

Advanced characterization of petroleum crude and products by high field Fourier Transform ion cyclotron resonance mass spectrometry

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Introduction

As worldwide petroleum reserves evolve toward heavier crude oils with rich heteroatomic content, effective processing of heavy petroleum becomes increasingly important. Heavy petroleum is a complex mixture (tens of thousands) of hydrocarbon molecules containing multiple aromatic rings, some of which contain heteroatoms, such as N, S and O. Variations in this petroleum composition directly impact all refinery processes; therefore compositional information is vital for advances in effective petrochemical processing. For example, heteroatomic hydrocarbons, particularly those containing nitrogen, are known to play a key role in catalyst deactivation through coke formation on the catalyst surface. Furthermore, in refineries, crude acids distill into the gas oil and vacuum gas oil fractions and cause liquid phase corrosion at process temperatures of 250-400 °C. Because naphthenic acids are surface active and marginally water soluble, their release to wastewaters is closely monitored but their identity is still largely unknown.

Our research takes advantage of the ultra-high resolving power and mass accuracy offered by high field FTICR to characterize and identify polar and non-polar species in petroleum **without** chromatographic pre-separation. The resolution and mass accuracy needed to directly resolve and assign elemental compositions to materials as complex as crude oil and other petrochemical products are currently obtainable only by FT-ICR mass spectrometry. For polar species, Electrospray Ionization (ESI) specifically targets polar compounds (those that contain heteroatoms and are of environmental concern, such as basic and neutral nitrogens, naphthenic acids, amides and phenols in petroleum and other fossil fuel products) thereby greatly simplifying the mass spectrum by eliminating the largely hydrocarbon matrix. In prior work we have been able to identify thousands of heteroaromatic compounds each in positive (basic species) and negative (acidic species) ion electrospray ionization analysis of crude oils.¹⁻³

Experimental

Sample Preparation. The extra heavy crude oils contain ~50% of >566 °C boiling point hydrocarbons, and 1-4% sulfur and 0.1-0.75% nitrogen. For sample preparation, 10 mg of the crude or asphaltene sample, is first dissolved in 3 mL of toluene. The toluene concentrate is diluted with methanol to bring the final volume to 20 mL. The final solution is spiked with 0.5% acetic acid to promote electrospray ionization (positive ion) or 0.5% ammonium hydroxide (for negative ions).

Electrospray Ionization High Field FT-ICR MS. The extra heavy oils and asphaltenes were analyzed at the National High Magnetic Field Laboratory (NHMFL) with a homebuilt 9.4 tesla Fourier transform mass spectrometer. Ions were generated externally by a micro-electrospray source and samples were delivered by a syringe pump at a rate of 300 nL/min. 2.2 kV was applied between the capillary needle and ion entrance. The externally generated ions were accumulated in a short (15 cm) rf-only octopole for 10-30 s and

then transferred via a 200 cm rf-only octopole ion guide to a Penning trap. Ions were excited by frequency-sweep (100-725 kHz @ 150 Hz/ms at an amplitude of 200 Vp-p across a 10-cm diameter open cylindrical cell). The time-domain ICR signal was sampled at 1.28 Msample/s for 1.63 s to yield 2 Mword time-domain data. Ten to two hundred data sets were co-added, zero-filled once, Hanning apodized, and fast Fourier transformed with magnitude computation. A continuous wave 40 W CO₂ laser (Synrad E48-2-115, Bothell, WA) was used to dissociate non-covalent ion complexes.

Results and Discussion

Variations in heteroaromatic content of heavy crude oils were first investigated by comparing of the negative ion ESI FT-ICR mass spectra of five unfractionated crude. Chinese crude consisted almost entirely of carboxylic acids whereas the North American crude is comprised of basic nitrogen-containing heterocycles. Figure 1 shows these differences in composition for a pair of crude oil samples (Chinese and North American crude). The Chinese crude showed predominately odd mass ions (indicating the species have zero or an even number of nitrogens) whereas the even mass ions result from the isotopic peaks of the odd mass (and higher relative abundance) peaks. Most of the species identified were naphthenic acids that are characteristic of immature, partially biodegraded crude. Conversely, the North American crude contained a large relative abundance of even mass ions (indicating species that have an odd number of nitrogens). In the present example, most species identified contained a single nitrogen. Based on ESI experiments of model compounds, we suspect that the majority of these are pyridine type compounds, since they are mildly acidic and electrospray well. Pyrrole containing structures are mildly basic and are predominately observed in positive mode ESI analysis. Three other crudes showed marked variations in heteroaromatic composition.

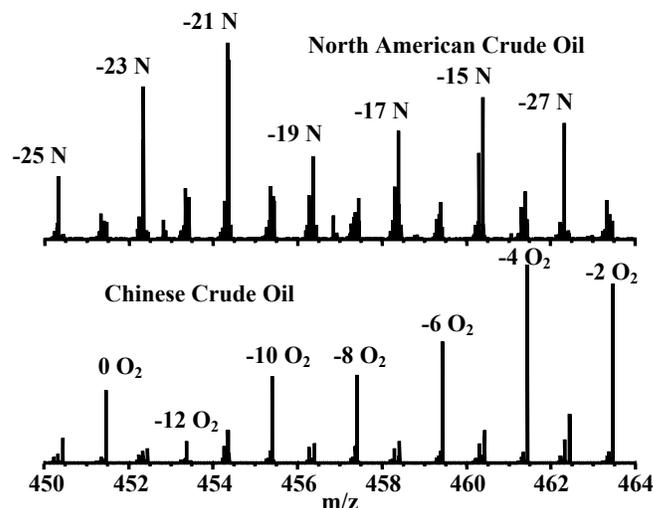


Figure 1. Broadband mass spectra of two crude oils (Chinese, top and North American, bottom), showing the compositional differences. Chinese crude consists primarily of carboxylic acids whereas North American crude is dominated by a -15 to -27N series.

Determination of the acidic asphaltene composition directly from the crude, without prior chromatographic separation, was investigated by analyzing a South American crude and its isolated acidic asphaltene fraction. Figure 2 shows the broadband mass spectra of both samples. Compositional comparison of the two

samples showed that some of the higher relative abundant species in the acidic asphaltene samples may be observed directly in the broadband whole crude sample.

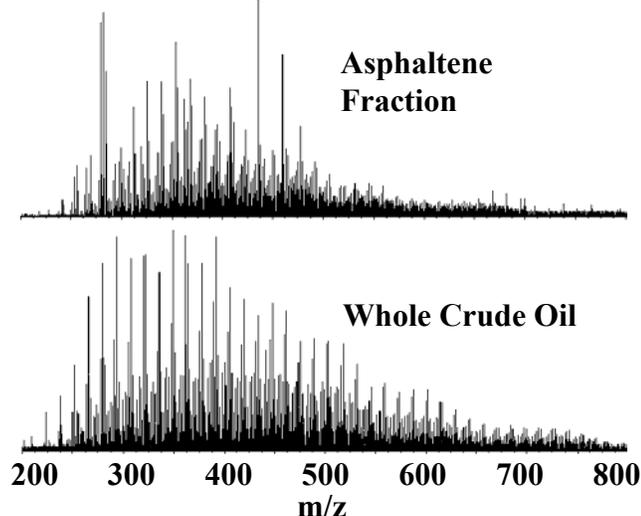


Figure 2. Broadband mass spectrum of both the whole crude (bottom) and acidic asphaltene fraction (top) from South American Crude.

Figure 3 compares the two samples of Figure 2 at a single nominal mass. Zoom mass insets at $m/z = 362$ show that some compounds present in the acidic asphaltene fraction are also seen in the whole crude. However, compounds are observed in the asphaltene fraction. Molecular formula assignment of species in the whole crude based on accurate mass identified more than 5000 compounds. The same analysis of the asphaltene fraction identified 2500 compounds, many of which were not observed in the whole oil sample because they are at or below the detection limit. The acidic fractionation procedure thus effectively extends the dynamic range of the technique and allows the identification of thousands of species not previously observed in the whole crude spectrum.

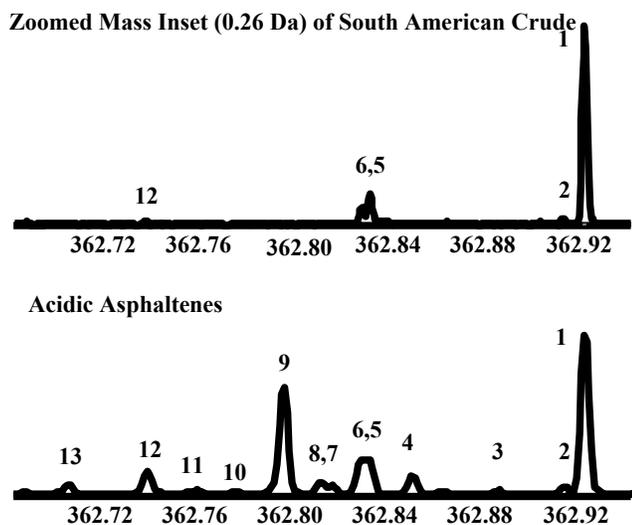


Figure 3. Zoom mass inset at $m/z = 362$ shows 13 different elemental compositions assigned in the acidic asphaltene fraction (bottom).

Separate high-resolution zoom mass scans were performed with a mass resolving quadrupole recently installed on the front end of the instrument. In this way, only a narrow range of masses is analyzed at a time, resulting in higher resolution and dynamic range. Figure 4 shows the results.

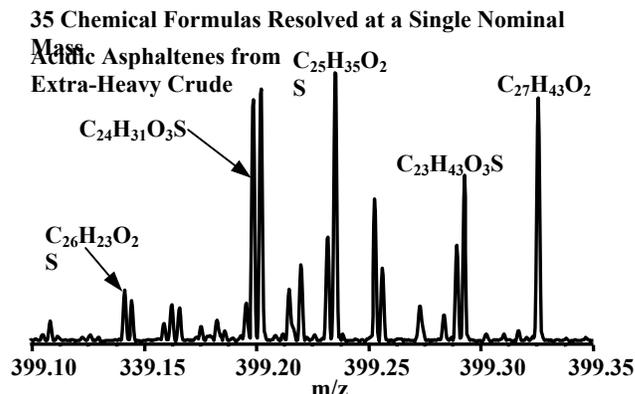


Figure 4. Zoom mass inset at $m/z = 399$ of the acidic asphaltene sample shows 35 peaks resolved at a single nominal mass. Elemental compositions could be assigned to 33 of the 35 resolved peaks.

We demonstrate that, under negative ion conditions, acidic hydrocarbons (mostly crude acids) and neutral nitrogen compounds can be ionized selectively in both whole crude and an acidic asphaltene fraction by electrospray ionization without interference from the hydrocarbon matrix. No prior chromatographic isolation or separation is needed. However, isolation of the acid asphaltene fraction does allow us to detect lower relative abundance species that were not observable in the whole unfractionated crude. We have determined detailed elemental compositions of whole crude and acidic asphaltenes by high field FT-ICR MS accurate mass measurements. Collectively, over one hundred acid homologues, ~10,000 chemical formulas (whole crudes) and ~2500 chemical formulas (acidic asphaltene fraction) containing O_2 , O_3 , O_4 , O_2S , O_3S and O_4S with carbon numbers ranging from 15 to 55, have been identified. New results coupling a Field Desorption (FD) ion source to the FT-ICR mass spectrometer will also be presented.

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ALTERNATIVE CALIBRATION AND STANDARDIZATION PROCEDURE OF IATROSCAN TLC-FID FOR SARA HYDROCARBON CLASS QUANTIFICATION: APPLICATION TO TAR-MAT ZONE IDENTIFICATION.

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INTRODUCTION

Thin layer chromatography-flame ionization detection (TLC-FID) is becoming increasingly popular in the crude oil industry. This technique is recognized as an efficient, fast and cost-effective way to obtain quantitative information about crude oil composition¹. Frequently, hydrocarbon group type analysis (Saturate, Aromatic, Resin and Asphaltene, (SARA)) involves the use of liquid chromatography after asphaltene precipitation and quantification by gravimetry². However, this preparative method is time consuming and is neither very precise nor accurate, if small sample amounts are analyzed²⁻³. For separation and quantification, correct use of Iatroscan TLC-FID offers good precision and accuracy, in addition to rapid analysis and low solvent consumption.

Cebolla et. al.², Karlsen et. al.⁴⁻⁵ and Sol et. al.⁶, are some of the researchers that have used this technique for the analysis of SARA constituents in crude oils and solvent extracts. Nevertheless, the common factor of these studies is the lack of suitable standards for calibration.

Previous works have relied upon synthetic compounds as standards to accomplish quantification⁷. However, Bharati et. al.⁷⁻⁸ have shown that TLC-FID response factors are not satisfactory when this kind of materials are employed to calibrate the Iatroscan Instrument. Considering the molecular complexity of crude oils, it is not surprising that the huge variety of compounds that they contain has a marked influence on the FID response. FID detector was found to be very sensitive to the structural features of the sample in addition to the heteroatom content⁹⁻¹¹. For instance, normal, branched, and cyclic alkanes show different response factors¹² as well as mono, di- and poly-aromatic hydrocarbons. These observations limit the use of synthetic standards. As a consequence, only crude oil based standards should be used for SARA quantification purposes.

Bharati et. al.⁷⁻⁸ have prepared standards derived from crude oils for calibration of the Iatroscan TLC-FID instrument. The major finding of these studies is that response factors of the separated SARA fractions are not unique for all oils, but are dependent on the composition of the fraction and the API gravity of the oil. From these studies, Bharati and co-workers⁷⁻⁸ recommend not to use bulk response factors because they are likely to give erroneous results. Different response factors for heavy oils, medium oils and light oils must be used instead.

In the present work, we describe an alternative procedure for the preparation of crude oil based standards and the calibration of the Iatroscan instrument for the analysis of SARA constituents in crude oils, and related materials. SARA distributions of representative crude oils, distillates and vacuum residues were compared to the respective preparative HPLC results. Additionally, a set of core solvent extracts from a reservoir from eastern Venezuela was analyzed in order to detect Tar-Mat zones and to establish their spatial distribution. Organic petrography analyses were performed to compare the obtained SARA TLC-FID results.

EXPERIMENTAL

Preparative HPLC SARA Separations

Prior to preparative HPLC fractionation, 220°C topped crude oils and vacuum residues were deasphalted with n-heptane following the IP-143 procedure¹³. The resulting maltene fraction was fractionated into Saturates, Aromatics, and Resins by the preparative HPLC methodology reported by Carbognani and Izquierdo¹⁴. Distillates (IBP>220°C) were analyzed as received by the same HPLC methodology.

Iatroscan TLC-FID Calibration Procedure.

The calibration protocol adopted in the present work involves the construction of three calibration curves as functions of the weight percentage of saturate, aromatic and asphaltene fractions. Resin content is calculated as a difference from the 100 wt.%. ($Wt.\%_{Resins} = 100 - (Wt.\%_{Saturates} + Wt.\%_{Aromatics} + Wt.\%_{Asphaltenes})$). Saturate and aromatic standards were prepared by mixing saturate and aromatic fractions isolated previously by preparative HPLC¹⁴ and derived from distillates (ranging from 220-510 °C), from n-heptane deasphalted distillation residues, and from deasphalted 220 °C topped crude oils with different API gravity. Samples were collected from different production facilities around the country to assure a representative population of the Venezuelan crude oils. Isolated saturate and aromatic fraction purity was verified by TLC-FID. If was necessary, they were re-separated by HPLC until no cross-contamination was detectable. Binary calibration standards were prepared weighing amounts of isolated saturate and aromatic fractions in relative proportions and adding the corresponding volume of Toluene/Chloroform 50:50 vol.% to reach a total concentration of 25.0 mg/mL.

Asphaltene calibration standards were prepared using a set of 35 samples (distillation residues and 220°C topped crude oils) from different places of the country. Asphaltene contents were determined previously by the IP-143 procedure¹³. Calibration standards were prepared dissolving a weighed amount of sample in Toluene/Chloroform 50:50 vol.% to reach a final concentration of 25.0 mg/mL.

Core Solvent Extracts

Core samples from a reservoir from a eastern Venezuela oilwell¹⁵ oilfield were collected at different depths, crushed and extracted with dichloromethane/methanol 93:7 vol.% as indicated by Karlsen et. al.⁵. After solvent evaporation, a 25.0 mg/mL sample solution was prepared dissolving a weighed amount of the extract in the corresponding volume of Toluene/ Chloroform 50:50 vol.%.

SARA TLC-FID Analysis.

Standards and core extract solutions were analyzed in an Iatroscan TH-10 instrument (Iatron Labs Inc.), equipped with a flame ionization detector (FID) and interfaced with a computerized acquisition system (DIONEX AI 450 Optimize). Pure hydrogen (190 mL/ min, supplied by a hydrogen generator) and pure air (2.0 l/min, supplied by an air cylinder) were used for the detector. Two sets of 10 silica rods, type Chromarod-SIII (pore diameter 60 Å, particle size 5µm) were used: One for the saturate and aromatic quantification and the other one for asphaltene quantification. Before sample application, Chromarods were passed twice through the FID to remove contaminants, and to obtain constant activity of the silica layer. Each rod was spotted by

1.0 μl of the standard or sample solution, applied dropwise by using a 1.00 μl syringe. For saturate and aromatic determinations, Chromarods were developed in n-heptane for 40 min; air dried (3 min) and developed again in toluene for 20 min. For asphaltene determinations, the second set of Chromarods was developed in n-heptane/ isopropanol 95:5 vol. % for 20 min. Each set of rods was dried for 3 min and then, pyrolyzed at a scan speed of 0,32 cm/s.

Organic Petrographic Analysis.

Visual characterization of the crude oil in the porous media was performed by a LEICA DMRXE microscope provided by a 340-380 excitation filter, a 400 dichroic mirror and, a LP425 quencher filter. Organic matter was observed using fluorescent light reflected at wavelengths over 425 nm.

RESULTS

Calibration

Investigating the variations of FID response of organic molecules, Christian¹² has pointed out that structural features play an important role in the formation and stabilization of organic ions produced into the flame of the detector. Most stable ions are more abundant and give a better response. Even though these variations cannot be eliminated at all, they can be controlled or reduced using the most appropriate standard for calibration.

Mixing saturate and aromatic fractions from different sources to yield representative standards, and using several crude oil and residue samples of different origins for asphaltene calibration, assure a great variety of molecules to be present. By this procedure, variations of the FID response due to structural factors and physical characteristics of the sample (i.e. API gravity) are expected to be considerably reduced. In consequence, calibration curves obtained could be considered universal and could be used indistinctly for SARA determinations of light, medium or heavy crude oils, residues, and distillates with IBP over 220°C.

Figure 1 shows the obtained TLC-FID calibration curves for each case. For Saturates and Aromatics, calibration curves (peak area % as a function of wt.%) followed third-order-polynomial response ($f(x)=ax^3+bx^2+cx+d$). Asphaltene calibration curve (peak area/Concentration as a function of wt.%) showed a second-order polynomial response ($f(x)=ax^2+bx+c$). As can be seen in Figure 1, all the calibration curves showed variations of response factors with the increase of saturate, aromatic, and asphaltene content, but in the cases of saturates and aromatics, variations were much noticeable.

The variation for saturate and aromatic response presumably was influenced by the structural factors mentioned before. However, if variations induced by such factors are controlled, samples should behave in accordance to the standards. Consequently, TLC-FID SARA results should compare with the preparative HPLC results.

Figure 2 shows the comparison of SARA distributions obtained by TLC-FID and HPLC for some samples (distillates, 220°C topped crude oil and vacuum residue). As expected, SARA distributions obtained with both techniques were very similar and no significant variations were observed among each hydrocarbon group type.

Another important finding is that API gravity of the sample seemed not to influence the TLC-FID results; otherwise, TLC-FID results would be quite different from those reported by HPLC. This observation is very advantageous, because calibration curves can be used for SARA determination of any kind of Venezuelan crude oil or related material.

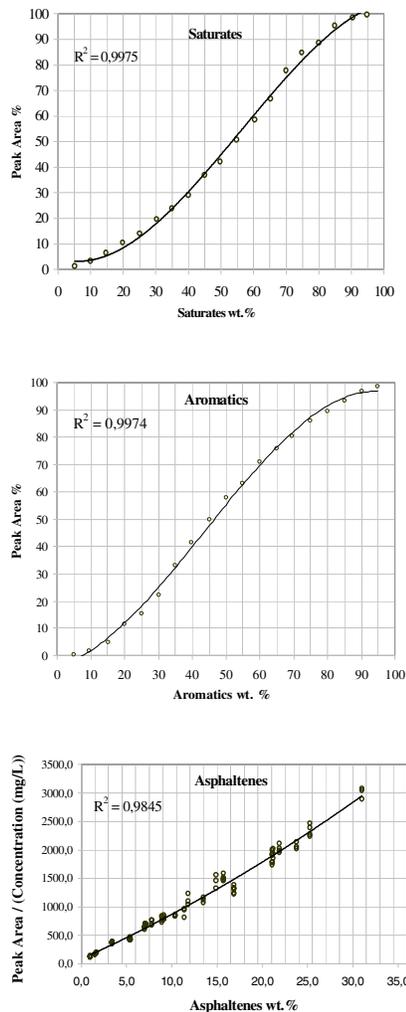


Figure 1. Calibration Curves for SARA group Type determinations by TLC-FID

SARA Distribution of Core Extracts: Identification of Tar-Mat Zones.

Tar-mats are considered as compositionally sharply defined zones of petroleum columns, which are enriched in asphaltenes up to 20-60 wt% of the C15+ extract.¹⁵ Due to their viscous nature caused by the enrichment in polar material, Tar-Mats may act as permeability barriers, which could possibly lead to or increase reservoir compartmentalization. Additionally, Tar-Mats represent dominantly non producible, low quality oil in place (OIP). For an accurate estimation of the recoverable reserves, a correct assessment of the amount of the OIP present in the form of Tar-Mats might be important¹⁶. Additionally, the location, areal extent, and thickness of Tar-Mats are important for secondary and enhance oil recovery.

Karlsen et. al⁴⁻⁵ have used TLC-FID as a fast way to describe vertically and laterally variations in crude oil composition into the reservoir, in order to obtain a preliminary discrimination of petroleum

populations and to reveal the existence of polar hydrocarbons enriched zones associated to Tar-mats.

In the present work, SARA distributions of core samples from an eastern Venezuela well were determined in order to assess the applicability of the TLC-FID methodology, and to compliment the geochemical information obtained by organic petrography.

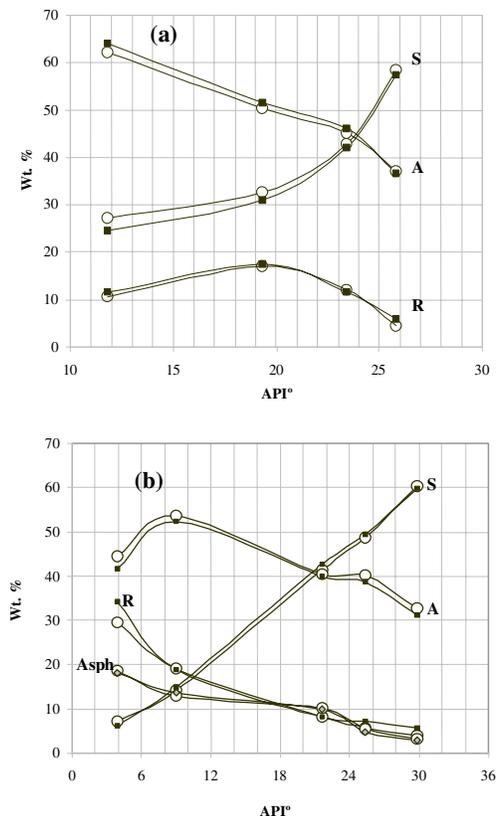


Figure 2. SARA distributions of some selected samples as a function of API gravity determined by TLC-FID and preparative HPLC. (a): Distillates. (b): Crude oils and Vacuum Residues. S= Saturates, A= Aromatics, R= Resins, Asph= Asphaltenes

Organic Petrography is a visual technique based upon measurements of the fluorescent properties of the petroleum components¹⁷. Thus, isolated asphaltenes do not show visible fluorescence due to the quenching effect produced by the strong molecular interactions among the existing aromatic moieties. As the bitumen or crude oil enriches in polar components, its fluorescent properties weaken and the fluorescent emission undergoes a shift to higher wavelengths.

Asphaltenes present complex structures and huge molecular sizes that are associated to poor mobility. Compared to saturates, aromatics and resins, asphaltenes present a low or almost zero mobility. This property together with their fluorescent properties are used to establish correlations between the petrographic characteristics of the fluid, its API gravity and the asphaltene content. Fluorescent properties are illustrated with the sample shown on Figure 3.

Figure 4 shows the comparison of asphaltene content obtained by TLC-FID and Organic Petrography. Regarding to the Tar-Mat zone, a good correlation was observed among both techniques. However, at 16480-ft. depth asphaltene content obtained by TLC-FID was higher than the value obtained by organic petrography. This discrepancy was

attached to the presence of residual drilling mud as a contaminant of the core. This contaminant is quantified by TLC-FID as an “asphaltene”, but it can be distinguished by organic petrography due to its own fluorescent properties. Despite of this advantage, organic petrography is less accurate than TLC-FID since this technique is based on visual inspections of the core sample. Additionally, quantification of resin fractions is impossible by this methodology. On the contrary, a complete characterization of core extracts can be obtained by TLC-FID (Figure 5).

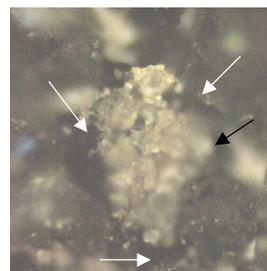


Figure 3. View of a core sample from the studied well under the petrographic microscope. White arrows indicate non-fluorescent asphaltenes. The black arrow indicates bitumen or mobile crude oil (fluorescent).

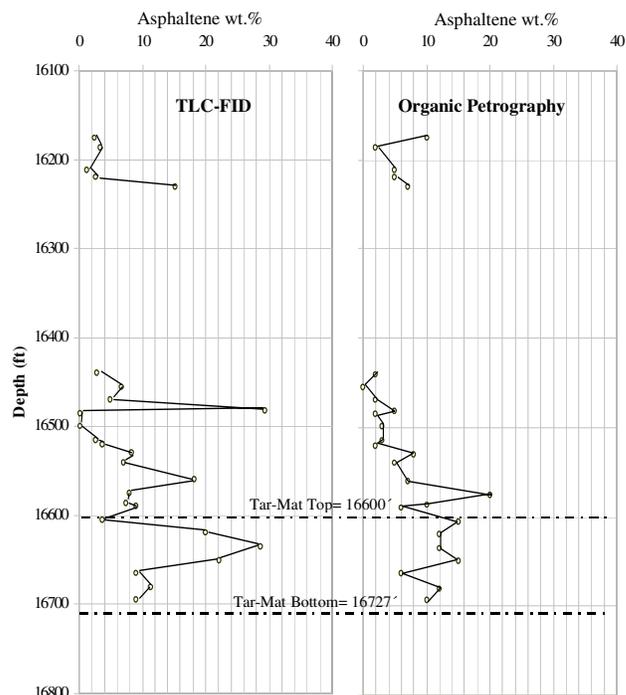


Figure 4. Comparison of the asphaltene content in core extract samples obtained by TLC-FID and organic petrography

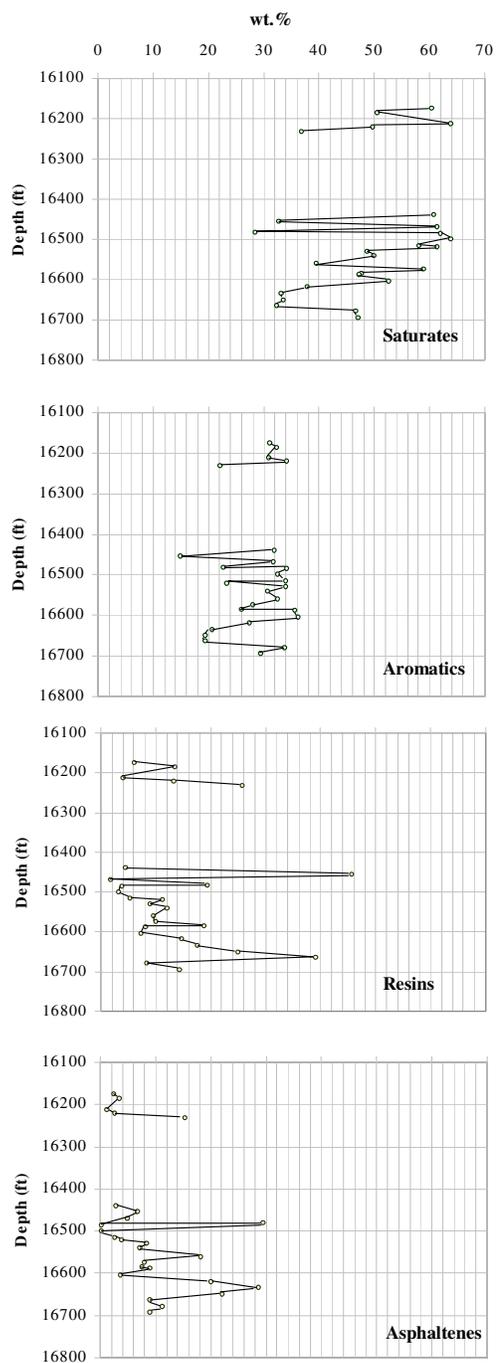


Figure 5. TLC-FID SARA distribution as a function of depth for the studied well.

CONCLUSION

Using crude oil based standards for calibration of the Iatroscan TLC-FID for determination of SARA group type distributions, allowed to control variations of the

FID response caused by structural characteristics of the sample. By following these standard preparation and calibration procedures, the influence of the API gravity on the TLC-FID results reported by Bherati et. al.⁷⁻⁸ is considerably reduced. In consequence, calibration curves can be applied for the analysis of to analyze light, medium, heavy or extra heavy crude oils and related materials.

TLC-FID can be used as an accurate way to obtain a preliminary description of petroleum basin formations and Tar-Mats identification. This technique gives quantitative SARA distributions that compare favorably with less accurate data obtained by organic petrography.

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APPLICATION OF THIN-LAYER CHROMATOGRAPHY WITH FLAME-IONIZATION DETECTION TO HEAVY OIL PROCESSING: FEEDS, PRODUCTS AND EFFECTS OF PROCESS VARIABLES

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Introduction

Heavy oil distillates such as light vacuum gas oils (LVGOs) and heavy vacuum gas oils (HVGOs) derived from different crude types were analyzed by thin-layer chromatography with flame-ionization detection (TLC-FID). TLC-FID chromatograms and resultant quantitative hydrocarbon type data for saturates, aromatics and polars show that these distillates vary markedly in the aromatic contents and aromatic ring types. Similar results were obtained from the analyses of fluid catalytic cracking (FCC) feeds. Compositional changes due to hydrotreating of a heavy oil feed were also studied by TLC-FID. The preferential reduction of higher polycyclic aromatic hydrocarbons and polars was observed with an increase of both hydrogen pressure and reactor temperature.

Heavy distillates such as vacuum gas oils and FCC feed are very complex, containing hundreds of individual hydrocarbons varying in size and molecular structure, polarity and functional groups. Almost all heavy distillates contain polar materials, a majority of them being sulfur, nitrogen and oxygen compounds. Since chemical groups determine the chemical properties, quality or processability of heavy distillates, the hydrocarbon type analysis has been a preferred choice for the characterization of these samples (1).

TLC-FID has been applied for the determination of hydrocarbon types in various high boiling materials (with initial boiling points at or above 260°C). These samples include lubricant base oils, high boiling residua or fractions derived from crude oils and coal tar pitches (1). The TLC-FID technique employs reusable quartz rods (Chromarods) coated with sintered silica particles. The sample is spotted on one end of each Chromarod for development with appropriate solvents to achieve the separation of saturates, aromatics and polars. The separated components are then detected with a special flame-ionization detector. Recently, a TLC-FID procedure was developed such that the above hydrocarbon groups are fully resolved from each other and aromatics are distributed based on the number of rings (2,3). The technique was capable of providing hydrocarbon type data for 12 oil samples in about 2 hours.

In this work, the TLC-FID technique has been applied to reveal appreciable differences in vacuum gas oils derived from different crude sources. FCC feeds are also found to display differences in both hydrocarbon group contents and aromatic types. TLC-FID is shown to be a useful technique to determine the effects of process variables such as temperature and pressure in the hydroprocessing of heavy oil by tracking changes in the total aromatics and aromatic compound types.

Experimental

Samples:

All LVGO and HVGO samples were actual refinery streams obtained as 345-455°C and 455-565°C cuts, respectively. FCC feeds were also refinery streams. Hydrotreated heavy gas oil samples were

obtained from a pilot plant study using a commercial heavy oil catalyst under differing operational severities.

TLC-FID Method:

The details of the TLC-FID procedure were provided elsewhere (2,3). A model MK-5 Iatroscan instrument (Iatron Labs, Tokyo, Japan) equipped with a specially designed flame-ionization detector was used. Hydrocarbon type separation was achieved on Silica SIII Chromarods. The FID hydrogen and air flow rates were 160 mL/min and 2000 mL/min, respectively. All samples were diluted with toluene to a concentration of 10 mg/mL. About 1 μ L (~10 μ g) of the diluted sample was spotted on the Chromarod. A rack of ten Chromarods with samples at the bottom was developed with toluene for 5 min. After drying the Chromarods at 70°C for 2 min, a second development was carried out with n-heptane for 30 min. With another drying, the Chromarods were scanned lengthwise under oxygen-hydrogen flame with a scan rate of 30 s per Chromarod.

Results and Discussion

Analyses of LVGO and HVGO:

Topped-off crude oil (or atmospheric residuum) is fractionated by vacuum distillation to obtain LVGO and HVGO. As mentioned in the Experimental section, four LVGOs used in this work are similar with respect to their boiling range of 345 – 455°C. All HVGOs fall within the boiling range of 455 – 565°C. However, as shown in Table 1 and Figure 1 hydrocarbon type compositions of these distillates vary widely depending on crude sources.

Examples of high-resolution TLC-FID separation of saturates, aromatics and polars as well as separation of aromatic compounds based on number of aromatic rings can be found elsewhere (2,3). In Figure 1, FID response is shown against Chromarod scan time inversely representing relative mobility of sample components during Chromarod development with toluene and n-heptane. Accordingly, saturates are resolved as a separate peak (at the scan time of 0.1 min), followed by a broad distribution of aromatics with a sequential elution of one-ring, two- and multi-ring aromatics (in the scan time range of 0.12 to 0.42 min). Finally, polars are obtained at around the scan time of 0.45 min.

Table 1. Properties of LVGOs and HVGOs

Crude Source	Sample Type	Sulfur (wt%)	Nitrogen (ppm)	Saturates (wt%)	Aromatics (wt%)	Polars (wt%)
South China Sea	LVGO	0.06	147	87.7	11.6	0.7
	HVGO	0.09	798	73.5	23.7	2.8
Mexico	LVGO	3.17	1524	42.5	35.0	22.5
	HVGO	3.68	2362	28.3	46.4	25.3
Central America	LVGO	4.81	809	30.1	66.3	3.6
	HVGO	5.49	1211	18.9	75.5	5.6
West Coast	LVGO	4.22	3107	39.6	54.3	6.1
	HVGO	4.94	3904	26.6	63.2	10.2

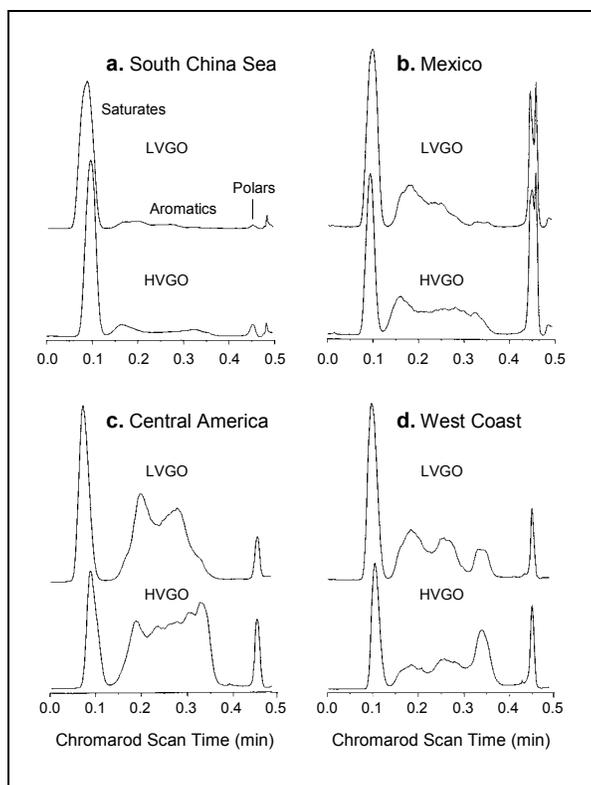


Figure 1. TLC-FID chromatograms of LVGO and HVGO from four crude oil sources.

Both Table 1 and Figure 1 show that relative amounts of aromatics and polars are higher in HVGO compared to those in LVGO for each crude oil type. Each of these gas oils also shows a wide distribution of aromatics, and a LVGO contains higher proportion of smaller ring aromatics than a HVGO.

Vacuum gas oils that provided chromatograms in Figure 1(a) are from a paraffinic crude from the South China Sea. These have the least amounts of aromatics and polars. Gas oils from other three crude sources have higher amounts of aromatics. Aromatic contents and TLC-FID profiles of all gas oils are quite different from each other. Similar observations can be made for the amounts of polars in the gas oils derived from four crude oils types.

Analyses of FCC Feeds

TLC-FID chromatograms of four FCC feeds are shown in Figure 2. Hydrocarbon type compositions of these feeds are as follows. Feed (a): saturates 41.4% (w/w), aromatics 55.2%, and polars 3.4%. Feed (b): saturates 53.8%, aromatics 43.9% and polars 2.3%. Feed (c): saturates 37.7%, aromatics 59.4% and polars 2.9%. Feed (d): saturates 41.7%, aromatics 55.4% and polars 2.9%. These quantitative compositional data reflect important differences among FCC feeds that may be useful for the selection of their processing options.

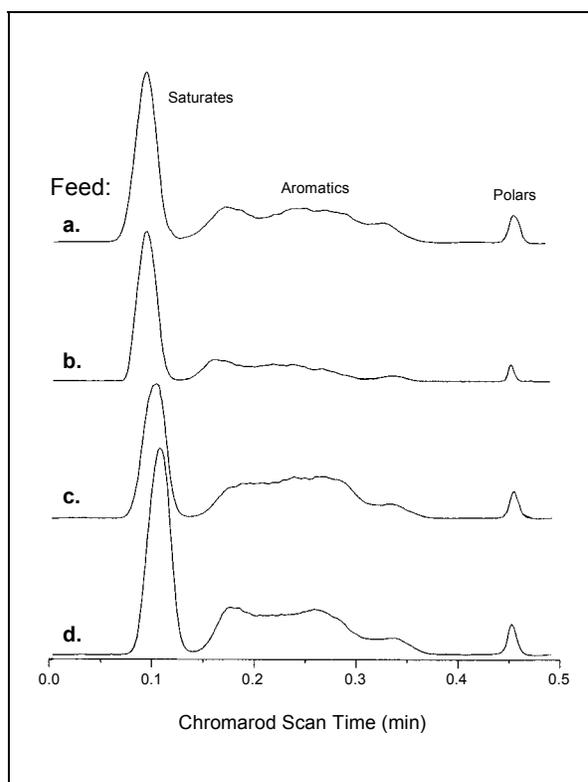


Figure 2. TLC-FID chromatograms of four FCC feeds.

Effects of Temperature and Pressure in Heavy Oil Processing

If all other process parameters are equal, effects of a variable such as temperature or pressure on aromatic saturation during hydroprocessing of a heavy oil feed can easily be determined by TLC-FID. Figure 3 suggests that saturation of aromatics continued as the weighted average bed temperature (WABT) was increased from 371°C to 388°C to 404°C. For this pilot plant study, pressure was maintained at 2250 psi and liquid-hourly space velocity (LHSV) was 1.2 h⁻¹. The polars were completely removed at both 388°C and 404°C. It appears that higher ring aromatics were reduced preferentially as the temperature was increased. The hydrocarbon type data obtained by TLC-FID showing the effects of temperature are as follows. Feed: saturates 28.3% (w/w), aromatics 64.4% and polars 7.3%. WABT = 371°C: saturates 52.1%, aromatics 47.0% and polars 0.9%. WABT = 388°C: saturates 68.2%, aromatics 31.8% and polars 0.0%. WABT = 404°C: saturates 71.6%, aromatics 28.4% and polars 0.0%.

Higher hydrogen pressure favors aromatics saturation. An example of such effect is shown in Figure 4. Using the same feed as in Figure 3, a pilot plant study was carried out by varying hydrogen pressure after maintaining WABT at 404°C and LHSV at 1.2 h⁻¹. The TLC-FID chromatograms (b) and (c) in Figure 4 were obtained at 1710 psi and 2250 psi, respectively. The hydrocarbon type data at these two pressures are as follows. Pressure = 1710 psi: saturates 60.4% (w/w), aromatics 39.3% and polars 0.3%. Pressure = 2250 psi: saturates 71.6%, aromatics 28.4% and polars 0.0%.

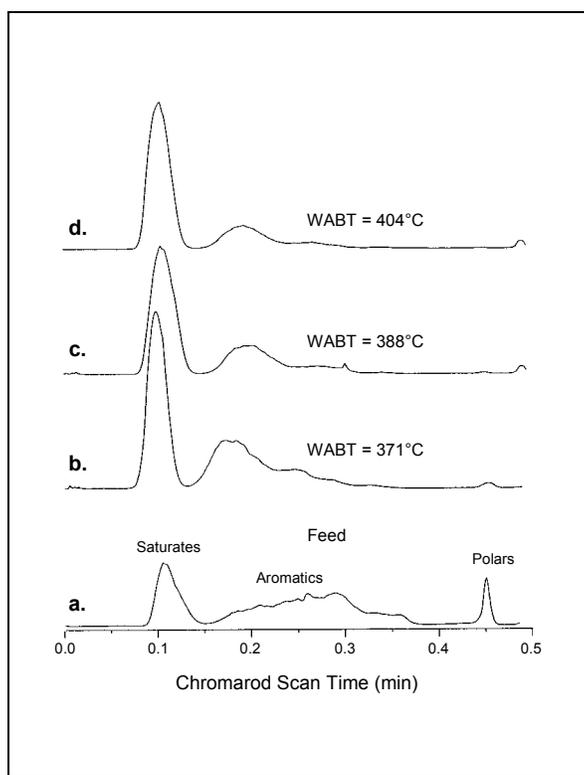


Figure 3. Effects of temperature on the hydroconversion of aromatics and polars.

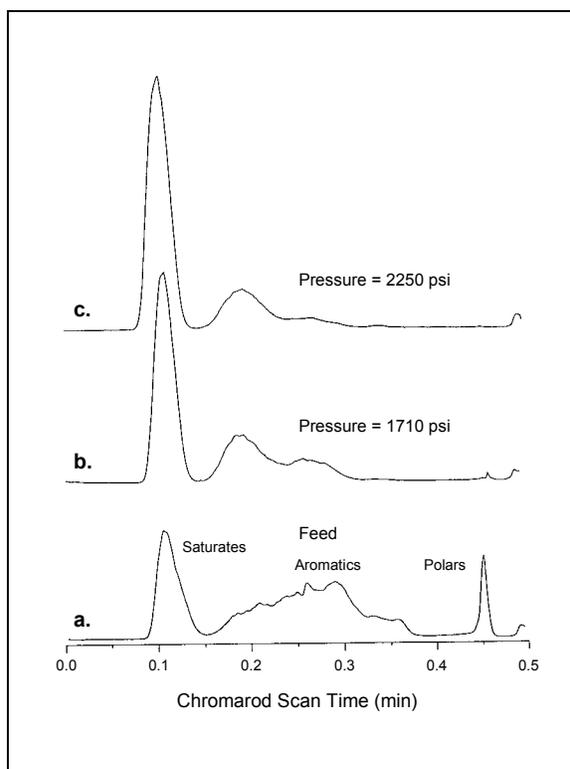


Figure 4. Effects of pressure on heavy oil hydrotreating.

Conclusions

TLC-FID is shown to be effective in providing differences in hydrocarbon group amounts and aromatic types in heavy oil distillates, feeds and products. As demonstrated in this work, this technique provides differential compositional data due to variations in process parameters. These should make TLC-FID an excellent method to evaluate variables for heavy oil hydroconversion processes and to elucidate reaction pathways and kinetics

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AVERAGE MASSES OF PITCH FRACTIONS OF NARROW POLYDISPERSITY FOR THE CALIBRATION OF SEC BY ASSESSMENT OF THEIR MALDI-TOF MASS SPECTRA.

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Introduction

This work attempts to establish that calibration of SEC with polystyrene standards provides a reasonable estimate of molecular masses (MMs) of coal liquids. Fractionation is necessary to reduce the polydispersity of the sample; too wide a polydispersity leads to the underestimation of the abundance of the high mass component [1]. Although polar components eluted early in a comparable SEC system [2], this was not the case for the present system [3,4] where a variety of standard molecules with different structural features eluted within about 1 min of the polystyrene calibration line. An alternative approach based on the calculation of signal from MALDI mass spectra of polymers of wide polydispersity [5] has been described in which the signal was considered to be real up to the point where the calculated mass averages failed to increase with increasing mass range of the spectrum.

In this work, narrow time-elution fractions (10 sec) of a coal tar pitch have been collected from a preparative size exclusion column using 1-methyl-2-pyrrolidinone (NMP) as eluent. MALDI mass spectra of these fractions using sinapinic acid as matrix have been evaluated by calculation of number (Mn) and weight (Mw) average molecular masses by three different methods [6], based on i) the standard deviation of noise at high mass, ii) the change of slope of baseline as signal exceeded noise at high mass and iii) the method used by Montaudo [5], for comparison with the peak intensity value of the spectrum (Mp). Analytical SEC, calibrated with polystyrene standards, has been used to determine the polystyrene MM equivalent to the elution time of each fraction.

The results show that the Mn and Mw values calculated by two of the three methods, those based on standard deviation and slope of the baseline, lie close to the Mp values and are very similar to the polystyrene standard masses, up to m/z 3000. The third method of calculation [6] greatly overestimated the Mn and Mw values. The quantitative divergence between MALDI and SEC above m/z 3000 will be discussed.

Experimental

Preparative size exclusion chromatography: A Perkin-Elmer LC 250 isocratic pump was used to maintain an NMP flow rate of 2 ml min^{-1} . The preparative SEC column (600 mm; 25 mm ID) used to fractionate the sample was maintained at 85°C and connected to a Perkin-Elmer LC 290 UV-absorbance detector at 450 nm. A single run of 100 mins gave enough sample. Narrow fractions corresponding to about ten second elution periods were obtained with three minutes intervals between the fractions. This method was used to minimise overlapping between different fractions and to restrict the total number of sample fractions collected.

Analytical size exclusion chromatography: A Polymer Laboratories Mixed-D ($5 \mu\text{m}$ particle size, 300 mm long, 7.5 mm id.) column was used with an NMP flow rate of 0.5 ml min^{-1} . The column has been calibrated using polystyrene standards of narrow polydispersity (Polymer Laboratories) with the detector set at 264 nm. The calibration

showed a linear relation between elution volume and $\log_{10}[\text{MM}]$ of the polystyrene between the permeation (low mass) limit at 23 min and the exclusion limit (mass of approx 200,000 amu) at 11 min. At higher masses, the relation between $\log_{10}[\text{MM}]$ and elution time showed a different relationship, with the polystyrene standard of MM 1.85 million eluting at about 9 min. Up to a MM of about ~ 1100 amu, the low mass calibration by polystyrene standards holds within about ± 1 min for a wide series of polycyclic aromatic hydrocarbons, nitrogen and oxygen containing molecules [3,4]. None of the small molecules used as standards - or components of coal liquids, biomass tars or petroleum residues, have been observed to elute after 23 min.

MALDI mass spectrometry: A Fisons VG TOFSPEC mass spectrometer (VG Organic Manchester, UK) fitted with a UV-laser (337 nm) and a VAX 4000-base data system with OPUS software has been used [cf Refs. 1,4 for details]. The spectrometer was used in the linear mode; the use of the reflectron was avoided to increase instrument sensitivity to high-MM. An accelerating voltage of 28 kV was used at maximum laser power. Prior to deposition on the target, sinapinic acid was premixed in NMP in a 4:1 matrix to sample solution volume ratio. The target was then dried in a vacuum oven at 150°C . The peak mass of each spectrum, Mp, was recorded for plotting against the elution time from SEC of the peak intensity of the fraction. The mass spectra were also evaluated by calculation of the standard deviation of the signal at the high mass limit of the spectrum [6]. The 'safe' upper limit of MALDI-signal was taken to be the signal level which exceeded five times the standard deviation of 'noise' level at high mass. The number and weight average MMs (Mn and Mw, respectively) were calculated up to the high-mass limit defined in this way.

UV-fluorescence The Perkin-Elmer LS50 luminescence spectrometer was set to scan at 240 nm min^{-1} with a slit width of 5 nm; synchronous spectra were acquired at a constant wavelength difference of 20 nm. A quartz cell with 1 cm path length was used. Synchronous spectra are shown in peak-normalised mode. Solutions were generally diluted with NMP to avoid self-absorption effects: dilution was increased until the fluorescence signal intensity began to decrease.

Results and Discussion

SEC and UV-fluorescence profiles of the narrow time fractions: Fractions of 10-sec interval effluent from the preparative SEC column were characterised by analytical-SEC (Figure 1). The fractions gave a set of successive narrow peaks in the retained region (15-22 min) and broader peaks in the excluded region (8-12 mins). The proportion of 'excluded' peak diminished with increasing elution time in the preparative column (i.e. with diminishing molecular mass). Fractions 1 to 8 gave only minor proportions of material in the retained region of the analytical column and were not analysed by MALDI. The retained peaks of fractions 9 to 18 however, showed a steady shift to longer elution times with increasing fraction number. Since the excluded material is indicated by the polystyrene calibration to be beyond the range of the MALDI mass spectrometer used, the mass spectrometry results are assumed to provide indications of MM's of the retained peaks. Synchronous UV-fluorescence spectra in Figure 2 show that the fluorescence shifted to shorter wavelengths with increasing elution times, indicative of progressively smaller polynuclear aromatic ring systems and decreasing MMs.

MALDI mass spectra: Spectra from the whole set of fractions analysed were relatively sharp indicating a relatively narrow polydispersity for the fraction, with the peak maximum shifting to smaller-MM with increasing retention time.

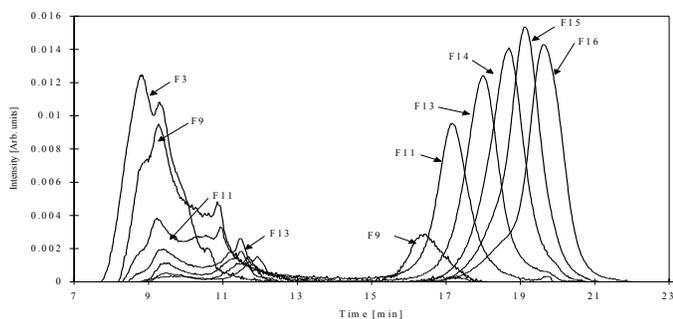


Figure 1 SEC chromatograms of narrow preparative SEC fractions [10 sec] of pitch

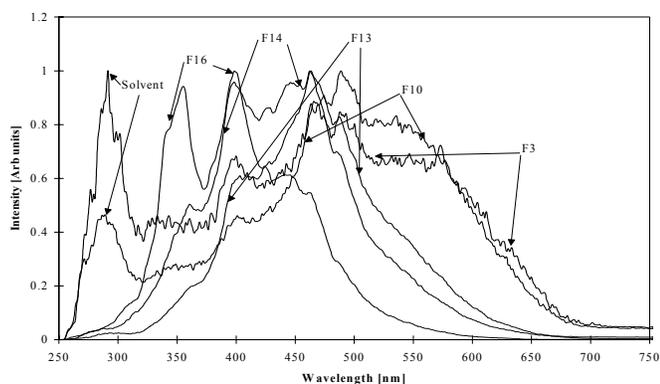


Figure 2. UV-f spectra of narrow preparative SEC fractions [10 sec] of pitch

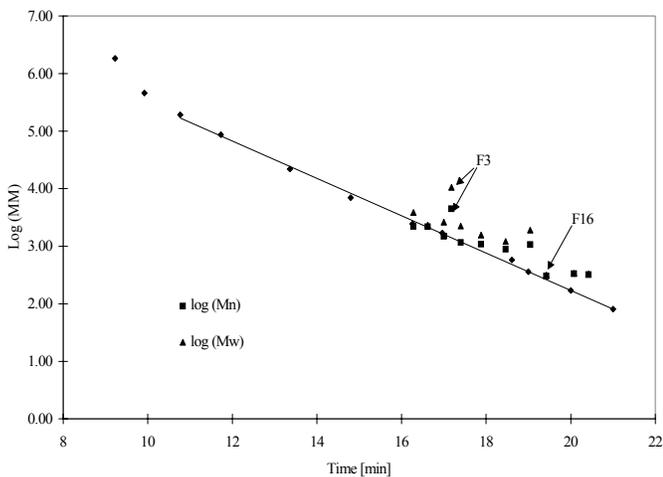


Figure 3 a) Comparison between polystyrene calibration line and Mn and Mw for pitch fractions calculated from MALDI mass spectra

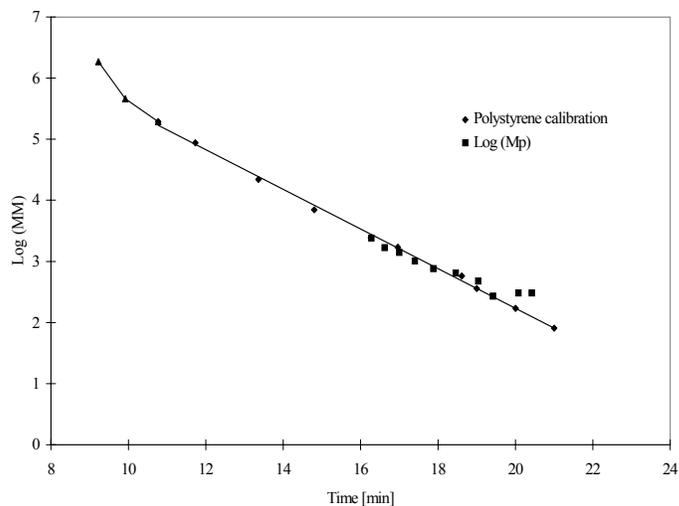


Figure 3 b) Comparison between polystyrene calibration line and Mp from MALDI mass spectra for pitch fractions

Figure 3 shows plots of the times of the peak maximum of the fraction, against the number and weight averages determined from MALDI-ms by each method and against the polystyrene calibration mass. Figure 3a compares the polystyrene calibration line with the Mp values from the MALDI mass spectra. Figure 3b compares the polystyrene calibration with Mn and Mw values calculated from the mass spectra. The Mp values appear to be a better match to the polystyrene equivalent mass values as defined by the elution times of the pitch fractions, although the calculated values gave only a slightly worse match. The polystyrene calibration is seen to give a reliable estimation of the masses of the fractions within the limited range of mass up to m/z 3-4000.

Conclusions

Preparative SEC of a pitch sample was used to collect fractions of narrow polydispersity. Mass spectra of the fractions have been obtained by MALDI-ms. Peak mass values (Mp), number and weight average masses (Mn, Mw) have been calculated from these spectra. These values have been compared with MMs of the fractions, calculated from their elution times in analytical SEC, using a calibration by polystyrene standards. The comparison shows quantitative agreement between molecular masses of pitch fractions from the polystyrene calibration and molecular masses found by MALDI-ms, up to about 3000 u.

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CAPILLARY COLUMN SELECTIVITY AND INERTNESS FOR SULFUR GAS ANALYSIS IN LIGHT HYDROCARBON STREAMS BY GAS CHROMATOGRAPHY

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Introduction

Unrefined C_1 to C_5 hydrocarbon streams typically contain significant to trace amounts of volatile sulfur compounds as impurities. Analysis of these sulfur compounds is critical to final product purity as well as avoidance of costly catalyst poisoning in the processing stream. Sulfur gas analysis is important not only in the petrochemical industry but also in environmental (EPA, CARB, etc.), industrial hygiene (NIOSH, OSHA) and food products applications (sulfur compounds in beer or wine, beverage grade CO_2 analysis, etc.). Detection limits are demanding for these applications, and it is not uncommon to require quantitation of sulfur gases such as hydrogen sulfide or methyl mercaptan down to low ppb levels.

Sulfur selective detectors are typically employed for these applications because of their high selectivity and sensitivity. Most commonly used are the Flame Photometric Detector (FPD), Pulsed Flame Photometric Detector (PFPD) and Sulfur Chemiluminescence Detector (SCD). More general "tunable" selective detectors may also be employed, such as the Atomic Emission Detector (AED) and Mass Spectrometer (MSD). Regardless of the detector selected for the application, possible quenching of response for low-level sulfur compounds may occur if they elute at the same time as large hydrocarbon peaks. Quenching makes accurate quantitation difficult due to detector response reduction and may also cause difficulties in compound identification. Thus, column selectivity is critical in these applications if accurate results are to be obtained.

Due to the high vapor pressure of target analytes, columns used for these applications must possess a high degree of retention if the analysis is to be performed without using cryogenic oven temperatures. Thick-film wall-coated open tubular (WCOT) columns and porous-layer open tubular (PLOT) columns can provide high enough retention to separate these volatile species at above ambient starting oven temperatures. While WCOT columns can exhibit high enough retention, phase selectivity is often not ideal. PLOT columns possess higher retention and selectivity for these compounds, however many PLOT phases available that exhibit acceptable elution patterns for sulfur and hydrocarbon compounds also exhibit unwanted stationary phase surface activity. This activity can dramatically affect the sensitivity of the system for active sulfur compounds such as mercaptans and hydrogen sulfide, producing higher detection limits. Hence, column inertness is just as critical as stationary phase selectivity in column selection for these applications.

This paper examines four different phases commonly used in light hydrocarbon and sulfur compound analysis. PLOT columns examined include a silica-based, a carbon molecular sieve and a divinylbenzene porous polymer. These PLOT columns are compared to a thick-film 100% dimethylpolysiloxane WCOT column.

Experimental

A Hewlett-Packard 5890 GC (Avondale, PA) equipped with a Flame Ionization Detector (FID; Hewlett-Packard, Avondale, PA) and a Pulsed-Flame Photometric Detector (PFPD; OI Analytical, College Station, TX) was used. Injection volume for each standard

was held constant at 1.0 mL. Data acquisition was performed via Hewlett-Packard Chemstation software. Split injection was used in this study to reduce residence time in the inlet and thus minimize potential peak tailing associated with inlet-related activity. Capillary columns used in this study were manufactured by Agilent Technologies (Folsom, CA).

Several hydrocarbon blend standards were used to generate retention times on each column. These standards were obtained from Scott Specialty Gases (Plumsteadville, PA) and Hewlett-Packard and were used for qualitative results only. Three different sulfur gas standards were used in this study: SO_2 was obtained from a permeation tube (GC Industries, Fremont, CA); a mixture of five sulfur gases was obtained from Scott Specialty Gases; and quantitative detection limit studies were performed with an H_2S standard also obtained from Scott Specialty Gases at 100 ppmV in nitrogen.

Results and Discussion

The conditions of analysis used for each column are summarized in Table 1. Elution order information for the four columns is summarized in Table 2. The sulfur compounds were *not* combined with the hydrocarbons to produce one analytical standard to produce the retention data in Table 2. This allowed for investigation of true retention times and peak shape without the influence of quenching on the PFPD. Each column was first installed into the PFPD and detector conditions were optimized for sulfur response. Retention time data was then obtained for each of the sulfur compounds on the column. The column was then removed from the PFPD, installed into the FID and retention time data was obtained for the hydrocarbons. Column head-pressure was held constant during this procedure so as to not affect carrier gas linear velocity. This allowed for generation of retention times using both detectors without introduction of possible activity associated with a glass Y-splitter or deactivated fused silica tubing.

An example chromatogram of sulfur and hydrocarbon analytes on the silica-based PLOT column (GS-GasPro) is shown in Figure 1.

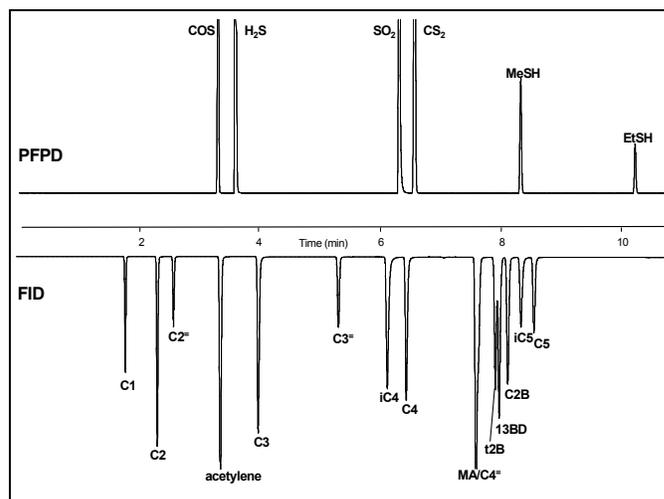


Figure 1. Sulfur and hydrocarbon analytes on GS-GasPro (silica-based PLOT phase).

Table 1. Analytical Conditions

DB-1
Phase: 100% Dimethylpolysiloxane WCOT
Dimensions: 30 m x 0.32 mm I.D., 5.0 micron
Carrier: Helium, 10 psig, 1.5 mL/min at 40°C (31 cm/sec)
Oven: 40°C for 5 min, 5°/min ramp to 75°C and hold
GS-GasPro
Phase: Proprietary, silica-based PLOT
Dimensions: 30 m x 0.32 mm I.D.
Carrier: Helium, 10 psig, 2.0 mL/min at 60°C (32 cm/sec)
Oven: 60°C for 2 min, 20°/min ramp to 260°C and hold
GS-Q
Phase: Divinylbenzene PLOT
Dimensions: 30 m x 0.32 mm I.D.
Carrier: Helium, 10 psig, 1.7 mL/min at 100°C (31 cm/sec)
Oven: 100°C for 2 min, 20°/min ramp to 250°C and hold
GS-CarbonPLOT
Phase: Proprietary, carbon-layer PLOT
Dimensions: 30 m x 0.32 mm I.D., 3.0 micron
Carrier: Helium, 10 psig, 1.7 mL/min at 100°C (31 cm/sec)
Oven: 100°C for 2 min, 20°/min ramp to 310°C and hold

Table 2. Retention Time Data

Compound	DB-1	GS-GasPro	GS-Q	GS-CarbonPLOT
Hydrogen sulfide	1.97	3.63	2.83	3.22
Carbonyl sulfide	2.20	3.34	3.21	5.03
Carbon disulfide	7.32	6.61	7.67	11.06
Methyl mercaptan	3.47	8.38	5.31	?
Ethyl mercaptan	5.77	10.29	7.42	?
Sulfur dioxide	2.20	6.35	9.06 *	5.03
Methane	1.61	1.82	2.07	1.95
Ethane	1.78	2.35	2.47	3.21
Ethylene	1.72	2.62	2.36	2.75
Ethyne	1.72	3.39	2.38	2.46
Propane	2.17	4.01	3.75	6.71
Propylene	2.13	5.34	3.60	6.28
Propyne	2.34	7.60	3.96	6.04
Propadiene	4.91	5.55	3.91	?
n-Butane	3.25	6.45	5.98	10.08
Butene-1	3.10	7.60	5.75	9.85
iso-Butane	2.75	6.14	5.48	9.57
cis-2-Butene	3.71	8.13	6.02	?
trans-2-Butene	3.42	7.92	6.16	?
1,3-Butadiene	3.15	7.99	5.88	?
n-Pentane	5.96	8.56	8.00	12.74
iso-Pentane	5.05	8.35	7.69	12.50
n-Hexane	10.56	10.30	9.62	15.44

Notes:
 * - Poor peak shape
 ? - Unable to determine

Selectivity of the GS-GasPro appears to be the most ideal for analysis of trace sulfurs in matrices such as methane, ethylene, propylene and propane. Target sulfur peaks are clearly resolved from potential hydrocarbon interference peaks likely to be present at significant concentrations. An important exception to this observation on the GS-GasPro is resolution between propane and H₂S. Increasing column length to 60 meters and changing the temperature program slightly can improve this resolution and allow quantitation of trace H₂S in LPG samples.

Figure 2 shows a comparison of approximate detection limits for hydrogen sulfide obtained on each column using this system setup. "On-column equivalent" denotes the approximate concentration delivered to the column after standard dilution and split ratios are

accounted for. Clearly, DB-1 and GS-GasPro exhibit the best inertness characteristics for active sulfur compounds in this application, making them the best choices for trace-level sulfur determination. While there are obvious differences in signal-to-noise present in the chromatograms shown in Figure 2, response was erratic at concentrations much lower than those shown on GS-Q and GS-CarbonPLOT. These two columns exhibited an apparent quenching phenomenon, whereby response improved for hydrogen sulfide after several injections of high-level standards. This quenching effect can make accurate quantitation difficult, as the effect may not be long lasting.

Absolute detection limits are very system dependent, and thus Figure 2 is shown only as a measure of relative inertness of the four columns tested. Lower absolute detection limits may be obtained by changing system parameters such as detector type and/or injection volume.

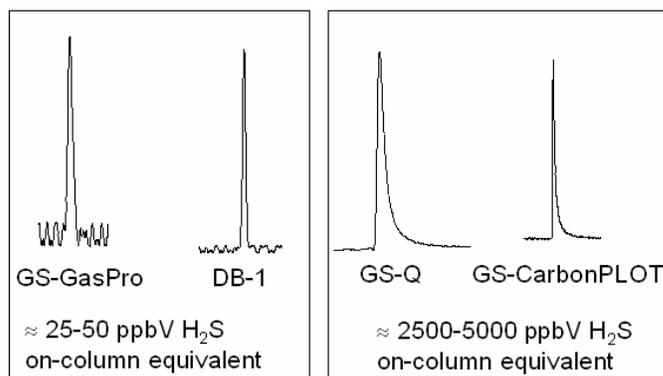


Figure 2. Hydrogen sulfide peak shape and approximate detection limit on the authors' analytical system.

Conclusions

Detector quenching can be a significant problem when quantitating volatile sulfur compounds in hydrocarbon streams such as propylene, ethylene or LPG. Column selectivity is important in these applications to allow for elution of sulfur compounds away from large hydrocarbon peaks in the sample matrix. As shown in this paper, the GS-Q and GS-GasPro appear to have the best selectivity for these applications.

Quantitation of low-level sulfur compounds requires inertness in the entire analytical system, including the capillary column. For truly trace-level sulfur analysis this paper showed evidence that DB-1 and GS-GasPro provided the most inert stationary phase surfaces for reactive sulfur compounds such as hydrogen sulfide and the mercaptans.

Of all four columns evaluated, the GS-GasPro was the only column that resolved sulfur dioxide from carbonyl sulfide under these analysis conditions. Sulfur dioxide was eluted from the GS-GasPro with good peak shape and response.

When elution pattern and inertness are both evaluated, it can be seen that the GS-GasPro appears to be an excellent column choice for trace-level quantitation of sulfur compounds in a variety of hydrocarbon streams.

Characterization of High-Boiling Petroleum Fractions using HPLC and HTGC

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Introduction

A better understanding of chemical structure of petroleum vacuum residues and their solvent separated fractions is of great importance to develop new and more efficient conversion processes. Characterization of residues is often carried out through spectroscopic and/or chromatographic techniques. However, some of the techniques are restricted to the study of separated subfractions and volatile fraction of the sample. High performance liquid chromatography (HPLC) enables the study of the entire sample if the sample is soluble in suitable organic solvent. HPLC offers advantages like fast analysis time, high resolution, low sample requirement and fractions of interest can be collected and used for detailed analysis by other characterization techniques. High boiling fractions having complex chemical structure of varying polarities are generally analyzed using amino, cyano, nitro etc. bonded silica columns (1-7). Simulated Distillation (SD) is generally performed by HTGC, which can handle samples boiling up to about 540°C. Higher boiling ranges can be covered by short, thin-film capillary columns up to final boiling point (FBP) around 800°C, with column temperature of 430°C (8-10). In this study, soluble fractions of petroleum vacuum residues (of two Indian crude oils) were characterized for hydrocarbon group type analysis using HPLC and boiling point distribution using HTGC. Method development for HPLC analysis involved study of parameters like columns, polarity of solvent and detectors, model compounds study, calibration, flow and solvent gradient programming.

Experimental

The soluble fractions have been fractionated from vacuum residues of two crude oils using different solvents and their elemental composition and characterization using NMR and FTIR have been discussed in previous study (11).

GC-SD was performed using a Chemito gas chromatograph equipped with a flame ionization detector and capillary column 6AQ5/HT5, 6m X 0.53 mm, coated with 0.10 µm thin film. The GC oven temperature program was 50-430°C at 10°C/min with 7 min hold at 430°C, injector temperature 50-400°C at 30°C/min, while detector temperature was set to 390°C. The helium carrier gas flow rate was 20 mL/min. 1 µL of 20% or more dilute solution in CS₂ solvent gave satisfactory results. During SIMDIS run, blank runs were automatically subtracted from sample runs with the help of software on Chemito SD data station, followed by integration of peak areas between perpendiculars to base line zero at the minima between peaks and accumulative area recorded throughout the run. Values so obtained are assumed to be directly proportional to the weight percent of sample eluted. The GC-SD system was calibrated by using n-alkanes from nC₁₂ to nC₉₄ covering the boiling range of 218°C (425°F) to 704°C (1300°F) (Figure 1). The actual boiling point distribution interval as obtained in SD report, was determined by chromatographic run time and boiling point information exceeding 704°C was obtained by extrapolation of curve fitted calibration data.

HPLC analysis was performed on a Waters modular system consisting of two pump (Waters 510) controlled by automated

gradient controller, differential refractive index (Waters 410), UV detector (DuPont), U6K injector, automated switching valve for backflushing and PC based Maxima 820 data station. Compound group type separation was achieved on two micro Bondapak amino bonded columns (300 x 3.9 mm) used in series. n-Hexane mobile phase at a flow rate of 1.0 mL/min gave satisfactory resolution. The sample solutions of 1.0 wt % were prepared in n-hexane and filtered through preweighed 0.45 µm syringe filters (Millipore, Bedford, MA), and the filters are dried and reweighed at room temperature to determine the weight of insolubles, allowing calculation of percent sample solubility. Response factor (RF) for each compound group (saturates, aromatics and polars) was determined for UVD at 254 nm and RI detectors from the isolated technical blend fractions for quantitative analysis of the HPLC data. 20 µL of sample solution was injected onto the HPLC column and eluted using hexane at a flow rate of 1.00 mL/min. Elution of the column with the forward flow yielded the saturate peak on RID, and aromatic peak on UVD 254 nm. Elution of polar fraction was accomplished by backflushing the column after the elution of the four ring aromatic hydrocarbons, at time, when aromatics peak comes down to baseline (RT 20 min.), which yielded a backflush peak of polars. The retention times of isolated group type concentrates prepared from technical blend of vacuum residues and model compounds were measured and used for identification and marking start and end of peaks of various compound group and classes.

Results and Discussion

Simulated TBP distillations were performed on two vacuum residues (JVR and HVR) and soluble fractions of JVR by high temperature gas chromatograph (HTGC). The typical chromatograms of HVR resulting from such a determination is shown Figure 2. The boiling points are calculated at 5 wt % intervals and include the initial (IBP) and final boiling point (FBP), which correspond to 0.5 and 99.5 wt % points (Table 1). JVR showed higher temperatures for almost all the cut points compared to HVR, which is due to heavy nature of JVR having more of high boiling components. JC7S fraction showed lower boiling components as compared to JVR, showing simplification of JC7S. JEAS, JC7C5S and JEAC5S have higher temperatures at all cut points compared to JC7S. In figure 2, a typical fine structure in the chromatograms due to high alkane content in the HVR can be discerned, while this is very less in case of the JVR sample. Similar trend is observed in JVR and its soluble fractions. Typical fine structures are most pronounced in JEAC5S, followed by JEAS, JC7C5S and least in JC7S, so the alkane content also decreases in the same order highest in JEAC5S, JEAS, JC7C5S, and least in JC7S.

In general, as the sample becomes heavier and heavier with AEBP increase, there occurs, a frequent loss of resolution of the aromatic envelope. To ensure baseline separation of hydrocarbon group types in vacuum residues, optimization was done with respect to different columns, mobile phase polarity, flow rates, column backflush time, wavelength of UV detector. Micro-porasil (silica column), energy analysis Bondapak amino column and Zorbax amino column were studied and best results were obtained with amino column in which polars were successfully eluted from residues and energy analysis amino column is good for group type separation. So detailed studies were carried out using this column. Although resolution becomes better by decreasing flow rate from 1.00 to 0.5 mL/min, but peaks become wider and poorer for quantitation. Even on increasing flow rate to 1.8 mL/min there seems to be no improvement in resolution. So n-hexane was used with flow rate of 1.00 mL/min for optimum column efficiency. The aromatic and polars envelop were measured using UV detector at 254 nm. The response of the saturate peak was obtained from a differential

refractive index (RI) detector. The NH₂ bonded silica column has been found not to adsorb irreversibly the resin materials commonly found in residues. However, precipitation of the asphaltene material from the residue samples in the column is not preventable using the n-hexane, which is used for group type separation of residues, so solutions are filtered prior to compound group separation by HPLC.

It has been shown that all alkanes including cholestane as well as separated normal, iso and cyclo-paraffins of BHVGO elute before monoaromatics (dodecyl benzene) (Table 2). Elution sequence of aromatics is strictly on the basis of number of condensed rings. It has been observed that an increase in alkyl chain length on aromatic ring leads to decrease in the retention time, whereas an increase in naphthenic content attached to aromatic ring tends to increase the same with respect to parent ring. The RF is obtained by dividing the peak area (expressed as units) by sample concentration in w/v %. Since sufficient model compounds are not available, the RFs for compound groups were determined from technically blended mixture of residues representative of Indian crude oils. Although most of the compound group types obtained were of high purity and quality, whereas some of the high boiling fractions contained a small amount of cross contamination, which could be accounted during calculation. The RFs are determined for total saturates (21.21 X 10⁶) and total aromatics (97.53 X 10⁶) on RI detector and aromatics (408.57 X 10⁶) and polars (539.78 X 10⁶) on UV detector at 254nm. The use of peak area percent rather than peak area is preferred for quantitation, because former remains unaffected by dilution of sample and day to day fluctuation in operating parameters, thus providing more reliable results. A broad aromatic peak with tailing was obtained on UV chromatogram. In residue and its soluble fractions, the column was backflushed at 20.0 min when aromatic peak comes nearly to baseline, to give a sharp backflush peak on UVD at 254 nm. This backflush peak contains polars as well as any higher ring aromatics (with more than four rings). While using RI detector, the column was backflushed after the saturates elute out (6.30 min) to give a very sharp peak of total aromatics constituting both aromatics and polars. Hexane insolubles are present only in residue and C7 soluble fractions. The polars and insolubles decreases in the order, residue > C7S > EAS > C6S > C7C5S > EAC5S, showing the effectiveness of insolubles removal in the same order (Table 3). The saturate and aromatic content increases in the same order with maximum in case of C7C5S. The soluble fractions represent a large range of composition from highly paraffinic (C7C5S) to highly polar (C7S). The saturate concentration varies from 15-18% with exceptionally high in C7C5 and EAC5 solubles (26-28%). Polar concentration is highest in C6S, while in others it is in range 27-50 wt %.

Partial separation of monoaromatics (MA), diaromatics (DA), triaromatics (TA), tetraaromatics (TTA), pentaromatics (PTA), and polars (PLR) was achieved using the flow and solvent (n-hexane and dichloromethane) gradient program, two chemically bonded silica -NH₂ columns in series and different wavelengths of UV detector. Elution of the column with forward flow yielded the aromatic ring type distribution, while polars peak was obtained by backflushing the column after the elution of the eight ring aromatic hydrocarbon. TA, TTA and PTA were resolved to some extent in UV 254 chromatogram, while MA and DA peaks merged to give a single peak (Figure 3). MA and DA peaks could be resolved to some extent, if UV 213nm was used in place of UV 254nm (Figure 4). Detection was accomplished, but quantitation was not done as peaks were not well resolved. Separation speed was increased by almost a factor of two by time programmable flow change and backflush for the polar constituents. The dominant aromatic compounds exist as 3-5 ring aromatic/ hydroaromatic compounds. These account for more than half of the aromatic compounds. 1-3 ring aromatic compounds account for very less percentage of aromatic compounds.

Table 1. Simulated Distillation Data of JVR, HVR and Solubles of JVR by HTGC

Samples	Cut points (°C)						
	IBP	5	25	50	75	90	FBP
HVR	94	187	434	548	630	693	740
JVR	93.2	197	470	572	646	694	737
JC7S	92.5	169	411	553	647	701	740
JEAS	92.5	280	521	589	650	692	737
JC7C5S	92.6	188	479	581	658	709	762
JEAC5S	108	239	477	576	652	702	747

Table 2: HPLC Elution Profile of Model Compounds on Amino Bonded Columns [2 X (300 X 3.9 mm)]

Model Compounds	Retention Time (min.)	Relative Retention
Saturates (n-paraffins of BHVGO)	6.43	0.89
Iso + Cyclo paraffins BHVGO	6.80	0.94
Mono-aromatics (1,3,5 tri isopropyl benzene)	6.92	0.96
Benzene	7.23	1.000
Di-aromatics (Naphthalene)	8.92	1.23
Fluorene	9.64	1.33
Tri-aromatics (Anthracene 1- methyl)	11.24	1.56
Anthracene	11.24	1.56
Phenanthrene	12.45	1.72
Tetra-aromatics (Pyrene)	13.37	1.85
Fluoranthene	14.51	2.01
Chrysene	18.06	2.50
Penta-aromatics (Benzopyrene)	25.14	3.48
Dibenzoanthracene	30.25	4.18
Octa-aromatics (Tetraphenyl Pyrene)	37.76	5.22

Table 3: Hydrocarbon Group Type Distribution of Residues and their Soluble Fractions by HPLC

Samples	Refractive Index Detector		UV Detector at 254 nm		Hexane Insoluble
	Total Saturate	Total Aromatic	Aromatic	Polar	
HVR	15.4	67.4	26.4	41.0	17.2
HC7S	15.7	76.1	32.6	43.5	8.2
HEAS	17.1	82.9	32.6	50.3	0.0
HC6S	18.4	81.6	34.0	47.6	0.0
HC7C5S	26.7	73.3	37.7	35.6	0.0
HEAC5S	25.6	74.4	38.9	35.5	0.0
JVR	15.3	47.1	20.2	26.9	37.6
JC7S	17.9	66.4	28.4	38.0	15.7
JEAS	18.0	82.0	35.0	47.0	0.0
JC6S	12.1	87.9	28.0	59.9	0.0
JC7C5S	27.8	72.2	36.0	36.2	0.0
JEAC5S	27.1	72.9	35.4	37.5	0.0

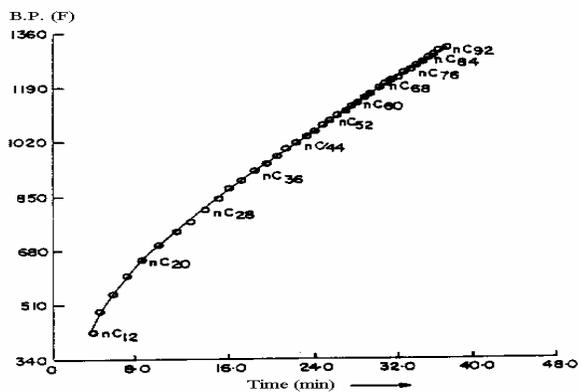


Figure 1. HTGC-SD calibration curve.

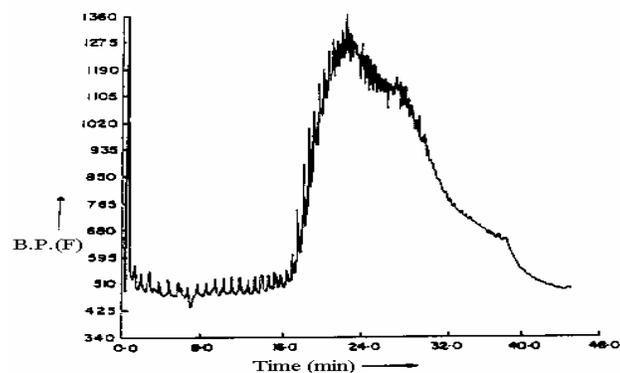


Figure 2. HTGC-SD chromatogram of HVR.

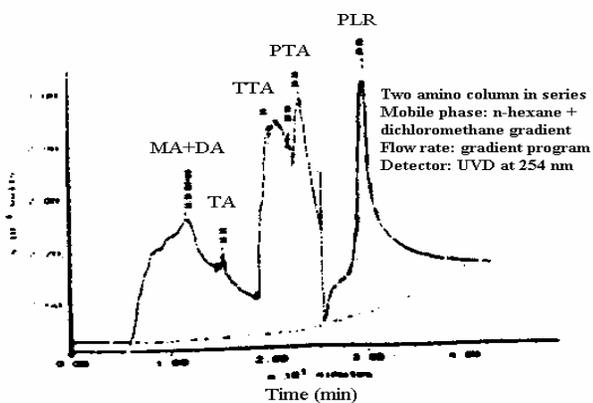


Figure 3. HPLC chromatogram of HVR C7C5 soluble on UV detector at 254nm.

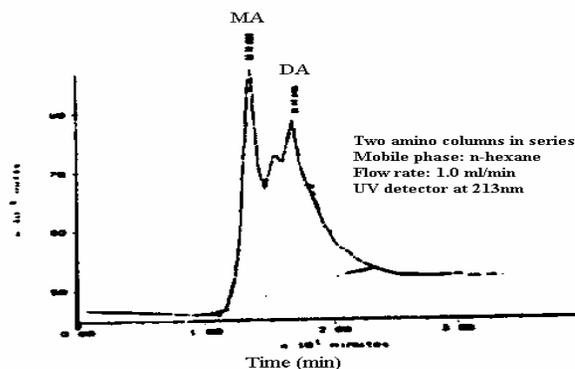


Figure 4. HPLC chromatogram of HVR C7C5 soluble on UV detector at 213nm.

Conclusions

The SD analysis showed that alkane content increases in the soluble fractions in the order C7S - EAS - C7C5S - EAC5S. HPLC demonstrated that polars + insoluble content decreases in the same order, with increase in saturates and aromatics. These changes in composition of residues as a result of solvent separation processes make the ultimate soluble fraction a good feed for conversion processes as shown by their simplified structure, which are more prone to cracking and upgradation processes. Simulated distillation by HTGC method utilizing a short, wall-coated open tubular capillary column provides an accurate and rapid means of determining boiling point distribution curves of petroleum vacuum residues. The use of amino bonded silica column has reduced the overlap between compound group fractions and it can be extrapolated for preparative separation. Aromatic ring distribution method needs further investigation in the direction of achieving good resolution between different aromatic peaks. The HPLC and HRGC method developed and standardized are fast, simple, accurate and suitable as first step to characterize residues and feeds used for conversion processes, thus making them an attractive and indispensable tool for the operation and control of secondary conversion processes.

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CHROMATOGRAPHIC SEPARATION OF LARGE QUANTITIES OF HIGH MASS MATERIALS FROM COAL DERIVED LIQUIDS.

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Introduction

Fractionation of coal liquids is an essential first step in concentrating material with similar structural features. Techniques used in this laboratory for characterising separated fractions include size exclusion chromatography (SEC) in 1-methyl-2-pyrrolidinone (NMP) eluent [1,2], UV-fluorescence spectroscopy (UV-F) and several mass spectrometric methods: heated-probe-ms, gc-ms and MALDI-ms. SEC in NMP eluent has been shown to operate by a size dependent method with only a small interference from surface effects. By contrast, Lafleur and Nakagawa [3] reported significant dependence of elution times on structural variations in sample molecules – whilst working with NMP as eluent, but with an apparently different column packing.

In previous work, we have found that the fluorescence of coal derived materials shifts to longer wavelengths with apparently increasing molecular mass, as determined by SEC elution times or diminishing solubility in common solvents [4,5]. The low fluorescence quantum yields are characteristic of large molecules with many ways in which the fluorescence energy can be dissipated to vibrational energy, while the red-shifted fluorescence points to increasingly complex aromatic ring systems. The MALDI-mass spectra of fractions of wide polydispersity tend to underestimate the proportion of high mass material. Better quality results are obtained when using narrow polydispersity coal derived fractions. Quantitative agreement has been found between SEC elution times of polystyrene molecular mass standards and fractions with MALDI-ms peak masses (Mp) up to m/z 3-4,000 [6]. The fractionation method described below is based on column chromatography using silica packing and sequential elution by acetonitrile, pyridine and NMP. This allowed fractionation of 1g quantities and near quantitative recovery of the separated fractions. The method produced enough sample in each fraction, to enable the use of several analytical methods, including NMR and py-gc-ms. The results strongly suggest the presence of large mass materials rather than molecular aggregates.

Experimental

Samples: (1) Coal tar pitch is the distillation residue of tars from high temperature coking. The present sample has been investigated extensively [1,2,7]. (2) A coal liquefaction extract, from the former British Coal Point of Ayr coal liquefaction pilot plant, corresponding to a coal solution in recycle solvent, following the filtration of undissolved coal and other solids. (3) A low temperature coal oil from the Coalite process, a low temperature distillation of coal to produce a smokeless solid fuel. Of the three samples used in the study, this material was expected to show the least thermal degradation.

Elemental analyses of the fractions from column chromatography were obtained by micro-analytical methods by determination of C, H, N and oxygen by difference (Table 1).

Column chromatography. The method to produce fractions from up to 1 gram of sample uses silica gel with sequential elution using acetonitrile, pyridine and NMP. Fifteen grams of SIGMA Silica Gel, of 15-40 μm particle size and 60 Angstroms average pore size, were heated in a vacuum oven at 200 °C overnight, cooled and stored. The

sample (1g) as a slurry (4% wt) in acetonitrile was added to 10 grams of silica gel and excess solvent removed by rotary evaporation under vacuum. The silica, coated with sample, was added to a column (20cm height x 3cm i.d.) containing the other five grams of the clean silica gel, held on a sintered glass plate. Acetonitrile (75ml) was added to the column and allowed to elute under gravity. A subsequent 75ml was eluted using vacuum. To avoid the possibility of elution by mixed solvents, air was drawn through the column to dry any residual solvent off, before commencing elution with pyridine. Two volumes (75ml each) of pyridine were used, one with gravity elution and the second under vacuum. The column was dried before adding NMP and eluting under vacuum (150ml). After elution, a small amount of sample remained on the silica gel, indicated by darker colouring. Mass balances for the fractionation are shown in Table 1.

Size exclusion chromatography [1,2]: NMP was used as eluent in the polystyrene/polydivinylbenzene 'Mixed-D' Column with 5- μm particle size, operated at a temperature of 80 °C and a flow rate of 0.5 ml min^{-1} . The samples and their fractions were examined with UV-absorbance detection at 280, 300, 350, 370 and 450 nm. The injected solution was prepared to contain less than 2 % by weight of sample, to avoid overloading of the excluded region of the column, which causes band broadening.

UV-fluorescence spectroscopy [4]. Synchronous spectra were acquired at a constant wavelength difference of 20 nm in NMP solution. Solutions were diluted with NMP to avoid self-absorption effects: dilution was increased until the fluorescence signal intensity began to decrease. However, it was necessary to examine the fluorescence from fractions eluted from the column by NMP, in relatively concentrated solutions because the fluorescence quantum yields were rather low; in these cases, sample was added until the fluorescence signal was significantly greater than background noise.

TGA analysis. Thermogravimetric analyses of the samples and their fractions was performed to measure their volatilities over successive temperature ranges, fixed carbon and ash contents (prox analysis).

Solid-state ^{13}C NMR: A Bruker MSL300 spectrometer was used with a standard Bruker magic angle spinning magic probe at 75.5 MHz (7.05T). The samples were studied as polycrystalline powder in zirconia rotors (7 nm external diameter) and a MAS frequency of 5KHz. The spectra were recorded at ambient temperature. Single pulse excitation was used with a repetition rate of 120 s to allow quantitative analysis.

Results and discussion

SEC chromatograms of the 'whole' pitch sample were acquired at five wavelengths (not shown). Two groups of peaks may be discerned, one in the excluded (8-11 min) and the other in the retained (16-23 min) region. The UV absorbance at 280 nm was the most intense. The *relative* intensity of the 450 nm absorbance was greater than those in the chromatograms (not shown) of the extract and of the LTT; that intensity appears to correlate with increasing severity of thermal treatment. The greatest intensity of excluded material was found in the digest and the least in the LTT. All three samples showed a valley of zero intensity between about 11 and 16 min.

The fractions. The relative abundance of fractions in the different solvents, Table 1, indicates that the effect of high temperature treatment is to increase the abundance of material soluble only in NMP; this was greatest in the pitch and least in the low temperature tar.

Elemental and thermogravimetric analyses of the fractions

Elemental analyses of the pitch sample and fractions are shown in Table 1. The other data (not shown) indicate that the hydrogen contents of the whole samples increase from pitch (4.1%) to the digest (6.8%) to the low temperature tar (7.8%), reflecting the effects

of different thermal treatments. The analyses of the unfractionated samples and their acetonitrile and pyridine soluble fractions gave mass balances, with sums of C, H and N greater than 90%; only the low temperature tar, pyridine solubles gave 85.8%. The apparently high oxygen values for the NMP solubles in particular imply that either the elemental analyses were low (sample not totally combusted) or the ash content was high. However, thermogravimetric analysis showed that ash levels were less than 0.1%; this suggests that combustion was not complete in the elemental analyser.

TGA data show that the acetonitrile fraction from each of the three samples produced more volatiles between 400-900 °C and gave the lowest fixed carbon content, compared to the other fractions. The pyridine solubles fractions of the pitch and the coal digest gave more volatiles between 400 and 900 °C, compared with the corresponding NMP solubles; however, that order was reversed in the case of the LTT. The fixed carbon content of the NMP solubles of the pitch was greater than that of the pyridine solubles. However, for the digest and the LTT, fixed carbon was greater for the pyridine solubles compared to the NMP solubles.

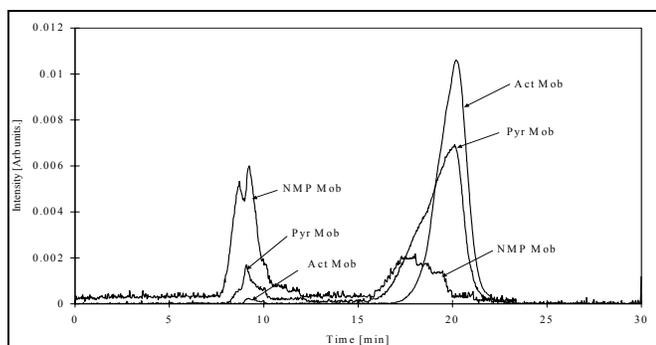


Figure 1. SEC chromatograms of pitch fractions

SEC profiles of fractions separated by column chromatography:

The pitch fractions are shown in Figure 1. The chromatogram of the acetonitrile soluble fraction was similar to that of the 'whole' pitch sample (not shown). For LTT and the digest samples (not shown) as well as the pitch, the NMP soluble/pyridine immobile fraction contained the greatest proportion of excluded material and the acetonitrile soluble/mobile fractions the least, indicating a systematic shift in molecular size from the acetonitrile solubles to the NMP-solubles.

UV-fluorescence spectrometry: Spectra of the three pitch fractions are shown in Figure 2. The fluorescence maximum was found to clearly shift to longer wavelengths and diminished in intensity, in the sequence going from acetonitrile to pyridine and to NMP-solubles. Similar shifts of fluorescence were observed for the coal digest and LTT (not shown). These shifts indicate that the aromatic chromophores become larger with increasing molecular size as observed by SEC. UV-F spectrometry does not measure molecular size directly; however, increasing chromophore sizes did correlate with increasing molecular size for all three samples.

Solid state ^{13}C NMR spectra of pitch fractions. Data from the single pulse experiments are summarised in Table 2. The results indicate that the carbon contents of the whole pitch, the acetonitrile and pyridine solubles were incompletely detected, while most of the carbon of the NMP solubles was detected. The aromaticity decreased and the aliphatic content increased in the solvent sequence acetonitrile, pyridine, NMP.

Conclusions: Column chromatography was shown to provide good separation by molecular size and polarity for three coal derived liquids (pitch, extract, tar). Analytical characterisation of the fractions suggest that for coal derived

samples, increasingly large PNA groups are being held together by aliphatic/hydroaromatic structures of increasing complexity in the larger molecules.

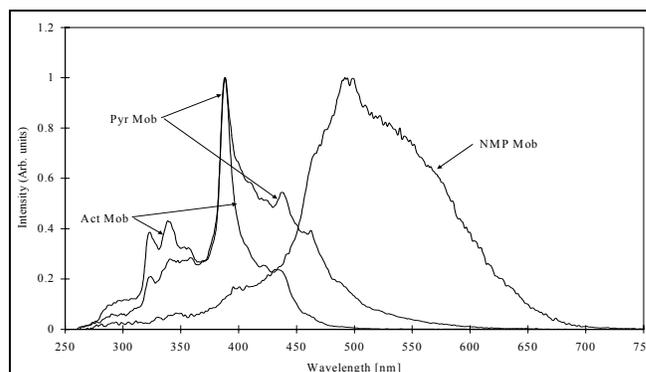


Figure 2. UV-f spectra of pitch fractions height normalised

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Table 1. Elemental analyses of pitch and fractions

Sample	Fraction	% wt	%C	%H	%N	Sum CHN	%O diff
Pitch		100	91.4	4.1	1.3	96.8	3.2
	Aceto. sols	26.1	90.7	4.8	1.3	96.8	3.2
	Pyrid. sols	47.9	89.8	4.2	1.3	95.4	4.6
	NMP sols	12.8	73.4	5.1	6.2	84.7	15.3

Table 2. Solid state ^{13}C NMR data for pitch and fractions

Sample	Aliph/Arom	%C	Aromaticity
Pitch	0.04	46	96%
Acet	0.08	91	92%
Pyr	0.08	47	92%
NMP	0.36	92	73%

COAL CLEANING VIA LIQUID-FLUIDIZED BED CLASSIFICATION (LFBC) WITH SELECTIVE PARTICLE MODIFICATION

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Introduction

Under liquid-fluidized conditions, particles segregate in height in a liquid-fluidized bed according to their density and size. For coal particles in water, the lighter/smaller particles accumulate near the top of the bed, and the heavier/larger particles populate the bottom of the bed. Immersion of coal particles in certain solvents causes them to swell to different extents. Those with the most organic matter will swell more than those with more mineral matter. This could improve the separation of organic/inorganic material in a LFBC. Here we report on an investigation of this approach in a 5-cm diameter LFBC.

Experimental

Coal Samples. Illinois #6 and Kentucky #9 coal samples from the Pennsylvania State University Coal Sample Bank were used in this study. Four particle size ranges were obtained by grinding and sieving the original 1/4" (nominal) sized particles for the LFBC studies: (A') 56-75 μm ; (B') 106-180 μm ; (C) 355-500 μm ; and (D) 840-1000 μm . A narrower A'-size range of 40-100 μm , as verified by image analysis, was obtained by decanting a slurry of the 56-75 μm sieve cut into a column filled with water. "Fines" from this sieve cut were removed in this manner, and the coal particles that remained in the initial container became the A" sample.

Coal Swelling and De-swelling. The solvents used in the LFBC experiments were selected based on swelling index measurements.¹ Small glass tubes of 3 mm inner diameter and 5 cm in length were filled with about 1 cm of ground coal. The tubes were then centrifuged at 7500 rpm. The initial heights of the coal samples were then measured with calipers and recorded. Excess solvent was added to the tube and the samples were stirred vigorously. The sample was covered with parafilm and allowed to sit for a predetermined time after which it was centrifuged again for 3 minutes, and the coal column height was determined once again. Coal samples were allowed to swell for 3-4 days while monitoring the resultant column height in this manner. For the LFBC experiments, larger samples of the coals were allowed to swell from seven to ten days. De-swelling of the coal was performed in a similar manner by simply replacing the solvent with DI water and then monitoring the decrease in the coal column height with time.

Acetone was selected based on the initial swelling test results that showed it to be an effective swelling solvent for the coals Investigated (SI \approx 1.31-1.39 for Illinois #6; 1.23-1.33 for Kentucky #9). Saturated phenol solutions in water (8g/100ml) were also selected because, in addition to being an effective swelling solvent (SI \approx 1.18-1.19 for Illinois #6; 1.13-1.22 for Kentucky #9), phenol is produced as an objectionable byproduct in paper pulping operation,² and thus could be available in large amounts at relatively low cost.

Since the coal particles are fluidized in water, it was important to ascertain how rapidly the particles de-swell by leaching the solvent into water. Small particles are expected to de-swell more rapidly than large particles. De-swelling results for the A'-size (56-75 μm) particles in water are presented in Figure 1. As shown, for both coals,

de-swelling occurred more rapidly for the phenol-swollen particles than for the acetone-swollen particles. This is to be expected, given the relatively high solubility of phenol in water. Particles swollen with phenol de-swelled to their original size in approximately 80 min. Even though leaching of phenol from the particles is about twice as rapid as for acetone, this time scale is still sufficient to allow LFBC separation of phenol-swollen particles. Other measures, such as decreasing the water temperature can also be implemented to minimize de-swelling if it should become a problem.

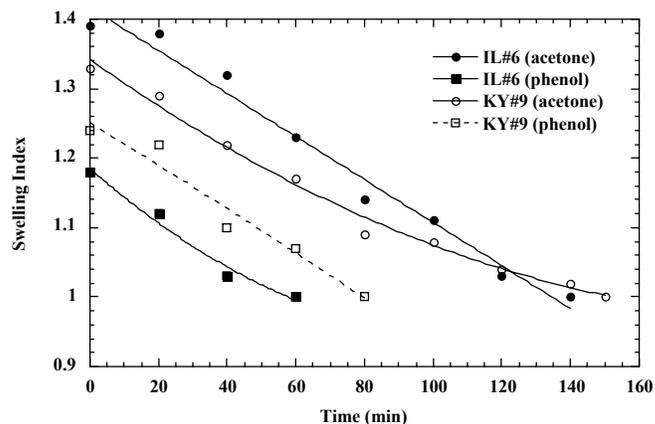


Figure 1. De-swelling rates in water for Illinois #6 and Kentucky #9 coal samples, A'-size (56-75 μm), swollen in methanol and acetone.

Liquid-Fluidized Bed Apparatus. The column was constructed of a clear Lucite tube. The fluidizing section is 1 m in length. Upstream of the fluidizing section is a 50 cm homogenizing section to provide a uniform flow field over the entire cross section of the distributor. The homogenizing section is composed of approximately 30 cm of packed straws, topped off with approximately 20 cm of 1/8" acrylic spheres. The fluidization and homogenizing sections are separated by the distributor. The distributor in the current work was a stainless steel wire mesh with a nominal opening of 56 μm . A 10 gpm centrifugal pump was used to provide water flow, and a paddle wheel flow meter was used to measure the flow rate.

Particles were loaded into the bed from an opening at the top of the column. Samples were removed from the column *via* sampling ball valves located along the side of the column. Particle size distributions were determined by image analysis (with IPLab Spectrum™ software) of images taken with an optical microscope (smaller particles) or with a digital camera (larger particles). A standard ASTM analysis procedure was followed.³

Results and Discussion.

"Larger" Coal Particle Samples. Coal samples, both swollen and unswollen, were fluidized in the LFBC, and three fractions (bottom, middle, top) were removed from each of the corresponding sampling ports, and particle size distributions were determined. Examples of these data are presented in Table 1.

From data such as these, it is apparent that the LFBC does indeed separate particles according to size, with the largest particles consistently appearing in the bottom fraction. In addition, the data showed that the LFBC separated the C- and D-size particles based primarily on ash content. The top fraction consistently had less ash than the bottom fraction for all the samples investigated. Thus, the LFBC naturally tends to separate coal particles according to mineral

Table 1. Mean Particle Diameters of LFBC fractions for Kentucky #9, 355-500 μm (C) and 840-1000 μm (D) Samples

Solvent	Bottom (μm)	Middle (μm)	Top (μm)
Unswollen (C)	419	358	339
Acetone	415	376	294
Phenol	409	361	335
Unswollen (D)	711	697	628
Acetone	816	714	711
Phenol	785	740	680

matter content, both due to density and size. However, for these larger coal particle sizes, it was found that solvent-swelling did not have a significant effect on improving beneficiation in comparison to that obtained for the unswollen coal particles.

“Smaller” Coal Particle Samples. It was hypothesized that the larger particles did not exhibit improved beneficiation due to solvent-swelling primarily because the mean organic/inorganic composition was relatively homogeneous with particle size. For distributions of ground coal particles, it has been reported that the organic matter is concentrated in the *smaller* particles.^{4,5} This same effect was demonstrated in the current work. The A"-size particles were further separated into three size fractions using the water-filled column approach that was used to eliminate a significant fraction of the “fines” from the original A'-size particles. These three samples were then ashed. The results are presented in Table 2. As shown, the smaller particles do indeed exhibit a larger fraction of organic matter than the larger particles.

Table 2. Ash Content of Unswollen A"-Size Particles

Sample	Fraction 1		Fraction 2		Fraction 3	
	Size (μm)	Ash (%)	Size (μm)	Ash (%)	Size (μm)	Ash (%)
Kentucky #9	70	8.2	88	9.9	114	11.8
Illinois #6	67	11.3	73	12.1	104	12.8

The data for the solvent-swollen particles were even more interesting. First of all, it was noted that the bed expansion observed for these solvent-swollen coal samples was considerably greater than that for the corresponding unswollen particle samples at the constant liquid velocity of 10.6 cm/min that was used for the smaller particles. At this fluidization velocity, the unswollen particle samples expanded to about two-thirds of the column height. For the same initial sample size for the solvent-swollen particles, the bed expanded essentially to the full column height. This behavior is consistent with a significantly decreased mean particle density. The latter decreases the particle terminal velocity, which increases the mean bed void fraction. Due to the large bed expansion, a direct comparison of the particle samples obtained from the same three fixed sampling ports could not be done. For this reason, only two fractions were analyzed for ash content: a sample from the bottom sampling port, and a sample of the particles overflowing the fluidized bed.

For the A"-size particles, for three of the four solvent-swollen samples, it was observed that the top LFBC fraction exhibited the *largest* particle size. This could only occur if the density of these particles was considerably less than the smaller particles at the bottom of the bed. This means that these particles were predominantly organic in nature and were sufficiently swollen to overcome the natural propensity of the larger particles (when of comparable densities) to accumulate at the bottom of the bed. This effect was observable only for the A"-size particles because of their narrower size distribution. The bulk of these particles had a mean diameter lying between about 60 μm and 80 μm . Consequently, upon

swelling, the original smaller (primarily organic) particles could exceed in size the original larger (primarily inorganic) particles. This behavior is a good indicator of the degree of the additional beneficiation effect of solvent-swelling.

Ash contents of these samples are summarized in Tables 3 and 4. As shown in all four cases, comparisons of the ash content of the top and bottom fractions clearly show a significant beneficiation effect for the solvent-swollen samples, ranging from ratios of 2-4 in bottom/top ash content.

Table 3. Weight % Ash in the LFBC Bottom Sample

Samples	KY#9 (A')	IL#6 (A')	KY#9 (A'')	IL#6 (A'')
Standard	10.4	12.3	8.2	11.3
Unswollen	12.7	15.5	8.8	11.8
Acetone	14.2	15.8	9.6	13.2
Phenol	13.1	15.9	9.4	12.5

Table 4. Weight % Ash in the LFBC Overflow Sample

Samples	KY#9 (A')	IL#6 (A')	KY#9 (A'')	IL#6 (A'')
Standard	10.4	12.3	8.2	11.3
Acetone	3.9	5.2	3.2	4.7
Phenol	3.8	4.3	4.9	6.4

Following LFBC segregation of the A'-size particle sample of Kentucky #9 swollen with phenol, the sample was allowed to remain immersed in water for five days, over which time most of the phenol was leached out of the particles. The sample was then re-fluidized under the same conditions, and samples were collected from the three sampling locations as usual. The ash content of the resultant samples were found to revert back to those obtained for the unswollen sample. These results underscore the significant effect of solvent-swelling on improving LFBC coal beneficiation.

It is also noted that the size range where solvent-swelling appears to be the most effective with respect to improving beneficiation is quite similar to the size of particles commonly used in pulverized coal combustion; i.e., a mass mean diameter of 50 μm with 70-80 wt % less than 75 μm , and 0.2-0.5 wt % larger than 300 μm . This is potentially quite fortuitous since LFBC with solvent-swelling could be performed directly on the power plant PC grind just before it is used, without incurring any additional grinding costs.

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COMBINED USE OF THIN-LAYER CHROMATOGRAPHY AND GC-SULFUR SELECTIVE CHEMILUMINESCENT DETECTION FOR EVALUATION OF SULFUR COMPOUNDS AND HYDROCARBON CLASSES IN THE COURSE OF HYDROTREATMENT OF DIESEL FUELS

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Introduction

A progressive reduction of the polyaromatics (PACs) content (< 5 w/w %), sulfur (50 ppm) and cetane number for commercialized diesel fuels has been programmed for 2005 in the European Union. In this context, research activity has focused on identifying the ultimate sulfur species that remain unconverted after conventional hydroprocessing^{1,2}. This is usually carried out by GC-Sulfur Chemiluminescence Detector (SCD) due to its linear dynamic range and its structure independent response. However, less effort has been directed towards the development of analytical protocols for evaluation of aromatics, and, in general, hydrocarbon-types. Sensitive determinations of these are necessary because, during HDS, sulfur compounds are transformed into the corresponding aromatic species, and the hydrotreatment conditions should affect the distribution of aromatics in the processed feed. The standard method for aromatic distribution is based on HPLC-Refractive Index detection. It suffers of some limitations, for example, its low sensitivity³.

In a previous communication in this issue⁴, several methods for sensitive and quantitative determination of alkanes, naphthenes, total aromatics and PACs (over three rings) in gas oil have been reported, which were based on high-performance thin-layer chromatography with fluorescence and UV scanning densitometry.

The aim of this work was to investigate the distribution of sulfur compounds and hydrocarbon classes during the catalytic HDS of a diesel oil, in order to establish the basis for determining the reactivity of the different classes of sulfur compounds, and to evaluate the concomitant evolution of aromatic hydrocarbons. The combined use of Thin Layer Chromatography-Densitometry (TLC) and GC-SCD has provided interesting quantitative information related with both the composition of a straight run gas oil and its HDS process.

Experimental

Samples. A straight run gas oil (1.32 %S) was hydrotreated in a micropilot unit with a CoMoS/Al₂O₃ catalyst under the following conditions: temperature 633 K, total pressure 3 MPa, hydrogen-to-liquid flow ratio 150. The Liquid Hourly Space Velocity (LHSV) was adjusted in order to reach the required level of desulfurization. The determination of total sulfur content in the processed products was carried out by XRF (Horiba SLFA-1800, Japan). Calibration was performed according to a previously published method⁵. The sulfur content for the hydrotreated derivatives was, respectively: 9060, 7000, 6000, 4000, 3100, 1700, 970, 610, 290 and 150 ppm.

Preparative TLC. The straight run gas oil was submitted to preparative TLC in order to isolate fractions of the identified hydrocarbon classes (alkanes, naphthenes, aromatics and noneluted

for a detailed quantitative analysis of sulfur compounds distribution by GC-SCD. Preparative conditions have been reported in this issue.⁴

An evaporation of some species during drying of preparatively isolated fractions cannot be discarded. Although the protocole of drying is milder at analytical than at preparative scale (i.e., plates are dried at room temperature instead of using a slight air flow), a correction can be included in the mass balances. The amount of evaporated saturates is obtained from the difference of the content of light hydrocarbons (< C₁₃) between the gas oil raw sample and the fraction of alkanes determined by GC-FID.

Analytical TLC. The following hydrocarbon groups have been determined in the straight run gas oil and its hydrotreated products by analytical high performance thin layer chromatography with UV and fluorescence densitometry: alkanes, naphthenes, total aromatics and polyaromatic compounds over three rings (PACs). Analytical conditions have been reported in this issue⁴

GC-Sulfur selective Chemiluminescent Detector (SCD) and simulated distillation (GC-FID). An HP 5890 gas chromatograph equipped with a standard FID coupled to a SCD (Sievers, USA) was used for the analysis of gas oil samples. The injected volume was 1 or 3 µl depending on total sulfur concentration. The capillary column (PONA, 50 m, 0.2 mm ID) was programmed at 5 K min⁻¹ from 323 to 623 K. The linearity of the SCD was checked in the range from 10 to 1500 ppm S, and the response was shown to be independent of the nature of the sulfur compound (thiophene, benzothiophene or alkylbenzothiophene). For the determination of the simulated distillation curves, the FID signal was integrated every 0.1 min. The signal corresponding to a blank run performed under the same conditions was subtracted after completion of the temperature program.

Results and Discussion

Quantitative sulfur analysis by GC-SCD. A quantitative determination of sulfur can be performed from the integration of the SCD signal over the corresponding ranges of retention time. In order to calibrate the SCD response, the integrated signal was compared to the corresponding FID signal. The response coefficient of the SCD was determined through calibration with a series of hydrotreated gas oils containing variable total sulfur contents in the range 150 to 13200 ppm, which were previously determined by XRF. The standard variation is 5 % and the mass balance of the determined sulfur compounds matches the total sulfur XRF data at ± 5 %.

Distribution of sulfur compounds as a function of HDS. A complete identification and quantitative evaluation of sulfur compounds has been performed as a function of the degree of desulfurization during hydrotreatment of a straight run gas oil by GC-SCD. Sulfur containing species have been classified into benzothiophenes (C₃- and C₄-BTs) and dibenzothiophenes (C₀, C₁, C₂ and C₃₊-DBTs). BTs and DBTs are easily eliminated at low HDS conversion. Substituted DBTs remain unconverted up to high total HDS level of conversion. The least reactive species are 4,6-disubstituted DBTs (Figures 1 and 2). This distribution pattern is not specific of a given feed, as it will be shown from the SCD chromatograms of several processed diesel oils from various origins.

Hydrocarbon classes as a function of HDS The following hydrocarbon groups have been determined in the hydrotreated products by analytical thin layer chromatography-densitometry: alkanes, naphthenes, total aromatics and polyaromatic compounds (PACs).

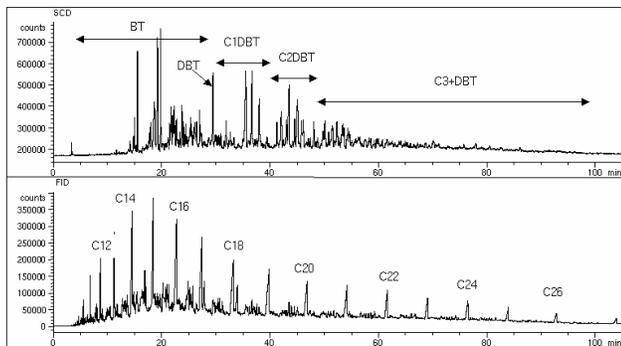


Figure 1. SCD and FID chromatograms of the straight-run gas oil (13200 ppm S)

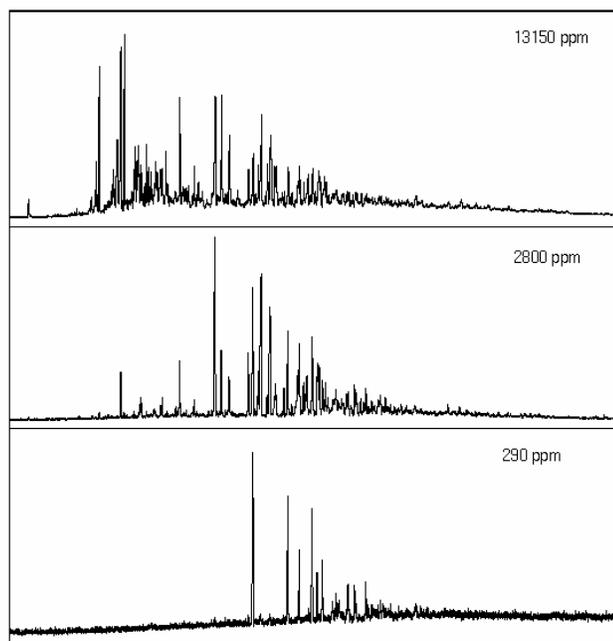


Figure 2. Evolution of SCD chromatogram of the straight-run gas oil in the course of HDS

Table 1 shows TLC distribution of hydrocarbon classes in the hydrodesulfurized gas oils with corrections concerning evaporation of some light products. Results indicates that PACs and naphthenes remain unconverted. The content of total aromatics decreases as sulfur is eliminated. In contrast, an increase of alkanes is observed.

Table 1. Corrected TLC distribution of hydrocarbon groups in desulfurized gasoils (w/w %)

Sample, ppm S	Total Alkanes	Total Aromatics	Naphthenes	PACs ^a	Total
13150	56.5	17	25.7	3.8	99.2
9060	60.2	11.6	25.3	3.5	97.1
6000	61	11.4	23.5	3	96
3100	63.5	10.8	25.3	3.4	99.6
610	65.1	7.9	24.5	3.8	97.5

Detailed composition of the straight run gas oil The straight run gas oil has been submitted to fractionation by preparative thin

layer chromatography and the resulting fractions of alkanes, naphthenes, aromatics, and noneluted fraction have been characterized by simulated distillation and gas chromatography with sulfur selective detection (GC-SCD). The quantitative distribution of sulfur compounds in these fractions is shown in Table 2.

Table 2. Distribution of sulfur compounds (w/w %) in the fractions of straight run gas oil

Fraction	BTs	C ₁ DBTs	C ₂ DBTs	C ₃₊ DBTs	Total S compounds
Alkanes	0,07	0,05	0,04	0,31	0,46
Naphthenes	0,50	0,94	0,81	4,32	6,6
Aromatics	2,29	10,58	10,29	33,77	56,9
Non eluted	1,66	1,53	2,79	15,54	21,5

Composition of each fraction will be discussed in detail during the oral presentation. The FID chromatogram of the naphthenic fraction exhibits the presence of numerous peaks between the series of *n*-alkanes, that complements the mentioned data concerning the cycloalkanic nature of this fraction⁴. The distribution is shifted towards higher retention time, as compared to that of the alkanes fraction. Similarly to the alkanes fraction, the total sulfur content is low, as evidenced by the SCD chromatogram.

One would expect an increase in naphthenes rather than an increase of the total alkanes content in the course of HDS process. However the hydrocarbons contained in the naphthenic fraction are heavy entities (> C₁₆) that are not affected by the HDS process, nor are they produced by HDS of DBTs which yields species containing less than 16 carbon atoms. Thus it must be admitted that the light cycloparaffinic species originated from the partial hydrogenation of aromatics are eluted along with the alkanes fraction.

It has also been observed that the sulfur compounds concentrate in the aromatic fraction (57 wt %). The FID chromatogram corresponding to this fraction is more complex than the SCD in the 10 to 30 min retention zone. This zone corresponds to the maximum of the distribution of the hydrocarbons in the whole gas oil. At higher retention times, the FID and SCD chromatograms are very similar, indicating that the species detected by the FID are sulfur-containing compounds.

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DETERMINATION OF CONJUGATED DIENES IN PETROLEUM PRODUCTS BY SUPERCRITICAL FLUID CHROMATOGRAPHY AND UV DETECTION

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Introduction

Aliphatic unsaturated hydrocarbons, like olefins and diolefins, are formed during both thermal and catalytic cracking of heavy petroleum fractions. Among these compounds, conjugated dienes are particularly reactive for polymerization and are known to contribute significantly to the instability of the resulting fuels. Nevertheless, the participation of cracking fractions in fuel blends of Petrobras tends to grow, since most of the Brazilian crudes are heavy ones. For this reason, CENPES – PETROBRAS R&D Center – is investigating ways either to minimize the formation of conjugated dienes during cracking operations, or to remove them from the end products. To support this research work a fast and precise analytical method for quantification of this hydrocarbon family is needed.

Gas chromatography with flame ionization detection (GC-FID) is the technique of choice for compositional analysis of most fossil fuel light fractions. Compound families like linear paraffins, olefins, naphthenic or aromatic hydrocarbons are quantified by summation of the peak areas of each component of a given family in the chromatogram. Each peak should be correctly referred to its corresponding structure, which is usually done by gas chromatography with mass spectrometry (GC-MS). However, problems inherent to the complexity of the matrix, like coelutions or lack of chromatographic standards, and the small concentration of the conjugated dienes make the unequivocal identification of the conjugated dienes, specially the heavy ones, by GC-MS, and quantification by GC-FID, very difficult. Although light distillates have typical distributions of components, the later can eventually change, which further complicates the recognition task.

The only way of measuring the content of total conjugated dienes in petroleum products available at Cenpes is the one stated in UOP method 326 (1). By this method, a fuel sample is refluxed with maleic anhydride, undergoing Diels-Alder reactions with the conjugated diolefins. Unreacted maleic anhydride is then hydrolyzed to maleic acid, which in turn is quantified by titration with a strong base. Consumed maleic anhydride is taken as a measure of the content of conjugated dienes present in the fuel. The result is reported as diene value, defined as the number of grams of I₂ equivalent to the amount maleic anhydride, on a 1:1 molar basis, that reacts with 100 g of sample. The determination is rather empirical, since some diolefins may not react completely, while certain compounds like vinyl aromatics or anthracene and its homologues may react as if they were conjugated diolefins. The method is cumbersome and requires too much manipulation. In addition, it takes more than three hours to be accomplished and its automation is impossible. It is not fitted, for instance, to analyze a large number of samples in a short period of time.

Supercritical fluid chromatography with flame ionization detection (SFC-FID) has been successfully used for determining total aromatics and aromatics by ring number in samples ranging from light fractions up to vacuum distillates and residua (2-5). Non-aromatics, which include saturated hydrocarbons, olefins and dienes, are

separated from aromatics on one or more silica columns and using CO₂ as mobile phase. This system may also be modified to allow the analysis of olefins, by adding a silver-containing column and two backflush valves to the flow path (6,7). Olefins and other non-aromatic, unsaturated hydrocarbons are retained on the silver-containing column and backflushed afterwards. Olefin content is normally much higher than diene content, and since both chromatographic systems do not separate them, a more selective way of detecting conjugated dienes, like UV detection, is needed.

Experimental

A supercritical fluid chromatograph from Berger Instruments was used, which included autosampler, high-pressure pump, and column oven. An Agilent UV diode-array detector, model 1100, with a high-pressure analytical cell, provided detection. Chromatograms for quantification of conjugated dienes were obtained at 240 nm. Samples were injected as received or diluted five times with toluene (HPLC grade), depending on the content of the conjugated dienes. An internal loop of 0.5 µL was used for injection. Chromatographic separation was performed on one or two silica columns (HP Group Separation, 250×2.0 mm), depending on the required resolution. The conditions of analysis can be the same as those used for determination of aromatics in diesel fuel (8), except that UV detection is used instead of FID.

Pure olefins, isolated and conjugated diolefins were diluted in hexane (HPLC grade) and were injected at the mentioned conditions. Calibration curves were constructed with pyperilene (1,3-pentadiene, mixture of isomers, Aldrich) and the concentration of conjugated dienes was reported in mol/L. The SFC method was tested with several samples, including FCC liquid products, FCC naphthas and respective hydrotreating products and hydrotreated delayed coking naphthas. Diene values given by UOP 326 standard method were also obtained for all these samples.

Results and Discussion

Overlaid UV spectra of some non-aromatic, unsaturated hydrocarbons are shown in Figure 1. While the absorbance of the olefins studied extinguishes around 225-230 nm, the UV absorption of both the conjugated dienes remains up to 250 nm. This is due to the delocalization of the electrons taking part in the conjugated double bonds, which reduces the energy gap between bonding and antibonding molecular orbitals. Therefore, photons with less energy are able to promote electronic transition. Isolated double bonds are not allowed to exhibit similar resonance and spectra of compounds like 2-methyl-1,5-hexadiene or 1,7-octadiene resemble those of

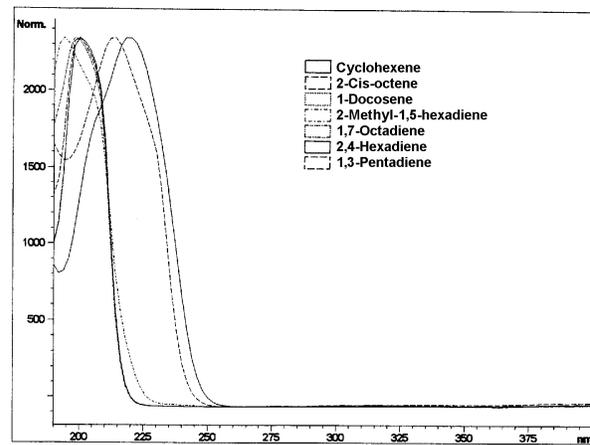


Figure 1. UV spectra of selected olefins, isolated dienes and conjugated dienes.

olefins. This offers the possibility to detect compounds with conjugated double bonds selectively in petroleum fractions. Since aromatic and non-aromatic hydrocarbons are easily separated in these chromatographic conditions, the only interfering substances are polyenes, which also cause instability in gasoline-range products and also react with maleic anhydride in UOP 326 method.

Retention times of the hydrocarbons tested are shown in Table 1, with only one silica column. All are non-aromatic hydrocarbons and elute very close to each other, which means that conjugated dienes are expected to elute as a single peak in the chromatogram. This can be confirmed by observing the chromatogram at 240 nm shown in Figure 2. The spectrum of a conjugated diene and a spectrum taken at the peak of conjugated dienes are overlaid in Figure 3. The later was obtained by the analysis of a non-hydrotreated FCC naphtha. They are rather similar except by the absorption below 200 nm exhibited in the spectrum of the naphtha, which is probably due to coelution of olefins.

Table 1. Retention Time of Selected Non-Aromatic, Unsaturated Hydrocarbons (Conditions: see text)

Substance	Retention time, min
Cyclohexene	1.384
2-Cis-octene	1.373
1-Docosene	1.383
2-Methyl-1,5-hexadiene	1.430
1,7-Octadiene	1.363
2,4-Hexadiene	1.450
1,3-Pentadiene	1.396

Several samples of petroleum products were analyzed by both SFC and UOP 326 methods, in order to test the suitability of the SFC method for measuring the content of conjugated dienes. The results were plotted in Figure 4 and were split in four groups, each of them representing samples generated from a given feed processed at different pilot-plant conditions. For example, square symbols in Figure 4 represent a set of samples produced from the same FCC naphtha, at different hydrotreating conditions. The results for samples belonging to the same set are well fitted by a straight line, which slopes are similar considering that each sample has a particular distribution of conjugated dienes. Therefore, the hypothesis of a constant average absorptivity, which is implicit in the proposed method, seems reasonable from these results. Assuming that the determination of conjugated dienes by SFC-UV is not subject to interfering substances, a negative intercept suggests that the reaction between conjugated dienes and maleic anhydride is not stoichiometric, at least during the reflux time specified in UOP 326.

On the other hand, a positive intercept indicates that substances other than conjugated dienes, like vinyl-arenes or anthracene and its

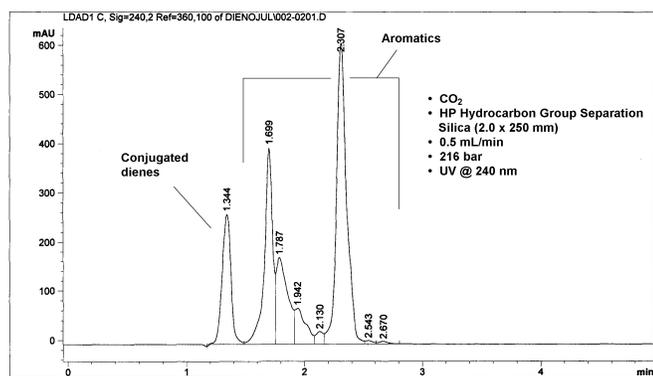


Figure 2. Chromatogram of a hydrotreated FCC naphtha.

homologues, reacted with maleic anhydride. Among the sample sets investigated, the one named "FCC liquid product" is the only which equation has a positive intercept. The whole FCC stream integrates these samples, so they are the only where substantial contents of these interfering substances are expected to exist.

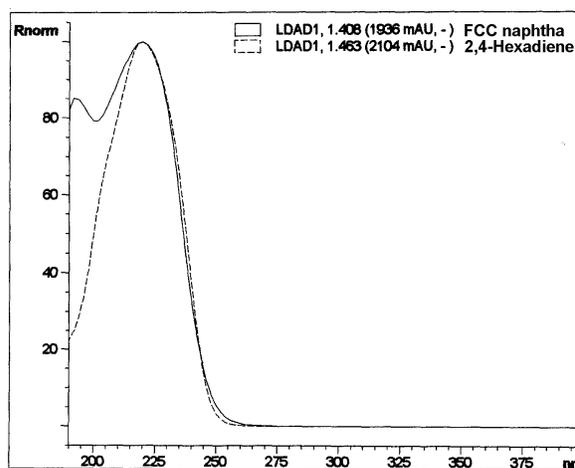


Figure 3. Overlaid UV spectra: 2,4-hexadiene and at the peak of conjugated diene.

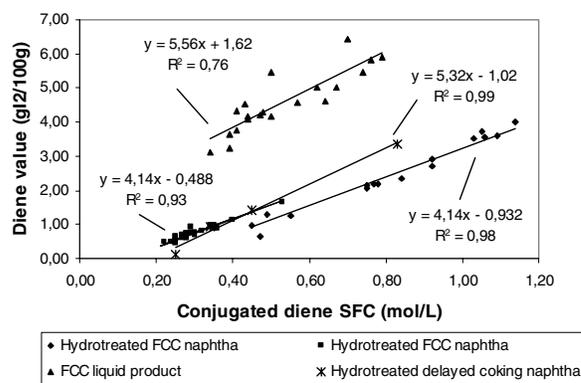


Figure 4. Correlation plots for samples with different origins.

Conclusions

A method for determination of total conjugated dienes in petroleum products by supercritical fluid chromatography and UV detection is presented. The method is accurate and faster (5 min) than the diene value method (UOP 326 method). Samples of both catalytic and thermal cracking naphthas were examined by both methods, with well-correlated results.

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ESTIMATION OF VISBROKEN AND SELECTIVE CATALYTIC STEAM CRACKED PRODUCT STABILITY USING IATROSCAN TLC-FID.

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INTRODUCTION

Crude oil vacuum residues are characterized by a high concentration of high-molecular-weight compounds such as asphaltenes. These compounds impart undesirable properties to the residue (i.e. low viscosity) and affect thermal and catalytic conversion processes¹. In many cases, the efficiency of conversion is related to the formation of insoluble carbon-rich deposits²⁻³. In visbreaking (VB) and selective catalytic steam cracking (SCSC) processes, severity of the operation is limited by heater fouling and product instability, which is dependent on the asphaltene content of the feed⁴.

An experimental measuring of the stability of the visbroken and selective catalytic steam cracked residues is given by the Shell P-value. This parameter is a measure of the flocculation potential of asphaltenes and their trends to form solid deposits. P-Value is directly proportional to the stability. Its determination involves the visual detection of the flocculated asphaltenes by using a microscope. In consequence, results depend on the operator ability and can vary from an analyst to another. Additionally, the procedure is time consuming.

One approach to determine the instability of heavy oil residues is through the colloidal instability index (CII), which is based on the chemical composition of the residue. The CII is defined as ratio of the sum of asphaltenes and saturates to the sum of the peptizing resins and aromatics⁵⁻⁶:

$$CII = (\text{Asphaltenes} + \text{Saturates}) / (\text{Resins} + \text{Aromatics})$$

Calculations of this parameter involve a hydrocarbon group type analysis. Saturate, Aromatic, Resin and Asphaltene (SARA) quantification can be achieved either by High Performance Liquid Chromatography (HPLC) or by Thin Layer Chromatography-Flame Ionization Detection (TLC-FID). The former requires the use of liquid chromatography after asphaltene precipitation and quantification by gravimetry⁷⁻⁸; besides, it is time consuming and needs considerable volumes of solvents.

TLC is becoming increasingly popular in the crude oil industry. This technique is recognized as an efficient, fast and cost-effective way to obtain quantitative information about crude oil composition⁹. For separation and quantification, correct use of Iatroscan TLC-FID offers good precision and accuracy, in addition to rapid analysis and low solvent consumption.

Cebolla et. al⁷, Karlsen et. al¹⁰⁻¹¹ and Sol et. al¹², are some of the researchers that have used this technique for the analysis of SARA constituents in crude oils and solvent extracts.

In this work, we evaluate TLC-FID as an alternative tool to estimate the stability of visbroken and selective steam cracked residues by CII calculations. Results were compared to the conventional P-Value.

EXPERIMENTAL

The samples studied in this work came from test carried out at a pilot plant of 1 barrel/day capacity, using a short Venezuelan residue operated both visbreaking and selective catalytic steam cracking. The reactions were stopped when the bottom (350°C+)

product reached a critical P-Value of 1.2. P-Value was determined using hexadecane titration, as indicated in reference 13.

SARA TLC-FID Analysis. An Iatroscan TH-10 instrument (Iatron Labs Inc.), equipped with a flame ionization detector (FID) and interfaced with a computerized acquisition system (DIONEX AI 450 Optimize) was employed. This instrument was calibrated for quantitative SARA analysis. Pure hydrogen (190 mL/min, supplied by a hydrogen generator) and pure air (2.0 l/min, supplied by an air cylinder) were used for the detector. Two sets of 10 silica rods, type Chromarod-SIII (pore diameter 60 Å, particle size 5µm) were used: One for the saturate and aromatic quantification and the other one for asphaltene quantification. Samples were prepared by dissolution in a mixture of toluene: chloroform 1:1 vol:vol to obtain a final concentration of 25 mg/mL. Before sample application, Chromarods were passed twice through the FID to remove contaminants, and to obtain constant activity of the silica layer. Each rod was spotted by 1.0 µl of the sample solution, applied dropwise by using a 1.00 µl syringe. For saturate and aromatic determinations, Chromarods were developed in n-heptane for 40 min; air dried (3 min) and developed again in toluene for 20 min. For asphaltene determinations, the second set of Chromarods was developed in n-heptane/ isopropanol 95:5 vol. % for 20 min. Each set of rods was dried for 3 min and then, pyrolyzed at a scan speed of 0,32 cm/s.

RESULTS

Selective catalytic steam cracking (SCSC) is a process based on chemicals reactions carried out in presence of steam and ultradispersed catalysts¹⁴. The technology based on SCSC is called Aquaconversion®. Table 1 shows the conversion achieved by the feedstock (350°C+) during VB and SCSC operations. P-values of the feedstock and its products are shown as well. When in VB a maximum conversion established by a critical P-Value of 1.15 is reached, the stability of the 350°C+ SCSC product (given by a P-Value of 1.45) allows to enhance the conversion by increasing the severity of the process. Even, under this severe condition, a new SCSC product is obtained with higher stability than VB product.

Table 1. Conversion and P-values of feed and products¹⁴

	Feed	VB	SCSC-1	SCSC-2 ^(*)
Conversion (wt.%)				
To 165°C-	---	2.9	5.2	7.5
Of 500°C+	---	28.2	28.5	36.3
P-Value	2.7	1.15	1.45	1.20

(*) SCSC-2 refers to severe conditions in SCSC process (5°C over the fixed temperature)

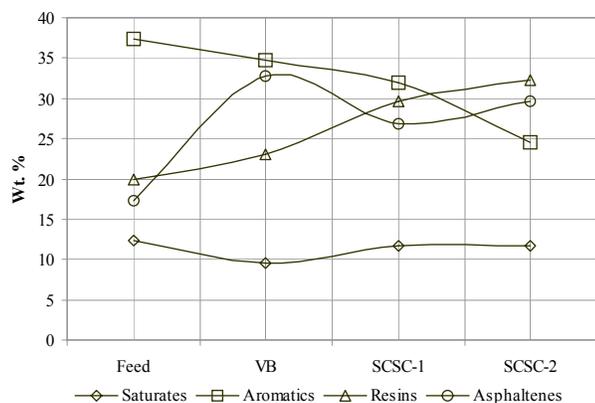


Figure 1. SARA distribution of the studied 350°C+ residue and the 350°C+ VB and SCSC products.

It is known that during VB, asphaltene formation increases with conversion. This is a consequence of thermal cracking reactions that follow a free radical mechanism, causing asphaltene condensation and formation of heavier products and coke¹⁵. On the contrary, the mechanism proposed for SCSC suggests the saturation of these free radicals by the incorporation of hydrogen free radicals formed by the catalytic dissociation of water. Thus, asphaltene formation is avoided as well as the early appearance of condensed products potentially unstable¹⁴.

Figure 1 shows TLC-FID SARA distributions of the feedstock studied and its VB and SCSC 500°C+ products. It is interesting to note that the addition of steam and catalysts to VB produces a residue with higher resin content and less quantity of asphaltenes. This observation indicates that, while asphaltenes are normally produced in VB, they are converted in SCSC. This particular behavior of SCSC favors the quality of the final product.

Some authors have pointed out that the nature of asphaltenes seem to play an important role in the stability of residues regardless their content¹⁶; however, others factors such as the content of asphaltenes, the presence of resins and the quality of the oil media must be taken into account¹⁷.

Considering the crude oil residues as colloidal systems, resins and asphaltenes comprise the dispersed phase while saturates and aromatics form the continuous phase¹⁹. The interaction among both phases and their influence on the stability of the system is related to the peptizing power of the resins, the solvent effect of the aromatics, the precipitant properties of saturates and the flocculation tendency of asphaltenes.

Lower values of CII indicate higher asphaltene stability due to the dispersant effect of aromatic and resins¹⁸. Figure 2 shows the CII values calculated from TLC-FID data and the P-Value. As can be observed, CII exhibits an inverse trend to the one showed by P-Value, giving surprisingly a mirror image. As can be seen in Figure 2, higher CII's correspond to lower P-Values. It is amazing the excellent correlation found between a chromatographic method such TLC-FID and the titration method (P-Value). This interesting correlation offers a potential tool to evaluate product stability in a very fast and accurate way.

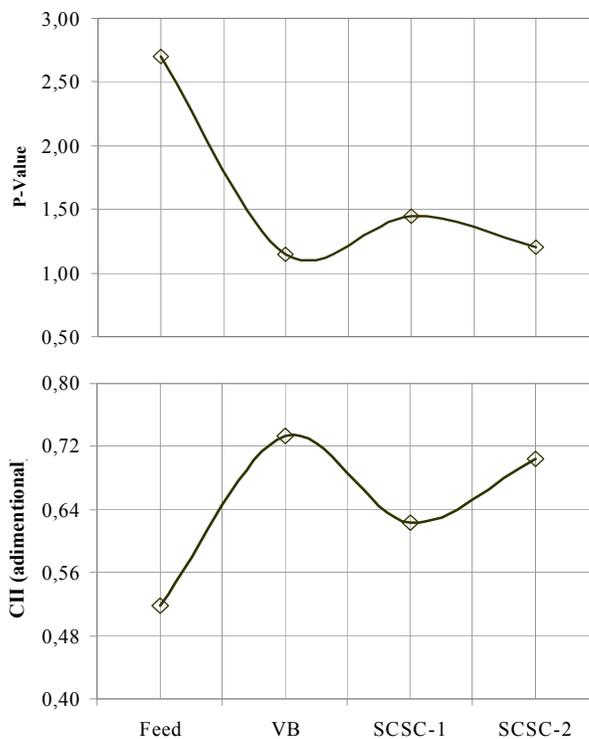


Figure 2. Comparison of CII values calculated from TLC-FID results with the P-Value of the VB and SCSC products of the studied 350°C+ residue.

On the other hand, an identical behavior was found when the P-Value was compared to the Theoretical Distribution of Solubility Parameter of these pure asphaltenes obtained by n-heptane precipitation⁴. These findings confirm that asphaltene nature plays an important role in the stability of the residues.

CONCLUSION

Stability of VB and SCSC products was evaluated by calculation of CII, using TLC-FID SARA distribution. Results obtained by this fast and accurate method are in total agreement with the conventional P-Value. Additionally, the CII showed the same trend found in the theoretical studies of the solubility parameter.

CII is proposed as a potential alternative parameter to obtain a rapid evaluation of the bottom product stability during VB and SCSC processes. However, a higher number of samples are being considered to confirm the results shown in this work.

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Novel Desulfurization and Denitrogenation Process for Fuel Oils Based on Alkylation and Precipitation Technique

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Introduction

Much attention has been focused on the deep desulfurization of light oil. To protect the environment against contamination, the sulfur level in diesel fuels is limited presently to 0.05 wt%, both in Japan and Europe and this will certainly be tightened to 0.005 wt% soon. The current technology of hydrodesulfurization (HDS) can desulfurize aliphatic and acyclic sulfur compounds quite adequately, when adopted on the industrial scale. The process however is limited, when treating dibenzothiophenes (DBTs), especially alkyl-substituted DBTs,¹ for deep desulfurization of light oil. In the development of alternative energy-efficient desulfurization process, a radical approach, which is not limited to conventional HDS, is needed.

Acheson and Harrison^{2,3} have reported that DBT are successfully methylated by CH₃I, in the presence of AgBF₄, to give rise at room temperature to crystalline powders of the corresponding *S*-methylthiophenium tetrafluoroborate. These thiophenium salts are highly polarized (water-soluble) and are insoluble in nonpolar solvents. Thus, such a synthetic method, if applied to the desulfurization of nonpolar light oil, might thus be able to remove the BTs and DBTs specifically from the light oil as a precipitate and under moderate conditions. This has now been demonstrated to be realized,⁴ and thus enabling the new desulfurization method for BTs and DBTs from light oil to be presented here.

Experimental

Commercial light oil (sulfur concentration: 0.179 wt %) was used as feedstock. To clarify the relative desulfurization reactivity of the sulfur compounds, *n*-tetradecane solutions, each containing DBTs, corresponding to a sulfur content of 0.05 wt %, were also employed as model light oils. Concentrations of total sulfur and of the individual sulfur compounds in light oil and of the sulfur and aromatic compounds in tetradecane were analyzed by ICP-AES, GC-AED, and GC-FID. Theoretical calculations of the electron density on sulfur atom for DBTs were performed with the PM3 semi-empirical method within the WinMOPAC ver3.0 software (Fujitsu Inc.)

Results and Discussion

To test the feasibility of this idea, a *n*-tetradecane solution (15 mL) containing DBT (0.81 mmol), corresponding to a sulfur content of 0.2 wt %, was used first for experiments. AgBF₄ (1.63 mmol) was added to the tetradecane solution under a nitrogen atmosphere. A tenfold molar excess of MeI (16.3 mmol) was then carefully added dropwise over a period of 10 min. The reaction mixture gradually changed forming heterogeneous mixture containing a yellow AgI precipitate. After stirring for 11 h, the AgI precipitate was recovered by filtration and was washed with CH₂Cl₂. The CH₂Cl₂ was then removed completely from the filtrate by evaporation. Upon cooling the resulting filtrate, using an ice bath at 273 K, a white powder of the dibenzothiophenium tetrafluoroborate^{2,3} precipitated successfully. In this procedure, the removal efficiency for DBT from tetradecane

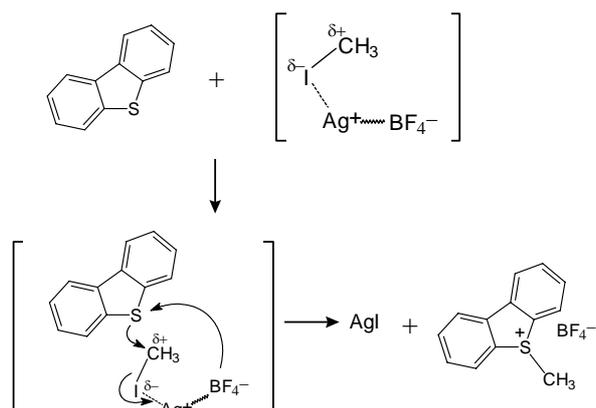


Figure 1. Reaction pathway for the methylation reaction occurring between DBT and alkylating agents (CH₃I and AgBF₄).

was however only 58% at a reaction temperature of 303 K. The methylation reaction proceeds via S_N2 displacement by the nucleophilic sulfur atom on the CH₃I–AgBF₄ complex,^{5,6} as shown in **Figure 1**. This low removal efficiency for DBT probably results since the tetradecane is poorly nucleophilic and a nonpolar solvent, and thus the highly polarized intermediates are not stabilized satisfactorily. To increase the polarity of the tetradecane solution, when an equal volume (15 mL) of CH₂Cl₂ was added, the desulfurization yield of DBT increased successfully to 85%. At higher reaction temperature than 320 K, the desulfurization yield of DBT decreased significantly, owing to the thermal decomposition of the thiophenium salts produced.⁷ These results therefore suggest that practical desulfurization should be carried out at room temperature conditions lower than 320 K.

The above procedure was then tested for the desulfurization of methyl-substituted DBTs, which are key compounds in the HDS technology.¹ The desulfurization yields of 4-methyl- and 4,6-dimethyl-DBT from tetradecane were smaller than that of nonsubstituted DBT, while higher desulfurization yield of 2,8-dimethyl-DBT being obtained. DBTs are methylated via the withdrawal of lone pair electrons on the sulfur atom. To clarify the methylation reactivities for DBTs, electron density on the sulfur atom of DBTs was calculated by MO calculation, and was compared with the relative desulfurization yield of DBTs. The frontier orbitals of DBT are sulfur π orbital with electron density lying perpendicular to the plane of the DBT molecule. However, no relationship between the desulfurization yield and the electron density calculated from the π orbital was observed. DBTs have a sulfur σ lone pair orbital with electron density lying parallel to the plane of the molecules on the lower energy-level orbital than HOMO.^{8,9} The electron density, calculated from this σ orbital, showed a linear relationship with the desulfurization yield of DBTs, as shown in **Figure 2**. The result therefore strongly suggests that the nucleophilic attack of the DBT molecule against the carbon atom of the CH₃I occurs, in a parallel direction to the DBT plane, and the electron density on the sulfur σ orbital governs the methylation reactivity for the DBTs. The present desulfurization process reveals that the DBTs, having methyl substituents on their 4 and/or 6-position, are difficult to be desulfurized, as in the case of HDS method.¹ The rate of the present S_N2 displacement reaction depends on the concentrations of both the sulfur compounds and of the CH₃I–AgBF₄ complex.^{5,6} Thus, when a larger amount of AgBF₄ and CH₃I was added, the desulfurization of these refractory DBTs was found to be accelerated significantly.

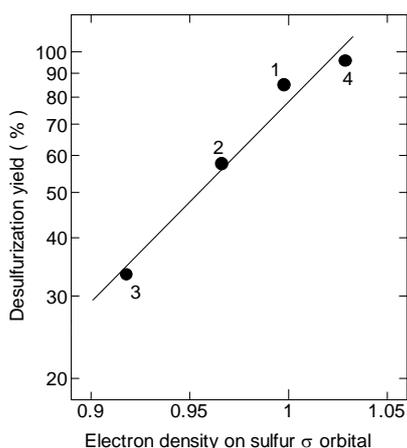


Figure 2. Correlation between the desulfurization yield for DBTs and BTs from tetradecane and the electron density on their sulfur atom. The electron density is calculated from (a) sulfur π lone-pair orbital and (b) sulfur σ lone-pair orbital. Key: **1**, DBT; **2**, 4-methyl-DBT; **3**, 4,6-dimethyl-DBT; **4**, 2,8-dimethyl-DBT.

The above process was applied to the desulfurization of light oil containing 0.78 mmol of sulfur. AgBF_4 (1.76 mmol) and CH_3I (15.7 mmol) were added to the homogeneous solution of light oil (15 mL) and CH_2Cl_2 (15 mL) under a nitrogen atmosphere and at 303 K. The resulting AgI precipitate was filtered off and washed with CH_2Cl_2 . The CH_2Cl_2 and CH_3I were then removed by evaporation. Upon cooling the resulting light oil, a dark green viscous liquid (0.1076 g) was found to adhere to the bottom of the flask, such that the light oil could therefore be recovered easily by decantation (recovery: 99.6%). By employing this procedure, the sulfur content of the light oil was thereby decreased from 0.18 wt% to 0.04 wt% for only 0.5 h of reaction time, and the 92% of sulfur removed from the light oil was contained in the precipitate. Using a sulfur-specific GC-AED analysis for the resulting light oil, it was found that 82% of the benzothiophenes and 76% of the DBTs in the light oil were desulfurized, thus suggesting that the present method can successfully desulfurize the benzothiophenes as well as DBTs. When a larger amount of AgBF_4 and CH_3I was added, the sulfur content of the light oil was decreased drastically to less than 0.002 wt%. The value of 0.002 wt% of sulfur content is below the present value (0.005 wt%), that is strictly legislated in Switzerland and Sweden, and thus the present novel method is satisfactory for application to the deep desulfurization of light oil.

The IR spectrum for the precipitate obtained from the light oil demonstrated a broad absorption band between 1000–1100 cm^{-1} which is ascribed to the counterion, BF_4^- .^{3,4} As shown in **Figure 3**, The ^1H NMR spectrum for the precipitate showed a strong resonance, due to a methyl protons adjacent to the S^+ atom at 3.00–3.60 ppm.^{2,3} These results thus indicate that the resulting benzothiophenes and DBTs, when removed from the light oil, occur as S-methylthiophenium tetrafluoroborates. The desulfurized light oil obtained by this new method exhibited the same distillation range data as the feed light oil, and thus any changes in the composition of the aromatic hydrocarbon content of the oil were found to be absent. The present method is therefore both selective and energy-saving and may be applied as a new deep desulfurization process for light oil.

The present study describes a novel desulfurization process for light oil, effected by the formation of thiophenium salts using CH_3I and AgBF_4 . The thiophenium salts produced are insoluble in nonpolar light oil, and are thus removed specifically from the light

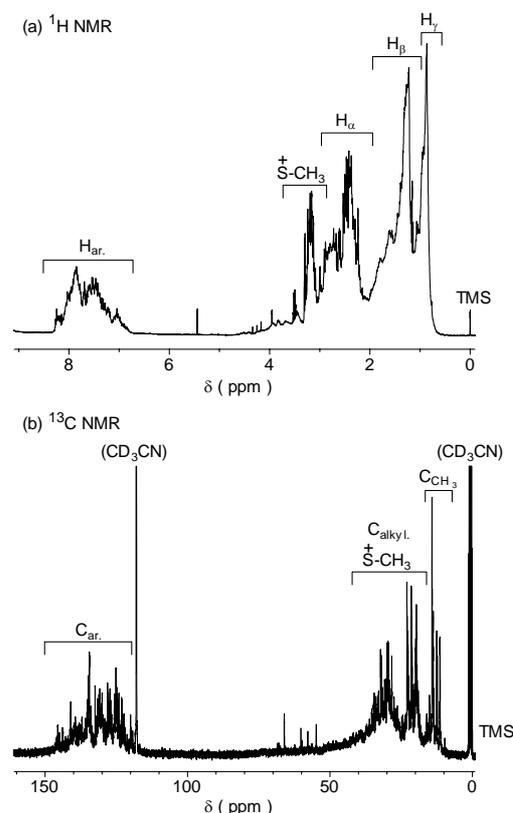


Figure 3. (a) ^1H NMR and (b) ^{13}C NMR spectra for the precipitate obtained by the desulfurization of CLO.

oil as a precipitate at room temperature conditions. It was recently found that the proposed method can also be applicable successfully to denitrogenation of light oil and desulfurization of other feedstocks, such as catalytic-cracked gasoline and vacuum gas oil.^{10–13} In this method, excess quantities of AgBF_4 and CH_3I are required for the desulfurization. Work is thus in progress to develop an integrated process, which includes the recovery of CH_3I , AgBF_4 , and CH_2Cl_2 .

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Novel Desulfurization Process for Light Oils Based on the Formation and Subsequent Adsorption of *N*-tosylsulfimides

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Introduction

Much attention has been focused on the deep desulfurization of light oil, since the sulfur oxy-acids (SO_x), contained in diesel exhaust gas are a cause of air pollution and acid rain. To protect the environment against the contamination, the sulfur level in diesel fuels is limited presently to 0.05 wt%, both in Japan and Europe. The current technology of hydrodesulfurization (HDS) can desulfurize aliphatic and acyclic sulfur-containing compounds quite adequately, when adopted on the industrial scale. The above process however is limited, when treating dibenzothiophene (DBT), especially DBTs having alkyl substituents on their 4 and/or 6-position, for the deep desulfurization of light oil.¹ Thus, the production of light oil, of very low level sulfur, inevitably requires severe high energy conditions and specially active catalysts. In the development of any alternative energy-efficient desulfurization process, a radical approach, which is not limited to conventional HDS technology, is required.

Various kinds of sulfur compounds have been reported to react with chloramine T, in hydrogen-donating solvents such as alcohol and water, to give rise at ambient temperature to crystalline powders of the corresponding *N*-tosylsulfimides.²⁻⁴ These sulfimides are highly polarized and are insoluble in nonpolar hydrocarbon solvents. Thus, such a synthetic method, if applied to the desulfurization of nonpolar light oil, might thus be able to remove the DBTs specifically from the light oil under moderate conditions. This has now been demonstrated to be realized,⁵ and thus enabling the new desulfurization method for DBTs from light oil to be presented here.

Experimental

Commercial light oil (sulfur concentration: 0.179 wt %) was used as feedstock. To clarify the relative desulfurization reactivity of the sulfur compounds, *n*-tetradecane solutions, each containing DBT (11 mmol/L), corresponding to a sulfur content of 0.05 wt %, were also employed as model light oils. Concentrations of total sulfur and of the individual sulfur compounds in light oil and of the sulfur and aromatic compounds in tetradecane were analyzed by ICP-AES, GC-AED, and GC-FID. Theoretical calculations of the electron density on sulfur atom for DBTs were performed with the PM3 semi-empirical method within the WinMOPAC ver3.0 software (Fujitsu Inc.)

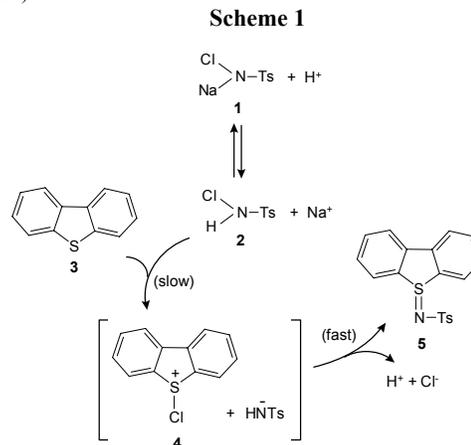
Results and Discussion

To test the feasibility of this idea, a *n*-tetradecane solution, containing DBT (11 mmol/L), was used for experiments. An alcohol solution, to which a required amount of chloramine T trihydrate was dissolved, was added to the above tetradecane solution at 323 K. In this procedure, the removal efficiency for DBT from tetradecane, following 3 h of reaction, was however only 5%, as shown in **Table 1** (entry 1). As reported⁴ and shown in **Scheme 1**, the sulfimide **5** is formed via the chlorination of the sulfur atom for the sulfur compound **3** by the free-state chloramine T **2**, produced by the hydrolysis of the chloramine T **1**. The rate of the chlorination is thus accelerated with decreasing pH of the solution, owing to the

Table 1. Desulfurization Yield of DBT from Tetradecane Following the Reaction with Chloramine T under Different Conditions^a

entry	alcohol	AcOH (mL)	chloramine T (mmol)	desulfurization (%)
1	MeOH	—	1.1	5.0
2	MeOH	1	1.1	70.6
3	EtOH	1	1.1	1.5
4	<i>i</i> -PrOH	1	1.1	6.7
5	MeOH	1	5.5	98.5
6	MeOH	1	2.75	95.2
7	MeOH	2	1.1	> 99.9

^a reaction temperature: 323 K, reaction time: 3 h, tetradecane volume: 50 mL, alcohol volume: 10 mL, initial DBT concentration in tetradecane: 11 mmol/L (0.55 mmol).



acceleration of the hydrolysis of **1**. The desulfurization of DBT, when a small amount of AcOH was added into the reaction mixture, was accelerated significantly (entry 2). The addition of the AcOH affects well for the desulfurization when used with MeOH, but is ineffective when used with the other solvents such as EtOH and *i*-PrOH (entries 3 and 4). This is because the hydrogen-donation ability of the latter two solvents is lower than that of MeOH. The desulfurization of DBT was also accelerated with increasing the concentrations of chloramine T and AcOH (entries 5–7). Both MeOH and chloramine T are insoluble in the nonpolar tetradecane, such that the resulting tetradecane is recovered easily using separation funnel. When an equal volume of water as that of the MeOH was added into the resulting MeOH solution, the *N*-tosylsulfimide of the DBT precipitated on the bottom of the flask, thus suggesting that the sulfimide formed is removed successively into the MeOH solution during the reaction.

The above procedure was then tested for the desulfurization of methyl-substituted DBTs, which are key compounds in the HDS technology.¹ In this process, as shown in **Figure 1**, the desulfurization rates for 4-methyl- and 4,6-dimethyl-DBT from tetradecane were higher than that of nonsubstituted DBT. This tendency differs completely from that obtained by the HDS method.¹ As shown in **Scheme 1**, the rate-determining step for the present reaction is the chlorination of the nucleophilic sulfur atom for the DBT **3** by the free-state chloramine T **2**. Semiempirical MO calculation showed that the electron density on the sulfur atom for DBTs lies in the order 4,6-dimethyl- (5.7597) > 4-methyl- (5.7586) > DBT (5.7577), which agrees well with the actual desulfurization reactivity (**Figure 1**). The result suggests that the rate of the chlorination depends on the electron density (nucleophilicity) on the sulfur atom for DBTs, and as a result, methyl-substituted DBTs, having high electron density, are desulfurized more easily than the

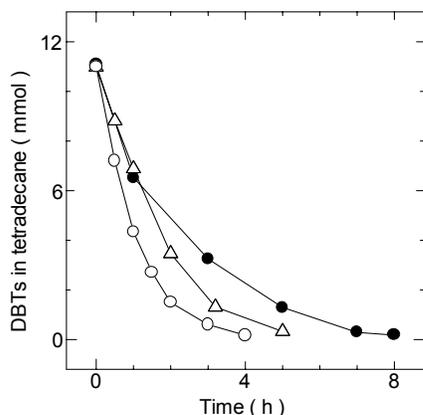


Figure 1. Time-course variation in the concentration of (●) DBT, (□) 4-methyl-DBT and (○) 4,6-dimethyl-DBT in tetradecane. Temperature: 323 K, tetradecane volume: 50 mL, MeOH volume: 10 mL, AcOH volume: 1 mL, initial DBTs content in tetradecane: 11 mmol/L (0.55 mmol).

Table 2. Variations in the Sulfur Concentration of Light Oil Following (a) Reaction with Chloramine T and (b) Subsequent Addition of Solid Adsorbents^a

Entry	(a)		(b)	
	chloramine T (mmol)	sulfur content (wt%)	adsorbent (g/ml-oil)	sulfur content (wt%)
1	4.65	0.099	–	–
2	11.6	0.079	0.2 (Al ₂ O ₃) 0.2 (SiO ₂)	0.054 0.050
3	23.3	0.066	0.3 (SiO ₂)	0.048

^a reaction temperature: 323 K, reaction time: 10 h, light oil volume: 50 mL, MeOH volume: 50 mL, AcOH volume: 2 mL, initial sulfur concentration of light oil: 0.190 wt% (2.47 mmol).

nonsubstituted DBT.

The above process was then applied to the desulfurization of light oil. The MeOH solution (50 mL) containing various amount of chloramine T was then added to the light oil (50 mL) in the presence of 2 mL AcOH, and was stirred at 323 K. Upon addition of water to the resulting MeOH solution, a yellow-white solid precipitate adhered to the bottom of the flask. As shown in **Figure 2b**, the IR spectrum for the precipitate demonstrated two intense absorption bands at 1180 and 1300 cm⁻¹ owing to the sulfonyl group and also a small band at 980 cm⁻¹ owing to S–N bond for the sulfimides. The spectrum is similar to that for *N*-tosylsulfimide of DBT (**Figure 2a**), thus indicating that the sulfimides, formed during the reaction, are removed successfully from the light oil into the MeOH solution. As shown in **Table 2**, the sulfur content of the light oil was decreased with increasing the chloramine T concentration. However, the deep desulfurization (0.05 wt %) was hardly achieved, even in the presence of 10-fold molar excess of chloramine T based on the initial sulfur concentration of the feed light oil (entry 3). The desulfurization yields obtained are significantly smaller than those as expected from the data for the model light oil, as shown in **Figure 1**.

The actual light oil contains a large amount of DBTs, with several types of hydrophobic alkyl substituents on the molecule, and the polarity of the DBTs is decreased with increasing the carbon number of the substituents.⁶ The low desulfurization efficiency of the light oil is thus probably because the low polarity sulfimides of DBTs having large carbon number of substituents, formed by the reaction with chloramine T, are not removed into the MeOH solution

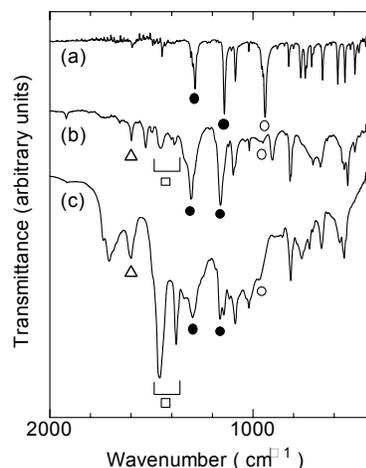


Figure 2. IR spectra for (a) *N*-tosylsulfimide of DBT, (b) precipitate obtained by the addition of water to the MeOH solution following the reaction of light oil with chloramine T, and (c) adsorbed material obtained by the addition of silica gel to the light oil following the reaction with chloramine T. (○) S–N bond, (●) sulfonyl group, (□) aliphatic hydrogen (C–H) and (Δ) aromatic hydrogen (C–H).

but remain in the resulting light oil. Since the sulfimides have a higher polarity as compared to the other constituents of the light oil, they might be removed by the addition of solid adsorbents, such as aluminum oxide and silica gel. As shown in **Table 2** (entry 2b), the sulfur concentration of light oil was actually decreased by the addition of the adsorbents, with the deep desulfurization (0.05 wt %) being achieved successfully. As shown in **Figure 2c**, the adsorbed materials showed absorption bands owing to the sulfonyl group and the S–N bond for sulfimides, respectively, as also for the spectrum of the precipitate (**Figure 2b**). The spectrum for the adsorbed material also showed larger absorption band at 1620 cm⁻¹, owing to alkyl group, as compared to that obtained for the precipitate, indicating that the sulfimides of the DBTs, having large carbon number of alkyl substituents, are adsorbed successfully.

The present study describes a novel desulfurization process for light oil, based on the removal of *N*-tosylsulfimides produced by the reaction of sulfur compounds with chloramine T. The deep desulfurization was achieved successfully at ambient temperature conditions. The refractory DBTs in the current HDS process are desulfurized easily by the present process, thus showing that the present process is both energy-saving and effective as a new deep desulfurization process for light oil. The sulfimides have been reported to have an antimicrobial, diuretic and hypotensive properties on tumor growth and activity as antidepressants and stimulants of the central nervous system. It may thus be interesting to use the recovered sulfimides from the desulfurization process, as novel materials for medicinal supplies.

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OCTANE NUMBER AND ANILINE POINT OF PETROLEUM FUELS

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Introduction

The quality of various petroleum fuels depends on their composition and types of hydrocarbons present in the mixture. Octane number is one of the characteristics of spark-ignition engine fuels such as gasoline and jet fuel. This number indicates anti-knock characteristic of a fuel and strongly depends on the hydrocarbon type. Octane number of fuels can be improved by addition of oxygenates such as TEL, MTBE or TAME. Octane number of fractions without additives is usually referred to as clear octane number. These additives are normally hazardous to the environment and for this reason methods to improve octane numbers through processes such as alkylation are used in refineries. Standards set in many countries and car manufacturers require a minimum octane number of 95. In Europe superstar gasoline should have minimum octane number of 98. Two commonly used octane numbers are research octane number (RON) and motor octane number (MON). RON is measured under low speed condition by ASTM D908 while the MON is measured under high speed condition by ASTM D 357 test method. The difference between RON and MON is called sensitivity and fuels with lower sensitivity are desirable. Conducting such experimental tests on every motor fuel is prohibitive in both time and cost. There are very few predictive methods for calculating octane number. Nelson methods are in the form of graphical correlations either in terms of boiling point and Watson characterization factor for naphtha fractions or in terms of boiling point and paraffin weight percent [1]. These methods have limited range of application and are not suitable for computer applications plus they produce high deviations in excess of 8 octane numbers. Other predictive methods that couple regression analysis with results from gas chromatography [2] or nuclear magnetic resonance [3] are also prohibitive in both time and cost which makes them unattractive for quick online analysis.

Aniline point (AP) is another characteristic of petroleum fractions that indicates the degree of aromaticity of hydrocarbon mixtures. Aniline point is defined as the lowest temperature at which equal volumes of aniline and the sample become completely soluble. As amount of aromatics in a petroleum fraction increase the aniline point decreases. Therefore, the aniline point is a parameter that is highly related to the hydrocarbon types in petroleum fractions. Aniline point is a useful parameter in calculation of heat of combustion, diesel index and hydrogen content of petroleum fuels. For non fuel products such as solvents aniline point is usually specified to quantify their effectiveness. Linden used the method of characterization of Watson and Nelson to develop a simple correlation for prediction of aniline point in terms of boiling point and API gravity [4]. However, the correlation was originally developed based on only 37 samples.

Most recently a set of data on crude assay and specification of petroleum products from around the world are collected and published by Oil and Gas Journal [5]. These data include boiling point, API gravity (or specific gravity), hydrocarbon type composition, kinematic viscosity, research and motor octane numbers, aniline point, flash, pour and cloud points for large number of various petroleum products. Although not all these specifications are given for a single fraction, but amount of information available

for each characteristic is sufficient to develop new predictive method or to re-evaluate the existing correlations. The main purpose of this paper is to use this data bank to develop new procedures for prediction of RON, MON and AP of various fuels with minimum information available.

Technical Development

Clear octane number of some pure hydrocarbons generally found in naphtha and gasoline are given in the API-TDB [6]. For the same carbon number or boiling point, octane number of n-alkanes (n-paraffins), 2-methylalkanes (iso-paraffins), n-alkylcyclopentanes (naphthenes) and n-alkylbenzenes (aromatics) vary significantly. As shown in Figure 1, octane number of aromatics is generally higher than n-paraffins, iso-paraffins and naphthenes.

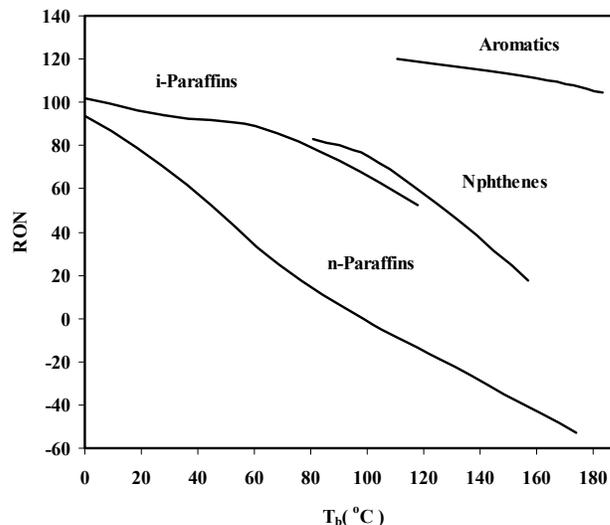


Figure 1. Research Octane Number of Pure Hydrocarbons from Different Families.

Even different types of iso-paraffins have different octane numbers. However, most petroleum fractions are olefin free and the main hydrocarbon families present in a fuel are n-paraffins (NP), iso-paraffins (IP), naphthenes (N) and aromatics (A). Clear research octane number of these homologous hydrocarbon families have been correlated to normal boiling point through the following relation:

$$\text{RON} = a + b(T) + c(T)^2 + d(T)^3 + e(T)^4$$

where $T = T_b/100$ in which T_b is the normal boiling point in °C and coefficients a-e are given in Table 1. To calculate RON of a fuel it is assumed that the mixture contain four model compounds from n-paraffins, iso-paraffins, naphthenes and aromatics families. Then the RON of the mixture is calculated as:

$$\text{RON} = x_{\text{NP}}(\text{RON})_{\text{NP}} + x_{\text{IP}}(\text{RON})_{\text{IP}} + x_{\text{N}}(\text{RON})_{\text{N}} + x_{\text{A}}(\text{RON})_{\text{A}}$$

where x_{NP} , x_{IP} , x_{N} and x_{A} are volume fractions of n-paraffins, iso-paraffins, naphthenes and aromatics groups, respectively. $(\text{RON})_{\text{NP}}$ is the clear RON of a hydrocarbon from n-paraffin family whose boiling point is the same as the mid-boiling point or ASTM D86 temperature at 50% point of the fraction and can be calculated from Equation (1). Similarly values of $(\text{RON})_{\text{N}}$ and $(\text{RON})_{\text{A}}$ are calculated from Equation (1) using boiling point of the mixture.

Table 1. Coefficients for Equation (1) for Estimation of RON

Hydrocarbon Family	a	b	c	d	e
n-Paraffins	92.809	-70.97	-53	20	10
iso-Paraffins					
2-Methylpentanes	95.927	-157.53	561	-600	200
3 - Methyl-pentanes	92.069	57.63	-65	0	0
2,2 - Dimethyl-pentanes	109.38	-38.83	-26	0	0
2,3 - Dimethyl-pentanes	97.652	-20.8	58	-200	100
Naphthenes	77.536	471.59	-418	100	0
Aromatics	119	144.8	-12	0	0

However, to calculate $(RON)_{IP}$, Equation (1) should be used for four different iso-paraffin families given in Table 1 and an average value (also shown in figure 1) is used for $(RON)_{IP}$. This is to account for the large differences in octane number for the various iso-paraffins in the gasoline fraction. When the amount of iso-paraffins is not reported, x_{NP} and x_{IP} are taken equal to half of volume fraction of paraffins. When experimental data on the composition are not available it can be estimated through methods proposed by Riazi et. al [7-10]. These correlations require refractive index, density and molecular weight all of which can be estimated from mid-boiling point and specific gravity of a petroleum fractions using methods proposed by Riazi and Daubert [6,11,12].

Once clear RON is known, clear MON can be estimated from the following correlation derived from the correlation proposed by Jenkins [13] for olefin free fuels.

$$MON = 22.5 + 0.83 RON - 20.0 SG$$

where SG is the specific gravity of the fuel at 15.5 °C. Summary of results for calculation of RON and MON using both experimental and predicted composition are given in Table 2 where AAD and MAD are average absolute and maximum absolute deviations, respectively. To develop a predictive method for the aniline point of petroleum fractions, we use parameters that quantify the amount of aromatics in a hydrocarbon mixture. It has been shown that parameters R_i and SG are suitable for prediction of aromatic content of petroleum fractions

where R_i is defined as:

$$R_i = n - d / 2$$

in which n is the refractive index and d is the liquid density in g/cm^3 both at 20 °C. These two parameters can be estimated from boiling point and specific gravity through available relations [11]. Based on a data bank consisting of 300 data points on aniline point of petroleum fractions from crude oils from around the world [5], the following relation is proposed to predict the aniline point.

$$AP = -9805.269 + 711.85761(R_i) + 9778.7069(SG)$$

where AP is in °C. This equation is compared with the following relation in terms of T_b and API gravity developed by Linden [4]:

$$AP = 0.4(API)T_b^{1/3} + 0.317T_b - 298$$

Table 2. Summary of Results for Prediction of RON and MON

	No. of Data Points	Method	API Gravity Range	RON Range	RON		MON	
					A A D	M A D	A A D	M A D
1	19	NP-IP-N-A	51 - 87	26 - 74	4	11	5	12
2	97	P-N-A	44 - 88	30 - 80	6	19	1	7
3	100	Pred. P-N-A	44-88	30-80	7	22	--	--
4	18	Nelson 1	58 - 78	45 - 73	5	19	--	--
5	39	Nelson 2	47 - 74	18 - 72	6	14	--	--

where AP is in °F and T_b is in °R. For 300 petroleum fractions with AP range of 45 to 106 °C and API gravity range of 14 to 56, the proposed method gives an AAD of 2.5 °C (AMD of 7 °C) while the Linden method gives AAD of 6.5 °C (AMD of 28 °C) for the same fractions. Results presented in this paper show that the proposed methods are capable of estimating octane number and aniline point of petroleum fuels with a wide range of data points from oils from around the world with accuracy greater than similar existing methods. The proposed methods require minimum information on boiling point and specific gravity, however, when additional data are available from experimental measurements the proposed methods predict RON and aniline point with higher degrees of accuracy.

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PLANAR CHROMATOGRAPHIC SEPARATION FOR THE RAPID DETERMINATION OF HIGH MASS MATERIALS IN COAL DERIVED LIQUIDS

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Introduction

Previous work [1-6] has shown that fractionation of coal liquids is an essential first step in revealing the presence of large molecules. The preferred separation method used was planar chromatography, where the large molecules tend to show little mobility in common solvents such as pyridine or tetrahydrofuran. The separated bands (fractions) of coal-derived samples show colours related to their mobility: the most mobile are yellow or orange, the partially mobile brown; the immobile materials were close to black. To characterise these samples, we used SEC with 1-methyl-2-pyrrolidinone (NMP) as eluent, UV-fluorescence spectroscopy (UV-F) and several mass spectrometric methods (heated-probe-ms, gc-ms and MALDI-ms). SEC in NMP eluent has been shown [2,7] to operate by a predominantly size dependent mechanism, with only low level interference from surface effects. UV-fluorescence spectra of unfractionated samples were mostly similar to the spectra of the lowest molecular weight fraction, most mobile in PC. Compared with the more mobile fractions, the fluorescence of the apparently higher molecular mass fractions (least mobile) normally showed lower quantum yields, with pronounced shifts towards red (longer) wavelengths [1-4]. These materials are not generally observed without fractionation.

Mass spectrometric methods such as heated probe-ms and gc-ms can only detect those molecules able to evaporate in the mass spectrometer vacuum (probe-ms) or undergo gas chromatographic separation (gc-ms); in general such molecules are small, <300 u for gc-ms and <600 u for probe-ms. This paper describes the separation by Planar Chromatography of a low temperature tar and gives some results on the larger molecular mass materials.

Experimental

The sample was a low temperature coal tar from the Coalite process, a low temperature distillation of coal to produce a smokeless solid fuel. The elemental composition of the sample was C 82.3%, H 7.83%, N 0.91%; it is expected to show much less thermal degradation than a pitch.

Planar chromatography. Preparative plates, 20 x 20 cm, coated with silica gel (thickness: 1000 μm) were used. The plates were washed in pyridine before the sample was applied as a slurry in pyridine. Developments were achieved after equilibration of the vapour for at least 30 min using first pyridine and subsequently, acetonitrile. The plates were dried between developments. Bands of silica coated with the relevant material were scraped off and extracted using cold NMP with ultrasonic agitation. The solutions were examined by SEC and by UV-fluorescence spectroscopy.

Size exclusion chromatography [1-8]. SEC using NMP as eluent was carried out using a ('Mixed-D') column, packed with 5- μm polystyrene/polydivinylbenzene beads, operated at a temperature of 80 °C and a flow rate of 0.5 ml min⁻¹. The whole tar sample and the fractions recovered from planar chromatographic separation were examined by SEC using UV-absorbance detection at 280, 300, 350,

370 and 450 nm. The sample solution contained less than 2% by weight of sample to avoid band broadening caused by the overloading of the excluded region of the column.

UV-fluorescence spectroscopy [9] The Perkin-Elmer LS50 luminescence spectrometer was set to scan at 240 nm min⁻¹ with a slit width of 2.5 nm; synchronous spectra were acquired at a constant wavelength difference of 20 nm. The spectrometer featured automatic correction for changes in source intensity as a function of wavelength. Synchronous spectra were obtained in NMP. Solutions were diluted with NMP to avoid self-absorption effects: dilution was increased until the fluorescence signal intensity began to decrease.

Results and discussion

The 'whole' sample: SEC chromatograms of the sample are shown in Figure 1 and the UV-fluorescence spectrum in Figure 2. Two groups of peaks are observed in SEC, the first in the 'excluded' region from 8-11 min and the other in the resolved region from 16-23 min. The UV absorbance at 280 nm was the most intense, with the relative intensities at the other wavelengths decreasing to 450 nm, suggesting the predominance of smaller PAH groups. The result is consistent with this low temperature tar having been produced by the distilling of lighter products from the parent coal. The valley of zero intensity between 11-16 min might indicate a change of structures possibly to three-dimensional structures at a polystyrene mass equivalent of about 4,000 u. The synchronous UV-fluorescence spectrum indicates a wide range of chromophores extending at low intensity up to 500 nm.

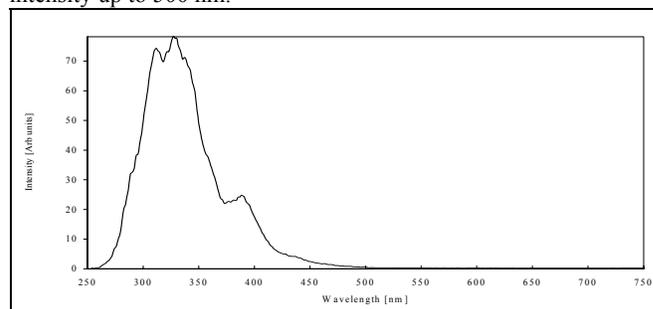


Figure 1. SEC of whole tar at 5 wavelengths 1:280, 2:300, 3:350, 4:370, 5:450 nm

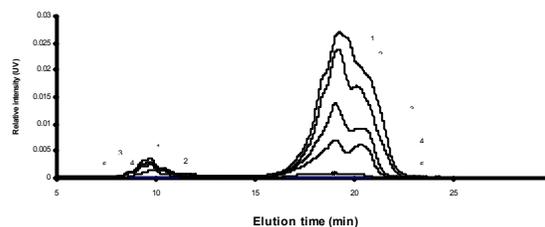


Figure 2. Synchronous UV-fluorescence of whole tar

Fractionation by planar chromatography: Quantitative planar chromatography is difficult to achieve since the addition of the sample as a slurry to the plate and the very small quantities of material recovered were not easily quantified. Sample may be lost because of incomplete removal by NMP of sample material from the coated silica, scraped off the plate. The silica containing the band of material immobile at the origin remained coloured after extraction by NMP. Furthermore, solvent removal from sample fractions by distillation under vacuum (NMP bp 202 °C), would lead to loss of some light ends from the samples. This can be seen by comparing Figures 1 and 3, where the low-mass cut-off extends to a later time in

Figure 1, compared to Figure 3. The partly resolved peak after 20 min in Figure 1 is also more clearly resolved in Figure 3. Another problem arises from the difficulty of completely removing NMP from the samples. NMP and some of its pyrolysis products could be identified in the pyrolysis-gc-ms spectra of the sample fractions [3,4,6]. However, the advantage of the method is the rapidity of operation, relative cheapness and the ability to observe visually the presence of material immobile at the origin. In our experience, this immobile material always represents large molecular mass material, which is liable to be lost either in the injection port (of a gc) or on the column packing (hplc) in solvents other than NMP.

SEC profiles of the fractions separated by planar chromatography are shown in Figure 3 with detection at 350 nm. The profile of the acetonitrile soluble fraction was similar to that for the whole sample. The 'immobile' fraction was in relatively dilute solution and signal to noise levels were low. For all fractions in Figure 3, an 'excluded' peak may be seen, indicating that each fraction contained *some* apparently high mass material, with a shift towards a greater proportion of 'excluded' material with diminishing mobility. Because of the increasing polarity of the solvent from acetonitrile to pyridine, this shift may also correspond to increasing polarity of the solute molecules in the retained region of SEC.

The synchronous UV-fluorescence spectra of the fractions are shown in Figure 4. The fraction mobile in pyridine showed close similarity to the acetonitrile mobile fraction, indicating that both materials contain similar chromophores. In contrast, the immobile fraction showed a prominent peak at 400 nm and an obvious shift to longer wavelengths. The spectra are height normalised; fluorescence of the pyridine 'immobile' material was of very low intensity. Also the weak fluorescence of the immobile fraction extends to longer wavelengths than is apparent in Figure 2. These data indicate that the chromophores in the heaviest fraction are more larger than in the two mobile fractions. The data contrast with those of a coal tar pitch [4] and a coal digest [3], where the pyridine mobile material showed a small shift to longer wavelengths compared with the acetonitrile mobile fraction, but not such a large shift as the pyridine immobile fraction. UV-F cannot measure molecular mass or size, but can indicate relative changes in chromophores, which in combination with data from SEC, suggests trends in structural changes with molecular size.

The excluded material observed in the present sample and its fractions appears to be present in most coal derived materials, biomass tars and petroleum vacuum residues. This material does not appear composed of aggregates of small polar molecules. Evidence for this comes from the UV-F and SEC data – indicating *differences in structure* with increasing apparent molecular mass. In addition, pyrolysis-gc-ms data [3,4,8] of the present tar, a pitch and a coal extract, have shown that the pyridine immobile fractions produce no detectable fragments on pyrolysis at 770°C, while the pyridine mobiles produced relatively weak signal compared to acetonitrile mobiles. The latter gave evidence of many well known aromatics in the mass range below 300 amu.

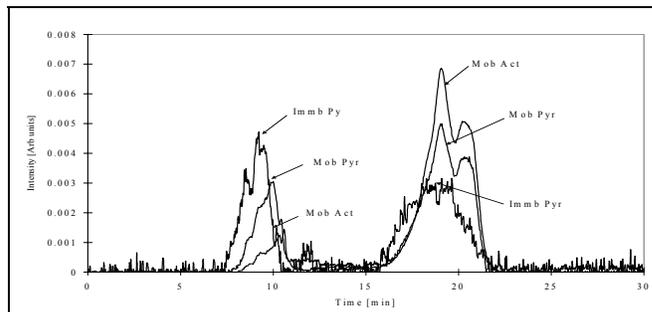


Figure 3. SEC of planar chromatography fractions

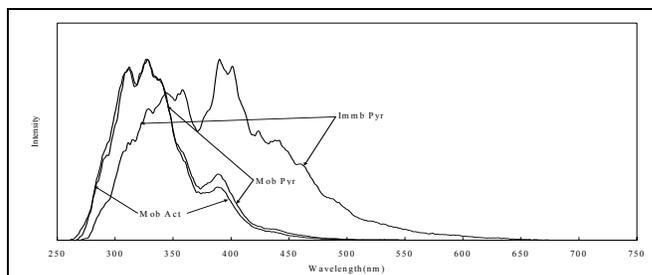


Figure 4. Synchronous UV-fluorescence spectra of fractions

Conclusions

Thin layer chromatography provides a rapid and inexpensive fractionation method for detecting large molecular mass material. Mass balances cannot easily be estimated because of the small quantities of material involved. Samples can then be made available for a wide range of structural characterization tests.

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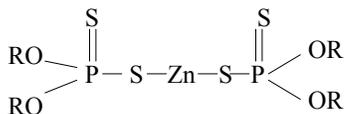
PREPARATIVE ISOLATION AND CHARACTERIZATION OF ZINC DIALKYL-DITHIOPHOSPHATES FROM COMMERCIAL ANTIWEAR ADDITIVES

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Introduction

Improvement of lubricant oil performance is achieved by additivition with taylor-designed products for specific purposes¹⁻². Zinc Dialkyl-Dithiophosphates (ZnDTP) exert antiwear actions over diverse components from internal combustion engines. Their synthesis comprises the generation of dithiophosphoric acid from P₂S₅, reaction of the acid with one alcohol and then with ZnO. Their structural formula is:



The efficiency, thermal stability and cost of ZnDTP's depend on the chosen alcohol². Derivatives can be easily identified by typical vibrational frequencies for the P-O-C bond in the infrared spectrum (IR)³. P-O-C moieties with R groups from primary alcohols display bands at 1000 cm⁻¹, from secondary at 980 cm⁻¹ and aryls at 920 cm⁻¹.

Preparative isolation of ZnDTP's has been reported by dialysis⁴⁻⁵, thin layer chromatography^{4,6-7}, open column liquid chromatography^{3,5,8}, high performance liquid chromatography (HPLC)^{3,4,9-10} and gel permeation chromatography¹¹. Supercritical fluid chromatography has been reported for analytical scale separation¹².

Spectrometric techniques are useful for determination of the distribution of ZnDTP mixtures. Mass spectrometry allows determining the alkyl length of the R substituents¹³. ZnDTP direct separation and characterization has been reported by coupled liquid chromatography-mass spectrometry¹⁴ and by selective ionization mass spectrometry without prior separation¹⁵. Nuclear magnetic resonance spectrometry has proven useful for elucidating ZnDTP intermolecular complexation and interaction between solvents and these organometallic compounds as well¹⁶.

Chemical derivatización and analysis of reaction products is another strategy followed for the characterization of ZnDTP. Lithium Aluminum Hydride gives origin to the original alcohols used during the synthesis of ZnDTP¹⁷. Alkyl-iodides are generated by the action of HI¹⁸. Dialkyl-methylthiophosphates are the products derived from the action of CH₃I¹⁹.

The objective of this work was to develop a fast, preparative and automated methodology for isolation of ZnDTP compounds from commercial additive packages. This was achieved by HPLC, allowing to quantify the total amount of these antiwear components in each received production batch. Further, isolated ZnDTP concentrates were characterized by IR and reverse phase HPLC for qualitative monitoring commercial ZnDTP batches employed for the formulation of end lubricant products.

Experimental

HPLC system and operating conditions for the preparative isolation of ZnDTP from commercial additives. The HPLC schematic is presented on Figure 1. A Waters 590 EF programmable pump delivers solvents and controls two pneumatic actuated valves, viz, a solvent select valve and a six-port switching valve used for

sample solution delivery. Sample solution was placed inside an Altex gas-tight glass column connected to a pressurized (5 psig) nitrogen source used for pushing the solution into the sampling loop. Typically, 500 mg were injected on each separation. A DVSP-4 digital valve sequence programmer from Valco commands the actuation of two pneumatic valves, viz, a Rheodyne 7010 injection valve provided with a 1 mL loop and a 4-port backflush N6 valve from Valco. A Glenco 5480 Uv-Vis detector set at 254 nm and a Knauer 98:00 RI detector were used for elution monitoring. Detector signals were registered with a Linear chart recorder. Separated fractions were collected with a Glenco 410 programmable fraction collector, provided with a 6+1 port Rheodyne 7060 distribution valve.

A bank of three silica columns connected in series was used to carry out the separations. The columns were slurry packed at 12000 psi with the aid of a Haskell air driven pump. Adsorbosil LC (10 μm, irregular) from Alltech was used as packing material. Adsorbent drying prior to packing was achieved inside an oven kept at 100°C (24h). Column dimensions were 25cm x 1cm.

Base oils (excipient) were eluted during 30 min with a mixture n-C6/CCl₄: 75/25: vol. in forward flow set at 5 mL/min. ZnDTP components were recovered under backflush (B.F) with CHCl₃ at 14 mL/min, during a 10 min period. Column regeneration with the initial solvent mixture was achieved by delivering the solvent at 16 mL/min during a period of 10 min. The whole separation was achieved in 50 minutes. Pooling of fractions separated during successive separations was possible. The 590 EF Waters pump was used to generate the pulses commanding the whole automated separation and collection sequence brought by the valve actuator/fraction collector.

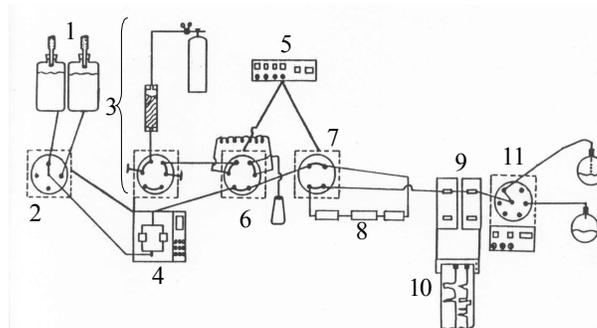


Figure 1. Preparative HPLC Schematic. 1: Eluents. 2: Solvent proportioning valve. 3: Sample delivery device. 4: Solvent pump. 5: Programmable valve controller. 6: Injection valve. 7: Backflush valve. 8: Column bank. 9: HPLC detectors. 10: Chart recorder. 11: Fraction collector.

Infrared spectrophotometry. IR spectra were acquired on a Pye-Unicam SP 1100 spectrometer in the range from 4000 to 400 cm⁻¹. Small amounts of neat separated base oils or isolated ZnDTP concentrates were compressed between a couple of KBr windows.

Reversed phase HPLC of ZnDTP concentrates. Isolated ZnDTP concentrates were dissolved in CH₂Cl₂ and injected in a stainless steel column (slurry packed at 12000 psig with the aid of a Haskell pneumatic pump). Spherical octadecyl derivatized silica (RPC18) of 5 μm from E-Merck was the column adsorbent. The silica was further end-capped by reaction with trimethylchlorosilane. Sample injection was performed with a Rheodyne 7410 valve provided with an internal built loop of 1 μL. Elution with CH₃CN at 250 μL/min was carried out with a Waters 590EF pump. Uv detection at 240 nm was achieved with an LDC Spectromonitor II

HPLC detector. Chromatographic signals were digitalized with an A/D converter and feed to an HP-1000 computer provided with a LAS (laboratory automation system).

Results and Discussion

Chromatographic conditions for the preparative separation and isolation of excipient (base oil) from active compounds (ZnDTP) present in commercial antiwear additives, were found during this study. Separations can be run in a reasonable time span (50 min). However, the most important advantage of the developed methodology lies on the fact that columns are reusable, aspect verified with one column bank used during a 1 month period for ca. 100 sample injections. A typical separation is presented on **Figure 2**. The preparative isolation gave the total amount of ZnDTP contained in each commercial batch of additive. This value is an important input for quality assurance for the end lubricant products. Further, the availability of mg-g quantities of the active compounds, allowed to characterize these materials in greater detail. Also, the physical availability of grams of these materials permitted their use in pilot studies conducted with combustion motors.

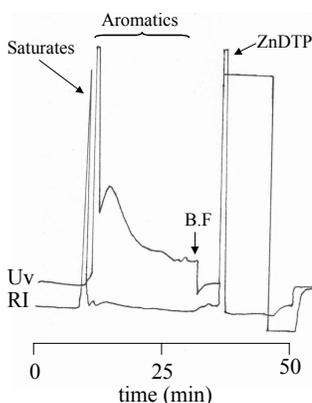


Figure 2. Typical chromatogram for the preparative separation of the active ZnDTP components from a commercial antiwear additive.

The repeatability of the preparative separations can be estimated by triplicate results for one sample, presented on **Table 1**. It was deemed reasonable for the aimed purposes of the study. The yields of ZnDTP components for some commercial additives can be appreciated on **Figure 3**. On the same figure, fraction recoveries are included. Recoveries were deemed good, averaging 98.4 ± 1.4 wt%.

Table 1. Repeatability for the HPLC Separation of a Commercial ZnDTP Additive (P5).

Run	% wt Oil	% wt ZnDTP	Recovery (%wt)
1	21.9	75.3	99.2
2	23.7	74.7	98.4
3	23.4	77.2	100.6

Separation of gram amounts of ZnDTP required the automated operation of the HPLC system. This commonly was carried out during overnight runs that allowed collecting ca. 5g of active materials in 12 separation cycles. **Figure 4** presents the initial portion for a typical chromatographic display of an automated separation sequence.

Characterization of ZnDTP mixtures can be practiced following different approaches, as cited in the introduction. With the preparatively isolated materials obtained in this work, qualitative

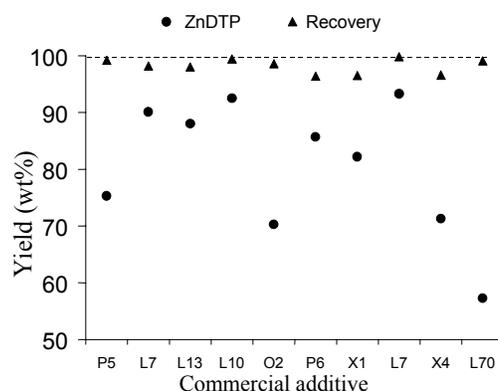


Figure 3. Yield of ZnDTP for commercial antiwear additives and recovery of separated fractions during the preparative HPLC isolation.

characterization was performed both by IR and reverse phase HPLC. On **Figure 5**, IR spectra of one oil fraction and three active (ZnDTP) fractions are presented. Absence of ZnDTP characteristic signals near 1000 cm^{-1} can be evidenced for the oil fraction, guarantee an efficient separation. IR spectra in the frequencies comprised between $1600\text{-}600 \text{ cm}^{-1}$ can be considered as fingerprints for each ZnDTP mixture. The examples included in **Figure 5** illustrate this aspect. Partial contribution of primary/secondary alkyl or aryl alcoholic R substituents can be deduced from the spectra, according to the literature assignments³ for the P-O-C band near 1000 cm^{-1} .

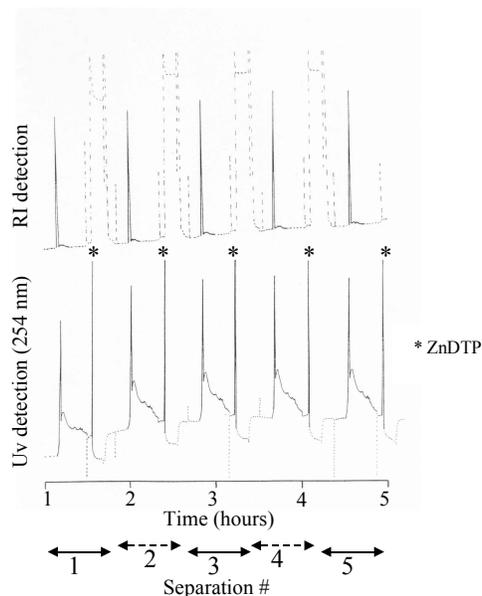


Figure 4. Chromatograms for a typical automated HPLC separation sequence of a commercial ZnDTP additive.

Reverse phase HPLC fingerprintings of ZnDTP active mixtures isolated from commercial additives are illustrated with the examples presented on **Figure 6**. The technique allows differentiating among diverse commercial ZnDTP. Also, subtle differences in mixture distributions can be detected among diverse batches of the same product, as evidenced with the example included in the same figure.

As a final remark it is to be said that the HPLC preparative separation methodology has been successfully applied for the isolation of the medium polarity components included in multipurpose additive mixtures used in lubricant products. It fails for high polarity compounds like sulphonates, which remain irreversibly adsorbed over the packing material. Recently, environmental constraints made CCl_4 disappear from the market. We have substituted it by MTBE (Methyltertbutylether). Equivalent polarity mixtures have been prepared following the procedures described by Snyder and Kirkland²⁰. With the n-C6/MTBE eluent, successful separations of end product lubricants have been carried out for exci-

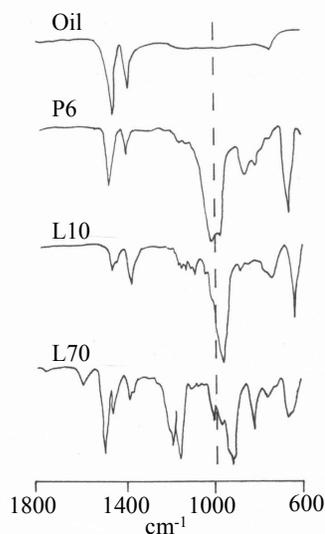


Figure 5. Infrared spectra for one separated oil fraction and for three active ZnDTP isolated active components.

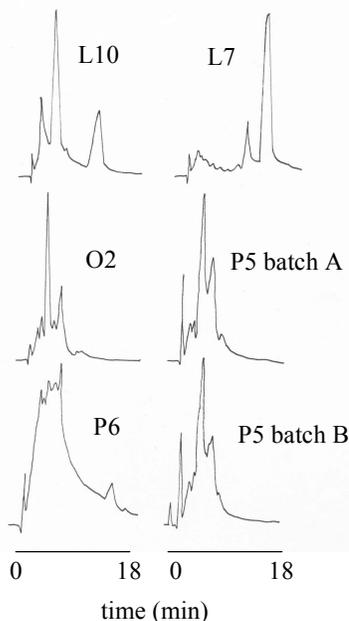


Figure 6. Reverse phase HPLC fingerprinting of isolated ZnDTP active components from commercial antiwear additives.

ipient isolation. However, no attempts have been made to recover the additives in these cases since base oils were the targeted analytes.

Conclusions

A preparative and automated HPLC separation methodology was developed for isolation of ZnDTP components from commercial antiwear additives. The methodology relies on rugged silica columns, which can be reused for long periods of time (months). Preliminary estimations suggest that separation repeatability and fraction recoveries were good.

Qualitative characterization of isolated ZnDTP mixtures was easily achieved by IR spectrophotometry and by HPLC. IR can assess the gross nature of ZnDTP alcoholic moieties. Fingerprints of diverse commercial mixtures and even subtle differences among diverse batches of the same product are obtained by reverse phase HPLC.

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QUANTITATIVE DETERMINATION OF ALKANES, NAPHTENES, TOTAL AROMATICS AND HEAVY PACS IN GAS OIL BY NORMAL PHASE HPTLC WITH UV AND FLUORESCENCE SCANNING DENSITOMETRY

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Introduction

Determination of hydrocarbon types is a classical analysis in petroleum industry^{1,2}. Determination of the contents in polycyclic aromatic compounds (PACs) and naphthenes in gas oil is especially important with regard to the development of hydrotreating processes (e.g., HDS), environmental requirements, and quality of fuels.

Generally, aromatic compounds in gas oil are determined by high performance liquid chromatography (HPLC) with refractive index detection³. However, this determination presents some technical drawbacks such as low sensitivity, and uncertainties in the calibration step. Moreover, determination of saturates is not directly carried out, but by difference after aromatics determination.

The purpose of this work has been to develop improved methods for separation and quantitative determination of hydrocarbon types (e.g. alkanes, naphthenes, total aromatics and heavy PACs) in middle distillates, based on normal-phase, high performance thin layer chromatography (HPTLC) with UV and fluorescence scanning densitometry. Planar chromatography is now a mature technique, particularly well adapted to complex samples.

Experimental

Material and reagents. Two middle distillates have been used throughout this work: a gas oil (GO) and a light cycle oil (LCO) which were provided by the Institut de Recherche sur la Catalyse (CNRS, Villeurbanne, France) and CEPSA (Madrid, Spain), respectively.

Samples were spotted onto the chromatographic layers using a Linomat IV application system. Solvent development of samples was carried out using a Camag horizontal developing chamber. The detection was performed with a CS-9301PC scanner (Shimadzu) either in fluorescence (excitation wavelength at 365 nm, emission measured between 450 and 550 nm with a filter) or UV (254 nm) mode.

The analysis of saturated fraction was performed on HPTLC silica gel glass plates (Merck, 10x10cm, pore size 60 Å, particle size 15 µm, thickness of layer 0.20 mm) impregnated with berberine sulfate before use (30 mg.L⁻¹ in methanol) during 20 sec. Plates were dried overnight at 40°C.

Non impregnated silica gel plates and caffeine impregnated plates from Macherey-Nagel (10x20cm, pore size 60 Å, particle size 2-10 µm, thickness of layer 0.20 mm) were used for the analysis of aromatic fraction and PACs respectively.

Preparative isolation of calibrating fractions. Preparative purifications were performed on TLC silica gel plates (20x20 cm, thickness of layer 2mm) from Merck. When required, a second purification is achieved using conventional TLC silica gel plates.

GO (100 to 500 mg) was applied as a 180 mm-band on a preparative layer and eluted with *n*-hexane (18 cm) in a conventional vertical development tank. The alkanes and

naphthenes were detected by fluorescence, using a slice of the plate impregnated with berberine to exclusively monitor the elution of saturates. The cutting point between alkanes and naphthenes was fixed by detection of naphthenes by UV at 210 nm. The distance of migration of the aromatic fraction was visualized in UV at 254 nm.

Preparative isolation of PACs (more than three rings) was performed under the same analytical conditions as described for the total aromatic fraction. However, the corresponding migration zone is determined according to the fluorescence properties of this family of molecules (wavelength_{exc} = 365 nm; wavelength_{em} between 450-550 nm). The distance of migration of PACs was also confirmed using aromatic standards.

After development, the zones corresponding to the different fractions were scratched and, subsequently, extracted from the silicagel with DCM in a Soxtec apparatus (Tecator, Hogånäs, Sweden) under mild conditions, and dried under N₂ until constant weight. Purity of isolated fractions was monitored by both HPTLC berberine-impregnated plates with fluorescence and HPTLC silica gel with UV scanning densitometry under the conditions of analytical separations.

Analytical separations of hydrocarbon-types. In all cases, samples and standards, dissolved in DCM, were applied as 2 mm bands. The conditions of analysis for the group types are summarized in **Figure 1** and analytical parameters in **Table 1**.

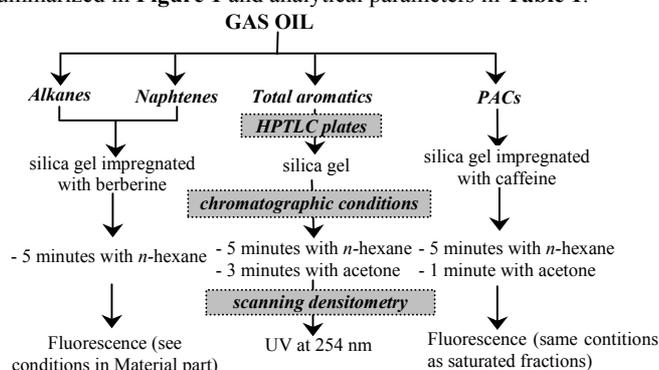


Figure 1. Analytical conditions for the separation of hydrocarbon types by HPTLC

Separation of aromatics from gas oil according to ring number. It was carried out using a caffeine-impregnated silica gel plate. Impregnation was performed exclusively in the sample application zone (4 cm). Samples were applied only on one of the sides of the plate. Elution was performed in two steps: the first one consists of two migrations with *n*-hexane (8 cm) in the same direction. The second step was a double elution with dichloromethane, as follows: on the caffeine-side of the plate, heavy PAHs are merged in a peak by dichloromethane (elution of 25 mm). Simultaneously, on the silica gel-end of the plate, a filter paper bridge is used to carry out a counter-elution from the point in which di- and triaromatics are overlapped (15 mm in opposite directions). The coordinates (x, y) of this point are previously fixed by the densitometer software from the *n*-hexane chromatogram. The baseline of the caffeine-side was subtracted using the densitometer software.

Results and Discussion

Determination of alkanes and naphthenes from gas oil. Although saturated hydrocarbons do not give any UV or fluorescent response under usual analytical working conditions, they give a fluorescent emission signal when they are spotted onto a silica gel TLC plate, previously impregnated with berberine sulfate and the system is irradiated using 365 nm-UV light. This fluorescent response depends on the mass and structure of the saturated hydrocarbon^{4,5}. The berberine-induced chromatogram of GO shows two peaks corresponding to saturated hydrocarbons (**Figure 2**). The

peak eluted at 20 mm has been assigned to naphthenes for several reasons: its R_f (cycloalkanes are slightly more polar than alkanes), its fluorescent response in the berberine system; its characteristic response in UV (no response at 254 and response at 210 nm); its ^1H NMR spectra which present chemical shifts and couplings constants which can be attributed to cyclic $-\text{CH}_2-$; and its GC-FID chromatograms. When the preparatively isolated fraction is reapplied on a berberine-impregnated HPTLC plate under analytical conditions, it presents a unique peak at 20 mm. All these results will be presented in the oral communication.

Table 1. Calibration Data for each Standard

Standard	Range (μg)	Slope / Intercept of the linear equation	R^2	LOD (μg)	LOQ (μg)
Alkanes	0.05 to 1.5	1163 / 744	0.9862	0.05	0.15
Naphtenes	0.6 to 2.4	655 / -89	0.9097	0.10	0.30
Total Aromatics	0.1 to 2.0	873 / 89	0.9684	0.06	0.18
PACs	0.1 to 1.2	898 / 8	0.9970	0.07	0.25

LOD : limit of detection and the *LOQ* : limit of quantification

Then, alkanes and naphthenes from GO can be quantitatively determined using external standard calibration. The calibration curves obtained, as well as linearity intervals, limits of detection (LOD) and quantification (LOQ), are presented in **Table 1**.

Response (Arbitrary Units)

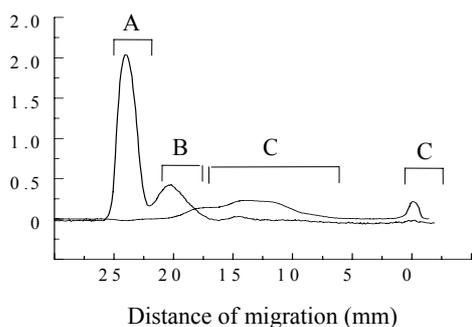


Figure 2. GO hydrocarbon group type identification on HPTLC. Detection in UV for the PAHs and in fluorescence for the saturated compounds. A: Alkanes; B: Naphtenes; C: Aromatics.

Determination of total aromatics from gas oil. As it was shown in the **Figure 2**, the use of *n*-hexane allows the separation of saturated compounds from aromatics on HPTLC silica gel plates to be carried out. However, the distribution of aromatics over the plate is very wide, this is due mainly to the different behavior of these molecules during the separation process: the distance of migration depends mainly on the solubility of the PAHs in this solvent and the compounds with the highest number of rings will migrate the less. Molecules with more than 4 rings stay at the injection point as it was checked using pure commercially available polyaromatic compounds. Then, the complete elution of aromatics of GO using acetone, after *n*-hexane elution allows to merge the aromatic peaks in one narrow, gaussian peak which enables the total aromatics to be quantified. No peaks remain at the sample application point. The data concerning the total aromatic determination for GO by external calibration are shown in **Table 1**.

Determination of PACs and separation of aromatics according to ring number from gas oil. The elution patterns of GO on silica gel HPTLC and caffeine-coated silica gel HPTLC plates are shown in **Figure 3** in UV and fluorescence detection mode. The use of pure aromatic standards has allowed to identify the distance of migration of the group types: three zones are identified as 2 rings (A), 3 rings (B) and more than 3 rings (C)

distance of migration. Fluorescence scanning enables a selective detection of the heavy fraction of aromatics. Then, the corresponding peaks are merged with acetone to be quantified, the results of calibration are summarized in **Table 1**.

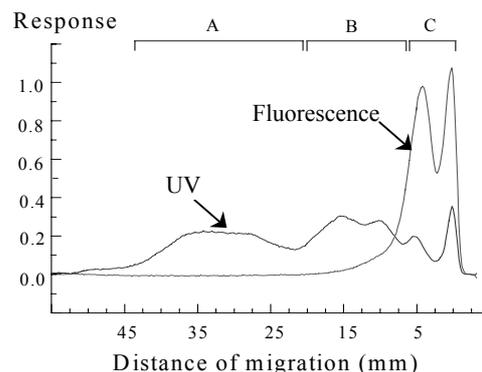


Figure 3. Chromatograms of the gas oil measured in UV (300 nm) and Fluorescence after separation on caffeine HPTLC plate. A : 1 and 2 rings. B : 3 rings. C : 4 and more rings.

Separation of aromatics from gas oil according to ring number The purpose of the procedure described in Experimental was to selectively retain heavy PACs in the caffeine zone of the plate with regard to the other aromatics, which migrate faster when arrive at the silica gel zone. Subsequently, a further separation of overlapped di- and triaromatics by counter-elution was carried out. Three narrow peaks corresponding to 1+2, 3, and more than four aromatic rings have been completely resolved from gas oil (**Figure 4**), and from mixtures of standards. The method proved to be repeatable and fast. As far as the authors know this is the first separation of aromatics according to ring number in a petroleum distillate using an HPTLC technique.

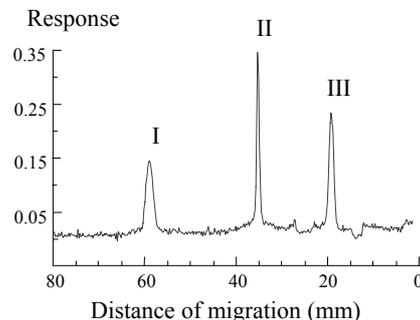


Figure 4. Separation of aromatics in a GO according to the number of rings. I: 1/2 rings ; II: 3 rings ; III: 4 and more rings

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SEPARATION OF AROMATIC SULFUR HETEROCYCLES FROM AROMATIC HYDROCARBONS BY USE OF A PALLADIUM ION COMPLEX

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Introduction

Acid rain and the poisoning of catalysts have driven the efforts to lower the amount of sulfur that can legally be present in fossil fuels. In coming years limits of ca 30 ppm can be expected in several countries and in the longer term even lower levels will be mandated such as the 10 ppm level required in Germany by January 2003. [1]

Sulfides and thiols may be present in crudes but are considerably more easily desulfurized than the aromatic sulfur. Thus the hydrodesulfurization processes used in refineries leave the sulfur essentially in the aromatic form. However, as the sulfur concentration is lowered, the analysis of the remaining polycyclic aromatic sulfur heterocycles (PASH) becomes increasingly difficult in the presence of the polycyclic aromatic hydrocarbons (PAH) whose concentration is unaffected by the hydrodesulfurization.

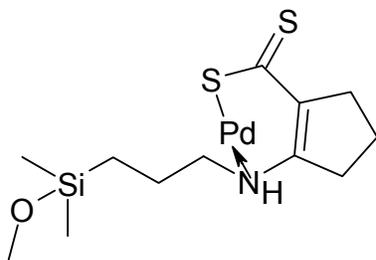
In future, as the world's crude reserves will not be as plentiful as today, heavier fossil materials may attract more attention as a resource for fuel production. Such materials are often heavier than the present-day crudes and high in sulfur.

In many analytical situations, it would be desirable to have a pure PASH fraction available in order to study its properties.

In this work we demonstrate how a liquid chromatographic stationary phase that includes palladium ions can be used to separate PAHs and PASHs, thus allowing the sulfur-containing fraction to be studied much more easily.

Experimental

The preparation of the stationary phase has recently been described. [2, 3] In short, a commercial aminopropyl substituted silica gel, as used for normal-phase HPLC, is derivatized with 2-aminocyclopentene-1-dithiocarboxylic acid (ACDA). This material is complexed with palladium(II) chloride in a subsequent step to give the phase used. (See **Figure 1**.) This is packed in the column using standard column-packing procedures.



Silica

Figure 1: The complex Pd-ACDA bonded to silica and used to separate PASHs and PAHs.

Chromatography. The polycyclic aromatic fraction of the material under study is preisolated through open-column chromatography on alumina and then injected onto the Pd-ACDA

column. The PAHs are eluted using a non-polar cyclohexane/dichloromethane mixture. A more polar solvent which includes isopropanol is used to elute the PASHs. After reduction of the volume of the solution (using a stream of nitrogen), gas chromatography with a universal detector as well as liquid chromatographic and other techniques can be used for detailed analysis.

If larger amounts of the PASH fraction are needed, a larger diameter column can be used with a higher sample capacity.

Results and discussion

Separations of PAHs and PASHs have been the target of research over the last decades and several methods have been published as reviewed in Reference 4. One of the more successful schemes was chromatography on palladium chloride deposited on silica, but due to several drawbacks this material now has lost much of its popularity. [4]

The Pd-ACDA phase shows more promising properties. Extensive determinations of the retention properties of PAHs and PASHs were carried on it out to ascertain that the two classes of compounds are completely separated from each other. Compounds with two, three and four aromatic rings were used, including such with extensive alkylation. Even sulfur aromatics bearing alkyl groups in immediate proximity to the sulfur atom, such as 4,6-dimethyldibenzothiophene, of particular importance in desulfurization studies due to their recalcitrance, exhibited long retention times on the Pd-ACDA phase and therefore good complexation. For instance, chrysene, a four-ring PAH, showed a retention factor of 0.7, dibenzothiophene 38 and 4,6-dimethyldibenzothiophene 14.

The interactions of PASHs with the palladium ions are considerably more selective for PASHs (vs. PAHs) than the interactions on the palladium chloride phase, especially for compounds with a terminal thiophenic ring. Benzothiophene elutes together with phenanthrene on PdCl₂/silica; however, on Pd-ACDA, the retention factor for benzothiophene is 5 - 7 times larger than that for phenanthrene.

The excellent separation of the two compound classes is illustrated in the chromatogram in **Figure 2**.

Gas chromatograms of the polycyclic aromatic fraction of crude oils showed that the PAH fraction thus isolated on Pd-ACDA did not contain any sulfur and the PASH fraction was free of non-sulfur

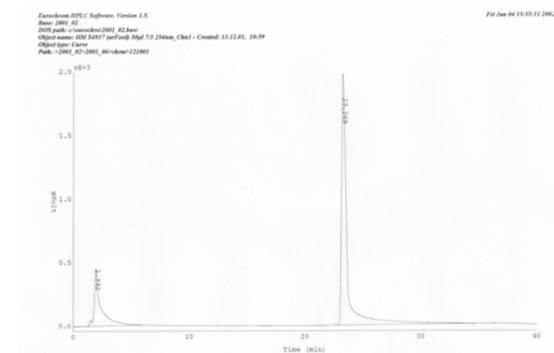


Figure 2. The polycyclic aromatic feed of a desulfurization unit, separated on Pd-ACDA. First peak: PAH, second peak: PASH

compounds, demonstrating the complete separation of the two classes of compounds.

The phase has shown its utility in extensive investigations of PASHs in gasolines and diesels, which mainly means alkylated

benzothiophenes and dibenzothiophenes. Fuels with a sulfur content of <10 ppm can be easily studied.

This stationary phase was also used to investigate sulfur-containing aromatic compounds in heavier distillation fractions and residues. Thus the preisolated polycyclic aromatic fraction of a vacuum residue (boiling range starting at ca 500 °C) was injected onto the column and the two separated fractions collected. They could now be investigated individually using off-line techniques. A marked difference in aromaticity was one of the major differences between the sulfur- and the non-sulfur-containing aromatic fractions, the sulfur-containing fraction showing a larger number of condensed aromatic rings.

Through this separation the opportunity to investigate the molecular mass distribution of the two classes of compounds is being opened. Common techniques such as size-exclusion chromatography or mass-spectrometric methods can now be employed on the separated fractions.

Conclusions

This palladium(II) containing column has shown itself to be a powerful tool in the separation of sulfur-containing aromatic compounds from non-sulfur analogs. Materials ranging from gasolines to heavy distillation residues have been successfully investigated. The properties of the sulfur-containing aromatics can now be studied without interferences of other components of the material. Likewise, the properties of the PAHs can be studied without interference of the PASHs.

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