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Coal Liquefaction Process Streams Characterization and Evaluation

Topical Report

Analytical Methods for Application to Coal-Derived Resids - A Literature Survey

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ABSTRACT

COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION TOPICAL REPORT: ANALYTICAL METHODS WITH POTENTIAL USEFULNESS FOR ANALYSIS OF COAL-DERIVED RESIDS - A LITERATURE SURVEY

A literature survey was made to identify analytical methods and techniques for application to the analysis of coal-derived resids. These analytical methods and techniques were chosen because they were shown to be useful in the analysis of coal-derived materials and other high molecular weight, fossil fuel-derived materials such as tar sands, shale oils, and petroleum resids. The survey is arranged by general analytical method. The survey is focused on literature published between 1980 and 1991; it contains a brief historical introduction.

I. INTRODUCTION

This literature survey was conducted to address an important question: What are the methods available in the realm of analytical chemistry that may have potential usefulness to the development of coal liquefaction technology? In an attempt to answer to that question, the emphasis of this survey was directed at analytical techniques which would be applicable to the high molecular weight, non-distillable residua of coal-derived liquids. It is this material which is most problematic to the analytical investigator and the developer of direct coal liquefaction processes.

This survey was conducted as part of a larger effort (US DOE Contract No. DE-AC22-89PC89883) to establish a bridge between the analytical technologist and his most modern methods of analysis, and the developer and operator of direct coal liquefaction processes, by the demonstration of various analytical methods with direct coal liquefaction-derived materials. In establishing this bridge, the gap that has heretofore existed between these two groups, should narrow to the benefit of both groups.

A number of comprehensive analytical reviews of literature dealing with coal and other fossil fuels are available.^{1,2} This literature survey will 1) be limited to articles published between 1980-1991, with some exceptions, 2) be limited to the use of analytical methods for high molecular weight, primarily non-distillable, fossil fuel-derived materials, except where the application of an analytical method to coals or distillates may show promise for application to non-distillable coal-derived materials, and 3) demonstrate the potential usefulness of an analytical method by showing how the method has been applied to high molecular weight, non-distillable materials, if not specifically to coal liquids.

The text is divided by type of methodology, i.e. spectroscopy, microscopy, etc. Each section will be essentially free-standing. An historical background is provided.

II. HISTORICAL BACKGROUND

Prior to 1940, the analyst of coal-derived residuum was primarily concerned with the "by-product" tars from gas works which were utilized as raw materials for the

production of pure organic compounds, primarily dyes, and for road building, roofing, and water-proofing materials. Tars were defined as "bitumens which yield pitch on fractionational distillation, and which are produced as distillates by the destructive distillation of bitumens, pyro-bitumens, or organic materials".³ In efforts to standardize the analysis of by-products (tars) from the gas works, papers of the early part of the twentieth century⁴⁻⁹ were devoted to the methodology for sampling tar reservoirs, specific gravity measurements, distillation techniques, fractionation of acids and bases from the distillation fractions, solubility fractionation, and physical testing. "Consistency" tests, "twist point" tests, melting points, evaporation, "slide" tests, and viscosity measurements were applied in an effort to better define and standardize the materials used for different applications. Additionally, by 1918, fixed carbon, ash, and total sulfur were determined on a regular basis in the coal-tar industry.⁹ Complex separation/characterization schemes were developed to characterize low-temperature tar (produced by distillation at <120 °F, 2 mm Hg) to avoid the cracking reactions which altered the starting material at higher temperatures.¹⁰ These schemes were based on solubility properties and acid/base properties of the tars and tar extracts. It was noted in 1930 by Chadder and Spiers¹¹ that many properties of tars for use as paving materials had no satisfactory standard method of analytical measurement, "...in other cases, though methods are available, sufficient knowledge has not been gained to enable the tests to be incorporated into testing specifications...This will, in course of time, be rectified when, as a result of the introduction of new methods for the testing of tar, it becomes possible to draw up the specifications on sound scientific lines."

In many respects, the analysis and implementation of analytical methods on a routine basis for coal-derived resids produced by the direct liquefaction of coal, is at the same juncture as Messrs. Chadder and Spiers described in 1930 for road tar. It is, at this time, necessary to determine which methods hold potential for process development, put them to trial, and select the best of them for routine use. The following sections deal with more recent analytical work, concentrating on the years 1980-1991. The emphasis in the last sixty years has shifted to spectroscopic techniques, many of which are discussed below. However, there are a number of separation techniques which have a basis in the work described in the early twentieth-century papers; these are also discussed below.

III. MOLECULAR WEIGHT DETERMINATION; MASS SPECTROMETRY, GEL PERMEATION CHROMATOGRAPHY, VAPOR PHASE OSMOMETRY

The molecular weight distributions of tars, shale oils, petroleum resids and other high molecular weight, complex mixtures are frequently determined by mass spectrometric (MS) techniques. Tao and Billimoria¹² used high resolution MS to identify aromatic and heterocyclic aromatic composition of the volatile (at 300 °C and 1×10^{-2} torr) components of coal liquefaction bottoms. However, only 16% of the total sample was vaporized, and subsequently analyzed, by this method. Hill et al.¹³ used low-voltage MS for the analysis of coal pyrolysis tars and coal tar pyrolysis products. The coal or coal tar was pyrolyzed in a heated Curie-point (610 °C wire) inlet and the pyrolysis products directly introduced to the mass spectrometer. Statistical analysis of the MS data (supported with other analytical data) show that rank-related trends in tar composition follow differences observed in the pyrolysis-MS patterns of the feed coal.

Interpretation of the mass spectra of the high molecular weight, non-volatile, coal liquefaction resids is extremely complicated, and is made more so by fragmentation of the molecules. Techniques which minimize the number of fragment ions and produce mostly intense parent peaks appear to be more applicable to high molecular weight mixtures. A number of techniques are currently in use; they differ in the method of ionizing the sample. Three of these MS techniques are field ionization (FI)-MS, field desorption (FD)-MS, and plasma desorption (PD)-MS. Whitehurst et al.¹⁴ demonstrated the use of FIMS with coal-derived liquids. They state that the primary limitation of the method is that, for materials to be analyzed, they must be volatile, without decomposing, at 13.3 μ Pa. This includes essentially all coal liquids boiling at <575°C (atmospheric equivalent). The molecular weight range that was investigated by FIMS was 100-800 Da. In another study, high-boiling distillates and non-distillable vacuum still bottoms (VSB) produced by direct liquefaction of Kentucky and Wyodak coals in the SRC-I process were analyzed by the FIMS technique after separation into solubility and compound classes.¹⁵ Molecular weight distributions were obtained and show that for the solubility fractions, oils have a molecular weight range of 200-400 Da, asphaltenes 300-800 Da. and preasphaltenes 300->2000 Da. FDMS is a method amenable to the analysis of high molecular weight, nonvolatile samples. FDMS was used to analyze coal liquefaction bottoms and petroleum resids.¹⁶ Field desorption extends the mass range

observable to -4000 Da for coal liquefaction bottoms, and from 200-600 Da for petroleum resids to 200 to 1200 Da. Although samples are usually introduced as solutions, even insoluble, suspended material could be analyzed. Larsen et al.,¹⁷ used Gel Permeation Chromatography (GPC) and Field Desorption Mass Spectrometry (FDMS), to examine the heavy constituents of deasphalted oil, resin, pitch, and furfural raffinate from a deasphalted petroleum (Mid-Continent U.S. Crude) residue. Number average molecular weights were obtained for all four fractions by GPC and FDMS, and for three of the samples (the deasphalted oil, the resin, and the pitch) by vapor phase osmometry (VPO). Detected by the FDMS analysis were individual masses above 3000 in the raffinate and above 5000 in the deasphalted oil and resin.

Two other methods of determining molecular weights in complex organic materials, such as coal-derived resids, are vapor phase osmometry (VPO) and gel permeation chromatography (GPC). Each of these methods has associated limitations. The VPO technique relies on the materials being dissolved in a solvent. Even with pure organic compounds, association can occur in solution to yield erroneous results. The GPC technique is a liquid chromatographic separation the selectivity of which is based on the criteria of molecular size and shape. Consequently, a molecule that has a higher molecular weight, but a smaller size than another lower molecular weight organic molecule (or class of molecules), will elute from the GPC column with the lower molecular weight species. Molecular weights determined by GPC are assigned on the basis of standards, usually linear polystyrene polymers. This, too, can pose problems when used with coal-derived materials, which are mostly non-linear structures.

GPC and VPO were used by Unger and Suuberg¹⁸ to determine the molecular weight distribution of coal tars produced by flash pyrolysis of coal. To get around the calibration problem with the GPC method, Unger and Suuberg calibrated their system with the same type of coal pyrolysis tars which they were attempting to analyze. These tars were produced under vacuum and then passed through a preparative scale GPC column. Each resulting fraction was analyzed by VPO for number average molecular weight. VPO determinations were made with pyridine as the solvent. Problems associated with the VPO technique were minimized by using dilute solutions (on the order of 0.1 to 1 g/dm³). The analyzed fractions were then passed through the analytical GPC column. A molecular weight vs. elution

volume curve was produced and used to as a standard for subsequent samples. Tao and Billimoria¹² used GPC to analyze tetrahydrofuran (THF) solutions of Exxon coal liquefaction bottoms produced in the Exxon Donor Solvent process. They used dilute solution and took advantage of THF's properties to reduce hydrogen bonding of the sample molecules in the solution. They did not, however, account for the hygroscopic nature of the THF.

IV. MASS SPECTROMETRY FOR COMPOUND IDENTIFICATION

High resolution MS methods were used by Gembecki et al.¹⁹ on atmospheric residuum of Tachning crude oil, vacuum gas oil (VGO) and a blend of VGO and demetalized oil (DMO) to identify specific hydrocarbons in the oils, and thus to determine the processability of the feedstock. ²⁵²Cf-PDMS was used by Zingaro et al.²⁰ to examine coal-derived asphaltenes. Periodicity in the ²⁵²Cf-PDMS spectra suggested that the ion groups apparent in the spectra had benzylic functionality.

MS techniques are often used with separation methods which serve to narrow the molecular weight range, or concentrate one class of compounds into a specific fraction of the sample being analyzed by the mass spectrometer. These techniques include supercritical fluid extraction (SFE)-MS²¹, supercritical fluid chromatography (SFC)-MS, gas chromatography (GC)-MS²²⁻²⁴, GC-FIMS²⁵, liquid chromatography (LC)-MS²⁶, and high performance liquid chromatography (HPLC)-MS²⁷ and HPLC-GC-MS.²³

Gas chromatography/mass spectrometry was used to identify the nitrogenous materials in a deasphalted Boscan (Venezuelan) crude.⁹⁰ Three major classes of compounds were identified; substituted pyridines, quinolines, and carbazoles. The same crude was retested after catalytic hydrotreatment. The alkylpyridines were eliminated and alkylanalines were found. Carbazoles were resistant to hydrotreating as were azarenes that were α -methyl substituted. Lamey et al.²³ employed a GC/MS technique to analyze a number of fossil fuel-derived materials, including a tar oil obtained from the Great Plains, ND fixed-bed coal gasification facility and an eastern shale oil. In the scheme used, the samples first underwent a solubility separation in CH₂Cl₂ or dimethylformamide (DMF); insoluble materials were filtered out and the soluble fraction was then treated with NaOH to remove phenols. The prepared samples were separated into compound classes by HPLC. The HPLC fractions were injected into the GC/MS and compound-class

identifications were made. The phenolic fraction of direct coal liquefaction distillates (175-425°C) were analyzed by gas chromatography/mass spectrometry.²⁹ The samples were analyzed both as whole materials and with preliminary separation into phenol-enriched fractions. In another study, the carbonyl-containing fraction of an Australian shale oil, isolated from the shale oil by a Girard-T reaction, was analyzed by GC/MS techniques²². Alkanones ranging from C₄ to C₂₉ were identified. Poirier and Das²⁴ used high performance liquid chromatography (HPLC) techniques to separate bitumens that boiled above 350°C into five fractions. The fractions enriched in polynuclear aromatics (PNAs) were subsequently acid/base extracted to remove the most polar material. The neutral PNA fractions were further separated and analyzed by capillary gas chromatography/mass spectrometry. Twenty-five model compounds were used to help identify the components of the bitumens; ninety-seven individual compounds were identified.

The compositions of a "conventional" oil and an Alberta tar sand bitumen were investigated by Strausz et al. utilizing GC-FIMS techniques.²⁵ Here, again, the more intractable samples (the tar sands) were first chromatographically separated (in this case into saturates, aromatics and polars). Saturated fractions were separated into n- and iso-alkane fractions by urea and thiourea adduction. Each of these materials was then analyzed by FIMS. It was found from the distribution of homologous series of hydrocarbons that the bulk (70-80%) of the thiourea adduct and non-adduct is made up of mono- to tricyclic compounds. In Boduzynski et al.,¹⁵ detailed interpretation of the FIMS spectra provided information on the composition of the solubility fractions of the high-boiling distillates and non-distillable VSB from the SRC-I process. Odd-numbered mass (nitrogen-containing) homologous series were apparent in all the spectra. Oxygen-containing homologous series were also evident in all the spectra. Although the compound classes were the same for oils and asphaltenes examined, the relative concentrations of the different classes differ between the oils and asphaltenes.

Herod et al.²⁶ used liquid chromatography/mass spectrometry (LC-MS) to analyze coal tar. Their intent was to avoid the volatility problems encountered in GC/MS analyses and to extend the range of materials analyzed by the mass spectrometer. However, volatility at the LC-MS interface was problematic. Compounds that had been previously undetected by GC/MS methods were, nonetheless, identified. Aromatic compounds with alkyl substituents up to C₂₀ and aromatic ring systems

up to seven rings were identified. Ueda et al.²⁷ utilized HPLC-FIMS as a method to monitor the chemical composition and molecular weight distribution of coal tar pitch produced from a coking process. The components of the coal tar (and an unidentified coal liquid) were classified into about forty chemical types.

Supercritical fluid extraction (SFE) coupled with off-line capillary gas chromatography (CGC)-MS was used to extract and analyze polynuclear aromatic hydrocarbons (PAHs) from coal.²¹ Neither the extraction yield or the extraction fluid were reported; however, compound class identifications were made via the SFE method and identification of components of those classes was made via the CGC/MS.

MS-MS techniques have been applied to shale oil extracts obtained from Fischer assay retorting experiments which had been carried out at different heating rates.³⁰ MS/MS is a method in which the ions selected in the first mass analyzer undergo dissociation in a collision cell. The fragments thus produced are then analyzed in a second mass analyzer. Prominent mass ions from the shale oil fractions were identified, and they varied in intensity among different samples.

V ELECTRON SPIN RESONANCE AND ELECTRON PARAMAGNETIC RESONANCE

The detection of free radicals in coal-derived residua could be an important tool for assessing the reactivity of the samples. It can also be a means by which the source of materials in the resid can be traced, as is the case with the work of Hocking and Premovic.³¹ Hocking and Premovic describe free radicals as being "trapped" in the resid. They demonstrated the use of electron spin resonance (ESR) methods to detect the presence of vanadyl porphyrins present in the coal inclusions in Athabasca tar sands. The coal particles were isolated from the tar sands and analyzed by ESR. They were able to show that the ESR technique is sensitive enough (with a lower limit of about 1 ppm) to quantify the vanadyl porphyrins present in the tar sands. ESR often is used to analyze coal at different stages of reaction, and thus to make inferences about the reactivity of coal and coal-derived materials. Seehra, Ghosh, and Mullins²⁸ looked at the variation of spin concentration as a function of temperature for three different bituminous coals as the coals were pyrolyzed. Three distinct stages of pyrolysis were observed. The activation energies (E_a) calculated for these three stages support the idea that the coal decomposes and produces free radicals in the

highest temperature stage. In the two lower temperature stages, E_a is too low to account for strong carbon-carbon bond breaking. It was postulated that the increase in free radical content at the lowest temperature stage (600 K) results from the release of CO, CO₂, and H₂O from the coal structure. At the next temperature stage (700 K), the decrease in free radical content was postulated to be a result of capping of free radicals by hydrogen. In a subsequent study, Ibrahim and Seehra³² compared the liquefaction yields of coals with ESR data, thermal parameters determined by use of thermogravimetry/differential thermogravimetry (TG/DTG), and coal composition. They found that the best correlations to coal conversion were made with H/C ratio, rate of TG mass loss and the formation rate of thermally generated free radicals. Yokono et al.³³ attempted to characterize the carbonization reaction of petroleum residua through the use of high-temperature ESR measurements. In their studies, a correlation was found between the free radical content, the hydrogen donor ability of the resid, and the mechanical texture of the resultant cokes. The free radical contents increased with decreasing hydrogen donor ability and with the formation of an isotropic coke. The relationship of the free radical density of coal extracts and the macerals in the native coal was investigated by Seehra et al.³⁴ It was found that the free radical density (N_g) decreases as the percentage of material extractable in N-methyl pyrrolidone and the H/C ratio increase. It also was found that the N_g value is lower for the extracted material than for the coal from which it was extracted and the sum of free radicals in the extract and residue of extraction add to nearly the initial value for the starting coal. The extractability is dependent on the relative concentration of exinite and vitrinite (both have low N_g) to inertinite (high N_g). This led the researchers to the conclusion that the extractability of the coal, and coal composition, could be predicted from the free radical content.

The use of electron paramagnetic resonance (EPR) spectrometry to describe the progress of maturation of oil shale kerogen was explored by Baker et al.³⁵ The EPR spectra were visually examined and the g values and peak widths were ordered to form a smooth progression from formation to destruction along a "progress of reaction/increasing temperature" scale. Visual inspection restricted the method to qualitative aspects of interpretation. However, mass spectral data supported the order of maturation of the samples.

VI INFRARED, RAMAN, AND LUMINESCENCE ANALYSIS

Fourier transform infrared spectroscopy was used by Robbins et al.³⁶ to determine the phenolic -OH content of direct coal liquefaction-process derived oils obtained from two different liquefaction facilities (Lummus and Hydrocarbon Research, Inc.) as a measure of process performance. The FTIR technique used monitored the height of the infrared peak produced by the stretching vibration of the O-H bond (around 3300 cm^{-1}) in THF solution. It was found that the phenolic -OH concentration of the THF-soluble portion of the process oil can be a good indicator of the performance of the coal liquefaction process. Petroleum pitches and coal slurries were characterized using FTIR³⁷ methods that reduced the large background signal and improved the quantitation of the method. The methods use ellipsoidal mirrors to increase the signal-to-noise ratio in the spectra. The methods are known as the scattering filter (SFM) and scattering dilution (SDM) methods. The petroleum pitch sample was molded into a pellet using CsI (60 wt %) and KBr (40 wt %) as dilution materials. The authors do not make it clear if the coal slurry was coal-water or coal-oil. Regardless, the slurry was coated on the surface of a KBr pellet before being examined. With the ellipsoidal mirror technique, a considerable amount of structure was seen in the IR spectrum using the scattering methods which was not discernable in a transmission spectrum.

Luminescence analysis was used to investigate the tar produced in a low-temperature carbonization of a Kuckersite shale.³⁸ The method is applicable to the determination of trace amounts of geochemical markers such as porphyrins and polyaromatic hydrocarbons in sedimentary and other source rocks. It is possible with this method to analyze complex mixtures and to detect homologous series in the lines of the luminescence spectra. Interpretation is based on model compound work. It was shown that the luminescence spectrum was dependent on the solvent matrix in which the sample was dissolved. The compounds of the shale that were identified had a low degree of condensation, mainly 2-3 six-membered rings. Brownrigg et al.³⁹ studied the low-temperature total luminescence contour spectra of six topped crude oils and their vacuum distillate and resid fractions. The advantage of low-temperature luminescence is that at the reduced temperatures employed (about 77 K), the spectral bandwidths sharpen and phosphorescence emissions appear making the spectral differences more pronounced. The two-dimensional contour plots of the emission wavelength vs. excitation wavelength

allow for recognition of spectral features and similarities and differences among samples. A common feature in all the spectra is a strong emission in the 330 to 340 nm region. The greatest differences found among the oils were the relative intensities of phosphorescence.

In a number of articles by Asher et al.,⁴⁰⁻⁴⁵ the technique of UV Resonance Raman (UVR) spectrometry was explored for use with complex hydrocarbon mixtures, specifically process-derived coal liquids. The UVR technique selectively enhances the vibrational spectrum of one molecular species of a complex mixture while maintaining the other species at background levels. Fluorescence does not interfere in the Resonance Raman measurements. Species that resonate in the ultraviolet region of the spectrum include polycyclic aromatic hydrocarbons, such as naphthalenes, substituted anthracenes and pyrenes. By changing the excitation wavelength, the authors showed, that it is possible to selectively enhance the spectrum of the different species in a complex mixture, thus allowing for identification of the species present by comparison to model compounds. Quantitation of the individual species is possible because the Raman intensities are directly proportional to the concentrations of the species in the mixtures.

VII THERMAL ANALYSIS

Thermogravimetric analysis (TGA) has been used to investigate the thermal oxidation/decomposition and competing polycondensation reactions of petroleum resids.⁴⁶ The slope of the TGA curve is dependent on the rate of decomposition, the formation of cross-linked structures, and autoretardation of the reformation of the bonds. Comparison of TGA curves of five different petroleum resids obtained in inert and oxidative atmospheres showed that in an inert atmosphere, weight loss followed a monotonic curve, whereas in air, the curve flattened (at about 275 °C) and remained flat until reaching higher temperatures (350 °C). This plateau is interpreted to correspond to the rearrangement of the resid structure to form thermally stable bonds. The temperatures of the initial weight loss, the start and end of the plateau, and the slopes of the lines are indicative of structural differences in the resids. Using TGA techniques, Schucker⁴⁷ investigated coking kinetics of Arab heavy vacuum residuum and of sub-fractions of the whole resid. It was found that the activation energies for the coking reactions of the various components of the residuum increase with conversion. This finding lends support to the idea that using a single

activation energy to model coking of petroleum residua would lead to erroneous results. Ibrahim et al.⁴⁸ correlated the liquefaction yield of four coals with differential thermogravimetric (DTG) measurements and found an excellent correlation (correlation coefficient, $r = 0.92$) between the rate of mass loss, as measured by DTG, and the percent of coal conversion. The authors propose that, with further verification of these findings, the DTG experiment could be used to quickly predict the liquefaction yield from any given coal.

VIII X-RAY TECHNIQUES

The solid nature of high molecular weight resids makes them amenable to analyses that are not applicable to liquid distillates. One example of this is the use of X-ray techniques to examine the dispersed colloids or particles in petroleum asphalts or resids. Asphalts are considered to be a two-phase system in which asphaltenes are dispersed in a resin or oil. In work performed by Kim and Long,⁴⁹ X-ray scattering techniques were successfully used for the characterization of the asphaltene structures in different heavy petroleum residua, as they exist in the whole residua without separation or dilution. The study of petroleum asphalts by small angle X-ray scattering techniques was undertaken by Posadov et al.⁵⁰ In their work, the size distribution of the inhomogeneities (asphaltenes) in the asphalts was determined by X-ray structure analysis. These data were used to develop a correspondence between a statistical-mean structural model of the asphaltene molecules and the dimensions of those dispersed-phase particles.

A state-of-the-art X-ray technique which is being used to explore sulfur in coal is X-ray absorption fine structure (XAFS) spectroscopy, and specifically, the X-ray absorption near edge spectroscopy (XANES) technique. Two principal approaches for the analysis of the XANES region have been developed. Huffman et al.⁵¹ have demonstrated that a least-squares analysis of their XANES structure can be made by fitting the data to two arctangent steps which represent the transition of the photoelectron to the continuum. The first represents the sulfur bound to carbon, and the second the sulfur bound to oxygen. The relative area under the peaks is used to assess the abundance of the different sulfur forms. The other technique was developed by Gorbaty, et al.^{52,53} and it entails a third-derivative treatment of the XANES spectra, which allows the approximate

quantification of the sulfidic and thiophenic sulfur components of model mixtures and coals to be obtained.

IX NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance (NMR) spectroscopy can be used to study the gross compositional changes which occur in complex fossil fuel materials in addition to the fine structural details customarily associated with the method when dealing with pure or model compounds. Netzel and Miknis⁵⁴ used both ^1H and ^{13}C high resolution NMR techniques to analyze shale oils produced by two different methods (the IGT Hytort process and Fischer assay) and hydrotreated shale oils from the Hytort process. Average molecular structural parameters were calculated from the normalized ^1H - and ^{13}C -NMR spectral areas. The authors state that the average structural parameters obtained from the shale oils are meaningless as representations of the molecular state of the materials studied. What they are, however, is a valuable way to quantitatively represent observed changes in ^1H - and ^{13}C -NMR spectra of the shale oils, and thus from them trends can be established. Snape⁵⁵ used a part-coupled spin echo (PCSE) ^{13}C -NMR method to obtain direct estimates of the aliphatic H/C ratio for fractions of two different coal liquefaction products. Use of the spin echo method allows for separation of the C, CH, CH_2 , and CH_3 signals. H/C values obtained by elemental analyses and normal accumulation NMR were found to be comparable to those obtained by PCSE ^{13}C -NMR. Two NMR techniques (INEPT and J-resolved two-dimensional Fourier transform (2-D FT) NMR) were applied to SRC-II distillate (b.p. 230-455 °C) and the hydrodeoxygenated products of the distillate in order to more fully understand the nature and the structure of the species present in the complex mixtures.⁵⁶ The multiplicity-dependent magnetization refocussing technique used (INEPT) makes it possible to determine the coupled nature of the carbon signal in the complex mixture. However, the authors state that the INEPT method does not provide adequate quantitative data. The J-resolved 2-D FT-NMR technique results in an array of data which, in principle, allows for the determination of the multiplicity of every line in the spectrum. The increased capability to discern structural detail was used to examine the SRC-II distillate and the catalytically upgraded products. Ware and Shram⁹¹ used ^{13}C -NMR spectroscopy to analyze the pentane-insoluble asphaltenes from a number of feeds and hydrotreated products. The hydrogen-to-carbon atom ratios, a calculated average chain length parameter, and the fraction of aromatic carbon were determined and used to

compare the samples. Samples were analyzed as CDCl_3 solutions. Both DEPT (distortionless enhancement by polarization transfer) experiments and J-resolved two-dimensional experiments were used to determine the fraction of nonprotonated carbon, but both methods were found to be too time consuming. Solid state continuous pulse/magic angle spinning (CP/MAS) ^{13}C -NMR experiments were also performed on the asphaltenes to directly obtain the carbon aromaticity of the samples. Structural group analysis of resids from Athabasca bitumen was accomplished by Gray et al.⁵⁷ The ^{13}C -NMR data were used as constraints in the computation of the concentrations of the structural groups. More detailed data, obtained by elemental analyses, ^1H -NMR, and infrared analyses, were combined with the ^{13}C -NMR data. It was shown that thermally treated samples differed significantly from virgin samples in the concentrations of various groups, and broader structural features, such as paraffin side chains. Solum et al.⁵⁸ utilized solid-state ^{13}C -NMR techniques to derive the proton spin-lattice relaxation time (T_1^H), the proton spin-lattice relaxation time in a rotating frame time ($T_{1\rho}^H$), the cross-polarization time T_{CH} , and the dipolar-dephasing time constants (T_G and T_L) for eleven different coals. These data, in conjunction with the normal CP/MAS integrations over different chemical shift ranges, were used to derive twelve parameters which describe the carbon skeletal structure of the coals. The twelve parameters, expressed as the fraction of carbon in the sample that is represented by a given skeletal structure, are: f_a = total aromatic carbon; f_{ar} = carbon in aromatic ring; f_a^C = carbonyl carbon; f_a^H = protonated aromatic carbon; f_a^N = nonprotonated aromatic carbon; f_a^P = phenolic or phenolic ether carbon; f_a^S = alkylated aromatic carbon; f_a^B = aromatic bridgehead carbon; f_{al} = total aliphatic carbon; f_{al}^H = CH or CH_2 aliphatic carbon; f_{al}^* = CH_3 or nonprotonated aliphatic carbon; and f_{al}^O = carbon bonded to oxygen. From these twelve parameters, the mole fraction of bridgehead carbon (X_b), the number of aromatic carbons per cluster (AC/Cl), the number of attachments per aromatic cluster (att/Cl), and the total molecular weight of an aromatic cluster (MW) could be derived for each coal. The authors speculate that structural parameters such as these could be useful for the assessment of coal devolatilization and liquefaction processes.

Gray⁵⁹ used data from catalytic and thermal hydrotreating of coker gas oil to study lumping of reaction kinetics based on aliphatic and aromatic carbon structural groups. These groups were defined by the elemental analysis as well

as the ^1H - and ^{13}C -NMR spectroscopic data. The author states that one of the most useful findings from this study is the observation that the stoichiometric relationships between groups can be deduced from rate data, even in complex mixtures. The maltenes (the pentane-soluble portion of the benzene-soluble portion) of an Athabasca oil sand were separated into different molecular weight fractions by gel permeation chromatography (GPC).⁶⁰ Each of these fractions was subsequently examined by ^{13}C -NMR using distortionless enhancement by polarization transfer (DEPT) pulse sequencing techniques. The results of these analyses were used to identify different types of CH_n ($n = 1-3$) multiplicities in the ^{13}C -NMR spectra and to allow a quantitative estimate of their distribution. Aliphatic carbon types identified and quantified include CH_3 as α -methyl and $\geq\text{C}_2$ alkyls; CH_2 in long aliphatic chains, CH_2 alkyl α and β to aromatic or naphthenic rings, and CH_2 in cyclic structures, including $\text{Ar}(\text{CH}_2)_n\text{Ar}$; CH in cyclic structures, and $(\text{CH}+\text{CH}_2)$ in cyclic structures. Aromatic carbon was identified as either CH , C , or the sum of both (determined directly by inverse gated heteronuclear decoupling (IGATED) pulse sequencing). The molecular weight fractions were found to follow a decreasing aromatic carbon content with increasing molecular weight from 315 to 800 Da and then an increasing aromatic carbon content from 800 to 2385 Da. Other trends in carbon types are noted by the authors for the different molecular weight fractions.

Wroblewski et al.⁶¹ briefly reviewed the literature on the use of NMR spectroscopy for the detection of nuclei other than ^1H and ^{13}C in coal-derived materials. They concluded that the direct determination of ^{17}O and ^{33}S resonance signals is hampered by the low natural abundance, and the ^{14}N , ^{17}O , and ^{33}S signals by their quadrupolar nature and low NMR receptivity. The derivatization of labile functional groups in coal-derived materials with ^{19}F containing reagents, silylation (^{29}Si), stannylation (^{119}Sn), and phosphorylation (^{31}P) is reviewed. The authors state the case for the use of ^{31}P -labeled reagents for the derivatization and subsequent analysis of coal-derived materials. The ^{31}P nucleus has a natural abundance 10-20 greater than the ^{119}Sn or ^{29}Si nuclei and it also possesses ca. 10-100 times more NMR receptivity. Additionally, the labile functional groups in coal materials are known to form O-P, N-P, and S-P bonds under mild conditions with a wide variety of phosphorous compounds. Five phosphorous-containing reagents were used to derivatize model organic compounds, the pyridine extracts of an Illinois No. 6 coal and the low-temperature

pyrolysate of the same Illinois No. 6 coal, a Kentucky No. 6 coal, and a Pittsburgh coal.⁶¹ The ^{31}P chemical shift ranges were determined for derivatized alcohols, phenols, carboxylic acids, amines, and thiols with model compounds. The coal-derived materials yielded broad ^{31}P -NMR spectral peaks; however, regions attributable to phenolics and carboxylic acids could be determined. In additional work with ^{31}P -NMR spectroscopy, Lensink and Verkade⁶² and Wroblewski et al.⁶³ explored a number of ^{31}P derivatizing agents for the analysis of labile functional groups in coal and coal-derived materials.

X SEPARATIONS AND CHROMATOGRAPHY

As was mentioned in the historical section of this review, many of the separation methods for the analysis of heavy fossil fuel-derived materials have their origins in the early twentieth century work. In general, separation techniques fall into three broad categories: phase equilibria, rate processes, and particle separation methods. Examples of these three categories are: distillation and chromatographic methods, osmosis and electrophoresis, and sedimentation and screening, respectively.⁶⁴ In this review, the majority of the separation techniques that are reported for application to fossil fuel materials fall in the first two categories. They are chromatographic separations, solubility separations, and distillation methods. In many studies, a combination of all or some techniques included in each of these broad categories is used for the analysis of single samples.

As an aid to process development engineers, solubility separations were used by Vercier et al.⁶⁵ for the subdivision of petroleum resids into asphaltenes, saturated hydrocarbons, aromatic hydrocarbons, and resins. Even though this separation scheme does not specifically separate acids, bases, and neutral nitrogen compounds, it was believed to provide the kind of information necessary for practical refining interests. In a comparison of West Coast and Kuwait vacuum resids before and after catalytic processing, Richardson and Alley⁶⁶ used adsorption chromatography to separate the resids into saturates, aromatics, polar aromatics, and asphaltenes. By analyzing each fraction, they could follow the distribution of sulfur-containing compounds in the resid. Prior to analyses by high performance liquid chromatography (HPLC), Amateis and Taylor⁶⁷ did a preliminary treatment of a coal-derived process solvent in order to provide simpler, but more concentrated fractions which differed primarily in polarity.

The treatment consisted of a sequential elution of increasingly more polar material from a silica gel column utilizing increasingly more polar solvents.

Reverse phase liquid chromatography (RPLC) was found to be an effective method to analyze the liquefaction products of an Illinois No. 6 coal.⁶⁸ The products collected from three different temperature stages (260, 340, and 420°C), in a process the authors call "temperature programmed solubilization", showed that the material produced at the highest temperature is decidedly more polar.

Distillation is a routine method for the characterization of the heavy ends of petroleum.⁶⁵ For the production of high boiling or "non-boiling" cuts, short path or molecular distillation techniques are required to prevent thermal cracking of the resids. Gas chromatographic simulated distillations are used to obtain characteristics of the distillation cuts. A middle distillate (473-723 K) of a Wandoan coal liquid was separated by spinning band distillation into narrow boiling point cuts with a 2-28 K range by Satou et al.⁶⁹ High performance liquid chromatography (HPLC) was then used for further separation of the fractions into six hydrocarbon classes according to the number of aromatic rings. The six classes are alkanes, monoaromatics, naphthalene-type aromatics, biphenyl-type aromatics, tri- and tetraaromatics, and poly-aromatic and polar compounds. Structural analysis of each compound class was performed by ¹H- and ¹³C-NMR. HPLC was used by Amateis et al. to separate the non-volatile polar fractions of coal derived materials.^{66,70} On-line FTIR and ultraviolet (UV) spectroscopies were used to characterize the material. Identification of hindered and unhindered phenols was made based on the FTIR results and the chromatographic retention times of the materials. In a study performed by Green et al.,⁷¹ the polar compound classes in SRC-II liquids were analyzed by HPLC with UV detection, as well as by non-aqueous titrametric methods and infrared spectroscopy. The study showed that HPLC is a rapid method which is applicable to a wide variety of compound types with a high degree of sensitivity. It also was shown, based on retention correlations developed for model compounds, that the HPLC-UV elution chromatograms can be "read", somewhat like spectra, to obtain information about the samples. However, ambiguities in assigning retention regions to specific compound classes, and the poor specificity of the detector for certain classes of compounds (including amides) are limitations of the method.

Hurtubise and Silver⁷² reported the results of a four-year study in which multiple separation techniques were developed for application to coal-derived materials. Among the techniques were several HPLC methods and solubility separation into oils, asphaltenes and preasphaltenes. The analytical methods developed in the study can be applied to nondistillable coal-liquid samples. Two samples that were analyzed were the SRC-I direct liquefaction products of a Wyodak subbituminous and a Kentucky bituminous coal.

Solubility separation, normal phase HPLC-FTIR, reverse phase LC, and gas chromatography-mass spectrometry were used to study the fate of basic nitrogen-containing solvents in bench and pilot plant scale coal liquefaction experiments.⁷³ Gas chromatography with both flame ionization and FTIR detection was used to analyze the distillate from selected coal liquefaction runs which used tetrahydroquinoline (THQ) and tetralin/THQ as solvents. The tetrahydrofuran-soluble portion of the liquefaction residua from these runs were analyzed in a number of ways, including HPLC with FTIR and UV detection. A cross-check of the normal phase LC method was made by using reverse phase LC. Good agreement was obtained between the two methods. By employing these techniques, the fate of the basic nitrogen solvent compounds could be described.

Green et al.⁷⁴ describe a scheme for the isolation and analysis of the hydroxyaromatic species from fossil fuel. The ultimate analysis is by gas chromatography-mass spectroscopy, thus the method is limited to materials boiling below approximately 500°C. However, the isolation techniques are not temperature limited. These techniques include an initial isolation of the total acid concentrate by nonaqueous ion exchange chromatography, followed by subfractionation of the acids into compound classes by HPLC. Derivatization by acylation or silylation and GC/MS analyses complete their analytical scheme. To study the sulfur containing species in coal extracts, Gundermann et al.⁷⁵ complexed the organic sulfur compounds with copper, mercury, palladium, and other metal salts. The silica gel support was converted to the metal-containing form by simply slurrying with an aqueous solution of metal salt. The complexed sulfur compounds elute from the chromatography column in the order of their Lewis-basicity. If the complex is too strong a Lewis base, it does not elute. Effective separation was achieved by appropriate choice of ligand.

A comparison of several analytical procedures for the analysis of catalytically hydrogenated and pyrolytic coal products was made by researchers in several laboratories (Delpuech et al.⁷⁶). These procedures included distillation, solvent extraction, sequential elution chromatography (SESC) on alumina, HPLC, chromatography by charge transfer complexation on grafted silica, and gas chromatography. Samples studied included a atmospheric flash distillation residue (300°C, 5 mm Hg) from a catalytic hydroliquefaction process (380-400°C, 220 bar), and three distillation cuts (102-215°C, 215-265°C, >265°C) from bench-scale (autoclave) liquefaction experiments. The authors conclude that although a variety of techniques can be applied to the characterization of coal products, it must be noted that some techniques are highly dependent on experimental procedure and suffer from poor reproducibility, other methods need to be optimized for each type of sample examined.

A rapid preparative liquid chromatographic separation is described by Burke et al.⁷⁷ for the analysis of the THF-soluble portion of the 850°F⁺ distillation resid from two different direct coal liquefaction facilities (the Wilsonville Advanced Two Stage Coal Liquefaction facility and the HRI Catalytic Two-Stage Liquefaction process development unit). The separation produces three classes of materials; they are oils (hexane soluble), asphaltenes (hexane insoluble, benzene soluble) and preasphaltenes (hexane-benzene insoluble, pyridine soluble).

Partition chromatography (Sephadex LH-20 or C₁₈-partition) followed by HPLC was used in a study designed to compare the chemical and mutagenic properties of shale oil, oil shale retort waters, and selected coal liquefaction products.⁷⁸ A Paraho shale oil, oil shale retort waters, an SRC-II distillate blend, and an SRC-I solid product were analyzed for known mutagens (among them, primary aromatic amines and aza-polynuclear aromatic hydrocarbons). The two coal-derived materials were found to have less polar mutagenic species than the shale oil or retort waters, although the number of different mutagenic species found in the coal-derived materials was much greater.

XI MICROSCOPY

The solid nature of several coal-derived products allows for the extension of well-defined microscopic techniques, used for the examination of coal, to the

analysis of these product materials. Microscopic analysis of several coal-derived materials has been successfully accomplished using a number of different techniques, including reflectance and fluorescence microscopy, and optical rotation polarimetry. Davis et al.⁷⁹ studied the dynamics of mesophase growth and coalescence of carbonizing pitch using reflected-light microscopy. The microscope was equipped with a heated stage and the real-time imaging was accomplished. In addition, solvent-refined coal (SRC) and SRC fractions were carbonized in small gold tubes. The pyridine-insoluble portion of the carbonized product was subsequently examined by reflected-light microscopy. The chloroform-insoluble residue obtained after the catalytic hydrogenation of hvA bituminous coal was examined by fluorescence microscopy and compared to the feed coal.⁹² The hydrogenation reactions were carried out in tubing bombs without solvent. It was found that the fluorescence intensity of the vitrinite in the unextracted coal after catalytic hydrogenation increased with increasing reaction temperature. This also corresponded with an increase in extraction yield. Ottenjann⁸⁰ described the alteration of fluorescence intensity in samples of Rhenish brown coal, a high volatile bituminous coal (from the Upper Westphalian C of the Ruhr area), Rundle oil shale (from Australia), and a high volatile bituminous coal from the Ruhr area as the samples changed as the result of photochemical reactions. In general, a relationship was found in which the lower the level of maturation of the initial sample, the more reactive is the organic matter and the stronger is the positive alteration of the fluorescence intensity. Davis et al.⁸¹ concluded that the vitrinite fluorescence intensity changes, within the bituminous coal rank, due to the development of a mobile phase in bituminous coal as the coal matures. In the same study, it was demonstrated that oxidation of the coal can lead to a reduction of fluorescence intensity. A study of the kinetics of the photochemical reactions which brings about the fluorescence alteration in crude oils (and chromatographic fractions of the oil) was undertaken by Pradier et al.⁸² They found that two basic forms of fluorescence alteration exist: a quick negative alteration (decrease) in the emission flux, and a generally slow positive alteration (increase).

Optical rotation by materials with biological origins can be used to investigate the geological maturity of the samples. It was proposed that optical rotation could be used to determine the thermal history of a shale oil sample in an in-situ retort. Retima et al.⁸³ characterized the highest optically active fraction

of a Green River shale oil from an above ground retort which was operated to simulate an in-situ retort process. The ultimate goal of the study was to develop an integrated approach using optical rotation and gas chromatography to track the shale oil samples in the in-situ retort. The most optically active compounds were successfully identified.

XII OTHER TECHNIQUES

Additional techniques which do not fit well into the categories described above include differential pulse voltammetry, polarographic characterization of aromatic structures, and standard (e.g., American Society for Testing and Materials (ASTM)) testing methods for fuels.

Differential pulse voltammetry was used for the analysis of the high molecular weight nitrogen-containing portion of coal derived materials, inclusive of a coal tar pitch, a direct coal liquefaction product, a pyrolysis liquid, and an SRC process residue.⁸⁴ Based on findings with polynuclear aromatic hydrocarbon (PAH) model compounds and the corresponding N-enriched PAHs, comparison of the asphaltenes and N-enriched portions of the coal-derived materials showed that the N-rich portions consist mainly of N analogues of hydrocarbon structures. These structures are found in the asphaltenes, except in the coal tar pitch, in which case the nitrogen was concentrated in smaller aromatic ring clusters.

Polarographic analysis was carried out on Synthoil coal liquid solvent fractions and on asphaltenes obtained from a number of other coal liquefaction products.⁸⁵ The solvent-separated fractions obtained from the Synthoil were designated gas oil, resin, asphaltene, carbene, and carboid. Correlations of the diffusion constant and the color and refractive indices of each fraction were made. The total polarographic reduction measurement per average molecule, as well as the color indices and refractive indices, increase in the order of the fractions as given. This trend agrees with the increase in the number of aromatic rings and total amount of aromatic carbon in each fraction.

In a program designed to measure the physical and chemical properties of product liquids from the SRC-I demonstration plant, ASTM fuel tests, and procedures designed specifically for coal-derived fuels, were screened to determine if they could provide meaningful results with SRC-I materials.⁸⁶ In addition, analytical

results obtained with the coal-derived materials were compared to ASTM fuel test results with petroleum-derived No. 2 and No. 6 fuel oils. It was found that certain analytical tests (such as bromine number, diene value, NMR for olefins, aniline point, neutralization number, and adsorption chromatography), which provide reliable results with petroleum products, are inappropriate for the SRC-I products. It also was concluded that the SRC-I middle distillate did not meet ASTM No. 2 fuel oil specifications for density, viscosity, and carbon residue. The SRC-I heavy distillate did not meet the ASTM specifications for No. 6 fuel oil because of a high sediment content. Sefer and Erwin,⁸⁷⁻⁸⁹ working under the U.S. Department of Energy Alternative Fuels Utilization Program (AFUP), successfully applied ASTM testing methods to seven different test fuels derived from both shale oils and coal liquids. The fuels included both diesel-type fuels and gasolines. ASTM tests which were used included those for API gravity (D 1298), distillation (D 86), cetane number (D 613), cetane index (D 976), pour point (D 97), flash point (D 93), viscosity (D 445), hydrocarbon type (D 1319), naphthalenes (D 1840), elemental analyses (D 3178, D 2622, D 3431), accelerated stability (D 2274), existent gum (D 381), octane number (research D 2699, and motor D 2700), Reid vapor pressure (D 323), heat of combustion (D 240), carbon residue (D 524), surface tension (D 971), particulates (D 2276), and refractive index (D 1218).

XIII CONCLUSIONS

This literature survey has described numerous methods and techniques for the analysis of high molecular weight fossil fuel-derived materials. Assuredly, not every method or technique currently being employed was described. However, this survey provides a broad overview of many useful ways to approach the complex problem of analyzing these difficult materials.

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