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John F. Schabron

Joseph F. Rovani

Mark M. Sanderson

Jenny L. Loveridge

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ABSTRACT

A series of volatile crude oils was characterized using the Asphaltene Determinator on-column precipitation and re-dissolution method developed at Western research Institute (WRI). Gravimetric asphaltenes and polars fractions from silica gel chromatography separation of the oils were characterized also. A study to define the differences in composition of asphaltenes in refinery desalter rag layer emulsions and the corresponding feed and desalter oils was conducted. Results indicate that the most polar and pericondensed aromatic material in the asphaltenes is enriched in the emulsions. The wax types and carbon number distributions in the two heptane-eluting fractions from the Waxphaltene Determinator separation were characterized by repetitive collection of the fractions followed by high temperature gas chromatography (GC) and Fourier transform infrared spectroscopy (FTIR). High resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICRMS) was conducted by researchers at the Florida State University National High Magnetic Field laboratory in a no-cost collaboration with the study.

EXECUTIVE SUMMARY

There is a significant interest by the petroleum industry in processing heavy oils to provide transportation fuels. In the current market, a refiner typically does not have the luxury of upgrading the same feedstock material year after year. Often, blends are used with different day-to-day compositions resulting in unexpected fouling. Some oils form persistent emulsions in refinery desalter units. Another important issue is fouling, which can result from blending of incompatible oils, during heating or from thermal processing, or combinations of these effects. To avoid fouling during distillation, many refiners select relatively conservative heating profiles, which result in less than optimal distillation efficiency.

Methods based on a new breakthrough on-column precipitation and re-dissolution separation technique developed at WRI offer significant advancement for the characterization of the pericondensed aromatic and polar materials and waxes in petroleum and residua (U.S. Patent 7,875,464 and patents pending). The methods provide solubility profiles for heavy oil components and solubility subfraction profiles for asphaltenes. The Asphaltene Determinator method separates oils into four solubility fractions at 30 °C: heptane, cyclohexane, toluene, and methylene chloride:methanol (98:2 v:v). The Waxphaltene Determinator method involves initial precipitation of waxes and asphaltenes in methyl ethyl ketone at -24 °C and then re-dissolves the precipitated material in heptane at -24 °C, heptane at 60 °C, toluene at 30 °C, and methylene chloride:methanol (98:2 v:v). In prior work under this project, both methods were optimized and standard conditions were established. They are now being used at WRI to evaluate both upstream and downstream oils from various processes related to process efficiency improvement. The new approach provides more detailed chemical information than conventional gravimetric techniques used to measure asphaltenes and waxes. Although our main focus for this project continues to be on refinery processing efficiency improvement, methods based on the new separation technique also have applications to the characterization of both upstream and downstream oils.

In the current effort, a series of volatile crude oils was characterized using the Asphaltene Determinator on-column precipitation and re-dissolution method developed at Western Research Institute (WRI). Gravimetric asphaltene and polar fractions from silica gel chromatography separation of the oils were also characterized. A study to define the differences in composition of asphaltenes in refinery desalter rag layer emulsions and the corresponding feed and desalter oils was conducted. Results indicate that the most polar and pericondensed aromatic material in the asphaltenes is enriched in the emulsions. The wax types and carbon number distributions in the two heptane eluting-fractions from the Waxphaltene Determinator separation were characterized by repetitive collection of the fractions followed by high temperature gas chromatography (GC) and Fourier transform infrared spectroscopy (FTIR). High resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICRMS) was conducted by researchers at the Florida State University National High Magnetic Field laboratory in a no-cost collaboration with the study.

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OBJECTIVES

The primary objective of this project is to enhance understanding of the chemical changes that occur during processing of heavy oils. This work is utilizing new tools for process monitoring and optimization which results in significant efficiency improvement and less down time and heat wasted in refinery operations. Additional objectives of the current effort are to characterize samples obtained from the co-sponsors, including crude oils and desalter rag layer emulsions. Another objective is to explore the chemical nature of the materials that comprise the various peaks in the Waxphaltene Determinator separation. Approaches include collection of analytical and/or preparative fractions for spectroscopic and chemical characterization.

INTRODUCTION

Background

Efficiency improvement in all facets of heavy oil recovery and processing is a major issue for the petroleum industry. New characterization and process monitoring tools are needed to enable significant improvements in production and processing. Partial upgrading for viscosity reduction, emulsion formation, separation of contaminants, compatibility, flow assurance, fouling, and upgrading are all relevant issues. Understanding and optimizing composition changes in processes such as pyrolysis, coking, and hydroprocessing to maximize efficiency and minimize fouling is of great importance to the industry. Since many refiners no longer have the luxury of upgrading the same feedstock material year after year, blends are used with different day-to-day compositions resulting in unexpected fouling. Fouling can result from blending of incompatible oils, during heating or from thermal processing, or combinations of these effects. Our oil company co-sponsors have stressed the importance of process analysis tools that can provide rapid information for refinery process control and efficiency improvement. There also is significant interest in enhanced understanding of the chemical nature of the most polar and pericondensed aromatic constituents of petroleum materials, and how these interact with the non polar matrix and with each other.

Methods based on a new breakthrough on-column precipitation and re-dissolution separation technique developed at WRI offer significant advancement for the characterization of the pericondensed aromatic and polar materials and waxes in petroleum and residua. The methods provide molecular based solubility profiles for heavy oil components. The development work and example separations with representative materials have been described in detail in earlier topical reports (Schabron et al. 2006, 2007, 2008, 2010, 2011) and in peer-reviewed publications (Schabron and Rovani 2008, Goual et al. 2008, Schabron et al. 2010, 2012). The separations are performed using an inert stationary phase consisting of ground polytetrafluoroethylene (PTFE). Although high-performance liquid chromatography (HPLC) instrumentation and detectors are used, there are no chromatographic interactions between the material being separated and the stationary phase. It is strictly solubility based.

The Asphaltene Determinator method separates oils into four solubility fractions at 30 °C: heptane, cyclohexane, toluene, and methylene chloride:methanol (98:2 v:v). The Waxphaltene Determinator method involves initial precipitation of waxes and asphaltenes in methyl ethyl ketone at -24 °C and then re-dissolves the precipitated material in heptane at -24 °C,

heptane at 60 °C, toluene at 30 °C, and methylene chloride:methanol (98:2 v:v) at 30 °C. In prior work under this project, both methods were optimized and standard conditions were established. Various methods for the separation of waxes and the development and optimization of the Waxphaltene Determinator separation have been provided previously (Goual et al. 2008, Schabron et al. 2012). They are now being used at WRI to evaluate both upstream and downstream oils from various processes related to process efficiency improvement. The new approach provides more detailed chemical information than conventional gravimetric techniques used to measure asphaltenes and waxes. Although our main focus for this project continues to be on refinery processing efficiency improvement, methods based on the new separation technique also have applications to the characterization of both upstream and downstream oils.

The work includes developing new applications for the methods and exploring various problem issues common to the industry. This includes possibly replacing gravimetric asphaltene determinations with new automated methods. There is a long list of issues that need to be addressed to fully understand the possibilities of the methods based on the new technique to improving refining process efficiency. Specific areas include atmospheric and vacuum, distillation, delayed coking, heat exchanger fouling, desalter emulsion stability, and establishing improved predictability criteria for processing various feeds from different sources. The new methods will be applied to specific processes or problem areas that are of interest to the oil industry. In addition, interest has been expressed by our oil company co-sponsors in developing an automated method to couple the automated Asphaltene Determinator separation with an automated SARA (saturates, aromatics, resins, asphaltenes) separation wherein the asphaltene separation step occurs in the Asphaltene Determinator separation.

EXPERIMENTAL

Samples and Solvents

Residua samples were Strategic Highway Research Program (SHRP) reference asphalts (Jones 1993). Tensleep and Dakota crude oils and residue materials were provided by Lamia Goual and Brian Towler, University of Wyoming (Goual et al. 2008). Crude oil samples and desalter emulsion samples were provided by ConocoPhillips. Solvents and chemicals used in the study were reagent grade.

Gravimetric Isolation of Asphaltenes

To prepare asphaltenes for the preparative Asphaltene Determinator separation, a sample of residuum or oil was weighed and mixed with an excess of heptane. The mixture was stirred overnight to allow full precipitation of asphaltenes. The mixture was then filtered using a medium frit (10 µm) sintered glass filter with repeated rinsing with heptane, and any residual solvent was removed using a vacuum oven at 110 °C. The precipitate was dried and weighed.

Saturates, Aromatics, and Resins (SARA) Separation

Open-column chromatographic separations of maltenes into saturates, aromatics, and resins fractions were conducted using a 400 mm x 19 mm ID glass column. The column was slurry packed with 35 g Aldrich grade 62, 60-200 mesh silica gel that had been activated overnight at 120 °C. Sample amounts of 350 mg maltenes in heptane solution (1 wt. % loading) were placed on the top of the column. Saturates, aromatics, and resins fractions were eluted with heptane, toluene, and toluene:methanol (80:20 v:v), respectively. The eluted fractions were rotovapped at 70 °C to near dryness, and then dried in a vacuum oven at 100 °C for 1 hour prior to weighing for gravimetric determination of the amounts in each fraction.

Emulsion Centrifugation

Desalter emulsions were centrifuged in a manner similar to ASTM D-4007-02 without adding a demulsifier. The emulsions were centrifuged in an International Centrifuge; Universal Model UV, with 100 mL centrifuge tubes at 2,500 rpm with a 16 inch tube tip to tube tip diameter while rotating. The centrifuging was performed in a series of three 10-minute intervals, with volume separations checked between each interval to ensure that there were no changes between the last two intervals.

Analytical Asphaltene Determinator Separation

The on-column asphaltene precipitation and re-dissolution experiments were conducted using a Waters 717plus autosampler, a Waters 60F pump with a model 600 controller, a Waters 2489 ultraviolet/visible absorbance detector, and a Waters 2424 evaporative light scattering detector (ELSD). Solutions of residua and asphaltenes in chlorobenzene were injected onto a 7 mm i.d. x 250 mm stainless steel column packed with 0.25-0.42 mm ground polytetrafluoroethylene (PTFE) (40-60 mesh). The optical absorbance detector in dual wavelength mode at 500 nm and 700 nm was used to monitor the separation profile for a standard reference oil (Lloydminster vacuum residuum), which was injected daily to detect the possible onset of adsorption effects in the stationary phase. If adsorption is observed, the in-line pre-filter disc (Supelco 5-9271, 0.5 µm) and/or the column PTFE packing material is replaced to restore proper operation. Solvent flow rates were 2 mL/min with step changes between solvents. Peak area integrations were performed using Waters Empower software. ELSD and optical absorbance peak areas were electronically blank subtracted prior to integration to correct for small blank peaks due to the step gradient solvent changes.

A 20 µL injection of 10% Lloydminster vacuum residuum is made daily as a QC check sample to ensure that there is no adsorption occurring on the column.

Solutions of the sample oils and residua are prepared as 10% (wt./vol.) or less solutions in chlorobenzene. Portions of 20 µL were injected in duplicate for the analytical scale Asphaltene Determinator separation. The optimized separation conditions are as follows:

Column: 7 mm ID x 250 mm stainless steel column

Packing: 40-60 mesh ground PTFE

Detectors:

Waters 2489 absorbance detector set at 500 nm and 700 nm

Waters 2424 evaporative light scattering detector (ELSD)

60 °C tube, 12 °C nebulizer, 35 psi nitrogen, gain = 1

Solutions: Sample and QC solutions are 10% wt/vol in chlorobenzene

Injection amount: 20 µL

Solvents used for step gradient changes: n-heptane, cyclohexane, toluene, methylene chloride:methanol (98:2) (v:v), all at 2 mL/min

Step gradient times:

0 min.	heptane
15 min.	cyclohexane
25 min.	toluene
35 min.	methylene chloride:methanol (98:2)
45 min.	heptane
60 min.	next injection

All separation profiles are electronically blank subtracted prior to peak integration

Analytical Waxphaltene Determinator Separation

The Waxphaltene Determinator precipitation and re-dissolution experiments were conducted using a Waters 717 autosampler, a Waters 60F pump with a model 600 controller, and a Waters 2424 evaporative light scattering detector (ELSD). Solutions of residua, waxes, and asphaltenes in chlorobenzene were injected onto a 7 mmID x 250 mm stainless steel column packed with 0.25-0.42 mm ground PTFE (40-60 mesh). The optical absorbance detector was not used due to optical cell plugging when waxes were separated from oil. The separation profile for a standard reference oil (Lloydminster vacuum residuum), which was injected daily, was used to detect the possible onset of adsorption effects in the stationary phase. Three column temperature baths were used. The -24 °C bath was a Julabo Model F-24 refrigerated temperature bath, and the 60 °C and 30 °C baths were both Lindberg Blue M Model WB11 20A-1 heated baths. The fluid used in all the baths was propylene glycol:distilled water (70:30 v:v). This was obtained by evaporating water from red RV antifreeze to achieve the optimal glycol to water ratio. The column was moved between temperature baths at pre-set times during the separations using a Thermo Fisher F-3 industrial grade robot. Solvent flow rates were 2 mL/min with step changes between solvents. Peak area integrations were performed using Waters Empower software. The ELSD peak areas were electronically corrected for small blank peaks due to the step gradient solvent changes prior to integration.

Solutions of the residua and devolatilized oils are prepared as 10% (wt./vol) solutions or less in chlorobenzene. Portions of 20 μ L are injected for the analytical scale Waxphaltene Determinator separation. The separation conditions for the optimized system are as follows:

Column: 7 mm ID x 250 mm stainless steel column

Packing: 40-60 mesh ground PTFE

Detector:

Waters 2424 evaporative light scattering detector (ELSD)

60 °C tube, 12 °C nebulizer, 35 psi nitrogen, gain = 1

Solutions: Sample and QC solutions are 10% wt/vol or less in chlorobenzene

Injection amount: 20 μ L

Solvents used for step gradient changes: methyl ethyl ketone, n-heptane, toluene, methylene chloride:methanol (98:2) (v:v), all at 2 mL/min.

Step gradient times and column temperatures:

0 min.	methyl ethyl ketone	-24 °C
10 min.	heptane	-24 °C
20 min.	heptane	60 °C
30 min.	heptane	30 °C
35 min.	toluene	30 °C
45 min.	methylene chloride:methanol (98:2)	30 °C
55 min.	methyl ethyl ketone	30 °C
65 min.	methyl ethyl ketone	-24 °C
80 min.	next injection	

All separation profiles are electronically blank subtracted prior to peak integration. A 20 μ L injection of 10% Lloydminster vacuum residuum is made daily as a QC check sample to ensure that there is no adsorption occurring on the column.

High Temperature Gas Chromatography

High temperature gas chromatography (GC) was conducted with an HP 5890 Series II GC with a flame ionization detector set at 395 °C. Injections were made with a flow inversion cup injector in the split mode at 375 °C. The column was a 15 m x 0.32 mm x 0.1 μ m thickness DB-1 column operated initially at 200 °C with a temperature gradient ramp up to 385 °C with helium carrier gas. Samples were prepared by adding 1 mL toluene to each fraction. The solutions were heated to 90 °C with a metal block heater, and shaken immediately before injection of a 1 μ L portion. To provide retention time points of reference, small amounts of n-hexacontane (nC_{60}), n-tetratetracontane (nC_{44}), and n-octacosane (nC_{28}) were spiked into the solutions.

Fourier Transform Infrared Spectroscopy

Attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy was performed with a Perkin Elmer Universal ATR Sampling Accessory by smearing a small amount of sample directly onto the ZnSe crystal and applying the pressure plate until the force gauge reaches a maximum of 150 (unitless). A total of 32 scans were performed on each sample.

RESULTS AND DISCUSSION

One focus of the current work involved developing approaches to apply the new separation methods to address problems relevant to the industry related to refinery efficiency improvement. This included characterizing various volatile crude oils, and examining the components of oils that appear to stabilize refinery desalter emulsions. In addition, the chemical nature of waxy materials eluting in the Waxphaltene Determinator separation was explored.

Asphaltene Determinator Evaluation of Volatile Petroleum Samples

The Asphaltene Determinator Characterization Tree described previously along with data for non-volatile residua materials was used to characterize a variety of volatile petroleum samples provided by the co-sponsors (Schabron et al. 2011). For the current FY 10 increment, the characterization was extended to volatile crude oils. The flow sheet for the characterization tree is provided in Figure 2-1. The characterization tree data include 10 μm and 0.45 μm asphaltene, and polars content from a gravimetric SARA separation to isolate resins / polars and asphaltenes for characterization. The maltenes varnish is brown colored material that coats the glassware after the heptane solution of maltenes has been filtered through the 0.45 micron filter and allowed to sit for a day or two (Schabron et al. 2010). This is asphaltene type material that remains in the heptane solution during the filtration steps. It is easily desorbed with methylene chloride for quantitative transfer to a small bottle for subsequent solvent removal and weighing.

To correct the ELSD peak area of maltenes for volatiles loss in the detector, the total area count for the ELSD profile for the daily QC check with Lloydminster vacuum residuum is measured. The total ELSD area for the injected oil is compared with the ELSD area for the QC injection. For nonvolatile oils and residua, these relative areas are typically within 1 - 5 % or less. The decrease in area is a quantitative measure of the wt. % volatiles lost from the maltenes fraction in the ELSD. A spreadsheet calculation is easily made to correct for volatiles loss and thus determine the solubility fraction distribution for the whole original oil including the asphaltenes. Separations results for a series of volatile crude oils from various sources are provided in Appendix A. The data for the various oils show significant differences between the oils and the components of their asphaltenes which can potentially be used to develop correlations with properties such as catalyst interaction, fouling, and blending characteristics.

Refinery Desalter Emulsion Study

Before an incoming crude oil is distilled in a refinery, the first step is to remove salt and sediment using a fresh water-based wash. The separated salt and sediment emerge from the unit in an aqueous outlet brine bottom layer. A generic diagram of a desalter unit showing “try layer”

sample port placement is shown in Figure 2-2. For some oils and conditions, a large undesired middle emulsion phase forms which interferes with efficient operation of the unit. This results in a rag layer or pudding-like emulsion of oil and water which is persistent and difficult to break. Components in the oil, especially the asphaltenes can contribute to the emulsion stability. Refinery desalter emulsions are believed to be water-in-oil emulsions that consist of spherical particles of water, each surrounded by a shell which stabilizes the emulsion structure (Figure 2-3). Spherical droplet diameters of 1-28 microns have been observed (Ortiz and Yarranton 2010). Asphaltenes have been shown to stabilize the emulsions, while intermediate polarity resins act as destabilizers (Spieker and Kilpatrick 2004). The emulsions also can be stabilized by fine inorganic particles such as clays in the oils (Sztukowski and Yarranton 2005).

In the current study, the Asphaltene Determinator method was used to study the contributions of polar and highly aromatic asphaltene component molecules that play a role in stabilizing emulsions. A main focus was to evaluate the amount and nature of asphaltenes in the original and desalter rag layer emulsion oils. Three good representative sample sets were provided by ConocoPhillips. These include incoming feed oils to the desalter, rag layer emulsions taken from the desalter units, and the desalted effluent oils, each set taken on the same day from a refinery desalter unit. One group of samples is for a light crude oil (API gravity ~40), and another group is for a mixture of heavy and light crude oils (API gravity ~25). A third group is for a much heavier oil than the first two groups (API gravity ~20). Differences in the Asphaltene Determinator solubility fraction profile distributions of the rag layer oil asphaltenes were observed in the current study when compared to the inlet and outlet oils. Results for the three sample sets are provided below.

Light Oil Sample Set Examples of results from the light oil group are provided in Tables 2-1 – 2-4. The incoming oil (Table 2-1) and desalted outlet oil (Table 2-2) appear very similar from the Asphaltene Determinator analyses corrected for ELSD volatiles losses. They also are similar in total heptane gravimetric asphaltenes content. However, the gravimetric asphaltenes from the desalted oil contain less toluene soluble and methylene chloride:methanol (98:2 v:v) soluble material than the asphaltenes from the feed oil (Tables 2-1 - 2-2). The gravimetric asphaltenes from the whole rag layer oil water emulsion (Table 2-3), which has the consistency of pudding, contain more methylene chloride:methanol (98:2 v:v) soluble asphaltene components than the asphaltenes from the incoming or desalted oils. To illustrate this, the area percent values for the 500 nm methylene chloride:methanol (98:2 v:v) peaks for the oils and 10-micron asphaltenes for the whole oil, the rag layer oil with water, and the desalted oil are summarized in Table 2-4.

The centrifuged emulsion contained 40 % oil by volume, 54% water, and 6% sediment. The centrifuged rag layer supernatant oil (Table 2-5) contains about 20 times more gravimetric asphaltenes than the inlet feed oil or the desalted oil and these asphaltenes contain significantly higher methylene chloride:methanol (98:2 v:v) soluble asphaltene components than the gravimetric asphaltenes from the incoming oil. These results for an emulsion set with a single oil suggest that the most pericondensed and highest surface energy components of oil could be involved in stabilizing oil / water emulsions.

Medium Oil Sample Set Results for the two medium oil sets collected from a refinery desalter unit on the same day are provided in Tables 2-6 – 2-9. The rag layer emulsions were centrifuged in a manner similar to ASTM D-4007-02 as described above, without adding a demulsifier. The

rag layer from Set 1 contains 60 % oil by volume, 38% water, and 2% sediment. The rag layer emulsion for Set 2 contains 80 % oil by volume, 14% water, and 6% sediment. The Asphaltene Determinator characterization data show that the inlet oils (Table 2-6) and outlet oils (Table 2-7) are similar in composition. The desalted effluent oil from Set 2 however has about half the amount of gravimetric asphaltenes as the incoming oil (Table 2-7). The explanation for this is not straightforward. It could be related to the timing of the sampling for the two materials. The gravimetric heptane asphaltenes from the whole rag layer oil / water emulsions, which have the consistency of pudding, contain significantly more methylene chloride:methanol (98:2 v:v) soluble asphaltene components than the incoming oils (Tables 2-6 and 2-8). This represents highly pericondensed and polar asphaltene material. The relative amounts of methylene chloride:methanol soluble material for the centrifuged emulsion oils are similar to the values for the inlet and outlet oils (Tables 2-6, 2-7 and 2-9). The supernatant oils from the centrifuged rag layer emulsions contain about half the amount of gravimetric asphaltenes relative to the incoming or effluent oils from Set 1 and about half the incoming oil from Set 2 (Tables 2-6, 2-7 and 2-9).

The area percent values for the 500 nm methylene chloride:methanol (98:2 v:v) peaks for the oils and 10-micron asphaltenes for the whole oil, the rag layer oil with water, and the desalted oil are summarized in Table 2-10. Enrichment of the most pericondensed and polar material represented by the methylene chloride:methanol soluble material in the rag layer emulsions suggest that the most pericondensed and highest surface energy components of oil could be involved in stabilizing oil / water emulsions.

Heavy Oil Sample Set For the heavy oil series, we were provided with samples from various try layer ports in a refinery desalter unit, as well as the incoming and desalted oils. The heavy oil sample set was for heavy oil (~20 API gravity) samples collected from the “try layer” ports of a refinery desalter. A photograph of some of these samples is provided in Figure 2-4.

As with the light and medium oil sample sets, the samples were analyzed using the Asphaltene Determinator separation and by gravimetric asphaltene precipitation followed by the Asphaltene Determinator. The samples that were analyzed included the whole samples shaken as received, the middle emulsion layers drawn from the samples, the oil from the centrifuged emulsions, and oily residue from the water which was evaporated from the centrifuged emulsions. The many tables of analysis results for this sample set are provided in Appendix B. The more significant results are provided in summary tables as described below. The oil, water, and sediment amounts in the emulsions obtained by centrifugation are provided in Table 2-11.

Data for the area percents of the methylene chloride:methanol (98:2) soluble material peaks with the 500 nm absorbance detector are provided in Table 2-12. The amounts of this most polar and aromatic material are significantly higher in the whole samples containing emulsions and in the emulsions themselves. The try layer 5 and 7 oil samples, which did not contain emulsions, are more similar to the inlet and desalted oils. Relative volatiles-corrected ELSD area percents for the most pericondensed material are provided in Table 2-13. For the emulsions, the ELSD volatiles correction for relative peak areas includes both the water and volatile oils materials. The evaporated emulsion centrifuged water residue samples contain a larger area percent of heptane insoluble material (asphaltene) than the whole samples or emulsions.

Selected non-volatile component ELSD area percents are provided in Table 2-14. The material represented by non-volatile ELSD components is in the boiling range slightly above the nominal initial boiling point for atmospheric residua ($> 640^{\circ}\text{F}$, $>340^{\circ}\text{C}$). The ELSD area percents of heptane insolubles and the total pericondensed aromatic contents are highest for the evaporated emulsion centrifuged water residue material when compared with the data for the whole oils or emulsions.

The relative 500 nm absorbance detector area percents for the gravimetric asphaltenes from the oils and emulsions are provided in Table 2-15. The percents for the toluene soluble asphaltene components are for the most part similar for all the oils and emulsions. However, the relative peak areas for the methylene chloride:methanol soluble materials are significantly higher for the samples that contain emulsions.

These results show that the most polar pericondensed aromatic pre-coke material in the oils, represented by the methylene chloride:methanol soluble peaks, are enriched in the rag layer emulsion samples relative to the incoming oil or the outlet desalted oil. The incoming crude oil and the desalted crude oils are similar in composition to each other as expected. The centrifuged emulsion oils are somewhat similar to the incoming and desalted oils. The results support the hypothesis that the most pericondensed material in the oils contribute to rag layer emulsion stability.

Waxphaltene Determinator Results and Peak Characterization

Example Separations Waxphaltene Determinator separation profiles with integrated peak areas for eight residua materials are provided in Figures 2-5 – 2-8. These materials are the strategic Highway research Program (SHRP) reference asphalts (Jones 1993). The profile for the West Texas residuum clearly shows the relatively high wax content (Figure 2-5). The SHRP sample designations and the relative ELSD area percents are provided in Table 2-16.

Another potential use for the new separation method is the predictability of wax fouling of pipelines at oil production sites (Goual et al. 2008). A separation profile for devolatilized Dakota crude is provided in Figure 2-9. This material shows the presence of significant wax content eluting with n-heptane at 60°C . This oil is known to develop chronic petrolatum type deposits in production site pipelines. A separation profile for one of the deposits is also provided in Figure 2-9. Some other oils in the region that do not exhibit the heptane peak at 60°C , such as Tensleep oil do not exhibit this type of fouling (Figure 2-10).

Waxphaltene Determinator Peak Characterization by Gas Chromatography An exploratory study of crude oils and pipeline fouling by an early version of the Waxphaltene Determinator with the 250 mm x 10 mm ID column is described in Goual et al. (2008). This includes a discussion of possible wax types and solubility considerations. Table 2-17 presents a summary of some likely chemical identity of the various peaks illustrated in Figure 2-11 for a waxy West Texas Intermediate residuum. The Waxphaltene Determinator separation is not readily amenable to being scaled up into a preparative mode because of the severe temperature changes involved. However, repeat separations can be made with the analytical system and fractions collected with an automated fraction collector (bypassing the ELSD) to provide small amounts of each fraction

for further characterization by various methods including high temperature gas chromatography to measure wax component.

To characterize the types of waxy composition eluting in the first three peaks of the Waxphaltene Determinator Separation, a series of 22 repetitive 2 mg injections with automatic fraction collection were made of a waxy West Texas Intermediate residuum on the Waxphaltene Determinator system (Figure 2-11). Tentative peak assignments in the figure are based on injections of standard materials in this study and in earlier work (Goual et al 2008). As described in the 2011 consortium report (Schabron et al. 2011), fractions from peaks 1, 2, and 3 were analyzed by high temperature gas chromatography (GC) according to the procedure described by Netzel and Rovani (2007). Peaks 4 and 5 represent the refractory pericondensed asphaltene material, which were not injected. The amount of sample in each fraction was: ~20 mg for Peak 1 (methyl ethyl ketone at -24 °C), ~20 mg for Peak 2 (heptane at -24 °C), and ~3 mg for Peak 3 (heptane at 60 °C), after solvent evaporation.

The high temperature GC profiles for the three peak fractions are provided in Figure 2-12. There was no wax hydrocarbon profile apparent for the material in Fraction 1. The MEK maltenes likely contains various aromatic, polar, and other materials that are soluble in MEK and do not freeze at -24 °C. The high temperature GC profile for the Peak 2 fraction shows two prominent regions of waxy hydrocarbon elution. Based on retention times, these correspond predominately to n-C₂₆ to n-C₄₀, and iso-C₄₀ to iso-C₆₀+ hydrocarbons, with some smaller peaks throughout the elution time range, which represent both iso- and n-paraffins. The separation profile for the Peak 3 fraction shows two prominent elution regions which correspond predominantly to a complex mixture of n-C₃₀ to n-C₆₀, and iso-C₅₀ to iso-C₆₀+ hydrocarbons, with some smaller peaks throughout the elution time range indicating the presence iso and n-paraffins. As discussed later, the high temperature GC profiles did not detect the significant amounts of material present with structures > C₆₀.

All three fractions had some brown color, which is likely due to the presence of highly alkyl substituted pericondensed aromatic material. In addition to the paraffins that were identified by high temperature GC, there are other molecules present that are not pure wax hydrocarbons. However, these exhibit freezing and solubility behavior similar to the wax components and they should not be ignored. Also, iso-paraffins include molecules with complex degrees of branching at various locations in the molecules. Components eluting above the *n*-hexacontane in the range larger than C₆₀ were not well resolved or detected.

Waxphaltene Determinator Fraction Characterization by Infrared Spectroscopy A series of 49 automated injections of 2 mg each of a waxy West Texas Intermediate residuum was conducted in a separate experiment, and the fractions were collected with an automated fraction collector. The approximate amounts of sample material in the fractions were: ~ 30 mg for Peak 1 (methyl ethyl ketone at -24 °C), ~ 40 mg for Peak 2 (heptane at -24 °C), ~ 10 mg for Peak 3 (heptane at 60 °C), ~7 mg for Peak 4 (toluene at 30 °C), and ~3 mg for Peak 5 (methylene chloride:methanol (98:2 v:v) at 30 °C). The Waxphaltene Determinator separation profile for this material was similar to the one shown in Figure 2-11. Portions of the fractions were analyzed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR). The FTIR spectra for the whole material and Fractions 2 and 3 are provided in Figure 2-13.

The Peak 1, 4, and 5 fraction materials showed significant carbonyl content near 1700 cm^{-1} and some hydroxyl material near 3300 cm^{-1} , and C-O absorbance near 1240 and 1160 cm^{-1} which is likely due to small amounts of aldol condensation products in the MEK solvent used in the separation or some oxidation during the repetitive fraction collection procedure. The Peak 2 material also shows some carbonyl, which is also likely due to the MEK (Figure 2-13). The spectra all show typical aliphatic C-H profiles from 3000 to 2899 cm^{-1} , $-(\text{CH}_2)_n$ - chain near 1465 cm^{-1} , and CH_3 near $1450 - 1375\text{ cm}^{-1}$. From the C=C absorbance near 1600 cm^{-1} and the aromatic C-H frequencies at 870 , 810 , and 743 cm^{-1} , the least amount of aromatic and other functional group structure of all the fractions is found in the Peak 3 material, followed by a little more in the Peak 2 fraction material. The FTIR spectrum of the Peak 3 material confirms that this is primarily aliphatic hydrocarbon waxy material, with very little aromatic content.

Waxphaltene Determinator Fraction Characterization by High Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry The fractions were also characterized and by high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT ICRMS) at the High Magnetic Field Laboratory at Florida State University in a no-cost collaborating with this project. This qualitative characterization was of the acidic and basic components of the Peak 2 and 3 materials. The results of these analyses provided significant new information than the high temperature GC or FTIR analyses. The report from the FSU researchers is provided in Appendix C. The results show that the high temperature GC separations described above did not resolve the material above about C_{60} . The actual molecular weights of the wax fractions components ranged from about 600 to above $1,600\text{ g/mol}$ (expressed as m/z ratio). All three fractions had some brown color which is likely due to highly alkyl substituted pericondensed aromatic material. In addition to the paraffins that were identified by high temperature GC, there are other molecules present that are not pure wax hydrocarbons. However, these exhibit freezing and solubility behavior similar to the wax components and they should not be ignored. Also, iso-paraffins include molecules with complex degrees of branching at various locations in the molecules.

CONCLUSIONS

Additional fine tuning optimization was made for the analytical Asphaltene Determinator separation. A new calculation method for determining Total Pericondensed Aromatic (TPA) content for residuum and whole oils was developed. A procedure for direct injection of volatile oils was developed. This provides rapid characterization of the asphaltene component molecules and their solubility distribution. A series of volatile crude oils is being characterized using this new approach. A study to characterize the differences in composition of asphaltenes in refinery desalter rag layer emulsions and the corresponding feed and desalter oils is currently underway. The wax types and carbon number distributions in the two heptane eluting fraction from the Waxphaltene Determinator separation were characterized by repetitive collection of the fractions followed by high temperature GC.

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Table 2-1. Asphaltene Determinator Characterization of Light Desalter Inlet Oil.

Sample:	WRI 1338-82-4			Date: 3/15/11					
Desalter Inlet Light Oil									
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA
Whole Oil 2.0016 mg	69.52	ELSD	98.95	0.47	0.43	0.14	3.4	0.55	2.0
		500 nm	47.99	14.08	26.23	11.71	1.2		
		700 nm	32.42	18.18	28.56	20.85	0.9		
		Whole Oil ELSD Area:			2016104	QC ELSD Area:		6615140	
Corrected for Volatiles Loss		ELSD	99.68	0.14	0.13	0.04	3.4	0.55	0.6
		500 nm	47.99	14.08	26.23	11.71	1.2		
		700 nm	32.42	18.18	28.56	20.85	0.9		
Gravimetric Asphaltenes Analysis									
Material/ Amt. Inj.	Wt.% of Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Area Percent Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Toluene + CH ₂ Cl ₂ :MeOH	Total Wt. % Asphaltenes
C7 Asphaltenes 10 μ ~0.6800 mg	0.05	ELSD	10.52	23.22	61.78	4.49	66.27	0.03	0.11
		500 nm	6.68	25.99	61.23	6.11	67.34		
		700 nm	4.44	26.38	62.46	6.72	69.18		
C7 Asphaltenes 0.45 μ ~0.8400 mg	0.06	ELSD	33.96	26.60	37.04	2.40	39.44	0.02	
		500 nm	14.50	35.48	45.88	4.14	50.02		
		700 nm	10.94	37.21	46.97	4.88	51.85		

Table 2-2. Asphaltene Determinator Characterization of Desalted Light Oil.

Sample:	WRI 1338-82-3								
	Desalted Light Oil							AD Asphalt	
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCI	Aging Index Ratio T/H	Percent TPA
Whole Oil 2.0000 mg	70.34	ELSD	99.01	0.41	0.41	0.17	2.4		1.8
		500 nm	46.38	14.09	26.99	12.53	1.1	0.58	
		700 nm	28.72	17.66	30.68	22.94	0.8		
		Whole Oil ELSD Area:		1961945		QC ELSD Area:		6615140	
Corrected for		ELSD	99.71	0.12	0.12	0.05	2.4		0.5
Volatiles Loss		500 nm	46.38	14.09	26.99	12.53	1.1	0.58	
		700 nm	28.72	17.66	30.68	22.94	0.8		
Gravimetric Asphaltenes Analysis									
Material/ Amt. Inj.	Wt.% of Whole Oil	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH	Area Percent Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Toluene + CH ₂ Cl ₂ :MeOH	Total Wt. % Asphaltenes
C7 Asphaltenes 10 µ ~0.9600 mg	0.07	ELSD	20.30	20.68	55.47	3.55	59.02	0.04	0.12
		500 nm	6.29	26.81	61.29	5.61	66.90		
		700 nm	4.07	26.82	63.10	6.01	69.11		
C7 Asphaltenes 0.45 µ ~0.6800 mg	0.05	ELSD	43.78	21.83	31.89	2.50	34.39	0.02	
		500 nm	16.46	32.84	45.66	5.04	50.70		
		700 nm	12.66	34.30	47.07	5.97	53.04		

Table 2-3. Asphaltene Determinator Characterization of Light Oil Desalter Whole Emulsion, Shaken.

Sample: WRI 1338-82-5		Light Oil Deesalter Emulsion with 40 vol. % Oil, Shaken						AD Asphalt	
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
	<u>Volatiles</u>	<u>Detector</u>	<u>Heptane</u>	<u>CyC₆</u>	<u>Toluene</u>	<u>CH₂Cl₂:MeOH</u>	<u>Ratio Cy/CCI</u>	<u>Ratio T/H</u>	<u>TPA</u>
Whole Oil 2.0018 mg	90.66	ELSD	97.67	1.34	0.62	0.37	3.6		na
		500 nm	Interference due to water turbidity for CH ₂ Cl ₂ :MeOH peak?					na	
		700 nm	Interference due to water turbidity for CH ₂ Cl ₂ :MeOH peak?						
		Whole Oil ELSD Area:		617842	QC ELSD Area:		6615140		
Corrected for Volatiles Loss		ELSD	99.78	0.13	0.06	0.03	3.6		na
		500 nm	na	na	na	na	na	na	
		700 nm	na	na	na	na	na		
Gravimetric Asphaltenes Analysis									
Material/ Amt. Inj.	Wt.% of Whole Oil	Asphaltene Determinator Area Percent					Area Percent Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Toluene + CH ₂ Cl ₂ :MeOH	Total Wt. % Asphaltenes
		<u>Detector</u>	<u>Heptane</u>	<u>CyC₆</u>	<u>Toluene</u>	<u>CH₂Cl₂:MeOH</u>			
C7 Asphaltenes 10 µ ~0.5600 mg	0.04	ELSD	17.92	18.35	57.11	6.62	63.73	0.03	0.11
		500 nm	6.40	22.00	62.24	9.37	71.61		
		700 nm	4.30	22.00	63.17	10.53	73.70		
C7 Asphaltenes 0.45 µ ~1.0000 mg	0.07	ELSD	28.55	25.55	42.86	3.05	45.91	0.03	
		500 nm	12.47	32.79	49.71	5.03	54.74		
		700 nm	8.90	33.78	51.35	5.97	57.32		

Table 2-4. Summary Results for the 500 nm Methylene Chloride:methanol Peak Areas for the Light Oil Series.

Asphaltene Determinator CH ₂ Cl ₂ :MeOH (98:2 v:v) Area Percent		
<u>Light Crude API ~40</u>	<u>500 nm Relative Area Percent</u>	
<u>Material</u>	<u>Whole Oil</u>	<u>10 Micron Asphaltenes</u>
Inlet Crude	11.71	6.11
Rag layer Emulsion	na	9.37
Centrifuged Rag Layer Oil	na	31.36
Desalted Outlet Crude	12.53	5.61

Table 2-5. Asphaltene Determinator Characterization of Light Supernatant Centrifuged Desalter Emulsion Oil.

Sample:		WRI 1338-82-5							
		Light Oil from Emulsion Separated by Centrifugation							
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	AD Asphalt Aging Index	Percent
	<u>Volatiles</u>	<u>Detector</u>	<u>Heptane</u>	<u>CyC₆</u>	<u>Toluene</u>	<u>CH₂Cl₂:MeOH</u>	<u>Ratio Cy/CCl</u>	<u>Ratio T/H</u>	<u>TPA</u>
Whole Oil	68.21	ELSD	97.95	1.10	0.25	0.70	1.6		na
2.0016 mg		500 nm	Interference due to water turbidity for CH ₂ Cl ₂ :MeOH peak?					na	
		700 nm	Interference due to water turbidity for CH ₂ Cl ₂ :MeOH peak?						
		Whole Oil ELSD Area:		2026156		QC ELSD Area:	6373174.0		
Corrected for		ELSD	99.35	1.10	0.25	0.70	1.6		na
Volatiles Loss		500 nm	na	na	na	na	na	na	
		700 nm	na	na	na	na	na		
Gravimetric Asphaltenes Analysis									
Material/ Amt. Inj.	Wt.% of	Asphaltene Determinator Area Percent					Area Percent	Wt. %	Total
	<u>Whole Oil</u>	<u>Detector</u>	<u>Heptane</u>	<u>CyC₆</u>	<u>Toluene</u>	<u>CH₂Cl₂:MeOH</u>	<u>Toluene + CH₂Cl₂:MeOH</u>	<u>Toluene + CH₂Cl₂:MeOH</u>	<u>Wt. % Asphaltenes</u>
C7 Asphaltenes	1.93	ELSD	12.58	28.32	35.61	23.48	59.09	1.14	2.32
10 μ (difcult to filter)		500 nm	5.00	15.02	48.63	31.36	79.99		
0.4007 mg		700 nm	na	14.32	45.70	39.98	85.68		
C7 Asphaltenes	0.39	ELSD	63.05	11.26	17.66	8.03	25.69	0.10	
0.45 μ		500 nm	14.18	22.66	46.18	16.97	63.15		
0.4051 mg		700 nm	9.60	22.71	44.54	23.15	67.69		

Table 2-6. Asphaltene Determinator Characterization of Medium Desalter Feed Oils from Sets 1 and 2.

Sample:	WRI 1338-94-21									
	Desalter Inlet Medium Crude Set 1							AD Asphalt		
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Toluene	Percent CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCI	Aging Index Ratio T/H	Percent TPA	
Whole Oil	54.33	ELSD	95.26	1.44	2.81	0.49	2.9			7.7
2.0012 mg		500 nm	38.64	18.00	34.34	9.02	2.0	0.89		
		700 nm	24.32	21.59	38.85	15.24	1.4			
		Whole Oil ELSD Area: 3096016			QC ELSD Area:		6779303			
Corrected for		ELSD	97.84	0.66	1.28	0.22	2.9			3.5
Volatiles Loss		500 nm	38.64	18.00	34.34	9.02	2.0	0.89		
		700 nm	24.32	21.59	38.85	15.24	1.4			
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total	
Material/ Amt. Inj.	Wt.% of Whole Oil	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Toluene	Percent CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Asphaltenes	
C7 Asphaltenes	4.27	ELSD	18.53	25.10	52.81	3.56	56.37	2.41		4.87
10 μ		500 nm	11.68	26.19	55.91	6.21	62.12			
0.4010 mg		700 nm	6.48	26.94	58.44	8.14	66.58			
C7 Asphaltenes	0.60	ELSD	22.94	25.25	47.72	4.10	51.82	0.31		
0.45 μ		500 nm	12.86	27.55	53.33	6.26	59.59			
0.4039 mg		700 nm	8.53	28.16	55.36	7.95	63.31			

Sample:	WRI 1338-94-22									
	Desalter Inlet Medium Crude Set 2									
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Asphaltene Determinator Detector	Area Percent Heptane	Percent CyC ₆	Percent Toluene	Percent CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA	
Whole Oil	54.87	ELSD	95.33	1.42	2.81	0.44	3.2		7.6	
2.0014 mg		500 nm	38.55	18.06	34.38	9.01	2.0	0.89		
4/15/2011		700 nm	23.93	21.51	39.18	15.38	1.4			
		Whole Oil ELSD Area: 3059784			QC ELSD Area:		6779303			
Corrected for		ELSD	97.89	0.64	1.27	0.20	3.2		3.4	
Volatiles Loss		500 nm	38.55	18.06	34.38	9.01	2.0	0.89		
		700 nm	23.93	21.51	39.18	15.38	1.4			
Gravimetric Asphaltenes Analysis										
Material/ Amt. Inj.	Wt.% of Whole Oil	Asphaltene Determinator Detector	Area Percent Heptane	Percent CyC ₆	Percent Toluene	Percent CH ₂ Cl ₂ :MeOH	Area Percent Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Toluene + CH ₂ Cl ₂ :MeOH	Total Wt. % Asphaltenes	
C7 Asphaltenes	4.32	ELSD	19.02	25.81	51.75	3.41	55.16	2.38	4.82	
10 μ		500 nm	11.94	27.16	54.78	6.12	60.90			
0.4008 mg		700 nm	6.45	28.07	57.50	7.98	65.48			
C7 Asphaltenes	0.50	ELSD	20.46	24.31	47.97	7.25	55.22	0.28		
0.45 μ		500 nm	13.49	26.11	52.51	7.89	60.40			
0.4076 mg		700 nm	6.74	26.84	55.43	10.99	66.42			

Table 2-7. Asphaltene Determinator Characterization of Medium Desalted Outlet Oils from Sets 1 and 2.

Sample:	WRI 1338-94-23											
	Desalted Medium Crude Set 1											
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Asphaltene Determinator	Area Percent				Coke Index	AD Asphalt Aging Index	Percent			
		<u>Detector</u>	<u>Heptane</u>	<u>CyC₆</u>	<u>Toluene</u>	<u>CH₂Cl₂:MeOH</u>	<u>Ratio Cy/CCI</u>	<u>Ratio T/H</u>	<u>TPA</u>			
Whole Oil 2.0002 mg	53.58	ELSD	95.27	1.49	2.78	0.45	3.3					
		500 nm	39.06	18.50	33.77	8.67	2.1	0.86				
		700 nm	24.16	21.99	38.53	15.32	1.4					
		Whole Oil ELSD Area:			3147093	QC ELSD Area:		6779303				
Corrected for		ELSD	97.80	0.69	1.29	0.21	3.3		3.6			
Volatiles Loss		500 nm	39.06	18.50	33.77	8.67	2.1	0.86				
		700 nm	24.16	21.99	38.53	15.32	1.4					
Gravimetric Asphaltenes Analysis										Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt. % Whole Oil	Asphaltene Determinator	Area Percent				Toluene + CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Total Wt. % Asphaltenes			
		<u>Detector</u>	<u>Heptane</u>	<u>CyC₆</u>	<u>Toluene</u>	<u>CH₂Cl₂:MeOH</u>			4.97			
C7 Asphaltenes 10 µ 0.4004 mg	4.22	ELSD	20.42	26.30	50.09	3.20	53.29	2.25				
		500 nm	11.99	27.51	54.49	6.01	60.50					
		700 nm	6.49	28.42	57.27	7.82	65.09					
C7 Asphaltenes 0.45 µ 0.4019 mg	0.75	ELSD	28.76	21.24	45.82	4.18	50.00	0.38				
		500 nm	13.01	24.80	55.31	6.87	62.18					
		700 nm	7.42	25.43	58.17	8.98	67.15					

Sample:	WRI 1338-94-24								
	Desalted Medium Crude Set 2								
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Asphaltene Determinator Area Percent					Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA
Whole Oil 2.0006 mg	53.40	ELSD	95.60	1.47	2.48	0.45	3.3	0.78	7.4
		500 nm	40.90	19.91	31.76	7.42	2.7		
		700 nm	26.69	24.00	37.83	11.48	2.1		
		Whole Oil ELSD Area:		2723177		QC ELSD Area:		5843181	
Corrected for		ELSD	97.95	0.69	1.16	0.21	3.3	0.78	3.5
Volatiles Loss		500 nm	40.90	19.91	31.76	7.42	2.7		
		700 nm	26.69	24.00	37.83	11.48	2.1		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt. % Whole Oil	Asphaltene Determinator Area Percent					Toluene + CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Asphaltenes
		Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes 10 µ 0.4002 mg	2.27	ELSD	10.93	23.33	62.27	3.46	65.73	1.49	2.6
		500 nm	8.51	24.60	61.87	5.03	66.90		
		700 nm	4.78	24.89	64.05	6.28	70.33		
C7 Asphaltenes 0.45 µ 0.4120 mg	0.31	ELSD	23.69	21.36	51.98	2.97	54.95	0.17	
		500 nm	11.10	25.55	58.25	5.10	63.35		
		700 nm	6.46	26.31	60.68	6.55	67.23		

Table 2-8. Asphaltene Determinator Characterization of Medium Oil Desalter Emulsions from Sets 1 and 2.

Sample:	WRI 1338-94-25									
	Medium Crude Emulsion Shaken (Contains 60 vol. % Oil) Set 1							AD Asphalt		
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent	
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCI	Ratio T/H	TPA	
Whole Oil 2.0000 mg	89.38	ELSD	93.87	1.61	3.21	1.31	1.2		8.7	
		500 nm	29.28	17.15	39.90	13.67	1.3	1.36		
		700 nm	14.85	18.09	45.02	22.04	0.8			
		Whole Oil ELSD Area:		620678	QC ELSD Area:		5843181			
Corrected for		ELSD	99.35	0.17	0.34	0.14	1.2		0.9	
Volatiles Loss		500 nm	29.28	17.15	39.90	13.67	1.3	1.36		
		700 nm	14.85	18.09	45.02	22.04	0.8			
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total	
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %	
	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes	
C7 Asphaltenes 10 µ 0.4075 mg	1.62	ELSD	13.04	18.00	58.62	10.34	68.96	1.12	1.76	
		500 nm	7.09	18.90	62.39	11.62	74.01			
		700 nm	3.90	17.92	63.30	14.88	78.18			
C7 Asphaltenes 0.45 µ 0.3900 mg	0.14	ELSD	30.96	23.48	39.62	5.93	45.55	0.06		
		500 nm	14.89	26.44	44.84	13.83	58.67			
		700 nm	7.93	24.62	42.63	24.82	67.45			

Sample:		WRI 1338-94-26							
		Medium Crude Emulsion Shaken (Contains 80 vol. % Oil) Set 2						AD Asphalt	
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil 2.0002 mg	89.76	ELSD	94.06	1.57	3.02	1.35	1.2		8.5
		500 nm	29.99	17.49	39.48	13.04	1.3	1.32	
		700 nm	19.13	19.43	41.43	20.00	1.0		
		Whole Oil ELSD Area:		598385	QC ELSD Area:		5843181		
Corrected for		ELSD	99.39	0.16	0.31	0.14	1.2		0.9
Volatiles Loss		500 nm	29.99	17.49	39.48	13.04	1.3	1.32	
		700 nm	19.13	19.43	41.43	20.00	1.0		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
C7 Asphaltenes 10 μ 0.4004 mg	2.16	ELSD	10.81	15.05	48.61	25.54	74.15	1.60	2.47
		500 nm	5.66	12.59	44.56	37.19	81.75		
		700 nm	2.69	9.01	34.39	53.91	88.30		
C7 Asphaltenes 0.45 μ 0.4160 mg	0.31	ELSD	14.73	20.01	47.44	17.81	65.25	0.20	
		500 nm	7.70	16.93	41.97	33.40	75.37		
		700 nm	3.50	12.89	32.36	51.25	83.61		

Table 2-9. Asphaltene Determinator Characterization of Medium Desalter Centrifuged Oils from Emulsions from Sets 1 and 2.

Sample: WRI 1338-94-25									
Medium Crude Emulsion Oil Separated by Centrifugation Set 1									
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Asphaltene Determinator Area Percent Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA
Whole Oil 2.0005 mg	56.51	ELSD	94.70	1.89	2.93	0.48	3.9	0.99	8.2
		500 nm	35.22	20.13	35.04	9.61	2.1		
		700 nm	22.71	23.39	39.16	14.74	1.6		
Whole Oil ELSD Area:		2979118		QC ELSD Area:		6849664			
Corrected for Volatiles Loss		ELSD	97.70	0.82	1.27	0.21	3.9	0.99	3.6
		500 nm	35.22	20.13	35.04	9.61	2.1		
		700 nm	22.71	23.39	39.16	14.74	1.6		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt.% of Whole Oil	Asphaltene Determinator Area Percent Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Asphaltenes
C7 Asphaltenes 10 μ 0.3981 mg	1.84	ELSD	14.87	30.22	51.76	3.15	54.91	1.01	2.69
		500 nm	10.67	31.85	52.36	5.12	57.48		
		700 nm	6.37	32.94	54.26	6.43	60.69		
C7 Asphaltenes 0.45 μ 0.4240 mg	0.85	ELSD	27.25	26.10	43.67	2.98	46.65	0.40	
		500 nm	12.35	31.39	51.06	5.20	56.26		
		700 nm	7.41	32.65	53.25	6.69	59.94		

Sample: WRI 1338-94-26									
Medium Crude Emulsion Oil Separated by Centrifugation Set 2									
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	AD Asphalt Aging Index	Percent
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil 2.0006 mg	56.52	ELSD	94.92	1.88	2.78	0.42	4.5	0.97	7.9
		500 nm	35.92	20.14	35.01	8.93	2.3		
		700 nm	22.77	23.54	39.58	14.11	1.7		
Whole Oil ELSD Area:		2978183		QC ELSD Area:		6849664			
Corrected for Volatiles Loss		ELSD	97.79	0.82	1.21	0.18	4.5	0.97	3.4
		500 nm	35.92	20.14	35.01	8.93	2.3		
		700 nm	22.77	23.54	39.58	14.11	1.7		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
C7 Asphaltenes 10 μ 0.4008 mg	1.96	ELSD	15.30	29.18	50.56	4.96	55.52	1.09	2.81
		500 nm	11.29	30.98	51.69	6.04	57.73		
		700 nm	6.80	31.86	53.39	7.94	61.33		
C7 Asphaltenes 0.45 μ 0.4012 mg	0.85	ELSD	21.55	28.34	46.90	3.21	50.11	0.43	
		500 nm	12.45	31.34	50.92	5.30	56.22		
		700 nm	7.27	32.67	53.43	6.63	60.06		

Table 2-10. Summary of Results for the 500 nm Methylene Chloride:methanol Peak Areas for the Medium Oil Sets 1 and 2.

Asphaltene Determinator CH₂Cl₂:MeOH (98:2 v:v) Area Percent		
Medium Crude 1 API ~25	500 nm Relative Area Percent	
<u>Material</u>	<u>Whole Oil</u>	<u>10 Micron Asphaltenes</u>
Inlet Crude	9.02	6.21
Rag layer Emulsion	13.67	11.62
Centrifuged Rag Layer Oil	9.61	5.12
Desalted Outlet Crude	8.67	6.01

Asphaltene Determinator CH₂Cl₂:MeOH (98:2 v:v) Area Percent		
Medium Crude 2 API ~25	500 nm Relative Area Percent	
<u>Material</u>	<u>Whole Oil</u>	<u>10 Micron Asphaltenes</u>
Inlet Crude	9.01	6.12
Rag layer Emulsion	13.04	37.19
Centrifuged Rag Layer Oil	8.93	6.04
Desalted Outlet Crude	7.42	5.03

Table 2-11. Amount of Oil, Water, and Sediment following Centrifugation of Emulsions.

Emulsions from Heavy Crude Set (API ~20)			
<u>Try Layer</u>	Centrifuged Volume Percent		
	<u>Oil</u>	<u>Water</u>	<u>Sediment</u>
T-1	50	34	16
T-2	40	49	11
T-3	56	30	14
T-4	56	35	9

Table 2-12. Relative 500 nm Absorbance Detector Peak Area Percents for the Most Pericondensed Material in the Heavy Oil Desalter Sample Set.

Asphaltene Determinator 500 nm CH₂Cl₂:MeOH (98:2 v:v) Peaks		
Heavy Crude API~20		
	500 nm Relative Area Percent	
<u>Sample</u>	<u>Whole Material</u>	<u>10 μ Asphaltenes</u>
Inlet Crude	4.31	3.03
Desalted Outlet Crude	4.12	2.86
<u>Try Layer 1</u>		
Whole Sample Shaken	5.74	11.23
Whole Emulsion	5.84	10.58
Emulsion Centrifuged Oil	3.73	3.91
Emulsion Centrifuged Water, Evaporated	7.71	na
<u>Try Layer 2</u>		
Whole Sample Shaken	5.37	13.71
Whole Emulsion	5.77	10.99
Emulsion Centrifuged Oil	3.95	3.94
Emulsion Centrifuged Water, Evaporated	6.82	na
Bottle 2 Centrifuged Emulsion Water, Evaporated	18.79	na
<u>Try Layer 3</u>		
Whole Sample Shaken	5.69	13.99
Top Layer Oil Only	4.69	3.70
Whole Emulsion	5.74	13.08
Emulsion Centrifuged Oil	5.79	4.13
Emulsion Centrifuged Water, Evaporated	4.48	na
Middle Bottle 2 Whole Emulsion	29.03	4.65
Middle Bottle 2 Water, Evaporated	8.16	na
<u>Try Layer 4</u>		
Whole Sample Shaken	5.45	8.74
Whole Emulsion	5.29	3.75
Emulsion Centrifuged Oil	4.00	3.75
Emulsion Centrifuged Water, Evaporated	3.39	na
<u>Try Layer 5</u>		
Whole Oil	4.13	4.14
<u>Try Layer 7</u>		
Whole Oil	3.93	4.14

Table 2-13. Relative Volatiles Corrected ELSD Peak Area Percents for the Most Pericondensed Material in the Heavy Oil Desalter Sample Set.

Asphaltene Determinator Volatiles Corrected ELSD Peaks		CH₂Cl₂:MeOH (98:2 v:v) Peak	
Heavy Crude API~20		ELSD Relative Area Percent	
Sample	Volatiles Corrected Area % C7 Insolubles	Whole Material	10 μ Asphaltenes
Inlet Crude	3.67	0.09	0.90
Desalted Outlet Crude	3.84	0.09	0.84
Try Layer 1			
Whole Sample Shaken	1.91	0.08	5.79
Whole Emulsion	2.06	0.11	6.40
Emulsion Centrifuged Oil	3.58	0.13	2.52
Emulsion Centrifuged Water, Evaporated	7.76	0.45	na
Try Layer 2			
Whole Sample Shaken	2.16	0.09	6.87
Whole Emulsion	2.19	0.10	5.90
Emulsion Centrifuged Oil	3.60	0.14	2.27
Emulsion Centrifuged Water, Evaporated	7.18	0.57	na
Bottle 2 Centrifuged Emulsion Water, Evaporated	31.99	2.20	na
Try Layer 3			
Whole Sample Shaken	2.30	0.10	6.89
Top Layer Oil Only	1.96	0.20	2.14
Whole Emulsion	2.15	0.34	7.29
Emulsion Centrifuged Oil	2.55	0.15	2.46
Emulsion Centrifuged Water, Evaporated	6.27	0.77	na
Middle Bottle 2 Whole Emulsion	0.31	0.17	2.20
Middle Bottle 2 Water, Evaporated	22.67	1.87	na
Try Layer 4			
Whole Sample Shaken	2.11	0.09	4.74
Whole Emulsion	2.60	0.10	1.82
Emulsion Centrifuged Oil	5.29	0.17	1.68
Emulsion Centrifuged Water, Evaporated	8.94	0.79	na
Try Layer 5			
Whole Oil	3.97	0.11	1.11
Try Layer 7			
Whole Oil	4.19	0.10	0.92

Table 2-14. Relative ELSD Non-Volatile Component ELSD Peak Area Percents for the Most Polar and Pericondensed Material in the Heavy Oil Desalter Sample Set.

Asphaltene Determinator ELSD Peaks for ELSD non-Volatile Components				CH ₂ Cl ₂ :MeOH (98:2 v:v) Peak	
Heavy Crude API~20	Area Percent	ELSD Non-Volatile		ELSD Relative Area Percent	
Sample	ELSD Volatiles	Area % C7 Insolubles	Percent TPA	Whole Material	10 μ Asphaltenes
Inlet Crude	41.02	6.22	9.8	0.16	0.90
Desalted Outlet Crude	40.85	6.49	10.2	0.16	0.84
<u>Try Layer 1</u>					
Whole Sample Shaken	74.29	7.43	11.5	0.31	5.79
Whole Emulsion	68.58	7.19	11.6	0.35	6.40
Emulsion Centrifuged Oil	50.91	7.29	11.4	0.27	2.52
Emulsion Centrifuged Water, Evaporated	70.88	26.64	37.1	10.41	na
<u>Try Layer 2</u>					
Whole Sample Shaken	69.82	7.17	11.1	0.29	6.87
Whole Emulsion	70.26	7.35	11.9	0.33	5.90
Emulsion Centrifuged Oil	51.69	7.45	11.6	0.28	2.27
Emulsion Centrifuged Water, Evaporated	79.21	34.53	51.3	11.84	na
Bottle 2 Centrifuged Emulsion Water, Evaporated	60.35	80.68	103.6	5.55	na
<u>Try Layer 3</u>					
Whole Sample Shaken	69.39	7.52	11.7	0.34	6.89
Top Layer Oil Only	79.99	9.80	14.3	1.01	2.14
Whole Emulsion	69.47	7.05	11.5	0.90	7.29
Emulsion Centrifuged Oil	69.11	8.25	12.6	0.47	2.46
Emulsion Centrifuged Water, Evaporated	56.33	14.35	22.9	0.77	na
Middle Bottle 2 Whole Emulsion	99.48	60.51	74.6	33.42	2.20
Middle Bottle 2 Water, Evaporated	58.54	54.68	84.4	1.87	na
<u>Try Layer 4</u>					
Whole Sample Shaken	73.87	8.06	12.1	0.36	4.74
Whole Emulsion	62.98	7.03	11.3	0.27	1.82
Emulsion Centrifuged Oil	33.04	7.90	12.4	0.25	1.68
Emulsion Centrifuged Water, Evaporated	48.87	17.48	29.0	3.38	na
<u>Try Layer 5</u>					
Whole Oil	40.24	6.65	10.5	0.18	1.11
<u>Try Layer 7</u>					
Whole Oil	37.91	6.75	10.5	0.16	0.92

Table 2-15. Relative 500 nm Absorbance Detector Peak Area Percents for the Gravimetric Asphaltenes from the Heavy Oil Desalter Sample Set.

Asphaltene Determinator 500 nm Peaks from 10 μ Gravimetric Asphaltenes			
<u>Asphaltenes from Heavy Crude API~20</u>		<u>500 nm Relative Area Percent</u>	
<u>Sample</u>	<u>wt.%</u>	<u>Toluene</u>	<u>CH₂Cl₂:MeOH</u>
Inlet Crude	7.51	54.14	3.03
Desalted Outlet Crude	8.21	52.35	2.86
<u>Try Layer 1</u>			
Whole Oil	2.86	51.94	11.23
Whole Emulsion	2.39	53.44	10.58
Emulsoin Centrifuged Oil	3.54	53.20	3.91
<u>Try Layer 2</u>			
Whole Oil	1.79	53.13	13.71
Whole Emulsion	1.72	54.05	10.99
Emulsoin Centrifuged Oil	6.92	52.08	3.94
<u>Try Layer 3</u>			
Whole Oil	2.95	52.78	13.99
Top 1.5 Inch Oil	0.78	57.17	3.70
Whole Emulsion	2.00	49.85	13.08
Emulsoin Centrifuged Oil	5.95	51.39	4.13
<u>Try Layer 4</u>			
Whole Oil	3.29	55.37	8.74
Whole Emulsion	4.88	57.21	3.75
Emulsoin Centrifuged Oil	9.06	51.55	3.75
<u>Try Layer 5</u>			
Whole Oil	8.97	52.63	4.14
<u>Try Layer 7</u>			
Whole Oil	8.98	50.33	3.82

Table 2-16. ELSD Peak Area Percents for Waxphaltene Determinator Separations of Eight Residua.

Residuum	SHRP Sample	Evaporative Light Scattering Detector Area Percent				
		-24 °C MEK	-24 °C Heptane	60 °C Heptane	30 °C Toluene	30 °C CH ₂ Cl ₂ :MeOH (98:2)
Lloydminster	AAA-1	79.99	8.00	0.71	9.61	1.71
WY Sour	AAB-1	78.64	10.22	1.79	7.58	1.78
Redwater	AAC-1	83.52	9.90	2.24	3.27	1.09
CA Coastal	AAD-1	77.49	7.68	0.83	10.44	3.56
W TX Sour	AAF-1	82.91	8.68	1.93	5.45	1.03
CA Valley	AAG-1	93.39	4.16	0.27	1.04	1.15
Boscan	AAK-1	76.11	9.25	1.18	10.81	2.64
W TX Intermediate	AAM-1	54.73	34.09	6.90	3.29	1.00

Table 2-17. Possible Chemical Structures Represented by Waxphaltene Determinator Peaks.

<u>Eluting Solvent</u>	<u>Temperature</u>	<u>Possible Chemical Structures</u>
Methyl Ethyl Ketone	-24 °C	relatively low molecular weight hydrocarbons, polar and aromatic functional groups, some alkyl substituted pericondensed aromatics
Heptane	-24 °C	<i>n</i> -paraffins C ₂₆ – C ₄₀ ⁺ (by GC) iso paraffins C ₄₀ – C ₅₀ ⁺ (by GC) highly alkyl substituted polar and aromatic functional groups
Heptane	60 °C	<i>n</i> -paraffins C ₃₀ – C ₆₀ ⁺ (by GC) iso paraffins C ₅₀ – C ₆₀ ⁺ (by GC) highly alkyl substituted polar and aromatic functional groups
Toluene	30 °C	alkyl substituted pericondensed aromatics with polar functional groups (asphaltenes)
Methylene Chloride: Methanol (98:2 v:v)	30 °C	highly pericondensed pre-coke aromatics; asphaltenes

Figure 2-1. Asphaltene Determinator Characterization Tree for Residua and Volatile Oils.

Figure 2-2. Generic Schematic for a Refinery Desalter Unit and Try Layers.

Figure 2-3. Drawing of Conceptual Water Droplets in Oil with Emulsion Stabilizing Skin.

Figure 2-4. Photograph of Heavy Oil Desalter Emulsion Samples from Try Layers 1 – 5.

Figure 2-5. Waxphaltene Determinator Separation Profiles for Lloydminster and West Texas Intermediate Residua.

Figure 2-6. Waxphaltene Determinator Separation Profiles for Boscan and Wyoming Sour Residua.

Figure 2-7. Waxphaltene Determinator Separation Profiles for Cosden, Oklahoma and California Valley Residua.

Figure 2-8. Waxphaltene Determinator Separation Profiles for Redwater, B.C. and California Coastal Residua.

Figure 2-9. Separation Profiles for Devolatilized Dakota Crude Oil and Waxy Deposit from Dakota Crude Oil.

Figure 2-10. Separation Profile for Devolatilized Tensleep Crude Oil.

Figure 2-11. Waxphaltene Determinator Separation Profile for 2 mg Waxy West Texas Intermediate Residuum.

Figure 2-12. High Temperature GC Separation Profiles for Peaks 1, 2, and 3 Materials.

Figure 2-13. ATR FTIR Spectra of Whole West Texas Intermediate Residuum and Fractions 2 and 3.

Appendix A

Separation Tree Data Tables for Volatile Crude Oils

Sample:		WRI 1270-67-20							
		Canadian Crude Oil A							
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Asphaltene Determinator Area Percent	Coke Index	AD Asphalt Aging Index	Percent				
		Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil	47.78	ELSD	91.08	4.11	4.48	0.34	12.1		14.5
2.0029 mg		500 nm	38.36	22.64	34.13	4.87	4.6	0.89	
11/17/2009		700 nm	26.88	25.65	39.92	7.55	3.4		
		Whole Oil ELSD Area:		5429411	QC ELSD Area:		10397542		
Calculated		ELSD	95.34	2.15	2.34	0.18	12.1		7.6
to		500 nm	38.36	22.64	34.13	4.87	4.6	0.89	
whole oil		700 nm	26.88	25.65	39.92	7.55	3.4		
Material/ Amt. Inj.	Wt. %	Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH			
C7 Asphaltenes	5.19	ELSD	12.43	29.41	55.11	3.05			
10 µ		500 nm	9.29	28.70	57.02	4.99			
0.4014 mg		700 nm	6.02	28.66	59.13	6.19			
C7 Asphaltenes	0.07	ELSD	16.48	25.15	44.43	N/A			
0.45 µ		500 nm	6.84	16.58	59.00	17.57			
0.1320 mg		700 nm	2.64	14.62	56.90	25.83			
Maltenes	1.24	ELSD	28.28	31.77	37.23	2.71			
Varnish		500 nm	17.43	34.66	44.86	3.06			
0.4160 mg		700 nm	12.55	36.04	47.50	3.91			
SARA Polars	6.39	ELSD	80.98	8.08	8.93	2.01			
Silica		500 nm	56.19	16.86	23.42	3.52			
0.2240 mg		700 nm	52.04	19.73	23.89	4.34			

Sample:		WRI 1270-67-23							
		Canadian Crude Oil B							
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Asphaltene Determinator Area Percent	Coke Index	AD Asphalt Aging Index	Percent				
		Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil	52.39	ELSD	92.31	3.02	4.30	0.38	7.9		12.7
2.0022 mg		500 nm	39.27	22.31	33.18	5.24	4.3	0.84	
11/17/2009		700 nm	27.43	25.49	39.03	8.04	3.2		
		Whole Oil ELSD Area:		4950444	QC ELSD Area:		10397542		
Corrected for		ELSD	96.34	1.44	2.05	0.18	7.9		6.0
Volatiles Loss		500 nm	39.27	22.31	33.18	5.24	4.3	0.84	
		700 nm	27.43	25.49	39.03	8.04	3.2		
Material/ Amt. Inj.	Wt. %	Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH			
C7 Asphaltenes	4.58	ELSD	13.19	29.94	53.83	3.04			
10 µ		500 nm	9.70	28.97	56.15	5.19			
0.4008 mg		700 nm	6.10	28.96	58.46	6.49			
C7 Asphaltenes	0.18	ELSD	14.26	24.26	56.22	5.26			
0.45 µ		500 nm	7.99	20.73	64.43	6.85			
0.3650 mg		700 nm	4.14	20.30	67.52	8.03			
Maltenes	1.29	ELSD	29.12	32.36	35.81	2.71			
Varnish		500 nm	17.53	34.71	44.57	3.19			
0.4011 mg		700 nm	12.91	35.99	46.87	4.23			
SARA Polars	6.95	ELSD	84.85	5.38	8.39	1.38			
Silica		500 nm	59.43	16.17	21.60	2.80			
0.2430 mg		700 nm	56.19	18.33	22.82	2.66			

Sample:		WRI 1270-67-9							
		Alveim Crude Oil						AD Asphalt	
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil 2.0001 mg	64.29	ELSD	98.43	1.18	0.31	0.09	13.1		3.2
		500 nm	50.99	10.78	28.02	10.21	1.1	0.55	
		700 nm	42.51	15.07	33.74	8.68	1.7		
		Whole Oil ELSD Area:		3668708	QC ELSD Area:		10272617		
Corrected for Volatiles Loss		ELSD	99.44	0.42	0.11	0.03	13.1		1.1
		500 nm	50.99	10.78	28.02	10.21	1.1	0.55	
		700 nm	42.51	15.07	33.74	8.68	na		
Material/ Amt. Inj.	Wt. %	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes 10 μ	0.005	ELSD		Insufficient Material					
		500 nm		Insufficient Material					
		700 nm		Insufficient Material					
C7 Asphaltenes 0.45 μ	0.009	ELSD		Insufficient Material					
		500 nm		Insufficient Material					
		700 nm		Insufficient Material					
Maltenes Varnish 0.4240 mg	0.05	ELSD		Insufficient Material					
		500 nm		Insufficient Material					
		700 nm		Insufficient Material					
SARA Polars Silica 0.4400 mg	0.06	ELSD	92.53	1.02	5.49	0.96			
		500 nm	59.17	14.94	22.88	3.00			
		700 nm	55.22	18.07	24.44	2.28			

Sample:		WRI 1270-67-10							
		Statfjord Crude Oil						AD Asphalt	
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil 2.0000 mg	65.97	ELSD	97.86	1.26	0.76	0.12	10.5		5.1
		500 nm	58.06	13.88	23.16	4.90	2.8	0.40	
		700 nm	43.64	17.98	28.79	9.59	1.9		
		Whole Oil ELSD Area:		3419603	QC ELSD Area:		10049213		
Corrected for Volatiles Loss		ELSD	99.27	0.43	0.26	0.04	10.5		1.7
		500 nm	58.06	13.88	23.16	4.90	2.8	0.40	
		700 nm	43.64	17.98	28.79	9.59	1.9		
Material/ Amt. Inj.	Wt. %	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes 10 μ	0.01	ELSD		Insufficient Material					
		500 nm		Insufficient Material					
		700 nm		Insufficient Material					
C7 Asphaltenes 0.45 μ 0.4886 mg	0.08	ELSD	31.47	27.47	39.26	1.79			
		500 nm	19.64	37.82	36.88	5.65			
		700 nm	17.09	39.67	36.52	6.72			
Maltenes Varnish 0.4300 mg	0.10	ELSD	74.67	12.27	11.87	1.20			
		500 nm	29.55	36.65	30.20	3.60			
		700 nm	24.57	39.27	31.74	4.42			
SARA Polars Silica 0.4660 mg	0.11	ELSD	89.87	2.29	6.99	0.85			
		500 nm	56.18	18.72	22.46	2.64			
		700 nm	51.43	21.09	23.91	3.58			

Sample:		WRI 1270-67-11							
		Grane Crude Oil							
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent				Coke Index	AD Asphalt Aging Index	Percent	
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil	41.60	ELSD	97.06	1.17	1.62	0.16	7.3		8.4
2.0032 mg		500 nm	64.80	13.56	18.75	2.89	4.7	0.29	
		700 nm	54.00	17.37	23.62	5.01	3.5		
		Whole Oil ELSD Area:		6071947	QC ELSD Area:		10397542		
Corrected for		ELSD	98.28	0.68	0.95	0.09	7.3		4.9
Volatiles Loss		500 nm	64.80	13.56	18.75	2.89	4.7	0.29	
		700 nm	54.00	17.37	23.62	5.01	3.5		
Material/ Amt. Inj.	Wt. %	Detector	Asphaltene	Determinator	Area Percent				
			Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes	0.86	ELSD	25.55	29.38	43.11	1.95			
10 μ		500 nm	20.72	37.39	39.64	2.25			
0.4005 mg		700 nm	16.36	39.28	41.40	2.96			
C7 Asphaltenes	1.15	ELSD	30.43	26.77	41.03	1.77			
0.45 μ		500 nm	21.62	36.28	39.84	2.26			
0.4164 mg		700 nm	17.09	38.09	41.72	3.11			
Maltenes	0.36	ELSD	58.22	22.50	18.50	0.78			
Varnish		500 nm	33.53	38.67	25.93	1.87			
0.4063 mg		700 nm	27.62	42.04	27.46	2.88			
SARA Polars	0.19	ELSD	95.04	1.34	3.24	0.38			
Silica		500 nm	72.81	11.35	13.26	2.58			
0.4122 mg		700 nm	66.21	14.87	15.40	3.52			

Sample:		WRI 1270-67-12							
		Troll Crude Oil							
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA
Whole Oil	60.12	ELSD	98.13	1.06	0.72	0.09	11.8		4.2
2.0003 mg		500 nm	55.57	11.12	23.52	9.79	1.1	0.42	
11/18/09		700 nm	40.70	13.62	28.12	17.56	0.8		
		Whole Oil ELSD Area:		4080367	QC ELSD Area:		10230804		
Corrected for Volatiles Loss		ELSD	99.25	0.42	0.29	0.04	11.8		1.7
		500 nm	55.57	11.12	23.52	9.79	1.1	0.42	
		700 nm	40.70	13.62	28.12	17.56	0.8		
Material/ Amt. Inj.	Wt. %	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes 10 μ	0.02	ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						
C7 Asphaltenes 0.45 μ	0.06	ELSD	25.43	23.15	50.04	1.39			
		500 nm	19.58	33.29	42.09	5.04			
0.4067 mg		700 nm	16.39	35.34	42.09	6.18			
Maltenes	0.13	ELSD	71.09	13.02	15.15	0.74			
Varnish		500 nm	31.24	35.65	30.89	2.21			
0.4138 mg		700 nm	26.16	38.25	32.13	3.46			
SARA Polars	0.06	ELSD	Insufficient Material						
Silica		500 nm	Insufficient Material						
0.4720 mg		700 nm	Insufficient Material						

Sample:	WRI 1270-67-13 Heidrun Crude Oil								
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Determinator Area Percent				Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA
			Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
Whole Oil	53.89	ELSD	97.72	1.20	0.96	0.11	10.9		5.8
2.0005 mg		500 nm	60.98	12.58	21.96	4.48	2.8	0.36	
		700 nm	49.55	15.86	26.55	8.04	2.0		
			Whole Oil ELSD Area:		4717879	QC ELSD Area:		10230804	
Corrected for		ELSD	98.95	0.55	0.44	0.05	10.9		2.7
Volatiles Loss		500 nm	60.98	12.58	21.96	4.48	2.8	0.36	
		700 nm	49.55	15.86	26.55	8.04	2.0		
Material/ Amt. Inj.	Wt. %	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes	0.25	ELSD	25.47	27.83	45.20	1.50			
10 µ		500 nm	19.14	37.18	42.12	1.55			
.4062 mg		700 nm	15.21	39.15	43.71	1.94			
C7 Asphaltenes	0.05	ELSD	49.47	16.79	33.18	0.56			
0.45 µ		500 nm	22.60	33.63	39.99	3.78			
		700 nm	18.18	36.24	40.98	4.60			
Maltenes	0.13	ELSD	75.54	10.75	13.09	0.62			
Varnish		500 nm	32.05	33.40	32.23	2.33			
0.4108 mg		700 nm	26.64	35.94	33.92	3.51			
SARA Polars	0.10	ELSD	95.33	1.20	3.01	0.46			
Silica		500 nm	69.23	12.64	15.81	2.31			
0.4080 mg		700 nm	62.15	15.11	18.04	4.69			

Sample:	WRI 1270-67-14 Slurry Oil								
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Determinator Area Percent				Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA
			Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
Whole Oil	19.07	ELSD	99.08	0.43	0.43	0.06	7.2		2.4
2.0005 mg		500 nm	62.00	4.15	29.03	4.82	0.9	0.47	
11/19/09		700 nm	34.78	na	46.88	18.33	na		
			Whole Oil ELSD Area:		8313526	QC ELSD Area:		10272617	
Corrected for		ELSD	99.26	0.35	0.35	0.05	7.2		2.0
Volatiles Loss		500 nm	62.00	4.15	29.03	4.82	0.9	0.47	
		700 nm	34.78	na	46.88	18.33	na		
Material/ Amt. Inj.	Wt. %	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes	1.93	ELSD	57.72	2.30	38.38	1.60			
10 µ		500 nm	32.95	6.06	55.38	5.62			
.4004 mg		700 nm	19.60	6.26	60.35	13.79			
C7 Asphaltenes	0.01	ELSD		Insufficient Material					
0.45 µ		500 nm		Insufficient Material					
		700 nm		Insufficient Material					
Maltenes	0.44	ELSD	66.41	1.28	30.65	1.65			
Varnish		500 nm	41.06	7.27	47.18	4.48			
0.4027 mg		700 nm	28.49	9.49	51.48	10.54			
SARA Polars	0.04	ELSD	91.72	0.36	7.09	0.83			
Silica		500 nm	48.76	5.61	32.81	12.82			
0.2840 mg		700 nm		Insufficient Material					

Sample:		WRI 1270-67-21							
		Rondacor Heavy Crude							
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA
Whole Oil	33.18	ELSD	95.92	1.66	2.04	0.38	4.4		9.0
2.0003 mg		500 nm	54.49	15.74	23.30	6.47	2.4	0.43	
11/23/09		700 nm	43.68	19.07	27.74	9.51	2.0		
Whole Oil ELSD Area:			6714572		QC ELSD Area:		10049213		
Corrected for		ELSD	97.27	1.11	1.36	0.25	4.4		6.0
Volatiles Loss		500 nm	54.49	15.74	23.30	6.47	2.4	0.43	
		700 nm	43.68	19.07	27.74	9.51	2.0		
Material/ Amt. Inj.	Wt. %	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes	3.04	ELSD	12.09	26.81	58.33	2.77			
10 µ		500 nm	12.48	31.20	50.56	5.76			
0.4000 mg		700 nm	9.07	31.98	52.09	6.86			
C7 Asphaltenes	0.23	ELSD	28.04	24.10	43.52	4.34			
0.45 µ		500 nm	17.63	32.12	42.96	7.30			
0.2753 mg		700 nm	12.98	33.40	44.61	9.00			
Maltenes	0.47	ELSD	38.52	28.16	32.36	0.96			
Varnish		500 nm	22.52	39.52	35.59	2.37			
0.4048 mg		700 nm	17.84	42.59	36.62	2.95			
SARA Polars	0.21	ELSD	95.10	1.18	3.39	0.33			
Silica		500 nm	71.94	12.65	13.39	2.01			
0.4074 mg		700 nm	67.92	14.70	14.59	2.78			

Sample:		WRI 1270-67-8							
		Coker Donor Oil							
Material/ Amt. Inj.	Wt. % Volatiles	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA
Whole Oil	42.66	ELSD	99.06	0.59	0.28	0.07	8.4		2.5
2.0006 mg		500 nm	63.09	4.21	25.76	6.93	0.6	0.41	
11/17/2009		700 nm	53.36	na	30.71	15.93	na		
Whole Oil ELSD Area:			5961537		QC ELSD Area:		10397542		
Corrected for		ELSD	99.46	0.34	0.16	0.04	8.4		1.5
Volatiles Loss		500 nm	63.09	4.21	25.76	6.93	0.6	0.41	
		700 nm	53.36	na	30.71	15.93	na		
Material/ Amt. Inj.	Wt. %	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes	0.12	ELSD	21.45	0.77	52.31	25.46			
10 µ		500 nm	11.27	2.82	57.62	28.29			
0.4017 mg		700 nm	4.44	2.03	46.61	46.91			
C7 Asphaltenes	0.02	ELSD		Insufficient Material					
0.45 µ		500 nm		Insufficient Material					
		700 nm		Insufficient Material					
Maltenes	0.17	ELSD	73.71	1.50	19.24	5.56			
Varnish		500 nm	29.51	8.16	49.91	12.42			
0.4138 mg		700 nm	20.77	9.67	46.67	22.90			
SARA Polars		ELSD	91.48	0.52	6.73	1.27			
Silica		500 nm	48.59	9.18	35.16	7.07			
		700 nm		Insufficient Material					

Appendix B

Asphaltene Determinator Data for Heavy Oil Desalter Emulsion Samples

Sample:	WRI 1338-131-9 (#4 Raw)		Heavy Oil Set 3						
	Desalter Inlet Oil							AD Asphalt	
Material/	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
Amt. Inj.	Volatiles	Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH	Ratio Cy/CCl	Ratio T/H	TPA
Whole Oil	41.02	ELSD	93.78	2.17	3.89	0.16	13.6		9.8
2.0000 mg		500 nm	36.39	23.64	35.66	4.31	5.5	0.98	
		700 nm	24.58	26.67	42.17	6.58	4.1		
		Whole Oil ELSD Area:		4478821	QC ELSD Area:		7594086		
Corrected for		ELSD	96.33	1.28	2.29	0.09	13.6		5.8
Volatiles Loss		500 nm	36.39	23.64	35.66	4.31	5.5	0.98	
		700 nm	24.58	26.67	42.17	6.58	4.1		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
Amt. Inj.	Whole Oil	Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH	CH₂Cl₂:MeOH	CH₂Cl₂:MeOH	Asphaltenes
C7 Asphaltenes	7.51	ELSD	13.34	25.76	60.00	0.90	60.90	4.57	7.54
10 µ		500 nm	13.87	28.96	54.14	3.03	57.17		
.4012 mg		700 nm	9.16	30.22	56.90	3.72	60.62		
C7 Asphaltenes	0.03	ELSD	Insufficient Material						
0.45 µ		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-27A (2nd Desalted)		Heavy Oil Set 3						
	Desalted Outlet Oil							AD Asphalt	
Material/	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
Amt. Inj.	Volatiles	Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH	Ratio Cy/CCl	Ratio T/H	TPA
Whole Oil	40.85	ELSD	93.51	2.31	4.01	0.16	14.4		10.2
2.0000 mg		500 nm	36.31	23.72	35.85	4.12	5.8	0.99	
		700 nm	24.61	26.80	42.47	6.12	4.4		
		Whole Oil ELSD Area:		4492090	QC ELSD Area:		7594086		
Corrected for		ELSD	96.16	1.37	2.37	0.09	14.4		6.0
Volatiles Loss		500 nm	36.31	23.72	35.85	4.12	5.8	0.99	
		700 nm	24.61	26.80	42.47	6.12	4.4		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
Amt. Inj.	Whole Oil	Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH	CH₂Cl₂:MeOH	CH₂Cl₂:MeOH	Asphaltenes
C7 Asphaltenes	8.21	ELSD	16.64	25.67	56.85	0.84	57.69	4.74	8.27
10 µ		500 nm	15.12	29.68	52.35	2.86	55.21		
.4002 mg		700 nm	10.31	31.03	55.03	3.63	58.66		
C7 Asphaltenes	0.06	ELSD	49.07	15.79	34.34	0.79	35.13	0.02	
0.45 µ		500 nm	23.04	26.17	46.33	4.46	50.79		
.2340 mg		700 nm	17.97	26.95	48.97	6.11	55.08		

Sample:	WRI 1338-131-10 (#1st Try Layer-1)				Heavy Oil Set 3				
	Whole Sample Shaken							AD Asphalt	
Material/	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
Amt. Inj.	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCl	Ratio T/H	TPA
Whole Oil 2.0008 mg	74.29	ELSD	92.57	2.80	4.32	0.31	9.0	1.01	11.5
		500 nm	35.42	23.19	35.65	5.74	4.0		
		700 nm	24.37	26.23	41.09	8.32	3.2		
		Whole Oil ELSD Area:			1952211	QC ELSD Area:		7594086	
Corrected for Volatiles Loss		ELSD	98.09	0.72	1.11	0.08	9.0	1.01	3.0
		500 nm	35.42	23.19	35.65	5.74	4.0		
		700 nm	24.37	26.23	41.09	8.32	3.2		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
Amt. Inj.	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
C7 Asphaltenes 10 μ 0.4014 mg	2.86	ELSD	7.26	25.01	61.94	5.79	67.73	1.94	2.88
		500 nm	11.73	25.10	51.94	11.23	63.17		
		700 nm	6.76	22.99	49.93	20.31	70.24		
C7 Asphaltenes 0.45 μ	0.02	ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-10 (#1st Try Layer-1)				Heavy Oil Set 3				
	Whole Emulsion Layer Shaken							AD Asphalt	
Material/	Wt. % ELSD	Asphaltene Determinator Area Percent				Coke Index	Aging Index	Percent	
Amt. Inj.	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCl	Ratio T/H	TPA
Whole Oil	68.58	ELSD	92.81	2.34	4.49	0.35	6.7		11.6
2.0016 mg		500 nm	37.95	20.49	35.71	5.84	3.5	0.94	
		700 nm	26.36	22.72	41.86	9.06	2.5		
		Whole Oil ELSD Area:			2532470	QC ELSD Area:		8060927	
Corrected for		ELSD	97.74	0.74	1.41	0.11	6.7		3.6
Volatiles Loss		500 nm	37.95	20.49	35.71	5.84	3.5	0.94	
		700 nm	26.36	22.72	41.86	9.06	2.5		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/	Wt. %	Asphaltene Determinator Area Percent				Toluene +	Toluene +	Wt. %	
Amt. Inj.	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes	
								2.40	
C7 Asphaltenes	2.39	ELSD	8.50	22.37	62.73	6.40	69.13	1.35	
10 μ		500 nm	12.07	23.90	53.44	10.58	64.02		
0.4004 mg		700 nm	8.23	24.04	55.08	12.64	67.72		
C7 Asphaltenes	0.01	ELSD	Insufficient Material						
0.45 μ		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-10 (#1st T-1)		Heavy Oil Set 3						
	Centrifuged Oil from Emulsion Layer								
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Asphaltene Determinator Area Percent					Coke Index Ratio Cy/CCl	AD Asphalt Aging Index Ratio T/H	Percent TPA
		Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH			
Whole Oil	50.91	ELSD	92.71	1.93	5.08	0.27	7.1		11.4
2.0016 mg		500 nm	36.02	23.02	37.23	3.73	6.2	1.03	
		700 nm	25.44	25.91	42.97	5.68	4.6		
		Whole Oil ELSD Area:		3850429	QC ELSD Area:		7842919		
Corrected for		ELSD	96.42	0.95	2.49	0.13	7.1		5.6
Volatiles Loss		500 nm	36.02	23.02	37.23	3.73	6.2	1.03	
		700 nm	25.44	25.91	42.97	5.68	4.6		
Gravimetric Asphaltenes Analysis									
Material/ Amt. Inj.	Wt. % Whole Oil	Asphaltene Determinator Area Percent					Area Percent Toluene + CH₂Cl₂:MeOH	Wt. % Toluene + CH₂Cl₂:MeOH	Total Wt. % Asphaltenes
		Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH			
C7 Asphaltenes	3.54	ELSD	11.12	22.17	64.19	2.52	66.71	2.37	3.55
10 µ		500 nm	14.51	28.38	53.20	3.91	57.11		
0.4020 mg		700 nm	9.68	28.94	56.19	5.18	61.37		
C7 Asphaltenes	0.01	ELSD	Insufficient Material						
0.45 µ		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-10 (#1st Try Layer-1)		Heavy Oil Set 3						
	Oil Residue from Evaporated Centrifuged Water Fraction from Emulsion Layer								
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Asphaltene Determinator Area Percent					Coke Index Ratio Cy/CCl	AD Asphalt Aging Index Ratio T/H	Percent TPA
		Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH			
Whole Oil	70.88	ELSD	73.36	3.02	13.20	10.41	0.3		37.1
0.2947 mg		500 nm	28.26	24.03	40.01	7.71	3.1	1.42	
		700 nm	23.00	25.75	40.50	10.76	2.4		
		Whole Oil 2mg ELSD Area:		2283936	QC ELSD Area:		7842919		
Corrected for		ELSD	92.24	0.88	3.84	3.03	0.3		
Volatiles Loss		500 nm	28.26	24.03	40.01	7.71	3.1		
		700 nm	23.00	25.75	40.50	10.76	2.4		
Gravimetric Asphaltenes Analysis									
Material/ Amt. Inj.	Wt. % Whole Oil	Asphaltene Determinator Area Percent					Area Percent Toluene + CH₂Cl₂:MeOH	Wt. % Toluene + CH₂Cl₂:MeOH	Total Wt. % Asphaltenes
		Detector	Heptane	CyC₆	Toluene	CH₂Cl₂:MeOH			
C7 Asphaltenes		ELSD	Insufficient Material						
10 µ		500 nm	Insufficient Material						
		700 nm	Insufficient Material						
C7 Asphaltenes		ELSD	Insufficient Material						
0.45 µ		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-11 (#1st Try Layer-2)				Heavy Oil Set 3				
	Whole Sample Shaken							AD Asphalt	
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCl	Ratio T/H	TPA
Whole Oil 2.0004 mg	69.82	ELSD	92.83	2.50	4.38	0.29	8.6		11.1
		500 nm	35.49	23.13	36.01	5.37	4.3	1.01	
		700 nm	24.04	26.30	42.04	7.62	3.5		
		Whole Oil ELSD Area:			2291864	QC ELSD Area:		7594086	
Corrected for Volatiles Loss		ELSD	97.84	0.75	1.32	0.09	8.6		3.4
		500 nm	35.49	23.13	36.01	5.37	4.3	1.01	
		700 nm	24.04	26.30	42.04	7.62	3.5		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
C7 Asphaltenes 10 μ 0.4028 mg	1.79	ELSD	4.48	23.95	64.70	6.87	71.57	1.28	1.80
		500 nm	9.62	23.54	53.13	13.71	66.84		
		700 nm	5.60	21.34	49.71	23.34	73.05		
C7 Asphaltenes 0.45 μ	0.01	ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-11 (#1st Try Layer-2)				Heavy Oil Set 3				
	Whole Emulsion Layer Shaken							AD Asphalt	
Material/	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
Amt. Inj.	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil 2.0000 mg	70.26	ELSD	92.65	2.42	4.59	0.33	7.3	0.93	11.9
		500 nm	38.03	20.73	35.48	5.77	3.6		
		700 nm	26.80	22.67	40.73	9.80	2.3		
Whole Oil ELSD Area:		2397115		QC ELSD Area:		8060927			
Corrected for Volatiles Loss		ELSD	97.81	0.72	1.37	0.10	7.3	0.93	3.5
		500 nm	38.03	20.73	35.48	5.77	3.6		
		700 nm	26.80	22.67	40.73	9.80	2.3		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
Amt. Inj.	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
C7 Asphaltenes 10 μ 0.4020 mg	1.72	ELSD	8.66	21.26	64.17	5.90	70.07	1.37	1.73
		500 nm	11.93	23.02	54.05	10.99	65.04		
		700 nm	8.43	23.05	55.24	13.28	68.52		
C7 Asphaltenes 0.45 μ	0.01	ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-11 (#1st Try Layer-2)				Heavy Oil Set 3				
	Centrifuged Oil from Emulsion Layer						AD Asphalt		
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCl	Aging Index Ratio T/H	Percent TPA
Whole Oil 2.0008 mg	51.69	ELSD	92.55	1.94	5.23	0.28	6.9	1.06	11.6
		500 nm	35.54	22.93	37.58	3.95	5.8		
		700 nm	25.40	25.71	42.94	5.95	4.3		
Whole Oil ELSD Area:			3789074		QC ELSD Area:		7842919		
Corrected for Volatiles Loss		ELSD	96.40	0.94	2.53	0.14	6.9	1.06	5.6
		500 nm	35.54	22.93	37.58	3.95	5.8		
		700 nm	25.40	25.71	42.94	5.95	4.3		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt. % Whole Oil	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Asphaltenes
C7 Asphaltenes 10 μ 0.4024 mg	6.92	ELSD	15.61	21.42	60.71	2.27	62.98	4.42	7.02
		500 nm	15.73	28.25	52.08	3.94	56.02		
		700 nm	10.84	28.98	55.15	5.03	60.18		
C7 Asphaltenes 0.45 μ	0.10	ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-11 (#1st Try Layer-2)				Heavy Oil Set 3					
	Oil Residue from Evaporated Centrifuged Water Fraction from Emulsion Layer							AD Asphalt		
Material/	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent	
Amt. Inj.	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCl	Ratio T/H	TPA	
Whole Oil	79.21	ELSD	65.47	5.77	16.92	11.84	0.5		51.3	
0.4633 mg		500 nm	32.71	25.12	35.35	6.82	3.7	1.08		
		700 nm	27.26	27.02	35.92	9.81	2.8			
		Whole Oil 2mg ELSD Area:		1630870	QC ELSD Area:		7842919			
Corrected for		ELSD	92.82	1.20	3.52	2.46	0.5			
Volatiles Loss		500 nm	32.71	25.12	35.35	6.82	3.7			
		700 nm	27.26	27.02	35.92	9.81	2.8			
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total	
Material/	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %	
Amt. Inj.	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes	
C7 Asphaltenes		ELSD	Insufficient Material							
10 μ		500 nm	Insufficient Material							
		700 nm	Insufficient Material							
C7 Asphaltenes		ELSD	Insufficient Material							
0.45 μ		500 nm	Insufficient Material							
		700 nm	Insufficient Material							

Sample:	WRI 1338-131-12 (#1st Try Layer-3)				Heavy Oil Set 3				
	Whole Sample Shaken							AD Asphalt	
Material/	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
Amt. Inj.	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCl	Ratio T/H	TPA
Whole Oil 2.0006 mg	69.39	ELSD	92.48	2.47	4.70	0.34	7.3	1.03	11.7
		500 nm	35.89	21.60	36.82	5.69	3.8		
		700 nm	23.98	24.29	43.47	8.26	2.9		
		Whole Oil ELSD Area:			2310376	QC ELSD Area:		7547625	
Corrected for Volatiles Loss		ELSD	97.70	0.76	1.44	0.10	7.3	1.03	3.6
		500 nm	35.89	21.60	36.82	5.69	3.8		
		700 nm	23.98	24.29	43.47	8.26	2.9		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
Amt. Inj.	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
C7 Asphaltenes 10 μ 0.4006 mg	2.95	ELSD	7.64	22.72	62.75	6.89	69.64	2.05	2.98
		500 nm	11.24	22.00	52.78	13.99	66.77		
		700 nm	6.12	19.94	50.67	23.27	73.94		
C7 Asphaltenes 0.45 μ	0.03	ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-12 (#1st Try Layer-3)				Heavy Oil Set 3				
	Whole Emulsion Layer Shaken							AD Asphalt	
Material/	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
Amt. Inj.	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCl	Ratio T/H	TPA
Whole Oil 2.0000 mg	69.47	ELSD	92.95	2.33	4.38	0.34	6.9	0.90	11.5
		500 nm	38.49	20.98	34.78	5.74	3.7		
		700 nm	26.92	23.44	40.18	9.46	2.5		
Whole Oil ELSD Area:		2461011		QC ELSD Area:		8060927			
Corrected for Volatiles Loss		ELSD	97.85	0.71	1.34	0.10	6.9	0.90	3.5
		500 nm	38.49	20.98	34.78	5.74	3.7		
		700 nm	26.92	23.44	40.18	9.46	2.5		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
Amt. Inj.	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
C7 Asphaltenes 10 μ .4020 mg	2.00	ELSD	12.05	21.97	58.69	7.29	65.98	1.29	2.02
		500 nm	13.42	23.64	49.85	13.08	62.93		
		700 nm	9.28	23.68	50.75	16.28	67.03		
C7 Asphaltenes 0.45 μ	0.02	ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-12 (#1st Try Layer-3)				Heavy Oil Set 3					
Emulsoin Centrifuged Oil Fraction										AD Asphalt
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent	
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCl	Ratio T/H	TPA	
Whole Oil 2.0012 mg	69.11	ELSD	91.75	2.34	5.44	0.47	5.0	1.09	12.6	
		500 nm	34.64	21.79	37.78	5.79	3.8			
		700 nm	24.22	24.30	43.18	8.29	2.9			
Whole Oil ELSD Area:				2602764	QC ELSD Area:		8427234			
Corrected for		ELSD	97.45	0.72	1.68	0.15	5.0			
Volatiles Loss		500 nm	34.64	21.79	37.78	5.79	3.8			
		700 nm	24.22	24.30	43.18	8.29	2.9			
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total	
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %	
	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes	
C7 Asphaltenes 10 μ 2.0036 mg	5.95	ELSD	12.95	27.08	57.51	2.46	59.97	3.57	5.97	
		500 nm	13.74	30.73	51.39	4.13	55.52			
		700 nm	8.86	31.43	54.44	5.27	59.71			
C7 Asphaltenes 0.45 μ	0.024	ELSD	Insufficient Material							
		500 nm	Insufficient Material							
		700 nm	Insufficient Material							

Sample:	WRI 1338-131-12 (#1st Try Layer-3)					Heavy Oil Set 3				
Oil Residue from Evaporated Centrifuged Water Fraction from Emulsion Layer										
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	AD Asphalt Aging Index	Percent	
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCl	Ratio T/H	TPA	
Whole Oil 1.1087 mg	56.33	ELSD	85.65	3.77	7.40	3.18	1.2	0.86	22.9	
		500 nm	37.36	25.86	32.31	4.48	5.8			
		700 nm	27.04	28.81	37.41	6.74	4.3			
Whole Oil 2mg ELSD Area:			3680435		QC ELSD Area:		8427234			
Corrected for		ELSD	93.73	1.65	3.23	1.39	1.2	0.86	10.0	
Volatiles Loss		500 nm	37.36	25.86	32.31	4.48	5.8			
		700 nm	27.04	28.81	37.41	6.74	4.3			
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total	
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %	
	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes	
C7 Asphaltenes 10 μ		ELSD	Insufficient Material							
		500 nm	Insufficient Material							
		700 nm	Insufficient Material							
C7 Asphaltenes 0.45 μ		ELSD	Insufficient Material							
		500 nm	Insufficient Material							
		700 nm	Insufficient Material							

Sample:	WRI 1338-131-13 (#1st Try layer-4)				Heavy Oil Set 3				
	Whole Sample Shaken								
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Heptane	Determinator CyC ₆	Area Percent Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCI	AD Asphalt Aging Index Ratio T/H	Percent TPA
Whole Oil	73.87	ELSD	91.94	2.73	4.96	0.36	7.6		12.1
2.0000 mg		500 nm	33.44	22.99	38.13	5.45	4.2	1.14	
		700 nm	21.55	25.27	44.67	8.51	3.0		
		Whole Oil ELSD Area:			1972189	QC ELSD Area:		7547625	
Corrected for	ELSD	97.89	0.71	1.30	0.09	7.6			3.2
Volatiles Loss	500 nm	33.44	22.99	38.13	5.45	4.2	1.14		
	700 nm	21.55	25.27	44.67	8.51	3.0			
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt. % Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Asphaltenes
C7 Asphaltenes	3.29	ELSD	6.60	18.02	70.64	4.74	75.38	2.48	3.31
10 μ		500 nm	11.83	24.06	55.37	8.74	64.11		
0.4028 mg		700 nm	8.01	23.83	56.69	11.47	68.16		
C7 Asphaltenes	0.02	ELSD	Insufficient Material						
0.45 μ		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-13 (#1st Try Layer-4)				Heavy Oil Set 3				
	Whole Emulsion Layer Shaken							AD Asphalt	
Material/	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	Aging Index	Percent
Amt. Inj.	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCl	Ratio T/H	TPA
Whole Oil	62.98	ELSD	92.97	2.26	4.50	0.27	8.4		11.3
2.0000 mg		500 nm	37.73	21.06	35.91	5.29	4.0	0.95	
		700 nm	26.28	23.63	42.09	8.00	3.0		
		Whole Oil ELSD Area:			2983869	QC ELSD Area:		8060927	
Corrected for		ELSD	97.40	0.84	1.67	0.10	8.4		4.2
Volatiles Loss		500 nm	37.73	21.06	35.91	5.29	4.0	0.95	
		700 nm	26.28	23.63	42.09	8.00	3.0		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
Amt. Inj.	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
									4.89
C7 Asphaltenes	4.88	ELSD	12.38	20.80	65.00	1.82	66.82	1.31	
10 μ		500 nm	12.36	26.67	57.21	3.75	60.96		
.4004 mg		700 nm	8.10	27.25	60.02	4.63	64.65		
C7 Asphaltenes	0.01	ELSD	Insufficient Material						
0.45 μ		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-13 (#1st Try Layer-4)		Heavy Oil Set 3						
	Emulsion Centrifuged Oil Fraction								
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Determinator Heptane	Area Percent CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCl	AD Asphalt Aging Index Ratio T/H	Percent TPA
Whole Oil 2.0010 mg	33.04	ELSD	92.10	2.50	5.16	0.25	10.0		12.4
		500 nm	36.15	22.64	37.21	4.00	5.7	1.03	
		700 nm	25.31	25.62	43.29	5.78	4.4		
Whole Oil ELSD Area:				5642749	QC ELSD Area:		8427234		
Corrected for Volatiles Loss		ELSD	94.71	1.67	3.46	0.17	10.0		
		500 nm	36.15	22.64	37.21	4.00	5.7		
		700 nm	25.31	25.62	43.29	5.78	4.4		
Gravimetric Asphaltenes Analysis							Area Percent Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Toluene + CH ₂ Cl ₂ :MeOH	Total Wt. % Asphaltenes
Material/ Amt. Inj.	Wt. % Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes 10 µ 2.0004 mg	9.0585	ELSD	20.48	23.96	53.87	1.68	55.55	5.03	9.09
		500 nm	15.18	29.52	51.55	3.75	55.30		
		700 nm	10.61	30.45	54.21	4.72	58.93		
C7 Asphaltenes 0.45 µ	0.0316	ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-13 (#1st Try Layer-4)		Heavy Oil Set 3						
	Oil Residue from Evaporated Centrifuged Water Fraction from Emulsion Layer								
Material/ Amt. Inj.	Wt. % ELSD Volatiles	Detector	Asphaltene Determinator Heptane	Area Percent CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Coke Index Ratio Cy/CCl	AD Asphalt Aging Index Ratio T/H	Percent TPA
Whole Oil 0.9160 mg	48.87	ELSD	82.52	5.71	8.40	3.38	1.7		29.0
		500 nm	39.75	24.80	32.07	3.39	7.3	0.81	
		700 nm	30.48	27.85	36.46	5.20	5.4		
Whole Oil 2mg ELSD Area:				4308742	QC ELSD Area:		8427234		
Corrected for Volatiles Loss		ELSD	91.06	2.92	4.29	1.73	1.7		14.8
		500 nm	39.75	24.80	32.07	3.39	7.3	0.81	
		700 nm	30.48	27.85	36.46	5.20	5.4		
Gravimetric Asphaltenes Analysis							Area Percent Toluene + CH ₂ Cl ₂ :MeOH	Wt. % Toluene + CH ₂ Cl ₂ :MeOH	Total Wt. % Asphaltenes
Material/ Amt. Inj.	Wt. % Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH			
C7 Asphaltenes 10 µ		ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						
C7 Asphaltenes 0.45 µ		ELSD	Insufficient Material						
		500 nm	Insufficient Material						
		700 nm	Insufficient Material						

Sample:	WRI 1338-131-14 (#1st Try Layer-5)				Heavy Oil Set 3				
	Whole Sample Shaken (all oil)								
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	AD Asphalt Aging Index	Percent
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil 2.0000 mg	40.24	ELSD	93.35	2.42	4.05	0.18	13.4		10.5
		500 nm	36.43	23.71	35.73	4.13	5.7	0.98	
		700 nm	25.02	26.84	41.94	6.20	4.3		
		Whole Oil ELSD Area:			4510300	QC ELSD Area:		7547625	
Corrected for		ELSD	96.03	1.45	2.42	0.11	13.4		6.3
Volatiles Loss		500 nm	36.43	23.71	35.73	4.13	5.7	0.98	
		700 nm	25.02	26.84	41.94	6.20	4.3		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
C7 Asphaltenes 10 μ 0.4036 mg	8.97	ELSD	12.00	22.50	64.38	1.11	65.49	58.70	9.40
		500 nm	13.93	29.30	52.63	4.14	56.77		
		700 nm	9.34	31.25	54.34	5.07	59.41		
C7 Asphaltenes 0.45 μ 0.4290 mg	0.43	ELSD	8.45	12.95	76.79	1.81	78.60		
		500 nm	9.10	20.14	66.11	4.65	70.76		
		700 nm	5.77	21.03	68.06	5.14	73.20		

Sample:	WRI 1338-131-16 (#1st Try Layer-7)				Heavy Oil Set 3				
	Whole Sample Shaken (all oil)								
Material/ Amt. Inj.	Wt. % ELSD	Asphaltene Determinator Area Percent					Coke Index	AD Asphalt Aging Index	Percent
	Volatiles	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	Ratio Cy/CCI	Ratio T/H	TPA
Whole Oil 2.0016 mg	37.91	ELSD	93.25	2.39	4.19	0.16	14.9	1.02	10.5
		500 nm	35.85	23.66	36.55	3.93	6.0		
		700 nm	23.79	27.08	43.39	5.74	4.7		
		Whole Oil ELSD Area:			4686428	QC ELSD Area:		7547625	
Corrected for Volatiles Loss		ELSD	95.81	1.48	2.60	0.10	14.9	1.02	6.5
		500 nm	35.85	23.66	36.55	3.93	6.0		
		700 nm	23.79	27.08	43.39	5.74	4.7		
Gravimetric Asphaltenes Analysis							Area Percent	Wt. %	Total
Material/ Amt. Inj.	Wt. %	Asphaltene Determinator Area Percent					Toluene +	Toluene +	Wt. %
	Whole Oil	Detector	Heptane	CyC ₆	Toluene	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	CH ₂ Cl ₂ :MeOH	Asphaltenes
C7 Asphaltenes 10 μ 0.4032 mg	8.98	ELSD	13.78	24.99	60.32	0.92	61.24	55.00	9.21
		500 nm	14.51	31.34	50.33	3.82	54.15		
		700 nm	9.97	33.51	51.95	4.57	56.52		
C7 Asphaltenes 0.45 μ 0.4550 mg	0.23	ELSD	5.58	11.53	80.73	2.17	82.90		
		500 nm	8.12	18.20	68.11	5.58	73.69		
		700 nm	4.86	19.25	69.82	6.06	75.88		

Appendix C

Waxphaltene Determinator Fraction Characterization at Florida State University

Characterization of Waxphaltene Determinator Fractions by High Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Leonard Nyadong, Amy M. McKenna and Alan G. Marshall

National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Dr., Tallahassee, Florida 32310 USA

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EXPERIMENTAL

Sample Preparation

Waxphaltene Determinator fractions were provided by WRI. All solvents were reagent grade (Sigma-Aldrich Chemical Co., St. Louis, MO). Prior to mass spectrometric analysis, ~1 mg of each fraction was diluted with toluene to make a stock solution (1 mg/mL) that was further diluted to yield a final concentration of 250 µg/mL equal parts (v/v) methanol spiked with 1% v/v formic acid (positive electrospray ionization, ESI) or 1% v/v tetramethylammonium hydroxide (25% by weight in methanol, negative ESI) prior to MS analysis.

ESI Time-of-Flight (TOF) MS

ESI TOF MS was performed with a Waters LCT Premier TOF mass spectrometer equipped with a Z-spray ESI source (Waters Corporation, Milford, MA, USA). The LCT was operated in the V-mode by use of MassLynx version 4.1 software. The electrosprayed ions were transferred from the source to the orthogonal acceleration TOF mass analyzer by use of two ion guides and a hexapole. The instruments settings were as follows: capillary voltage, ± 2.8 kV; cone voltage, 60 V; source temperature, 120 °C; desolvation temperature, 350 °C; and desolvation gas flow, 500 L/h. The sample was introduced by use of a built-in syringe pump at a flow rate of 25 µL/min.

ESI 9.4 tesla FT ICR MS

Sample solutions were introduced into the mass spectrometer through a microelectrospray source (1) (50 µm i.d. fused silica emitter) at 400 nL/min by a syringe pump. Typical conditions for negative ion formation were emitter voltage, -2.5 kV; tube lens, -350V; and heated metal capillary current, 4 A. Positive ion formation occurred at the same conditions as for negative ions, but with positive voltages. The electrosprayed ions were analyzed with a custom-built FT-ICR mass spectrometer (2) equipped with a 9.4 tesla horizontal 220 mm bore diameter superconducting solenoid magnet operated at room temperature (Oxford Instruments, Abingdon, Oxfordshire OX13 5QX United Kingdom). A modular ICR data station (Predator) facilitated instrument control, data acquisition and data analysis (3) Ions generated at atmospheric pressure were accumulated in an external linear octopole ion trap for 1-3 s and transferred by rf-only octopoles (2.0 MHz and 240 V_{p-p} amplitude) to the ICR cell. ICR time-domain transients were collected from a 7 segment open cylindrical cell with capacitively coupled excitation electrodes based on the Tolmachev configuration.(2,4) 150 individual

transients of 5.6 s each were collected for each fraction and averaged, apodized with a full-Hanning weight function, and zero-filled once prior to fast Fourier transformation. ICR frequencies were converted to ion masses based on the quadrupolar trapping potential approximation (5). Each m/z spectrum was internally calibrated with respect to an abundant homologous alkylation series differing in mass by integer multiples of 14.10565 Da (mass of a CH_2 unit) confirmed by isotopic fine structure based on the "walking" calibration equation (6). Experimentally measured masses were converted from the International Union of Pure and Applied Chemistry (IUPAC) mass scale to the Kendrick mass scale to identify homologous series for each heteroatom class (i.e., species with the same $\text{C}_c\text{H}_h\text{N}_n\text{O}_o\text{S}_s$ content, differing only by their degree of alkylation). Peak assignments were performed by Kendrick mass defect analysis as previously described (7). For each elemental composition, $\text{C}_c\text{H}_h\text{N}_n\text{O}_o\text{S}_s$, the heteroatom class, type (double bond equivalents, $\text{DBE} = \text{number of rings plus double bonds involving carbon}$) and carbon number, c , were tabulated for subsequent generation of heteroatom class relative abundance distributions and graphical DBE vs. carbon number or H/C ratio vs. carbon number images.

RESULTS AND DISCUSSION

Electrospray Ionization (ESI)

ESI is a soft ionization, semi-quantitative technique that allows the generation of unfragmented ions for mass spectrometric analysis. With this technique, every molecular formula in a complex mixture can be identified. Negative ESI with tetramethylammonium hydroxide (TMAH) was used to ionize and characterize acidic components because it minimizes drastic differences in ionization efficiency that are otherwise observed by ammonium hydroxide (NH_4OH) deprotonation, which primarily ionizes only highly polar naphthenic acids (8). Positive ESI with formic acid was used to ionize and characterize basic components. Neither of these techniques can ionize the hydrocarbon wax molecules, but can nevertheless provide insight into the carbon backbone structure of the polar species in the fractions. The two asphaltene fractions 4 and 5 failed to produce sufficient signal due to poor solubility and the tendency of asphaltenes to self-associate into stable aggregates at concentrations required for ESI MS. However, the Peak 1, 2, and 3 fractions were characterized based on acidic species (negative ESI) and basic species (positive ESI) for compositional differences. Solvent modification with TMAH increases the compositional coverage of acidic species to include five-membered ring nitrogen species (pyrrolic) compounds that are otherwise masked by the much higher ionization efficiency of carboxylic acids (O_2) with conventional solvent modification with ammonium hydroxide.

Fraction Characterization

Figure 1 shows the negative ion ESI TOF mass spectra of peaks 1, 2 and 3 fractions. Mass analysis by TOF exhibits minimal mass discrimination because all ions of essentially all mass-to-charge ratio (m/z), reach the detector to provide an accurate representation of the molecular weight distribution of the sample. A striking feature in the TOF MS spectra is the difference in the m/z distributions $m/z = 250 - 1800$ for Peak 1, vs. $m/z = 500 - 2700$ for Peak 2 and $m/z = 650 - 2750$ for Peak 3. Those broad m/z distributions could represent n -alkane and branched backbone structures that melt and elute with n -heptane at 60°C . Thus, the high-

temperature GC experiments discussed earlier accessed only relatively low molecular weight components.

Figure 1. Negative Ion ESI TOF mass spectra of Waxphaltene Determinator Peak Fractions 1, 2, and 3.

Figure 2 presents the TOF and FT-ICR m/z distributions for the Peak 1 material. The distributions are similar, except for somewhat lower signal magnitude at the high mass end in the FT-ICR spectrum, presumably due to time-of-flight mass discrimination in the transfer octopole. However FT-ICR MS provides ultrahigh resolution and mass accuracy to resolve and identify the thousands of peaks in the spectrum as demonstrated by the corresponding mass scale expanded insets across a 0.5 Da m/z range. At a mass resolving power of $\sim 5,000$, TOF MS exhibits a single unresolved peak, FT-ICR MS, at an average mass resolving power of $\sim 500,000$, enables resolution and assignment of 41 peaks of magnitude greater than 6 times the standard deviation of the baseline noise. Similar results were obtained for the peak 2 and 3 materials (data not shown).

(-) ESI (1 % TMAH) TOF MS
Peak 1 Fraction

(-) ESI (1 % TMAH) 9.4 T FT-ICR MS
Peak 1 Fraction

Figure 2. Negative Ion ESI TOF mass spectrum (top) vs. FT-ICR mass spectrum (bottom) of Waxphaltene Determinator Peak Fractions 1. The corresponding zoom insets show the necessity for ultrahigh resolution provided by FT-ICR MS to resolve and identify the thousands of peaks in the spectrum.

The relative abundances for several acidic species in the three fractions are provided in **Figure 3**. In petroleum, nitrogen-containing compounds detected by negative ion ESI consist of pyrroles, carbazoles, and indoles (9). Compounds with oxygen can include carboxylic functional groups. In general, ionization efficiency in negative ion ESI increases with the relative acidity of the analytes. Only a small portion of sulfur-containing compounds are ionized by negative ion ESI,²² including thiophenols, benzylic thiols, and other acidic compounds containing neutral sulfur. Electrospray-ionizable hydrocarbons include species with an acidic hydrogen moiety such as the acidic aliphatic hydrogen on the five member ring of indene and fluorene. Figure 19 shows that the most prominent heteroatom compositions are: N₁ (one nitrogen), N₁O₁ (one nitrogen, one oxygen), O₁ (one oxygen) and O₂ (two oxygens) and HC.

Figure 3. Negative Ion ESI Heteroatom Distribution of Acidic Molecules for Waxphaltene Determinator Peak Fractions 1, 2, and 3.

Three-dimensional abundance-contoured plots of H/C ratio vs. carbon number for the N₁ and N₁O₁ species are shown in **Figure 4**. The H/C ratio and the carbon number range for the Peak 2 and 3 materials are greater than for the Peak 1 material, indicating greater relative aromatic content in the Peak 1 material, and more aliphatic chain components in the Peak 2 and 3 materials. Similar plots (**Figure 5**) show that the O₁ and O₂ classes in the Peak 2 and 3 materials are highly aliphatic. For the O₂ class material, the H/C ratio is near 2, which is diagnostic of oxygenated highly aliphatic waxy material.

Figure 4. Distribution of Acidic N and NO Heteroatom Classes for Waxphaltene Determinator Peak Fractions 1, 2, and 3.

Figure 5. Distribution of Acidic O and O₂ Heteroatom Classes for Waxphaltene Determinator Peak Fractions 1, 2, and 3.

Positive ion ESI FT-ICR mass spectra (**Figure 6**) represent the basic compounds in the three fractions. As for the acidic species, the Peak 1 material has a lower m/z range than the Peak 2 and 3 materials.

Figure 6. Positive Ion ESI FT-ICR mass spectra of Waxphaltene Determinator Peak Fractions 1, 2, and 3 (Bases).

Figure 7 shows the relative abundances for several basic species in the three fractions. In petroleum, the basic nitrogen-containing compounds are primarily pyridinic.

Figure 7. Positive Ion ESI Heteroatom Distribution of Basic Molecules for Waxphaltene Determinator Peak Fractions 1, 2, and 3.

Three-dimensional isoabundance contoured plots of H/C ratio vs. carbon number for N_1 and N_1O_1 species are shown in **Figure 8**. As for the acidic species, the H/C ratio and carbon number range for the Peak 2 and 3 materials are greater than for the Peak 1 material, which is diagnostic of greater relative aromatic content in the Peak 1 material, and much more aliphatic chain content in the Peak 2 and 3 materials.

Figure 8. Distribution of Basic N and NO Heteroatom Classes for Waxphaltene Determinator Peak Fractions 1, 2, and 3

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