ASPHALTENE SUBFRACTIONS: NEW INSIGHT INTO HEAVY OIL CHEMISTRY

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Introduction

Traditional SARA (saturates, aromatics, resins, and asphaltenes) methods provide separations of maltenes into three or more subfractions, however, there is no routine provision for separating asphaltenes further into subfractions. The new solubility-based on-column precipitation and re-dissolution technique developed at Western Research Institute allows for the rapid separation of asphaltenes into chemically meaningful subfractions (1). SARA separations are performed with a variety of combinations of adsorbents such as alumina, silica, clay gel, etc. and a variety of different solvent sequences. The precipitation and filtration of asphaltenes also is performed by a variety of standard methods, and there are different variants of the methods in use by different oil companies (Table 1). Each provides different results.

Table 1. Asphaltene Separation Methods

Method	Solvent	Solvent to Oil Ratio	Stirring Temperature and Settling Time	Filter Media
ASTM D-3279-07	Heptane	100:1	Reflux 30 min., Settle Ambient 1 hr., Filter at 38-49 °C	Fiberglass 1.5 micron
ASTM D-4124-01	Heptane	100:1	Heat on Steam Bath 30 min., Settle Ambient Overnight	Slow / Med Paper ~ 10 micron
ASTM D-4124-09	Isooctane	100:1	Reflux 2 hours, Ambient 2 hr., Settle Ambient 2 hr.	Med. Glass Frit, 10 micron
WRI	Heptane	40:1	Heat to 80 °C for 5 min., Stir Ambient 16 hr., Settle 30 min.	Med. glass Frit, 10 micron
ASTM D-6560-00	Heptane	30:1	Reflux 60 min., Settle at Ambient 90-150 min.	Whatman 42 Paper 2.5 micron
ASTM D-2007-03	Pentane	10:1	Ambient 30 min	Rapid paper 20 micron
IFP 9313 Absorbance vs. Maltenes at 750 nm	Heptane	20:1 to 200:1	Heat to 80 °C 5 min. Filter Ambient	Cellulose Ester Filter 0.45 micron

The use of the term asphaltenes is a catch-all designation for insoluble material, depending on the experiment. Methods optimization work has been completed to standardize the automated Asphaltene Determinator method into a routine standardized separation that is now being used extensively to gain insight into the contributions of asphaltenes subfractions in various process applications. The new standardized conditions are provided in the Experimental section.

Experimental

The Asphaltene Determinator on-column and re-dissolution method configuration was optimized with a smaller column and a decreased solvent flow rate 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. Elution solvents were reagent grade, with step gradients between solvents. Peak area integration was performed on blank subtracted separation profiles using Waters Empower software. Separation conditions are provided below.

- 250 x 7 mm SS column (Alltech 96511) at 30 °C
- 0.25-0.42 mm PTFE stationary phase (40-60 mesh)
- Solvent flow rate: 2 mL/min
- Step gradient times: 0 min heptane, 15 min cyclohexane, 25 min toluene, 35 min methylene chloride:methanol (98:2 v:v)
- Sample solutions: Up to 10 wt. % in chlorobenzene
- Amount injected: 5-20 µL
- Daily QC check: 20 µL 10 % (w:v) Lloydminster VR in chlorobenzene.

Results and Discussion

Some Asphaltene Determinator peaks show slight tailing due to slow re-dissolution of some components. Although peak tailing is undesirable in chromatography, slight tailing in the solubility based separations is normal. An example separation for a Lloydminster residuum is provided in Figure 1.

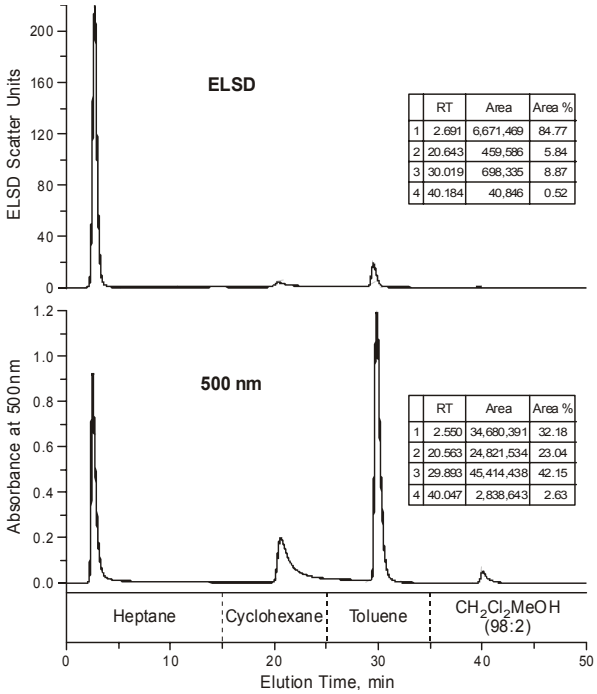

Figure 1. Separation of 2 mg Lloydminster VR.

In past work the emphasis was on using the ELSD separation profiles since peaks for both asphaltenes and maltenes are present. For ELSD profiles in which the areas under the all the peaks are integrated, however, the oil must not contain any volatile material since it evaporates with

solvent in the detector. For full ELSD profiles, crude oils must first be devolatilized in a rotary evaporator followed by vacuum oven at full vacuum at 200 ºC. If an ELSD profile is not required for the application, a viable alternative detector is an optical absorbance unit. Both asphaltenes and SARA polars can be detected in this manner and volatiles losses from the maltenes are not an issue. Pericondensed asphaltene material comprising the cyclohexane, toluene, and methylene chloride:methanol (98:2) peaks can be detected using visible wavelengths such as at 500-700 nm. The less pericondensed resins / polars are expected to absorb more at the shorter wavelengths within this range. The potential of using the separation to study samples for various applications was confirmed for the new optimized system. These are summarized in the following sections.

Oil / Water Emulsions In a feasibility study with emulsions between Minnelusa (Wyoming) topped separator crude oil and brine, Asphaltene Determinator separations were conducted on heptane asphaltenes separated from maltenes sequentially filtered using 10-micron followed by 0.45-micron filters. SARA separations using activated silica were performed on the resulting maltenes. The SARA resins / polars fractions were injected onto the Asphaltene Determinator column also. Separation profiles for the supernatant and rag layer oils are provided in Figures 2 and 3, respectively. Detection at 500 nm was used since in some cases only very small amounts of material (< 8 µg) was available and this was too little for accurate ELSD detection.

Results of a representative set of experiments are provided in Table 2. The data show that the amount of asphaltenes in the supernatant oil is less than that of the original oil, while the amount of asphaltenes in the rag layer oil is greater than the amount in the original oil. The asphaltenes in the original and supernatant oils are primarily between 0.45 and 10 microns in size, while the asphaltenes from the rag layer oil are greater than 10 microns. The Asphaltene Determinator profiles for the various asphaltenes are not identical. The profiles for the SARA resins / polars appear to be essentially the same for both supernatant and rag layer oils. A systematic series of oil / water experiments is needed before definitive conclusion can be made about the contributions of the various subfractions to emulsion stability. However, it appears that the Asphaltene Determinator results can provide new insight into oil / water emulsion chemistry.

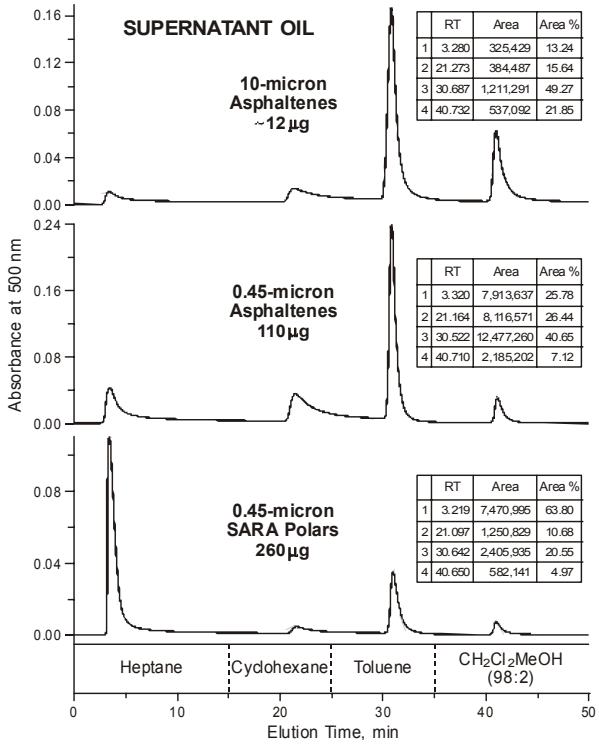

Figure 2. Separations of Emulsion Supernatant Oil.

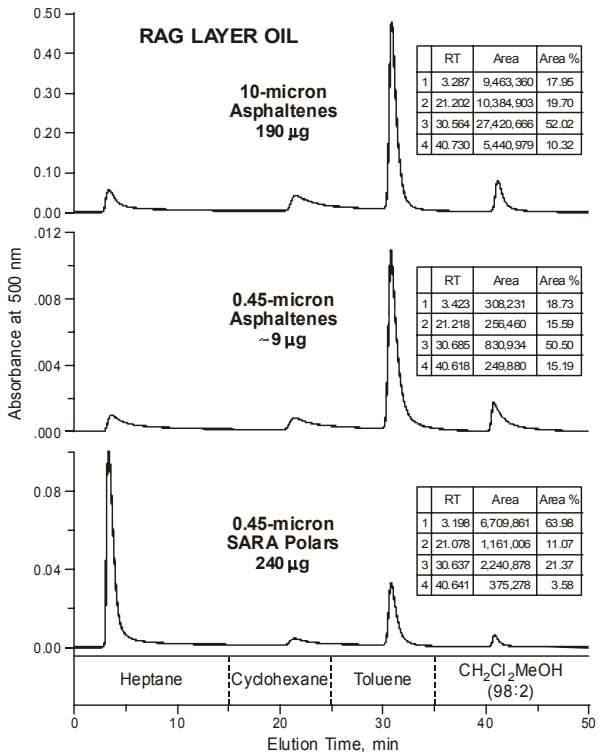

Figure 3. Separations of Emulsion Rag Layer Oil.

Table 2. Asphaltene Determinator Data from Oil / Brine Emulsion Experiments

Sample	Fraction	Weight %	Asphaltene Determinator 500 nm Area % Heptane	CyC6	Toluene	CH_2Cl_2:MeOH
Minnelusa	Asphaltenes 10 µ	0.25	15.41	19.27	50.10	15.23
Topped Oil	Asphaltenes 0.45 µ	1.20	22.90	23.99	45.87	7.24
	Total (calculated)	1.45	21.61	23.17	46.60	8.61
Supernatant	Asphaltenes 10 µ	0.10	13.24	15.64	49.27	21.85
Oil	Asphaltenes 0.45 µ	1.09	25.78	26.44	40.65	7.12
2:1 oil:brine	Total (calculated)	1.19	24.62	25.44	41.40	8.46
	SARA Polars 0.45 µ	2.56	63.80	10.68	20.55	4.97
Rag Layer	Asphaltenes 10 µ	1.91	17.95	19.70	52.02	10.32
Oil	Asphaltenes 0.45 µ	0.08	18.73	15.59	50.50	15.19
2:1 oil:brine	Total (calculated)	1.99	17.98	19.53	51.96	10.51
	SARA Polars 0.45 µ	2.38	63.98	11.07	21.37	3.58

Pyrolysis The ability of the Asphaltene Determinator separation to monitor the severity or pyrolysis during the coke formation induction period for whole residua and visbroken oils which was originally demonstrated in prior work (1) was confirmed with the new optimized system. Separation profiles at 500 nm for pyrolysis of two vacuum residua at 400 ºC are shown in Figure 4 for residence times up to 50 minutes. The point at which the area under the cyclohexane soluble material peak is less than the area for the more highly pericondensed aromatic pre-coke methylene chloride :methanol (98:0) soluble material is where the system is very unstable and coke formation is imminent.

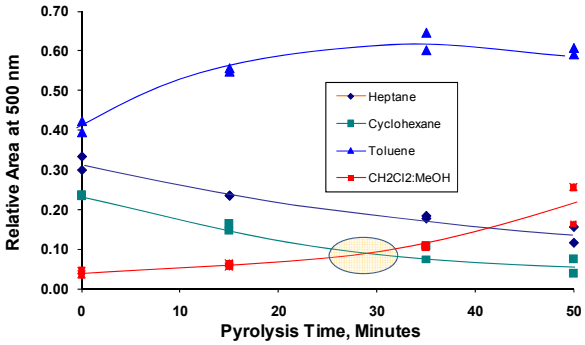

Figure 4. Separations of Two Residua Pyrolyzed at 400 ºC.

Asphaltene Determination Correlations can be made for particular systems between Asphaltene Determinator peak areas and the weight percent asphaltenes from a particular gravimetric method. These correlations are somewhat empirical since gravimetric asphaltenes contain some associated or entrained heptane-soluble material and maltenes contain some heptane-insoluble materials when separated using the Asphaltene Determinator. The correlations can be made using either two-solvent profiles or four-solvent profiles. Some sort of line equation is developed to create the correlation. This can be a function of the absolute asphaltene peak area with external calibration, or it can be a correlation with the relative area percent of the asphaltene peak(s). In a recent study with various original and processed oils, a two solvent separation was used with an evaporative light scattering detector (2). The calibration equation has the form:

$$\log M = (D * \log A) + E$$

where A is the absolute asphaltene peak area and M is the mass of asphaltenes. The area under the heptane (maltenes) peak is not measured. D and E are calibration constants. This approach has the advantage that whole oils containing volatile components can be injected.

Alternatively, relative percent area of asphaltenes ELSD peaks can be used with either a two-solvent or four-solvent separation profiles. The calibration equation for this system has the linear form:

$$Y = M * X + B$$

where X is the total percent area of asphaltene peaks relative to the total ELSD peak areas, and Y is the weight percent of asphaltenes. The line slope M and intercept B are constants relative to the particular system. This approach requires that the samples contain no volatile maltenes material that can evaporate in the detector. An example for a 2-solvent separation of residua is shown in Figure 5.

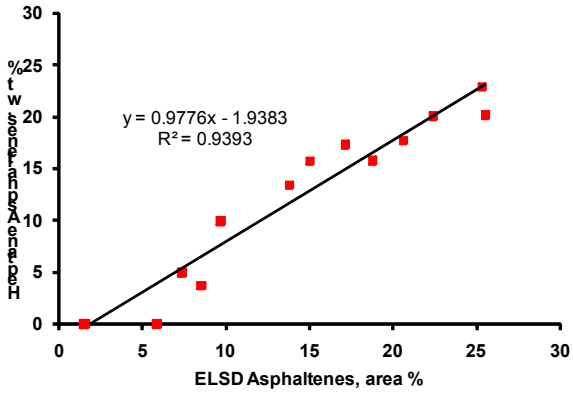

Figure 5. Calibration Line for Unpyrolyzed Residua.

Attempts to correlate gravimetric asphaltene content with the more detailed AD separation data can be frustrating since the material precipitated in gravimetric separations consists of highly associated species, and the associations are dependent on the precipitation conditions. On the other hand, the AD separation provides chemically meaningful subfractions on a molecular basis. Many aspects of the potential utility of the information provided by the AD separations remain to be explored and developed.

Another approach that we are investigating is the potential use of optical absorbance at both 500 and 700 nm (which is the upper limit of our absorbance detector). An unrelated method, IFB 9313 is a filtration / absorbance method that uses differential light absorption between maltenes and whole oils at 750 nm to determine weight percent asphaltenes. Absorbance at this wavelength is attributed to pericondensed ring systems in asphaltenes that

cause the brown color of oil. Possibly a combination of the Asphaltene Determinator separation with optical absorbance at two wavelengths can be used to measure both asphaltene subfractions and resins / polars from a single Asphaltene Determinator separation. An example is provided in Figure 6 wherein the heptane peak at 500 nm has a greater relative area percent than at 700 nm. The relative peak areas for the three asphaltene peaks (cyclohexane, toluene, methylene chloride:methanol (98:2) are essentially identical at 500 nm and 700 nm. The difference in relative absorbance peak areas for the heptane (maltenes) could be due to the presence of a less pericondensed intermediate polarity material, which absorbs light more at 500 nm than at 700 nm. Since it appears that the majority of SARA resins / polars material elutes with the heptane peak (Figures 2-3), the possibility exists that this material causes the enhanced absorbance at 500 nm for the heptane peak. More work is in progress to examine this possibility further.

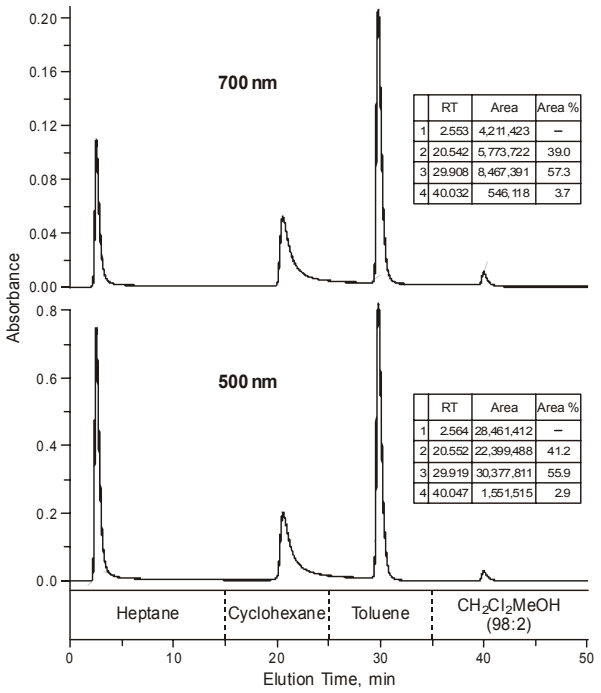

Figure 6. Separation Profiles for 2 mg Lloydminster VR at 500 nm and 700 nm.

New Characterization Approach The Asphaltene Determinator separation provides a new fractionation approach to the polar and pericondensed aromatic components of oil. The separation is not dependent on the isolation of highly associated materials that are separated to various degrees depending on precipitation conditions such as in gravimetric separations of asphaltenes. In this regard, it provides more consistent and chemically meaningful information than gravimetric precipitation of bulk asphaltenes. Also, resins / polar materials can possibly be characterized in a different manner without requiring a chromatographic SARA separation which is dependent on sorbent type. With a single injection and the judicious use of ELSD and optical absorbance detectors, it appears that an approach can be developed to define the distribution of these components in an oil by the four solubility peaks: heptane, cyclohexane, toluene, and methylene chloride:methanol (98:2). The optical absorbance detector can be used alone if the sample contains volatile material that is lost in the evaporative light scattering detector.

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