

Comparison of Precipitation and Extrography in the Fractionation of Crude Oil Residua

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Four different crude oils—Arab Heavy (AH), Arab Berri (AB), Alaskan North Slope (ANS), and San Joaquin Valley (SVJ)—were characterized by separating the crudes into compound classes by two different fractionation methods—extrography (ext) and asphaltene precipitation followed by extrographic isolation of the resins (ppt + ext). The fractions derived from these two methods of separation were characterized and compared in order to determine the most complete and discriminating compositional analysis for subsequent use in studies concerning the stability of emulsions or sludges which are produced by these crudes in refinery processing. The resin and asphaltene fractions are of primary interest due to their polar, surface-active nature, the central role these fractions play in stabilizing emulsions and sludges, and their resulting influence on crude processability. Preparatory-scale separations were developed and utilized to provide sufficient amounts of the polar fractions of these crudes for further studies. The H/C ratio and concentrations of S, N, and O as well as V and Ni contents were determined for each of the crudes and their respective fractions. The results of this investigation also provided useful information regarding the H-bonding capacity (as gauged by the functional group types and content) and aromaticity of the polar fractions of these particular crude oils. The polar functional groups and carbon types were identified and quantitated by FTIR and ¹³C NMR spectroscopy. FTIR analysis also provided an indirect measure of the polarity of substituent groups attached to the aromatic core of these molecules when comparing the results of the integration of the aromatic C=C stretch with the aromaticity as measured by ¹³C NMR analysis. Both the H-bonding capacity and the aromaticity are considered to play a central role in determining the solubility of asphaltenes in the crude medium which in turn has a significant effect on the emulsifying potential of the crude oil. In the comparison of the two fractionation methods, the resin and total asphaltene yields were very similar for most of the crude types; however, the characteristics of these polar fractions varied considerably in all the crudes depending upon the method used to isolate them. There was strong evidence to support the prevailing sentiment that the fraction which is coined “asphaltenes” is greatly influenced and defined by the very method utilized to isolate this fraction. When considering and analyzing the characteristics of the polar materials in their totality (i.e., resins + asphaltenes), these materials were very similar in nature regardless of the fractionation method used to isolate them. However, irreversible adsorption of asphaltenic components (up to ~0.8 wt % of whole crude) on the silica gel does occur when employing the extrographic technique. Thus, the ppt + ext fractionation method appears to be the simplest and most robust method to provide further understanding of the mechanisms which govern the stability of emulsions produced from different crude types.

Introduction

Waste minimization has become the focus of environmental policies in the petroleum industry.^{1–5} In particular, the formation of stable emulsions and sludges in petroleum refineries comprised of water, crude oil,

and solid particles has become a serious environmental concern. As the EPA continues to redefine specific petroleum-derived components which will be targeted as listed wastes, the need to minimize the formation of emulsions and the impetus to develop new methods for effective demulsification or alternative treatments of them have become more acute.

Despite years of research, there is a lack of a fundamental understanding of the mechanisms governing the stability of oil-continuous emulsions. With crude oil emulsions, the importance in long-term stability of a rigid and protective film surrounding the water droplets is clear.^{6–11} The detailed properties of this film, together with a fundamental knowledge of the chemistry of the interfacially active components in the crude

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oil, are far from understood.¹² However, studies have shown the importance of components such as asphaltenes and resins which, because of their surface-active and structure-forming properties, accumulate at the interface and hence have pronounced effects on emulsion stabilization and breaking.¹³⁻¹⁷ Therefore, it is of interest to isolate and characterize these components in order to determine their roles in forming these interfacial films.

Many attempts have been made to separate crude oils into groups or classes of compounds.¹⁸⁻²¹ The most generally accepted approach has been to divide the sample initially into the following fractions: (i) aliphatic hydrocarbons, (ii) aromatic hydrocarbons, (iii) resins, and (iv) asphaltenes. Such a separation has been called the SARA (for saturates, aromatics, resins, and asphaltenes) technique. This method has many variations (e.g., ASTM D893-69, D2007-80, Modified D2007-80)²² but is based on removal of asphaltenes by precipitation with a paraffinic solvent such as *n*-pentane or *n*-heptane prior to chromatographic separation of the remaining crude oil on Attapulgite clay and/or silica gel. The SARA separation is convenient and inexpensive and has been utilized extensively in the oil industry.²³⁻²⁵ There is debate, however, whether the method yields accurate

information on asphaltenes.²⁶ The many variations in the recommended procedures which have been employed may all have some influence not only upon the yield but also upon the chemical nature of this fraction. For example, the yield and chemical properties of asphaltenes have been shown to be affected by the temperature, precipitating solvent, solvent-to-oil ratio, reprecipitation, and separation time.²⁷ In addition, the solubility of a substance is not a function of its general carbon-hydrogen skeleton and its chemical functionality alone but depends on interactions with other substances which can act as cosolvents. Therefore, a given compound can appear as an "oil" or an "asphaltene" depending upon the presence or absence of other substances in a particular crude oil.²⁸

Since a detailed understanding is required of the structure of petroleum compounds concentrated chiefly in the heavier ends of crude oil (i.e., resins and asphaltenes), it is essential that these particular components be separated into reproducible fractions according to their specific chemical characteristics (heterocyclic composition, aromaticity, polarity, molecular weight). One technique for the characterization of low-volatile petroleum residues, called extrography (i.e., extraction and chromatography), is the best known method to attain such a separation.²⁹⁻³³ This method combines chromatographic separation and subsequent extraction of tightly bound petroleum components from the adsorbent. Slight variations of this method are often referred to as gradient elution chromatography or sequential elution fractionation. This type of separation is purported to provide a more consistent and precise definition of asphaltenes and a more accurate measure of the asphaltene content in crude oils in comparison to asphaltene precipitation due to the presence of asphaltene micelles in the crude oil.³³ These micelles contain lighter and/or less polar, but still very aromatic, components which may be incompletely removed from the precipitated asphaltenes. On the other hand, when the asphaltene micelles are adsorbed onto the silica gel prior to extrographic separation, the micellar arrangement may become destabilized, thus releasing any associated saturate, aromatic, and resin molecules which would then elute with the previous fractions.³⁴

The mechanism of an extrographic separation arises from orderly adsorption of the components in the sample, together with selective extraction by solvents

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of increasing polarity (i.e., solvent strength). Orderly adsorption means that the most polar components are adsorbed by the most active sites on the surface of the adsorbent, the least polar compounds probably being retained in the pores.³⁵ Thus, saturated hydrocarbons, which are only weakly bound to silica, are the first to be eluted; asphaltenes, which interact strongly with silica and have low solubility in the less polar eluents, are the last to be eluted.³⁶ Therefore, extrography provides a given number of fractions of well-defined chemical composition according to aromaticity, polarity, and molecular weight.³⁵ However, there are those who cite some difficulties with extrography (and other sequential elution fractionation techniques) in fractionating petroleum crude oils. These difficulties are primarily associated with recovering the most polar petroleum components which are tightly bound to the adsorbent material.^{28,37,38}

The molecular structures in petroleum and similar complex mixtures have never been completely defined by analytical techniques.³⁹ Molecular types in crude oils range from nonpolar, nonaromatic hydrocarbons to highly aromatic hydrocarbons, the molecular structures of which contain varying amounts of certain so-called heteroatoms, predominantly oxygen, nitrogen, and sulfur, together with parts-per-million amounts of metals. Because the number of molecules in crude oils with different chemical structures is extremely large, determination of crude oil composition by separation into its molecular components is generally considered impractical if not impossible by present-day techniques. However, if the different chemical functionalities that compose and dominate the properties of the various petroleum molecules are considered, the number of types of functionalities that need be considered quickly narrows to a manageable number. We have conducted this study with this perspective in mind.

Quantitative IR spectroscopy provides the ability to identify and quantify chemical functionalities in complex mixtures such as petroleum.⁴⁰ Specifically, it has been used to estimate the type and amount of different chemical functional groups present in polar fractions of high-boiling distillates,^{41,42} in asphaltene fractions,⁴³

and in acidic, basic, and neutral fractions of asphalts.⁴⁴ With the exception of basic nitrogen compounds (predominantly pyridine types), sulfides, thiophenes, ethers, and furans, which have poorly defined or weak infrared bands and cannot be analyzed by infrared alone, the following functionalities make up the important polar heteroatom-containing functionalities occurring naturally in crude oils or formed during oxidative aging: carboxylic acids, amides, phenols, pyrroles, ketones, esters, anhydrides, and sulfoxides.

¹³C nuclear magnetic resonance spectroscopy has also become a useful, nondestructive tool in the analysis of crude oils and petroleum products.⁴⁵⁻⁴⁷ This technique is very attractive in that it provides an accurate value of "aromaticity" or aromatic carbon content as a fraction of the total carbon and consequently affords an excellent characterization of complex, multicomponent petroleum fractions.^{48,49} In ¹³C NMR spectroscopy, the carbon types are observed directly and, under appropriate conditions, can be readily quantified. There are two inherent problems in ¹³C spectra which must be taken into account to ensure the quantitative reliability of the data: (1) the great difference in relaxation times for different molecules observed in the same crude oil fraction and (2) the extensive variations in the nuclear Overhauser enhancement (NOE) parameter. The addition of paramagnetic agents such as Cr(acac)₃ provides an alternative relaxation mechanism via the unpaired electron's magnetic field, thus significantly reducing data acquisition time.⁵⁰ In many studies, all samples containing a high degree of condensed aromatic ring systems (i.e., asphaltene samples) are prepared with Cr(acac)₃.^{51,52} To suppress NOE effects, an inverse gated decoupling microprogram is normally used in which the broad band proton decoupler is gated off during the delay time.^{47,51} These recent improvements in instrumental techniques to obtain high-quality ¹³C spectra have thrust ¹³C NMR into a position where it promises to play a central role as a structure-determining tool.

The purpose of this study was to determine and

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Table 1. General Properties of Crude Oils

property	test methods	SJV	ANS	AB	AH
gravity, °API	ASTM D 287	12.2	27.5	38.6	27.4
viscosity, ^a SUS at 100 °F	ASTM D 445	15,025	71	41	118
nitrogen, wt %	GC combtn	0.90	0.31	0.07	0.25
sulfur, wt %	GC combtn	1.20	1.42	1.52	3.16

^a Viscosity of distilled water at 68 °F is 31 SUS.

compare the composition of four different crude types as defined by two different fractionation techniques: (1) extrography and (2) asphaltene precipitation followed by extrographic separation of the deasphalted crude oil. This comparison would reveal the method which provides the most reproducible and complete recoveries as well as the most chemically distinct compositional analysis of the surface-active material in crude oils. These interfacially active compounds, primarily resins and asphaltenes, are of principal interest to our further investigations concerning the stability of water-in-crude-oil emulsions. The crude oils chosen for this study—Arab Heavy, Arab Berri (Extra Light), Alaskan North Slope, and San Joaquin Valley—were selected in such a way to obtain crudes with a range of heavy residua. The extrography technique was employed to yield five distinct fractions: saturated and aromatic hydrocarbons (satd/arom), resins, asphaltenes, and polar asphaltenes 1 and 2. The latter technique provided only three fractions: satd/arom, resins, and asphaltenes. Preparatory-scale versions of these techniques were developed to provide ample amounts of the interfacially active materials (i.e., resins and asphaltenes) which will be required for further fractionation and characterization via ion exchange chromatography and model emulsion stability studies. These crude oils and their fractions were analyzed by element to determine structural information regarding their relative aromaticity (H/C) and heteroatomic distribution (%N, %S, and %O). FTIR spectroscopy was used to quantify the functional groups and aromatic carbon content in these polar fractions. The polar functional groups which were identified by this technique include carbonyls/carboxylic acids, phenols, sulfonyls (sulfoxides), amide carbonyls, and pyrroles. Spectra of model compounds were obtained in order to determine the apparent integrated molar absorptivities (B) of these functional groups. These values were used to calculate the weight percentages of these functional groups in the various crude fractions. The aromatic carbon content in these fractions was also determined by ¹³C NMR spectroscopy. Comparisons between the aromaticity as determined by different methods (i.e., elemental analysis, FTIR spectroscopy, and NMR spectroscopy) were made to provide further insight into the structural characteristics and polarity of the resins and asphaltenes isolated from the different crude oils under study.

Experimental Section

Materials Studied. The general properties of the crude oils selected for this study (Arab Berri, Arab Heavy, Alaskan North Slope, and San Joaquin Valley) are presented in Table 1. Arab Heavy (AH) is a medium °API gravity, high-sulfur crude produced from an off-shore field, Safaniya, known to be

the world's largest offshore field.^{41,53} Arab Berri (AB) is a high °API gravity, low-sulfur crude produced from Upper Jurassic Arab zone reservoirs in Berri, Saudi Arabia.^{53,54} Alaskan North Slope (ANS) is produced from fields in the North Slope of Alaska, predominantly in the Prudhoe Bay region. The nitrogen-rich San Joaquin Valley (SJV) crude oil (a blend of crudes from San Joaquin Valley, CA) is a crude of very low °API gravity and unusually high viscosity.¹⁸

Two different fractionation methods were employed: (1) extrography and (2) precipitation of asphaltenes followed by extrographic isolation of resins.

Extrographic Separation of Crude Oil. Before fractionation via extrography, the crude oil was pretreated by dissolution in methylene chloride (Fisher-Scientific HPLC Grade) and subsequent evaporation in a nitrogen-flushed vacuum oven at 70 °C. The percent of mass loss was determined and the process repeated until little or no mass loss (<3%) was observed. To obtain large amounts of the polar compounds of interest, 8–10 g of pretreated crude oil was adsorbed to 50 g of silica gel (Fisher-Scientific Chromatographic Grade, 35–60 mesh, Davisil) in a solution of methylene chloride for 24 h or until the solvent above the silica gel was optically transparent. Prior to adsorption of the crude oil, the silica gel was activated at 120 °C in a nitrogen-flushed vacuum oven for 24 h. After adsorption of the crude oil, the solvent was driven off by rotary evaporation at 50 °C. The adsorbed crude oil was then dried in a nitrogen-flushed vacuum oven at 70 °C for 24 h.

The adsorbed oil samples were charged to a standard set of chromatography columns. A schematic illustration of a packed extrography column along with the fractions obtained and the solvents used to elute them is provided in Figure 1. All solvents used were the purest HPLC grade available. The required solvent volume to separate the crude oil into distinct reproducible fractions was determined via UV–visible spectrophotometric analysis. The material remaining on the column after elution with THF:acetone was then Soxhlet-extracted with chlorobenzene at ~60 °C for 24 h. The residual, strongly adsorbed components of the crude oil were then extracted with 300 mL of pyridine at room temperature for 8 h and isolated from the silica gel matrix by positive-pressure filtration. Care was taken to avoid contamination of this last fraction with silica gel during the filtration process. The solvents were removed from the crude oil fractions via rotary evaporation (except for the asphaltene fraction), and the fractions were then dried in a nitrogen-flushed vacuum oven at 70 °C for 48 h. The asphaltene fraction is eluted with a solvent mixture containing THF which is known to form peroxides in the presence of air.⁵⁵ To prevent reaction of the asphaltenes with peroxides, the eluted asphaltenes are sparged with argon for ~18 h to evaporate the solvent before vacuum-drying.

Asphaltene Precipitation and Resin Isolation. In the second fractionation method, the asphaltenes were first precipitated with an excess of *n*-heptane (40:1) prior to extrographic isolation of the resins. The asphaltenes were precipitated by shaking them in the heptane solution for 8 h at room temperature followed by vacuum filtration using Whatman 934-AH filter paper. The asphaltenes were washed on the filter with heptane until the filtrate was colorless and dried under vacuum at 80 °C until constant weight. The heptane solubles were then adsorbed to silica gel (as explained above), charged to the extrography column, and eluted as shown in Figure 1 to obtain the saturate/aromatic and resin fractions.

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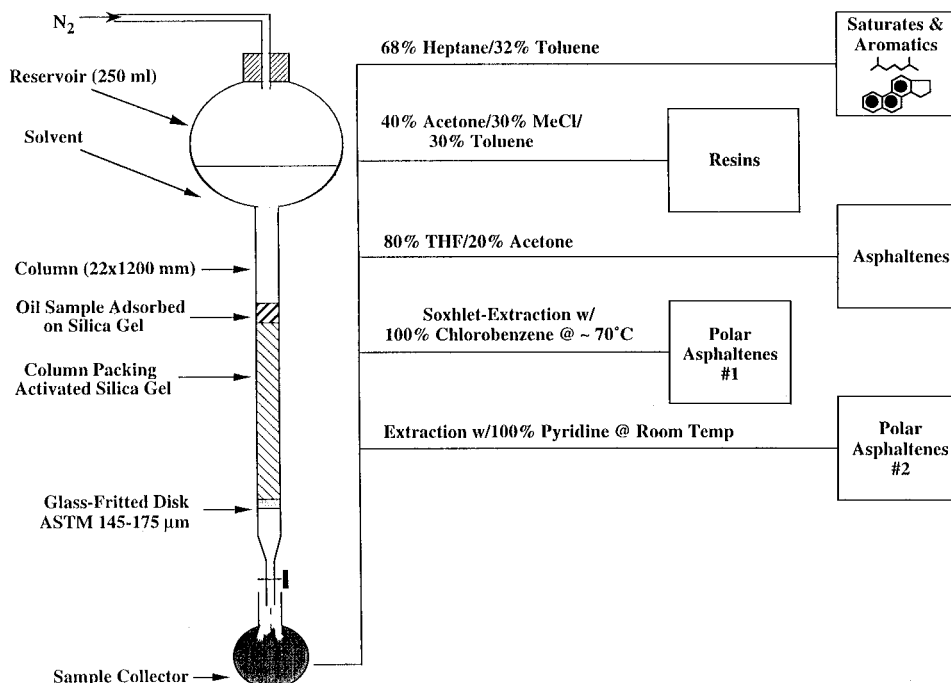


Figure 1. Schematic of extrographic fractionation of crude oil.

Elemental Analysis. Elemental analyses (C, H, N, S, and O) of these crude oils and their fractions were obtained with a Perkin-Elmer 2400 Series II CHNS/O analyzer. A combustion method is employed to determine C, H, N, and S content while the sample is pyrolyzed in a helium/hydrogen mixture to determine O content. In both methods, the homogenized gases are depressurized through a column where they are separated by gas chromatography and detected as a function of their thermal conductivities. Metals content (V, Ni, and Fe) was determined via neutron activation analysis (NAA) with 20 s and 12 h irradiations of 1.5×10^{13} n/(cm² s). Decay was monitored from 200 to 1200 s counts on Ortec 38% and 42% GeLi detectors coupled to Ortec Omnigram-N computerized γ detection systems. NIST/NRC-certified standards were irradiated and analyzed as unknowns along with samples.

FTIR Spectroscopy. In the Fourier-transform infrared (FTIR) studies, a Nicolet Magna IR 750 spectrometer was used with a TGS detector. Spectra were obtained from dilute solution (10 g/L) of polar fractions dissolved in CH₂Cl₂ (Fisher-Scientific HPLC Grade) using a 0.2 mm fixed-path-length CaF₂ cell. All spectra were run consecutively in the same cell to allow spectral comparisons without minor baseline shifts caused by variations in cell transmittancy or minor differences in peak heights caused by variations in cell thickness. The background spectrum of pure CH₂Cl₂ was integrated and subtracted from the sample spectra. Sixty-four scans were taken of each sample recorded from 4000 to 800 cm⁻¹ at a resolution of 2 cm⁻¹ in the transmission mode. Due to the high clarity of the spectra in preliminary experiments, no smoothing techniques were needed. Peak positions and areas were determined by using available software packages.

The areas under the absorption bands of interest were used to evaluate quantitative estimates of functional group concentrations via Beer's Law. Apparent integrated absorption intensities (B) of functional groups that are similar to those of compound types found in the crude oils were determined from FTIR spectra of model compounds. The values of B were obtained in the following manner.⁵⁶ Spectra were recorded using the linear transmission mode of the spectrometer. Absorption band areas having the units cm⁻¹ were then

calculated by a software package integration feature. B was determined by substituting the values of the absorption band area for the integral in Beer's law, shown below, and solving the following equation:

$$B = (1/c) \int_{\text{over band}} A_{\nu} d_{\nu}$$

With concentration (c) expressed in mol/L and the cell path length (l) in cm, B has units of L/(mol cm²). In the form of Beer's law shown above, A_{ν} is the absorbance when the spectrometer is set at wavenumber ν . The values of B for each functional group of interest were the result of several runs to be made at different concentrations, for two or three different compound types, between 10⁻² and 10⁻³ M. The infrared curves of the various functional groups had areas which were directly proportional to concentration in this range.

Then each of the spectral features of interest in the "unknown" samples were integrated and quantified as weight percentage by dividing the integrated area of the peak by B , the apparent integrated absorption intensity, and by the cell path length of 0.02 cm to obtain the molar concentration of the functional group in the FTIR cell. This concentration was then multiplied by the molecular weight of the particular functional group and divided by the total mass concentration of 10 g/L to obtain the weight fraction of functional group. These values were then multiplied by 100 to obtain weight percentages of each of the functional groups.

¹³C NMR Spectroscopy. A General Electric GN 300 Omega nuclear magnetic resonance (NMR) spectrometer with a C/H dual 5 mm probe was utilized for all experiments at an observed frequency of 75 MHz. The ¹³C spectra were normally accumulated overnight in order to obtain the best possible signal-to-noise ratio. A total of 8000 scans were acquired for each sample using an 8 μ s (~90°) pulse and a 4 s delay time between scans. During the delay, the proton decoupling power was turned off to facilitate more complete relaxation of slowly relaxing carbons. It has been shown that the relaxation time of petroleum asphaltene is less than 1 s, even in the absence of the relaxation agent, largely because of the presence of

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Table 2. Weight Percentage Yields of Various Fractions from Extrographic Separation of Crudes^a

crude oil	SJV	ANS	AB	AH
% loss after pretreatment	21.7 ± 1.90 ^b	41.5 ± 1.29	45.7 ± 0.97	33.1 ± 1.12
satd/arom + pretreatment loss	71.56 ± 1.66	83.59 ± 1.66	94.77 ± 0.67	79.01 ± 2.75
resins (R)	18.84 ± 0.33	7.81 ± 0.27	3.65 ± 0.18	11.86 ± 0.24
asphaltenes (A)	2.04 ± 0.12	0.68 ± 0.01	0.36 ± 0.02	1.59 ± 0.06
polar asphaltenes 1 (PA 1)	3.04 ± 0.56	1.66 ± 0.15	0.43 ± 0.03	2.19 ± 0.07
polar asphaltenes 2 (PA 2)	0.52 ± 0.16	0.59 ± 0.01	<0.05	0.56 ± 0.04
% recovery	96.00 ± 1.32	94.33 ± 1.50	99.21 ± 0.65	95.21 ± 2.31
total asphaltenes (A + PA)	5.60 ± 0.36	2.93 ± 0.09	0.79 ± 0.03	4.34 ± 0.06
total polars (R + A + PA)	24.44 ± 0.34	10.74 ± 0.22	4.44 ± 0.15	16.20 ± 0.19

^a All numbers are weight percentages based on the whole crude oil. ^b Reproducibility as measured by average deviation from mean.

Table 3. Weight Percentage Yields from Heptane Precipitation and Extrography of Heptane Solubles^a

crude oil	SJV	ANS	AB	AH
% loss after pretreatment	21.7 ± 1.90 ^b	41.5 ± 1.29	45.7 ± 0.97	33.1 ± 1.12
satd/arom + pretreatment loss	71.75 ± 2.22	85.25 ± 2.99	90.69 ± 2.45	79.99 ± 0.87
resins (R)	20.26 ± 0.26	9.47 ± 0.07	3.49 ± 0.17	9.56 ± 0.87
ppt asphaltenes (A)	4.57 ± 0.12	3.35 ± 0.01	0.68 ± 0.04	8.27 ± 0.12
% recovery	96.58 ± 1.71	98.07 ± 2.61	94.86 ± 2.35	97.82 ± 0.81
total polars (R + A)	24.83 ± 0.23	12.82 ± 0.05	4.17 ± 0.15	17.83 ± 0.52

^a All numbers are weight percentages based on the whole crude oil. ^b Reproducibility as measured by average deviation from mean.

paramagnetic species such as V³⁺ and Ni³⁺.⁵⁷ A spectral width of 25 kHz was used, and the free induction decay was stored as 16K data points. Inverse-gated hydrogen decoupling was used throughout to minimize the residual nuclear Overhauser effect (NOE). All samples were approximately 30–80 mg diluted with 0.5 mL of deuteriochloroform in 5 mm sample tubes.

Results and Discussion

Extrography. The results from the extrographic (ext) separation of the four crude oils studied are summarized in Table 2. These results are the average of at least six, reproducible extrography runs. Percent loss due to pretreatment of the crudes varied from 21.7% for SJV to 45.7% for AB. Percent recoveries (including the crude loss due to pretreatment) varied from 94.3% to 99.2%. The results from fractionation via asphaltene precipitation followed by extrographic isolation of the resins (ppt + ext) of these same four crude oils are shown in Table 3. Percent loss due to pretreatment and percent recoveries are similar to that obtained by ext. The unrecovered material was most likely volatile hydrocarbons as these fractions—saturates and aromatics—showed the largest variations. A small amount of the material (<1%) may also have been irreversibly adsorbed on the silica gel matrix after the extrographic separation in both fractionation methods. Also computed are total asphaltenes (A + PA) and total polar components (R + A + PA).

To place these results in the proper perspective, Figure 2 shows the composition on a ternary diagram of approximately 640 different crude oils (after removing the crude fraction boiling below 210 °C (~450 °F)).⁵⁸ The three coordinates are total saturated hydrocarbons (paraffins and naphthenes), total aromatic hydrocarbons (pure aromatics, naphthenoaromatics, and usually cyclic sulfur compounds), and total polar components (resins which are retained on alumina and asphaltenes which are insoluble in *n*-hexane). In our study, total saturates

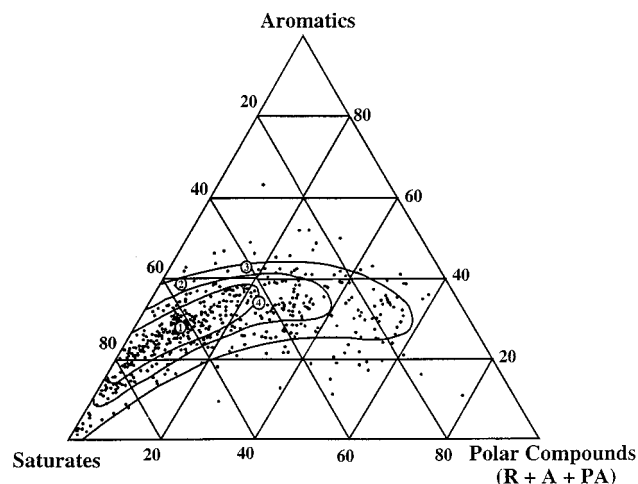


Figure 2. Compositional representation on ternary diagram of ca. 640 different crudes. Compositions are in wt % and represent the 210 °C+ fraction. Crudes in this study are 1 (ANS), 2 (AB), 3 (AH), and 4 (SJV).

and total aromatics were determined by an analytical version of the extrographic technique. AB falls very close to the polar-free edge of the diagram. AH is modestly higher in polar component content and is somewhat more aromatic than AB. Finally, SJV is extremely high in polar components which are primarily resinous compounds. This figure clearly illustrates the diversity in the properties of the crude oils under investigation.

The percent yields (including total asphaltenes) using both separation methods (i.e., ext and ppt + ext) presented in Tables 2 and 3 are plotted graphically for the four crude oils in Figure 3. AH yields more asphaltenes and fewer resins from ppt + ext than by ext (~4% and 2%, respectively) while the asphaltene and resin yields from SJV displays the opposite trend, although to a lesser extent (~1% and 1.5%, respectively). ANS yields both more resins (~1.5%) and asphaltenes (~0.5%) from ppt + ext than by ext while AB has similar yields for both methods. This could be due to the difference in the aromaticity and polarity distributions of AH and SJV and the difference in the governing separation mechanisms between the two fractionation techniques to be discussed later.

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(58) Tissot, B. P.; Welte, D. H. *Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration*; Berlin: Springer-Verlag, 1984; p 527.

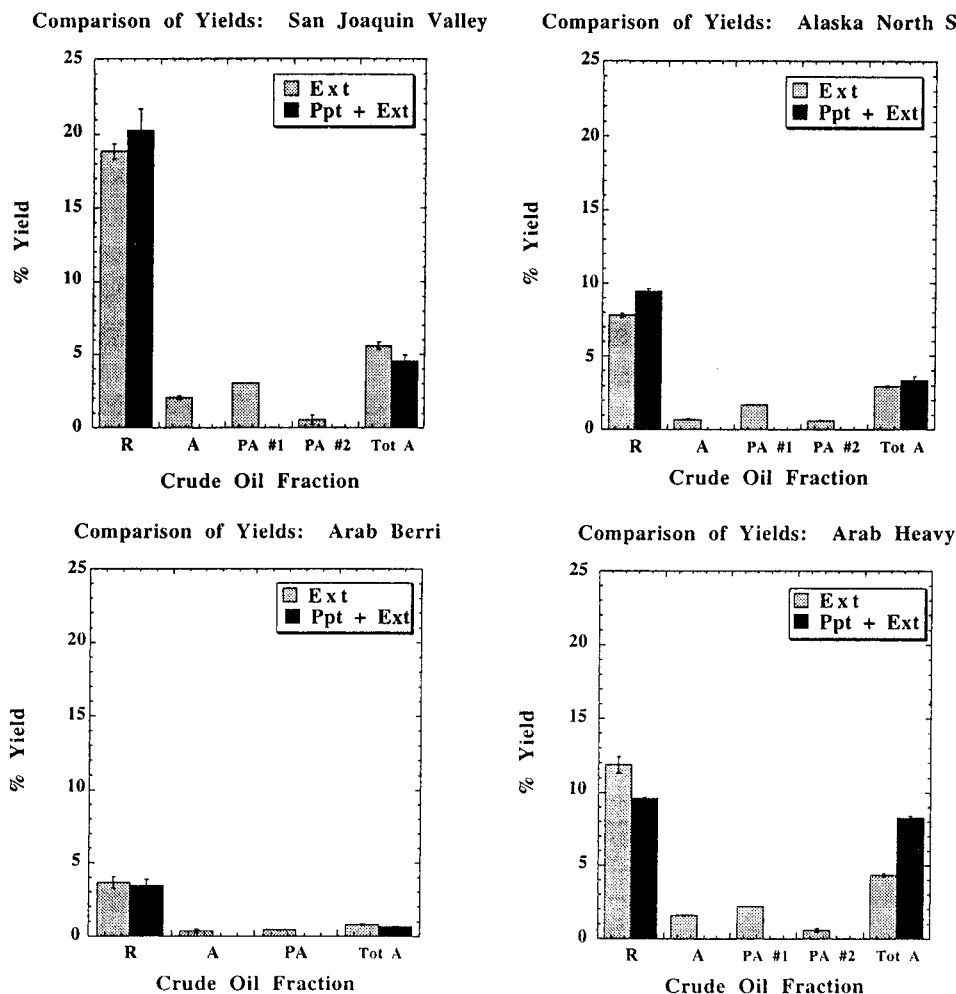


Figure 3. Comparison of yields from four crude oils using extrography and precipitation + extrography fractionation methods.

Elemental Analysis. The elemental compositions (carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O)) of the crudes and crude fractions obtained from both the ext and ppt + ext separation techniques were measured. These values are collected in Tables 4 and 5, respectively, in terms of H/C, %N, %S, and %O. For the sake of comparison, Table 4 also presents the "average" parameter values for the total ext asphaltenes as a sum of the weighted values (i.e., as a function of the respective yields) of each of the ext asphaltene fractions.

There is excellent consistency among the H/C ratios of the ext polar fractions of the crudes, with the exception of SJV crude. The H/C ratio of the resin fraction falls between 1.27 and 1.32 with the exception of SJV, which is 1.36. Similarly, the H/C ratio of the asphaltene and polar asphaltene fractions falls between 1.09 and 1.14. Again, SJV crude has significantly higher H/C ratios for these two fractions: 1.33 for the asphaltene fraction and 1.31 and 1.24 for polar asphaltene fractions 1 and 2, respectively. The H/C ratio of the ppt resins from the four crudes all fall between 1.36 and 1.39 while the values for the ppt asphaltenes range anywhere from 1.03 for AB to 1.17 for SJV. Again, SJV asphaltenes are found to have the highest H/C ratio, although the difference among the crudes is considerably less with ppt + ext vs ext. Two explanations seem plausible: (1) the asphaltenes in SJV crude are considerably more aliphatic and/or less condensed than in the other crudes and (2) the asphaltene fractions are so

strongly solvated (i.e., peptized) by the resins that some of the resins are retained on the column and elute with the asphaltene fractions in the ext method.⁵⁹⁻⁶¹ The latter would explain the greater difference in H/C ratios between SJV asphaltenes and those from the other crudes when employing the ext method as compared to the ppt + ext asphaltenes. In Figure 4, we see that the H/C ratios of the ppt + ext asphaltenes are much lower than their ext counterparts for both SJV and AB. Whereas we observe the opposite trend for the resins between the two methods where the H/C ratio of the ppt + ext resins is significantly higher than that of the ext resins, excepting SJV. Since the ppt + ext asphaltenes appear to be much more aromatic (i.e., lower H/C value) than the asphaltenes isolated via extrography, one might suspect the irreversible adsorption of condensed, polyaromatic compounds on the silica gel matrix during the extrographic fractionation as mentioned in the literature review.

If nitrogen (N) content is any indication of polarity, SJV appears to be the most polar of the crude oils in this study. SJV is clearly highest in N content of the

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(60) Al-Jarrah, M. M. H.; Al-Dujaili, A. H. Characterization of Some Iraqi Asphalts II. New Findings on the Physical Nature of Asphaltenes. *Fuel Sci. Technol. Int.* **1989**, 7 (1), 69-88.

(61) Reynolds, J. G.; Biggs, W. R. Effects of Asphaltene Precipitation and a Modified D 2007 Separation on the Molecular Size of Vanadium- and Nickel-Containing Compounds in Heavy Residua. *Fuel Sci. Technol. Int.* **1986**, 4 (6), 749-777.

Table 4. Elemental Analysis Summary: Extrography Fractions^a

crude type	SJV	ANS	AB	AH
H/C Ratio				
satd/arom	1.55	1.54	1.70	1.63
resins	1.36	1.27	1.29	1.32
asphaltenes	1.36	1.10	1.11	1.14
polar asphaltenes 1	1.31	1.13	1.13	1.11
polar asphaltenes 2	1.24	1.12		1.09
avg asphaltenes ^b	1.31	1.12	1.13	1.12
% Nitrogen				
satd/arom	0.41	0.16	0.02	0.04
resins	2.15	1.20	0.98	0.82
asphaltenes	1.60	1.05	0.74	0.82
polar asphaltenes 1	1.64	0.89	0.61	0.89
polar asphaltenes 2	3.14	3.43		1.83
avg asphaltenes	1.79	1.33	0.67	0.99
% Sulfur				
satd/arom	0.79	0.89	1.69	3.10
resins	1.87	2.47	4.51	6.29
asphaltenes	1.64	2.65	5.99	6.77
polar asphaltenes 1	1.20	2.38	4.44	6.64
polar asphaltenes 2	1.42	2.17		6.26
avg asphaltenes	1.43	2.43	5.15	6.64
% Oxygen				
satd/arom	0.25	0.30	0.17	0.22
resins	2.11	0.86	1.54	1.33
asphaltenes	4.29	3.19	3.18	1.87
polar asphaltenes 1	2.84	2.91	2.79	1.11
polar asphaltenes 2	3.10	4.64		1.90
avg asphaltenes	3.39	3.32	2.97	1.49

^aAll number are weight percentages except H/C ratio which is an atomic ratio. ^bParameters for average asphaltenes are determined as a function of yield distribution among asphaltene fractions.

Table 5. Elemental Analysis Summary: Precipitation + Extrography Fractions^a

crude type	SJV	ANS	AB	AH
H/C Ratio				
satd/arom	1.46	1.56	1.63	1.56
resins	1.38	1.38	1.36	1.39
ppt asphaltenes	1.17	1.08	1.02	1.11
% Nitrogen				
satd/arom	0.46	0.24	0.03	0.04
resins	1.89	0.94	0.67	0.66
ppt asphaltenes	2.44	1.11	0.77	0.94
% Sulfur				
satd/arom	0.65	1.07	1.46	2.91
resins	1.90	3.29	4.76	5.95
ppt asphaltenes	1.60	3.06	5.84	7.17
% Oxygen				
satd/arom	0.54	0.59	0.65	0.52
resins	2.30	2.91	2.44	2.39
ppt asphaltenes	3.52	2.67	2.49	1.46

^aAll number are weight percentages except H/C ratio which is an atomic ratio.

four crudes and varies from 1.8 to 2.5% for the polar fractions whereas the N content of the polar fractions for the other three crudes varies from 0.7 to 1.5%. The N content of the ppt + ext asphaltenes from SJV is considerably higher than its ext counterpart (2.5 vs 1.8%). The values for the fractions in the other crudes are similar, however, the N content of the polar asphaltene 2 fractions from ext are suspiciously high and could be the result of incomplete evaporation of its eluting solvent, pyridine. So, in actuality, the N content of the ppt + ext asphaltenes may be higher than their ext counterparts for all the crudes. From Table 4, we see that the oxygen (O) content of the ext asphaltene fraction is notably higher than the other ext or ppt +

ext polar fractions (excepting the ANS polar asphaltene 2 fraction). This is to be expected since the solvent mixture used for the elution of the asphaltenes is primarily comprised of THF. A mobile phase of this type would selectively elute compounds commensurately richer in oxygen. The O contents of the total asphaltene fractions from both methods are similar, but the resins derived from the ppt + ext method are consistently higher in O content than those obtained via the ext method, especially for ANS. This could be the result of oxidation during the extraction and subsequent workup of the ppt + ext resins and/or incomplete evaporation of the extraction solvent, a mixture which includes acetone. AH and AB are clearly the most sulfur-rich crudes while SJV is the leanest in sulfur. It is also evident that the asphaltenes recovered by ppt + ext are higher in sulfur (S) content than the ext asphaltenes while the resins derived from both methods are closely matched in comparison. These results on the heteroatom distribution suggest that the presumed irreversibly adsorbed asphaltenes remaining on the silica gel after the ext procedure are rich in both nitrogen and sulfur content.

Metals Analysis. The metals content (vanadium (V) and nickel (Ni)) of the crudes and their polar crude fractions (i.e., resins and asphaltenes) obtained from both separation techniques are presented in Table 6. For comparison with the ppt + ext method, the values for the ext asphaltenes have been averaged over the total asphaltene fraction as a function of the yields of each of the ext asphaltene and polar asphaltene fractions.

As expected, the asphaltenes are higher in metals content than the resins regardless of the employed separation technique except in the case of the V distribution observed in the extrographic separation of SJV. AH asphaltenes have the highest V contents from 530 to 760 ppm depending on the method of fractionation while SJV asphaltenes are richest in Ni with values between 350 and 940 ppm. The greatest difference between the fractionation methods in terms of metals content is observed in the SJV asphaltenes. SJV asphaltenes as derived by precipitation were much higher (by a factor of 2) in both V and Ni content than the asphaltenes obtained by extrographic separation. In general, the ppt asp fractions were higher in metals content than the ext asp while the converse is true for the resins obtained by the different methods. The Ni content distribution among the crude fractions obtained from AB and AH was very similar for both methods. The comparative trends among the resins and asphaltenes obtained by the different separation techniques are not surprising given the expectation that the metal-containing species would be among the first to precipitate out of solution when subjected to a very nonpolar environment such as the addition of an excess of *n*-heptane during the asphaltene precipitation.

Table 7 compares the results of an overall balance on the polar fractions derived from both separation techniques. These results reveal that the recovery of metal-containing components is not definitively better when employing precipitation vs extrography for a given crude oil. To determine a more conclusive answer in addressing the issue of irreversible adsorption, the metals content of the silica gel (with any potentially irreversibly

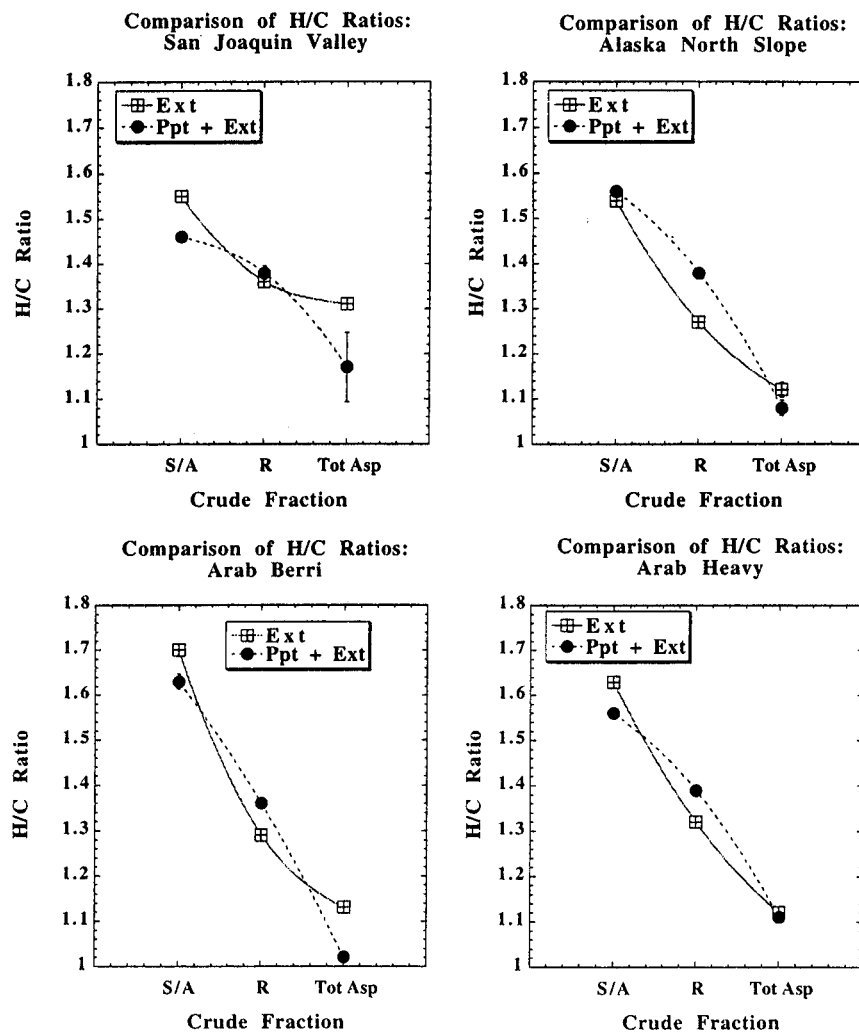


Figure 4. Comparison of H/C ratios in crude oil fractions isolated via extrography and precipitation + extrography.

Table 6. Summary of Metals Analysis: Weight Percentage of Vanadium and Nickel in Polar Fractions

crude oil fraction	SJV	ANS	AB	AH
Vanadium (ppm)				
extrography				
resins	281.3	216.1	82.5	370.4
asphaltenes	229.2	438.0	181.9	528.7
polar asphaltenes 1	178.6	398.9	232.0	647.7
polar asphaltenes 2	419.4	286.2		764.5
avg asphaltenes ^a	219.5	385.3	209.2	619.2
ppt + ext				
resins	187.7	117.9	62.8	205.0
asphaltenes	463.8	516.4	352.8	667.6
Nickel (ppm)				
extrography				
resins	322.4	117.5	66.6	135.1
asphaltenes	458.5	306.1	128.0	271.0
polar asphaltenes 1	348.3	317.0	155.4	415.2
polar asphaltenes 2	943.1	240.0		568.0
avg asphaltenes	443.8	299.0	142.9	382.1
ppt + ext				
resins	268.0	64.4	43.0	85.8
asphaltenes	873.1	386.0	130.5	352.1

^a Parameters for average asphaltenes are determined as a function of yield distribution among extrographic asphaltene fractions.

adsorbed "residual" polar materials) after the final extraction of both fractionation techniques was measured for all the crude oils under study. The results for SJV, AH, and ANS crude oils are presented in Table 8 in terms of the mass of V and Ni per gram of silica

Table 7. Comparison of Overall Balance on Metals Composition of Resins and Asphaltenes Isolated via Extrography and Precipitation + Extrography

pretreated crude oil	composition	V (ppm)	Ni (ppm)
SJV	from balance on extrog	65.3 ± 0.5	85.6 ± 4.0
	from balance on ppt + ext	59.2 ± 0.6	94.2 ± 6.3
ANS	from balance on extrog	28.2 ± 0.3	17.9 ± 2.8
	from balance on ppt + ext	28.5 ± 0.3	19.0 ± 3.8
AB	from balance on extrog	4.7 ± 0.1	3.6 ± 0.8
	from balance on ppt + ext	4.6 ± 0.1	2.4 ± 0.8
AH	from balance on extrog	70.8 ± 0.6	32.6 ± 3.2
	from balance on ppt + ext	74.8 ± 0.5	37.3 ± 3.0

Table 8. Comparison of Metals Analysis of "Residual" Si Gel after Fractionation via Extrography and Precipitation + Extrography

crude oil	"residual" Si gel after extraction method	V (μg/g Si)	Ni (μg/g Si)
SJV	extrog	0.67	1.68
	ppt + ext	<0.30	1.18
ANS	extrog	0.71	0.24
	ppt + ext	<0.44	<0.24
AH	extrog	0.90	2.45
	ppt + ext	<0.55	<1.36

gel submitted. These results are NOT the actual concentration of metals in the remaining adsorbed crude oil components and are, therefore, only quantitative in a comparative sense. AB crude oil left no detectable traces of metals on the silica gel after extraction using either method. In looking at these results, it is quite

clear that higher concentrations of irreversibly adsorbed polar materials are found on the silica gel after extrography than following the ppt + ext method. Also, if we assume that the irreversibly adsorbed material is at least as rich in V content as the last fraction extracted from the silica gel in the extrographic separation (i.e., polar asphaltene 2), an upper bound for the extent of the unrecovered material is ~ 0.8 wt % (based on the whole crude) for SJV and AH crude oils. If the metals concentration in the adsorbed materials is higher, as would be expected, then the amount of unrecovered polar materials would be less. Given that the extrography on the deasphalted crude oil leaves very little, if any, irreversibly adsorbed material, it would seem logical that the unrecoverable materials from the ext method are indeed asphaltenic in nature.

FTIR Spectroscopy. FTIR transmission spectra (inverses of absorbance spectra) were obtained of all of the polar fractions—resins, asphaltenes, and polar asphaltenes—derived from both methods of the four crudes studied here—AB, AH, ANS, and SJV. (Typical FTIR spectra are shown in Figure 5.) These spectra reveal a number of significant similarities among the polar fractions of these crudes. Virtually every spectrum of these three polar fractions contains identifiable and integrable absorbance peaks of the following functional groups: aliphatic CH_2 and CH_3 stretch, aromatic C—C ring-breathing stretch, methyl CH_3 asymmetric and symmetric stretches, carbonyl and carboxyl stretch, pyrrolic NH stretch, and sulfoxide stretch. In addition, many of the spectra contain one of the following absorbances: free OH stretch, phenolic OH stretch, and amide-carbonyl stretch. Each of these absorbances has been carefully identified in the spectra and integrated according to the technique described in the methods section. All of these spectra are similar qualitatively in the following three characteristics: (1) they all exhibit large absorbance intensities (50–60%) for aliphatic CH_2 and CH_3 stretches in the wavelength range from 2800 to 3000 cm^{-1} , (2) all exhibit significant absorbance intensities (15–20%) for symmetric and asymmetric CH_3 bending modes in the wavelength range from 1350 to 1500 cm^{-1} , and (3) all exhibit reproducible and integrable aromatic C—C ring-breathing stretches at a frequency of approximately $1600\text{--}1605\text{ cm}^{-1}$. The absorbances corresponding to polar functional groups are considerably more variable in their intensity than these three carbon-related absorptions. In what follows, we will discuss the semiquantitative characterization of the aromatic carbon and polar functional groups and discuss the implications of these integrations.

Spectra of model compounds which represent the functionalities typically found in petroleum products were obtained and integrated to determine their apparent integrated absorption intensities (B) as outlined in the methods section. A summary of the key absorbances, their characteristic frequency of absorbance, and their apparent integrated absorption intensities are provided in Table 9. The chemical environment has a substantial effect on the B value for certain functional groups (e.g., C=O and S=O). The S=O B values range from 8000 to $22\,400\text{ L}/(\text{mol cm}^2)$ depending upon the model compound. Since alkyl sulfides (which are most likely close in proximity to aromatic rings) have been found to be the predominant sulfur-containing struc-

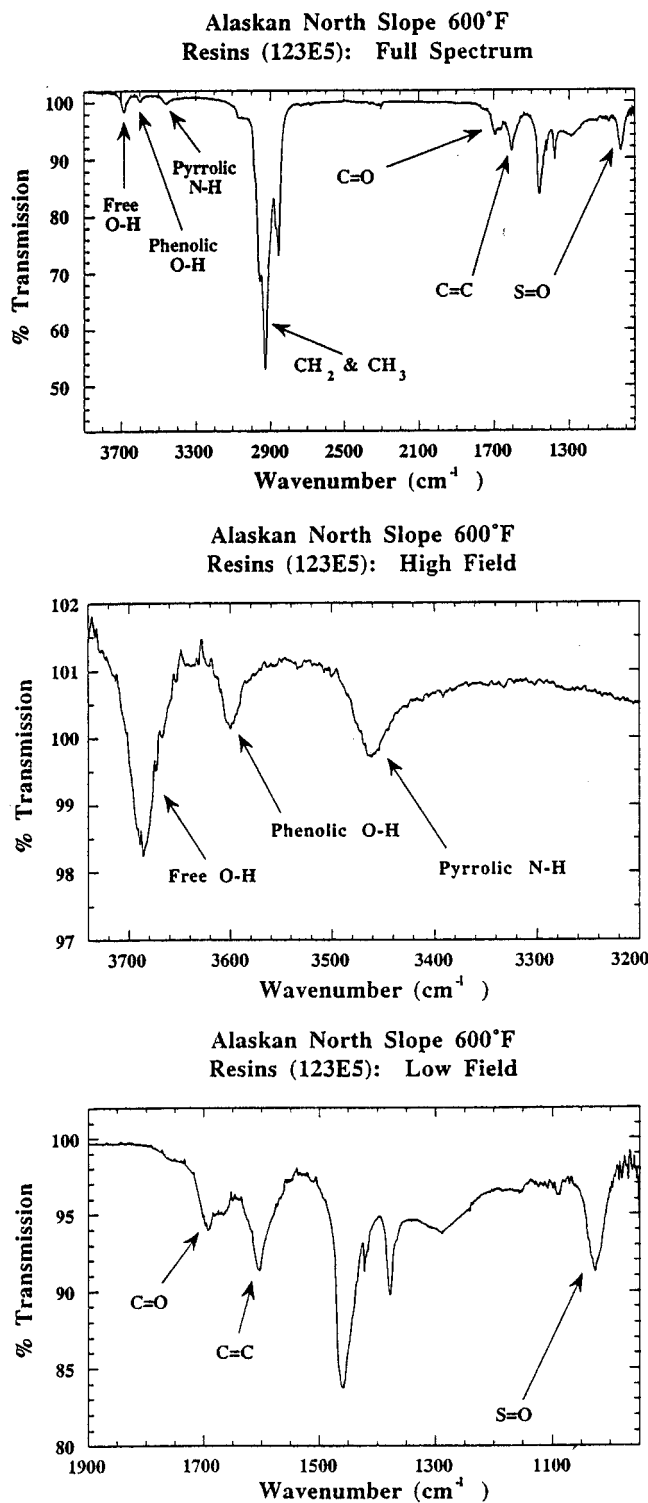


Figure 5. FTIR spectra of extrographic resin fraction isolated from ANS $600\text{ }^\circ\text{F}+$ atmospheric residue.

tural types to undergo oxidation during oxidative aging of petroleum residues,⁶² the B value for dibenzyl sulfoxide has been utilized to determine sulfoxide concentrations in this study. Aside from the effect of the chemical environment of the functional groups, the apparent discrepancy in B values between our study and others in the literature may be attributed to differences in the frequency range of integration. For example,

(62) Petersen, J. C.; Dorrence, S. M.; Nazir, M.; Plancher, H.; Barbour, F. A. Oxidation of Sulfur Compounds in Petroleum Residues: Reactivity-Structural Relationships. *Prepr.-Am. Chem. Soc., Div. Pet. Chem.* **1981**, 26 (4), 898–906.

Table 9. Apparent Integrated Absorption Intensities (*B*) of Selected Functional Groups from Model Compounds

functional group	compound	group type	frequency (cm ⁻¹)	<i>B</i> (L/(mol cm ²))
C=O	acetanilide	amide	1696	47 000
	benzoyl BA	ketone	1675	27 000
	benzyl acetate	ester	1740	35 500
	cyclohexaneacetic acid	carboxyl (sym)	1707	15 700
	cyclohexaneacetic acid	carboxyl (sym + asym)	1707 & 1750	26 900*
	cyclohexanecarboxylic acid	carboxyl (sym)	1704	16 200
	cyclohexanecarboxylic acid	carboxyl (sym + asym)	1704 & 1750	27 900*
	pyrrolecarboxaldehyde	aldehyde	1660	47 400
	N-H	carbazole	pyrrole	3462
O-H	1-naphthol	phenol	3580	13 200*
	di- <i>tert</i> -butylphenol	phenol	3580	16 700*
S=O	dimethyl sulfoxide	sulfoxide	1040	8 000
	diphenyl sulfoxide	sulfoxide	1040	13 400
	benzyl sulfoxide	sulfoxide	1045	22 400*
arom C=C	acetanilide	amide	1600	1 700
	acetophenone	ketone	1590 & 1600	1 200
	benzamide	amide	1590 & 1600	3 500
	benzoic acid	carboxyl	1600	800*
	benzoyl BA	carboxyl	1600	800*
	carbazole	pyrrole	1605	600
	dibenzofuran	aromatic ether	1590 & 1605	500
	1-naphthol	phenol	1580 & 1600	700
	phenanthrene	condensed aromatic	1600	50

integrating the symmetric stretch vs integrating both the symmetric and asymmetric stretches for a particular functional group. For the case of the carbonyl-type *B* values, the absorption intensities determined in this study were found to compare very well with the literature values when exclusively integrating the symmetric stretch of the carboxylic absorbance region. Since most of our "unknown" samples did not exhibit distinct symmetric and asymmetric peaks in this region, we determined *B* values over the entire absorbance range for the carbonyl functional group (i.e., symmetric + asymmetric stretches). Since the *B* values determined from the C=O symmetric stretches for both cyclohexane acetic acid and cyclohexane carboxylic acid are very similar to other literature values,^{39,56,63,64} we will utilize the average of the *B* values determined from these two compounds over both the symmetric and asymmetric stretches. The apparent integrated absorption intensities used to determine the respective polar functional group concentrations in this study are highlighted with an asterisk in Table 9 (if more than one value is highlighted within a particular functional group, the average of these values was used). Weight percentages of the aromatic carbon type and carbonyl, pyrrolic, and sulfoxide functional groups in the polar fractions derived from both fractionation methods are collected in Table 10.

The weight percentages of carbonyl (C=O) functional groups are roughly 1–3% for all the polar fractions (ext resins (R), asphaltenes (A), polar asphaltenes 1 (PA 1), and polar asphaltenes 2 (PA 2); and ppt + ext resins (ppt res) and asphaltenes (ppt asp)), with the exception of the ext SJV A and PA 2 and ANS PA 2 fractions. Both the ext and ppt + ext polar fractions of SJV crude have C=O weight percentages which are substantially higher than the C=O contents of the polar fractions derived from the other crude oils and could very reason-

Table 10. Summary of FTIR Analysis: Weight Percentage of Aromatic Carbon and Polar Functional Groups

crude oil fraction	SJV	ANS	AB	AH
Aromatic C=C				
resins	38.1	30.4	24.7	23.5
asphaltenes	47.0	40.8	44.8	55.0
polar asphaltenes 1	56.8	40.4	43.1	56.6
polar asphaltenes 2	68.7	61.4	49.1	49.1
avg ext asphaltenes ^a	54.3	44.7	43.9	55.0
heptane-soluble resins	17.0	11.9	11.7	18.4
ppt asphaltenes	62.8	38.2	46.9	28.7
Carbonyl C=O				
resins	1.7	1.2	1.4	0.8
asphaltenes	4.9	1.4	2.1	1.7
polar asphaltenes 1	2.5	1.9	1.9	1.5
polar asphaltenes 2	3.8	5.4	2.6	2.6
avg ext asphaltenes	3.5	2.5	2.0	1.7
heptane-soluble resins	2.3	1.5	1.7	1.3
ppt asphaltenes	1.5	1.0	1.7	0.6
Pyrrolic N-H				
resins	0.8	0.3	0.5	0.2
asphaltenes	0.7	0.2	<0.1	0.2
polar asphaltenes 1	0.4	0.2	<0.1	0.2
polar asphaltenes 2	0.3	0.1	0.2	0.2
avg ext asphaltenes	0.5	0.2	<0.1	0.2
heptane-soluble resins	0.6	0.3	0.3	0.3
ppt asphaltenes	0.5	0.2	0.2	0.1
Sulfoxide S=O				
resins	0.6	1.6	1.8	1.5
asphaltenes	1.8	2.4	4.1	3.4
polar asphaltenes 1	1.6	0.4	1.7	1.6
polar asphaltenes 2	1.8	<0.1	0.6	0.6
avg ext asphaltenes	1.7	0.8	2.8	2.1
heptane-soluble resins	1.7	3.1	3.2	2.5
ppt asphaltenes	<0.1	<0.1	1.5	<0.1

^a Parameters for average asphaltenes are determined as a function of yield distribution among extrographic asphaltene fractions.

ably account for the strongly resin-solvated character of the SJV asphaltenes. It stands to reason that if SJV asphaltenes contain high concentrations (relatively speaking) of C=O groups and if the resin fraction is rich in carboxylic acid functional groups, then intermolecular hydrogen bonding could lead to strong solvation of asphaltenes by resin molecules. In fact, the high H/C ratio of asphaltene and polar asphaltene fractions of

(63) Petersen, J. C. Quantitative Method Using Differential Infrared Spectrometry for the Determination of Compound Types Absorbing in the Carbonyl Region in Asphalts. *Anal. Chem.* **1975**, *47* (1), 112–117.

(64) Bunger, J. W.; Thomas, K. P.; Dorrence, S. M. Compound Types and Properties of Utah and Athabasca Tar Sand Bitumens. *Fuel* **1979**, *58* (3), 183–195.

SJV could be accounted for, in part, by strongly adsorbed (due to high concentrations of polar C=O functional groups) resin molecules of high H/C ratio (1.40) which do not desorb until elution with the more polar solvents used to elute the asphaltenes during the extrographic fractionation process. The total asphaltenes from the ext method are all notably richer in C=O content (by ~1.2–2% higher for SJV, ANS, and AH) than the precipitated asphaltenes. This makes sense since the extrographic asphaltene solvent selectively elutes materials which are higher in oxygen-containing functional groups. Conversely, the ppt + ext resin fractions contain somewhat higher concentrations of C=O functional groups than the ext resins.

Table 10 shows the sulfoxide (S=O) weight percentages in the polar fractions range anywhere from 0 to 4.1% with the highest concentrations found in the ext asphaltene and ppt res fractions. These values seem higher than what might be reasonable. The bulk of the organic sulfur in polar crude fractions should be concentrated in sulfidic and thiophenic structures.^{65–67} In fact, only as much as 10% of the organic sulfur was found to be in the form of sulfoxides in these studies. However, exceptions can arise according to the specific operational definitions of the fractions obtained or other artifacts.^{62,68,69} The likeliest explanation for our results is listed in order of likelihood: (1) an underestimation of *B* for the sulfonyl group, (2) some oxidation of thiophenic to sulfonyl sulfur occurred during the workup and analysis of extrographic fractions (despite the precautions taken to ensure no inadvertent oxidation), or (3) the integrated band intensities at 1040 cm⁻¹ contain other absorbances, such as ether bands, within the sulfonyl band vibration. For example, the ext asp fraction is eluted with THF which is an aliphatic ether. The aliphatic C–O stretch is also observed at ~1025 cm⁻¹ and could be contributing to the assigned S=O peak if all of the THF was not divested from the ext asp fraction. Also, polar maltenes (such as the ppt res fraction) are known to be selectively enriched in sulfide compounds which are readily susceptible to significant oxidative degradation.⁶⁵ In addition, extremely fine, suspended mineral matter has also been found to make a significant contribution to the 1030 cm⁻¹ band.⁶² All of these possibilities are feasible and until these values are confirmed by some other complementary technique, these results should be viewed as semiquantitative at best and will not be included in further characterization analyses or in any potential correlations with emulsion stability.

The pyrrolic nitrogen content is fairly low for most of the crude fractions (0.3% or less for all fractions except-

(65) Waldo, G. S.; Carlson, R. M. K.; Moldowan, J. M.; Peters, K. E.; Penner-Hahn, J. E. Sulfur Speciation in Heavy Petroleum: Information from X-ray Absorption Near-Edge Structure. *Geochim. Cosmochim. Acta* **1991**, *55* (3), 801–814.

(66) Waldo, G. S.; Mullins, O. C.; Penner-Hahn, J. E.; Cramer, S. P. Determination of the Chemical Environment of Sulphur in Petroleum Asphaltene by X-ray Absorption Spectroscopy. *Fuel* **1992**, *71* (1), 53–57.

(67) Gorbaty, M. L.; George, G. N.; Kelemen, S. R. Direct Determination and Quantification of Sulphur Forms in Heavy Petroleum and Coals 2. The Sulphur K Edge X-ray Absorption Spectroscopy Approach. *Fuel* **1990**, *69* (8), 945–949.

(68) Andersen, S. Effect of Precipitation Temperature on the Composition of *n*-Heptane Asphaltene. *Fuel Sci. Technol. Int.* **1994**, *12* (1), 51–74.

(69) Snyder, L. R. Nitrogen and Oxygen Compound Types in Petroleum: Total Analysis of a 400–700 F Distillate from a California Crude Oil. *Anal. Chem.* **1969**, *41*(2), 314–323.

ing the AB ext res and SJV fractions). This is consistent with the relatively low nitrogen content of the polar crude fractions. Moreover, pyrrolic nitrogen is frequently cited to be the dominant nitrogen form in polar petroleum fractions.^{70,71} An interesting trend which emerges from the FTIR analysis is that the pyrrolic nitrogen content of the asphaltene fractions appears to be considerably lower than that of the resin fractions. As with the carbonyl content discussed above, this may play an important role in determining the relative emulsion stability of SJV crude as compared to other crudes. If the polar pyrrolic nitrogen groups are good sources of hydrogen bond donors and acceptors, then the strength of solvation of asphaltene by resinous molecules may be strongly mediated by the relatively high concentrations of pyrrolic nitrogen in SJV polar fractions relative to the other crudes. Also, amides were found to be present in the SJV polar fractions at concentrations from 1.1 to 1.7 wt %. Once again, this observation supports the notion that there may be considerably greater solvation by intermolecular hydrogen bonding of SJV asphaltene fractions by SJV resins than with the other crudes.

The final FTIR analysis is of the aromatic carbon content, and several items should be noted about these values: (1) the general trend is of increasing aromatic carbon content as one moves from resins to asphaltene fractions, (2) the apparent aromatic carbon wt % of AH ppt asp is lower than that of the other crudes, which is *inconsistent* with the low H/C ratio of this fraction, and (3) the apparent aromatic carbon weight percentages of SJV fractions are generally higher than those of the other crudes. The first observation is very consistent with a considerably more fused-ring aromatic character to the asphaltene fractions than to the resin fractions. The latter two observations are somewhat perplexing until one realizes that the apparent integrated absorbance intensities of the aromatic carbon ring-breathing modes are very sensitive to the polarity of aromatic substituent groups. In fact both Bellamy⁷² and Lin-Vien et al.⁷³ point out the highly variable absorbance intensities of these ring-breathing modes, depending on the electron-donating and electron-withdrawing strength of any substituent groups attached to the aromatic core. This clearly manifests itself when one considers the *B* values of benzoic acid (800 L/(mol cm²)) versus acetanilide (1700 L/(mol cm²)). Thus, the apparent low values of aromatic carbon in AH ppt asp as determined by integration of the aromatic ring-breathing stretch at 1600 cm⁻¹ is to some extent a result of the low degree of polar substitution in this fraction, relative to the other crudes. Also, the *apparently* high aromatic carbon content of SJV polar fractions is likely an artifact of the strong polarity of these fractions, as indicated by the polar functional group content already cited. It there-

(70) Wilhelms, A.; Patience, R. L.; Larter, S. R.; Jorgensen, S. Nitrogen Functionality Distributions in Asphaltene Isolated From Several Oils From Different Source Rock Types. *Geochim. Cosmochim. Acta* **1992**, *56*, 3745–3750.

(71) Patience, R. L.; Baxby, M.; Bartle, K. D.; Perry, D. L.; Rees, A. G. W.; Rowland, S. J. The Functionality of Organic Nitrogen in Some Recent Sediments from the Peru Upwelling Region. *Org. Geochem.* **1992**, *18* (2), 161–169.

(72) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; John Wiley & Sons: New York, 1975; p 433.

(73) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: Boston, MA, 1991; p 503.

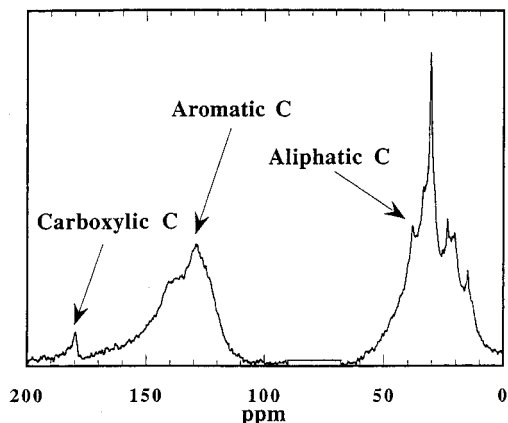


Figure 6. ^{13}C NMR spectrum of extrographic asphaltene fraction isolated from SJV whole crude oil.

Table 11. Aromatic Carbon Content of Crude Oil Extrographic and Ppt + Ext Fractions as Measured by ^{13}C NMR Spectroscopy

crude fraction	SJV	ANS	AB	AH
whole	25.5	23.8	15.6	25.9
extrography				
satd/arom ^a	21.6	21.8	14.4	22.8
resins	37.0	39.4	39.5	40.2
asphaltenes	36.2	45.0	46.8	45.3
polar asphaltenes 1	41.3	44.4	43.8	48.8
polar asphaltenes 2	42.1	43.1	---	46.5
total ext asphaltenes	39.5	44.1	45.6	47.2
ppt + ext				
satd/arom ^a	20.8	21.2	14.5	22.2
resins	38.5	38.1	38.8	37.9
asphaltenes	45.9	51.9	54.7	49.2

^a Calculated by difference between whole and polar fractions.

fore appears that the integration of aromatic carbon ring-breathing modes in the infrared spectrum of polar petroleum fractions is *not* a reliable way to quantify aromatic carbon and other spectroscopic means should instead be used.

^{13}C NMR Spectroscopy. ^{13}C NMR spectroscopy was utilized primarily for quantifying % aromatic carbon. A typical spectrum is shown in Figure 6. The ^{13}C NMR spectra of these fractions were divided into two general categories, the aromatic region from 110 to 160 ppm and the aliphatic region from 5 to 60 ppm. The aromatic region was characterized by a broad, featureless resonance, whereas the aliphatic region consisted of several relatively sharp resonances overlapping a broad resonance. The integrated areas of these regions were used to obtain the aromatic and aliphatic carbon contents present in the sample. There was also a peak of notable intensity at 180 ppm in the spectrum of the SJV asphaltene fraction which reveals the presence of carboxylic carbons in this particular fraction. The relative percentages of all these carbon types were calculated by the ratio of the area of the resonances for each carbon type over the total area, excluding the solvent and reference peak areas.

The aromatic carbon content of the fractions derived from both fractionation methods from each of the four crudes and of the whole crudes are reported in Table 11. The aromatic carbon content of the satd/arom fractions was determined by difference from an overall mass balance since a considerable amount of volatile material was lost during pretreatment and workup of the crudes and their fractions. Not reported in Table

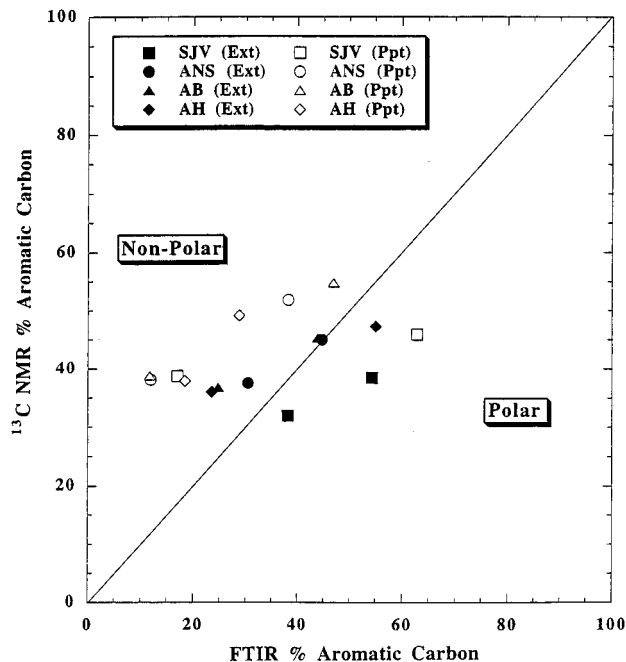


Figure 7. Comparison of aromatic carbon content of polar crude oil fractions (ext and ppt + ext) as measured by FTIR and ^{13}C NMR spectroscopy.

11, the SJV ext asp was found to contain 1.22 wt % carboxylic carbon which is equivalent to 4.6 wt % carboxylic acid functional group concentration. This compares favorably with the value of 4.9 wt % as determined by FTIR spectroscopy. Of the whole crudes, AB is the least aromatic at 15.6% aromatic carbon content while AH and SJV are the most aromatic at 25.9 and 25.5%, respectively. The aromatic carbon content of all the polar SJV fractions is less than 43%, with the exception of the ppt asp fraction which is at 46%. The similarity in structural characteristics (e.g., aromaticity) between the resins and asphaltenes could play a role in determining the solubility state of the asphaltenes and, ultimately, the emulsifying propensity of the crude oil. This result suggests that the asphaltenes in SJV would tend to be more soluble in the presence of the resins and the surrounding crude medium due to their similar aromaticities and, consequently, less prone to forming stable emulsions. Based solely on this conjecture, SJV would appear to form the least stable emulsion of the crudes in this study since the aromaticity among its polar fractions are much more similar, regardless of the fractionation method employed, in contrast with the other crude oils. From a comparison standpoint of the two different fractionation methods in terms of the aromatic carbon content, the ppt asp are considerably more aromatic (by 2–9 wt %) than their extrographic counterparts. The resins are very similar in aromatic carbon content regardless of the method of fractionation.

The aromatic carbon content of all the fractions as determined by ^{13}C NMR spectroscopy is contrasted with the integration of the aromatic ring-breathing modes by FTIR spectroscopy in Figure 7. Considering the effect of polar substituents attached to the aromatic core on the results obtained by FTIR analysis as discussed previously, this plot provides a measure of the relative polarity of the fractions from the different crude oils. The FTIR results significantly overestimate the actual aromatic carbon content for the SJV ext res and asp and

Table 12. Apparent Integrated Absorption Intensities (B) of Crude Oil Fractions Derived from Extrography and Precipitation + Extrography Determined from FTIR and ^{13}C NMR Spectroscopy

B_2 ($B_1 = 800$)	SJV	ANS	AB	AH
extrography				
resins	825	620	500	470
asphaltenes	1100	810	770	930
ppt + ext				
resins	350	250	240	390
asphaltenes	1100	590	690	470

ppt asp fractions. This suggests that these particular fractions are rich in polar functional groups which are attached to the aromatic core of the molecules. On the other hand, the FTIR results underestimate the actual aromaticity of AH ext res and ppt res and asp fractions, which implies these molecules are lean in polar functional groups altogether or are found in other positions relative to the aromatic core (e.g., at the end of aliphatic side chains along the periphery of these molecules). In general, the extrographic fractions are all more "polar" than the ppt res and asp fractions with the exception of SJV asphaltenes. This is most likely a result of the difference in the operational definitions of these fractions. It would be plausible that structural characteristics such as aromatic carbon content would play a greater role in determining the identity of asphaltenes which are based solely on their solubility in paraffinic solvents (as is the case for precipitation) than asphaltenes which are isolated by an extraction method (e.g., extrography) where the activity of the sorptive matrix would necessarily impose separations which are governed to a greater extent by the polarity of the adsorbed crude oil components.

This effect is further elaborated by determining the apparent integrated absorption intensities of the resin and asphaltene fractions obtained from the two different fractionation methods assuming the "true" aromatic carbon content is as determined by ^{13}C NMR spectroscopy. These B values are presented in Table 12. The B value used to determine the aromatic carbon concentrations was $800 \text{ L}/(\text{mol cm}^2)$; therefore, B values higher and lower than 800 suggest that these fractions contain compounds of higher and lower polarity, respectively. As found in Figure 8, the SJV asphaltenes are the most polar with a B value of $1100 \text{ L}/(\text{mol cm}^2)$. This value is very similar to those found for the aromatic carbon stretch in acetanilide and in acetophenone in Table 9 which suggests that these fractions may be rich in amides, ketones, or other polar nitrogen- and oxygen-containing functional groups. This is not surprising given the high nitrogen and oxygen contents of the SJV fractions relative to those of the other crudes in this study. This table also reveals that AH ext res and ppt asp are the least polar fractions with B values which suggest the presence of highly condensed fused aromatic compounds in these particular fractions. Notice that the B value for phenanthrene, which is three fused six-carbon aromatic rings, is only $50 \text{ L}/(\text{mol cm}^2)$.

A strong correlation exists between the aromaticity of these fractions as gauged by ^{13}C NMR and the H/C ratio (see Figure 8). For all crudes, the ppt res are more "saturated" (i.e., less condensed) than their extrographic counterparts given that the H/C ratios of the ext res

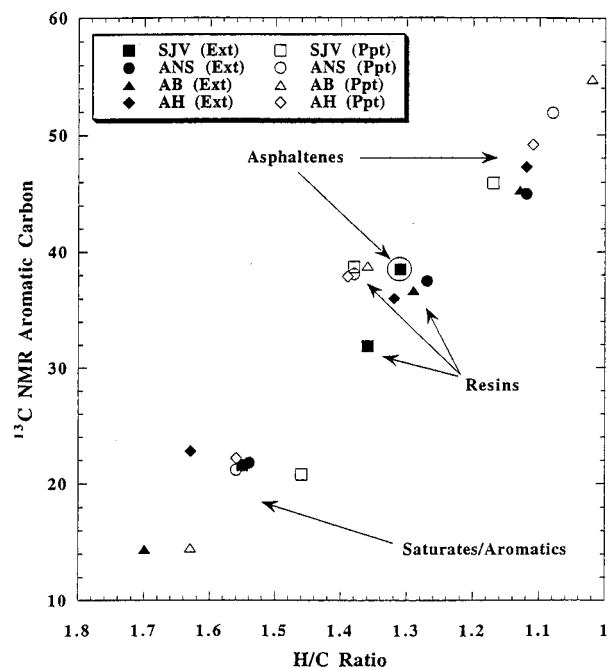


Figure 8. Comparison of H/C ratio and aromatic carbon content as measured by ^{13}C NMR spectroscopy of all fractions (satd/arom, resins, and total asphaltenes) isolated by ext and ppt + ext methods.

are higher than those of the ppt res while the aromatic carbon content of all the resin fractions are practically the same.

Summary of Analyses. To gain a broader and perhaps more focused perspective on the comparison of characterization results from the two fractionation techniques (ext vs ppt + ext), all the key characterization parameters of the resins and asphaltenes isolated both via ext and ppt + ext are presented in Table 13. When comparing the characterization parameters, bear in mind the effect of the differences in yields which are listed for that particular fraction. Starting with the resins, the ext resins have lower H/C ratios than the ppt + ext resins yet are generally similar in aromatic carbon content as determined via ^{13}C NMR. This suggests that the ext resins are more condensed than those obtained by extrography, as was also illustrated in Figure 8. The differences in %N, % aromatic carbon content (as determined by FTIR spectroscopy), % pyrrolic N-H, and metals content all suggest that the ext resins are also more polar than those isolated after precipitation of asphaltenes, although the ppt + ext resins appear to be richer in oxygen in the form of carbonyl/carboxylic functional groups. In comparing the asphaltenes, the trends in the differences between the two methods are not quite so general (i.e., more crude specific). The ppt asphaltenes from all the crudes are lower in H/C ratio and higher in aromatic carbon content. Also, the ppt asphaltenes appear to be somewhat lower in oxygen content and in carbonyl concentration. With the exception of SJV, the N, S, and O contents of the asphaltenes from each method are very similar. Ppt asphaltenes from SJV are higher in N content than its ext asphaltenes (2.44 vs 1.79%). They also exhibit a stronger absorbance in the FTIR aromatic carbon stretch and are higher in both V and Ni contents which all point to a higher degree of polarity. With AH, the ppt asphaltenes appear to be less polar than its ext asphaltenes considering the large difference in FTIR

Table 13. Summary of Characterization Analysis of Resins and Asphaltenes Isolated via Extrography and Precipitation + Extrography

characterization		resins				asphaltenes			
parameter	method	SJV	ANS	AB	AH	SJV	ANS	AB	AH
% yield	extrog	18.84	7.81	3.65	11.86	5.60	2.93	0.79	4.34
	ppt + ext	20.26	9.47	3.49	9.56	4.57	3.35	0.68	8.27
H/C	extrog	1.36	1.27	1.29	1.32	1.31	1.12	1.13	1.12
	ppt + ext	1.38	1.38	1.36	1.39	1.17	1.08	1.02	1.11
%N	extrog	2.15	1.20	0.98	0.82	1.79	1.33	0.67	0.99
	ppt + ext	1.89	0.94	0.67	0.66	2.44	1.11	0.77	0.94
%S	extrog	1.87	2.47	4.51	6.29	1.43	2.43	5.15	6.64
	ppt + ext	1.90	3.29	4.76	5.95	1.60	3.06	5.84	7.17
%O	extrog	2.11	0.86	1.54	1.33	3.39	3.32	2.97	1.49
	ppt + ext	2.30	2.91	2.44	2.39	3.52	2.67	2.49	1.46
% arom C (NMR)	extrog	31.9	37.5	36.7	36.0	38.5	45.0	45.3	47.3
	ppt + ext	38.7	38.1	38.8	37.9	45.9	51.9	54.8	49.2
% arom C (FTIR)	extrog	38.1	30.4	24.7	23.5	54.3	44.7	43.9	55.0
	ppt + ext	17.0	11.9	11.7	18.4	62.8	38.2	46.9	28.7
% carbonyl	extrog	1.7	1.2	1.4	0.8	3.5	2.5	2.0	1.7
	ppt + ext	2.3	1.5	1.7	1.3	1.5	1.0	1.7	0.6
% pyrrole	extrog	0.8	0.3	0.5	0.2	0.5	0.2	<0.1	0.2
	ppt + ext	0.6	0.3	0.3	0.3	0.5	0.2	0.2	0.1
V (ppm)	extrog	281.3	216.1	82.5	370.4	219.5	385.3	209.2	619.2
	ppt + ext	187.7	117.9	62.8	205.0	463.8	516.4	352.8	667.6
Ni (ppm)	extrog	322.4	117.5	66.6	135.1	443.8	299.0	142.9	382.1
	ppt + ext	268.0	64.4	43.0	85.8	873.1	386.0	130.5	352.1

Table 14. Comparison of Characterization Analyses: Overall Element Balance of Resins + Asphaltenes

characterization		resins + asphaltenes			
parameter	method	SJV	ANS	AB	AH
% yield	extrog	24.44 ± 1.17 ^a	10.74 ± 0.21	4.44 ± 0.34	16.20 ± 0.12
	ppt + ext	24.83 ± 0.22	12.82 ± 0.06	4.17 ± 0.14	17.83 ± 0.50
H/C	extrog	1.35 ± 0.009	1.23 ± 0.010	1.27 ± 0.007	1.27 ± 0.006
	ppt + ext	1.35 ± 0.027	1.30 ± 0.006	1.30 ± 0.004	1.26 ± 0.007
%N	extrog	2.06 ± 0.024	1.24 ± 0.057	0.93 ± 0.040	0.86 ± 0.012
	ppt + ext	1.94 ± 0.063	1.00 ± 0.026	0.71 ± 0.019	0.77 ± 0.022
%S	extrog	1.76 ± 0.059	2.46 ± 0.050	4.62 ± 0.040	6.38 ± 0.060
	ppt + ext	1.78 ± 0.061	3.23 ± 0.041	4.97 ± 0.072	6.53 ± 0.094
%O	extrog	2.40 ± 0.094	1.34 ± 0.327	1.80 ± 0.068	1.37 ± 0.090
	ppt + ext	2.52 ± 0.065	2.85 ± 0.094	2.45 ± 0.114	1.96 ± 0.197
% C=O	extrog	2.11 ± 0.150	1.60 ± 0.045	1.51 ± 0.195	1.05 ± 0.165
	ppt + ext	2.15 ± 0.071	1.40 ± 0.042	1.70 ± 0.186	0.98 ± 0.071
% pyrrolic N-H	extrog	0.73 ± 0.135	0.27 ± 0.074	0.42 ± 0.020	0.20 ± 0.037
	ppt + ext	0.58 ± 0.032	0.27 ± 0.024	0.28 ± 0.037	0.21 ± 0.013
V (ppm)	extrog	267.1 ± 1.9	262.3 ± 2.9	105.0 ± 0.9	437.1 ± 3.5
	ppt + ext	234.8 ± 2.8	222.0 ± 1.8	110.1 ± 1.1	419.6 ± 2.5
Ni (ppm)	extrog	350.2 ± 11.2	167.0 ± 15.7	80.2 ± 16.6	201.3 ± 16.7
	ppt + ext	371.1 ± 24.9	148.4 ± 21.5	57.3 ± 12.1	209.3 ± 20.3

^a 90%+ confidence interval.

aromatic carbon content. The ppt asphaltenes from ANS and AB are similar in polarity as measured by the FTIR aromatic carbon stretch but do exhibit higher concentrations of vanadium than their Ext asphaltenes. For the most part, in comparing the resins and asphaltenes derived from the two methods, they appear to be qualitative "converses" of each other to the extent that if one method isolates asphaltenes that are notably higher in a particular characterization parameter than the other method, then the resins tend to "make up" for the difference by exhibiting similar but opposite trends.

This point is further illustrated by performing an overall balance of pertinent characterization parameters on all the material which is classified as resins and asphaltenes from both fractionation methods. The results from this overall balance are presented in Table 14 in order to compare the characteristics of the "polar" materials isolated by these two fractionation methods. These polar materials, in their entirety, should be essentially the same from a characterization standpoint regardless of the type of separation performed in this

study. This does indeed appear to be the case when comparing the data presented in Table 14. Again, bear in mind any differences in yields for the combined fractions when comparing the characterization parameters, especially with ANS. The only parameter which is not consonant between the two fractionation methods is the oxygen content. As discussed earlier, this may be an artifact of oxidation during the extraction of the ppt + ext resins. For the most part, the results from this study lend credence to the belief that the asphaltenes that appear to be *missing* from the extrographic fractionation are really not missing in the sense of being unrecoverable irreversibly adsorbed material. While this may be true to a limited extent, it is more accurate to assert that they are *misplaced* or simply defined differently according to the specific operation used to isolate them.

Conclusions

A set of four crude oils of diverse compositions were separated into compound classes via two different

fractionation methods—ext and ppt + ext—in order to determine which method provides the most complete and insightful analysis. The characteristics of these polar fractions varied considerably according to the method of fractionation. Using characterization tools such as elemental (including metals) analysis and spectroscopic methods, we found evidence to suggest that ext resins are both more “condensed” and more polar than those isolated via ppt + ext. The comparisons between the asphaltenes from the different methods are not quite so broad and general in nature (i.e., more crude specific); however, the ppt asphaltenes from all the crudes are higher in aromaticity and lower in oxygen-containing components such as carbonyls and carboxylic acids. For the most part, it appears that, if one method isolates asphaltenes that are somewhat different in regard to a particular characterization parameter, then the resins tend to “make up the difference” by exhibiting similar but opposite trends.

Elemental analysis of the ext fractions showed a remarkable consistency among the H/C ratios of the polar crude fractions, with the exception of SJV crude. This exception is most likely due to strong hydrogen-bonding interactions between the resins and asphaltenes specific to SJV crude. FTIR spectroscopy further affirms this notion since SJV polar fractions were found to be rich in functional groups capable of strong H-bonding interactions (i.e., carbonyl, carboxylic, and pyrrolic types). SJV polar fractions also possessed strong intensities in the aromatic carbon region ($\sim 1600\text{ cm}^{-1}$) which is an indirect measure of the presence of polar functional groups attached to aromatic rings when used in conjunction with ^{13}C NMR spectroscopy.

In the final analysis, extrography proved to be somewhat more selective in its fractionation given the higher concentration of oxygen-containing compounds such as carbonyls, carboxylic acids, and possibly sulfoxides within the ext asphaltene fraction. This is effected through the use of a mixture of THF and acetone as the eluting solvent for this particular fraction. There does appear to be a problem with this method concerning irreversible adsorption of polar components (up to 0.8 wt % of whole crude) on the silica gel (as determined by metals analysis of the “residual” silica gel). This material, which appears to be asphaltenic in nature, cannot be recovered without compromising the silica gel matrix and/or subjecting to the tightly bound species to harsh conditions which may induce oxidation and/or reaction of the components of interest. However, upon performing an overall balance of pertinent characterization parameters on all the polar material (resins + asphaltenes) derived from both fractionation methods, the results show that there is virtually no measurable difference in the characteristics of these polar, surface-active materials as a whole with regard to the method of fractionation. This leads us to believe that the asphaltenes that were once thought to be *lost* in the form of unrecoverable irreversibly adsorbed species (which may be true to a limited extent) were actually *found* upon consideration of the operational definition of both the resin and asphaltene fractions. Given the simplicity, universality, and more complete recovery afforded through the precipitation technique, we will employ this fractionation method (along with subsequent, more discriminating fractionation techniques

such as ion exchange chromatography) to help provide further insight into the mechanisms which govern the stability of emulsions produced from these crude oils.

This is part of an ongoing investigation designed to study the interactions between the polar components (i.e., resins and asphaltenes) in crude oils. The resins are known to support the dispersion of asphaltenes in the crude oils.^{59,74,75} Although the mechanism is not fully understood, it appears that the extent of aromaticity and the heteroatom content of the resins control the solubility of the asphaltene in the crude oil.^{76–78} Based on IR, solubility, and molecular weight data, one of the determining forces in the solvent power of the resins appears to be hydrogen bonding.⁵⁰ For example, hydrogen bonding between a phenolic hydroxyl group in a resin molecule and a donatable proton bonded to O or N (e.g., pyrrole, pyridine, carboxyl, etc.) in the asphaltene molecule results in a resin–asphaltene agglomerate. These agglomerates, and more generally the state of dispersion of the asphaltenes, are known to have a pronounced effect on the emulsifying ability of a particular crude.^{8,79} Since the asphaltenes are known to be the most aromatic portion of the crude oil, the aromaticity of the resins and the crude medium can also affect the solubility of the asphaltenes. This information on composition as identified by compound class and the functionality and aromaticity of the polar, surface-active constituents will be useful in the search for potential correlations between the extent of these interactions and the emulsifying ability of crude oils, one of the ultimate goals of the research in our laboratory.

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