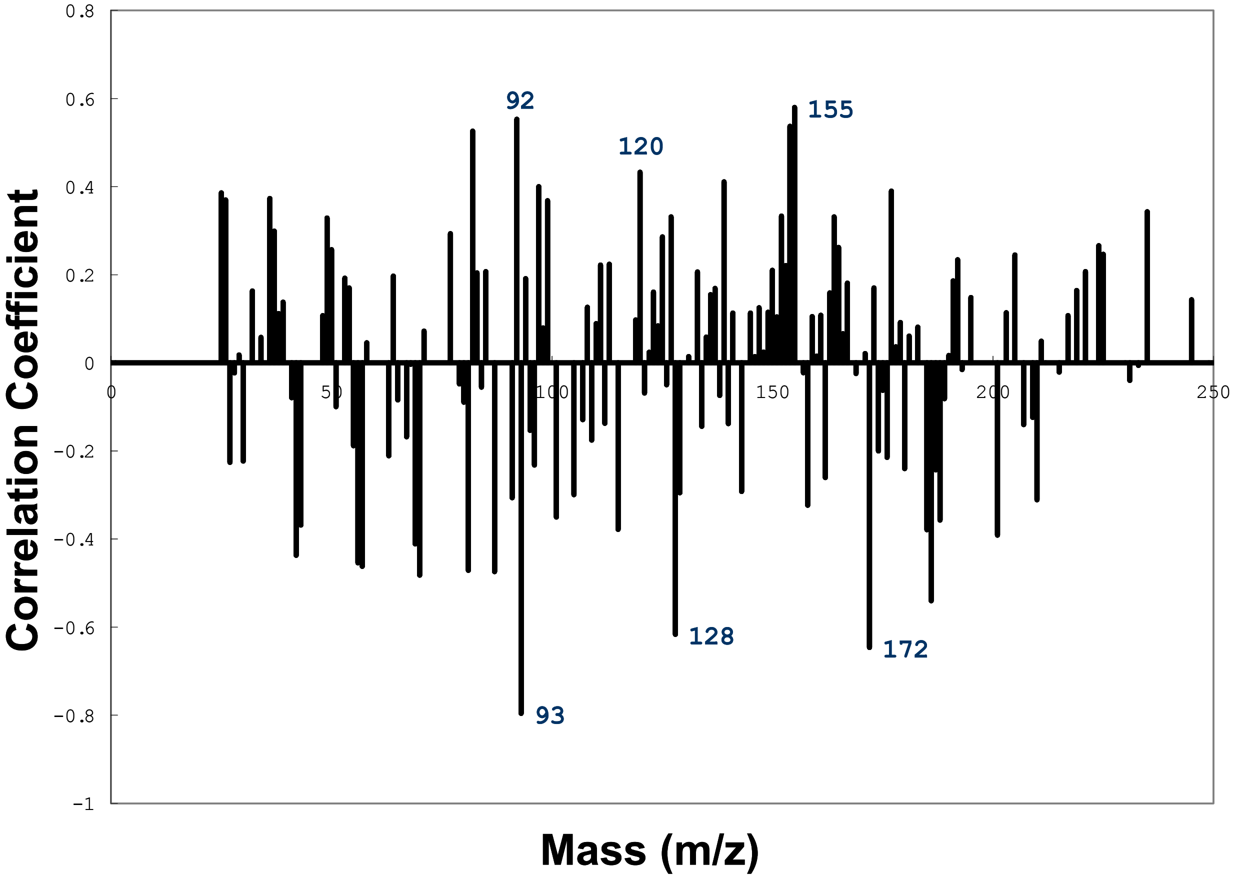

Figure 11. Correlation coefficient of pyrolysis-MBMS variables with asphaltenes, resulting from partial least square regression analysis.