HIGH RESOLUTION MASS SPECTROMETRIC ANALYSIS OF COAL LIQUIDS

Thomas Aczel, Steve G. Colgrove, and Stephen D. Reynolds

Exxon Research and Engineering Company
Baytown Research and Development Division
P. O. Box 4255
Baytown, TX 77522-4255

INTRODUCTION

Development of new industrial technologies requires meaningful cooperation among many scientific disciplines, including several branches of chemistry, physics, engineering, economics, and others. This is particularly true for coal liquefaction technology, that involves complex operations, deals with rather refractory materials, and represents a potentially large impact on overall consumption patterns.

Analytical chemistry is a key player in this team effort. It seeks and obtains, to an extent commensurate with effort and circumstances, information on the composition of feed, product and intermediate streams. This information is utilized for fundamental understanding of the reactions involved in coal liquefaction and the upgrading of coal liquids, for monitoring day-to-day pilot plant operations, for evaluating end-products quality and for assessing process and product impact on the environment.

This paper reviews some of the analytical approaches we use in our laboratories for the in-depth characterization of coal liquids. Emphasis will be placed on methods determining organic composition. Issues discussed will include the overall nature of coal liquids, analytical strategy and methodology, the scope of the analyses, the role of separation, mass spectrometric and other techniques, and on the calculation and/or prediction of useful physical parameters from compositional data.

DISCUSSION

Overall Nature of Coal Liquids

Coal liquids are very complex liquids that contain a large variety of chemical classes and compounds. A non-exhaustive list is given in Table I. In-depth analysis generally requires the use of a variety of analytical tools, although, as we will see, these can be often reduced to mass spectrometry alone, provided that one is willing to use some assumptions and clearly understands the limitations of the short-cut method selected.

Composition is a function of both coal origin and liquefaction and/or upgrading conditions. Liquids from some western coals contain significantly lower concentrations of sulfur compounds than those from some eastern coals; while the type and severity of the upgrading process changes significantly the ratios between saturate, hydroaromatic, aromatic, and polar components. Gross composition of end-products in most cases is more affected by the type of upgrading than by coal origin.

Analytical Strategy

Selection of the best analytical strategy for the analysis of coal liquids depends on the nature of the information needed, the availability of analytical tools, funding for a particular project, and time. Information content and time/cost restraints are most often balanced with a compromise. A typical analytical scheme that is often used in our laboratories is shown on Figure 1. This scheme provides the user with a

very large body of information that is generally sufficient for most studies involving reaction kinetics, process behavior, end-product quality. The main roles of the various steps are summarized in the following paragraphs.

Separation into saturates, aromatics and polars yields valuable information on the overall amounts of these classes of compounds. It also facilitates the subsequent analysis. For example, saturates are difficult to characterize in detail in the presence of aromatics; and separation of aromatics and polars reduces the mass spectrometric resolving power requirements for the analysis of most nitrogen and oxygen compounds. Separation also eliminates structural uncertainties between furanic and phenolic oxygen types that even high resolution MS can not cope with in complex mixtures. Furans are concentrated in the aromatic fraction, phenolics in the polar fraction; separation thus allows a reliable structural assignment.

Low resolution, high voltage compound type analysis of the saturates determines total paraffins and one to six ring naphthenes. GC distillation and subsequent analysis of trapped cuts yields this type of information as a function of boiling range.

The main feature of the overall analysis is the high resolution, low voltage characterization of the aromatic, polar aromatic, and asphaltene fractions. As will be shown in the remainder of this presentation, this approach yields detailed information of several thousands of individual components and provides the user with a number of physical parameters that are related to composition.

Time and funding constraints might restrict the scope of the analytical scheme. If the separation step is not carried out, total saturates, aromatics and polars can be determined with reasonable accuracy from high voltage, low resolution MS data (Table II), while the aromatic and polar components can be measured accurately from the high resolution, low voltage analysis of the total stream. The decrease in information content will affect only the saturate type distribution, the relationship between saturate composition and boiling range, and the specific identification of some of the oxygenated types. This reduced approach is the only one feasible for materials in the gasoline range; separation of these streams would involve unacceptable losses of volatiles.

A further simplification consists of the substitution of a low resolution, low voltage analysis to the high resolution procedure. This approach is generally applicable to only rather severely hydrogenated coal liquids, as it determines only a few heteroatomic components, such as phenols. Separation of more and less condensed aromatics, that usually requires a resolving power of at least 1000 per 100 MW units, is accomplished through computerized deconvolution of the interfering homologous series, for example alkyltetralins and alkylpyrenes. The deconvolution calculations are based on a large number of high resolution analyses. The low resolution approach, using high voltage for determining saturates/aromatics/polars and low voltage for the determination of aromatic types and carbon number homologs, yields fast and highly reproducible analyses. The method was used extensively in monitoring the large coal liquefaction pilot plant at Baytown, Texas, with an average of two analyses every four to six hours each day, and with a response time of about one hour (1980-1982).

Special nature of some samples and research projects requires occasionally a more extensive analytical treatment than that outlined in Figure 1. These include separation of the aromatics into one, two, three, and four ring concentrates; separation of the polars into weak and strong acids, weak and strong bases, and neutral polars; and analysis of all the fractions by GC/MS, ^{13}C NMR, and proton NMR. The more specific separations facilitate interpretation and yield information on components in the parts per billion range (Table III); GC/MS yields important information on individual isomers; NMR corroborates and extends the structure assignments made by MS.

High Resolution, Low Voltage MS Analysis

This method is the cornerstone of our procedures. It has the unique ability to give both detailed quantitative data on a very large number of components and to summarize and sort these into process and/or product quality related parameters.

The underlying principle of the method is the simultaneous use of high resolution and low voltage. High resolution separates the very large number of hydrocarbons and heterocompounds that have the same nominal molecular weight but possess different formulas and thus slightly different precise masses. Such multiplets consist of six to eight peaks on the average at every mass from about mass 150 to mass 500 or 600 in coal liquids. Examples are given in Table IV. Low voltage greatly simplifies the spectra of complex mixtures by ionizing only aromatic and polar aromatic molecular ions. Low voltage is an open-ended approach that allows one to analyze as many components as are present in a sample; and calibration sets can be set up based on theoretical considerations and extrapolations. This is particularly important in complex natural products, that contain thousands of components that are not available in pure form for calibration.

The procedures involved in high resolution, low voltage analysis can be summarized as follows:

- The sample and a blend of halogenated aromatic mass reference standards are charged to a high resolution mass spectrometer, in our case a Kratos MS50, and are run at an effective voltage of 10-11 electron volts (measured by a ratio of 50 to 100 between the molecular ion, 106, and a strong fragment, 91, in m-xylene).

- A computerized data acquisition system, Kratos DS55 plus Exxon proprietary programs determines the mass and intensity of each component, assigns formulas, and sorts the components according to formula or compound type and carbon number.

- A second set of Exxon proprietary computer programs quantitates all individual concentrations and also summarizes the data into overall structural parameters. The scope of the analysis is shown in Table V; typical summary parameters calculated are listed in Table VI.

A very useful feature of the analysis is the calculation of physical and process related parameters from composition (Table VI). For samples available only in very small amounts, this is often the only means to obtain these parameters. Most of the calculations use simple stoichometric equations; distillation is calculated by assigning each component a boiling range derived either from the literature or extrapolations; carbon and hydrogen types are expressed in NMR terms by assigning theoretical values to each component. In all cases, total sample values are obtained by weighing the theoretical values of all components by the corresponding concentrations in a particular stream and by compositing the data.

The physical parameters calculated are generally quite accurate. Table VII shows typical data for elemental analysis, Table VIII for distillation, Table IX for NMR type parameters.

DEVELOPMENTS IN PROGRESS

While mass spectrometry is certainly the technique that yields the most detailed information on coal liquids, it also has some limitations. The major ones are the need to heat and volatilize the materials to be analyzed, and the difficulty of identifying specific isomers in complex mixtures. The volatility limitation applies to heavy ends boiling above approximately 1100°F; specific isomer identification is a

problem mainly in total coal liquids. Work is continuing in our laboratories to reduce or eliminate the impact of these factors.

The volatility requirement can be eliminated by using field desorption or fast atom bombardment for ionization. Preliminary data obtained in our laboratories show that field desorption can be used to reproducibly analyze heavy ends with molecular weights as high as 3000 for coal liquids and 4000 for petroleum liquids. The approach requires use of a high-field magnet for mass measurements up to 6000+ molecular weight and very careful standardization of the numerous experimental steps involved, including preparation of the special emitters, sample loading, source alignment, scanning and computerized data acquisition. Recognition of individual isomers can be accomplished through the use of GC/MS, in particular for the lighter components up to C_{12}, and the more outstanding ones beyond that range. GC/MS data in our labs are generally normalized to high resolution MS data on the corresponding homologs in order to account for the components that can only be identified non-specifically. We are now working on methods to interpret GC/MS data in the absence of pure compound calibrants.

CONCLUSION

The analytical methodology discussed above was used for literally hundreds of thousands of samples in the past decade. Many were run with the standard aproach outlined in Figure 1; more with the simplified, "MS only" alternative; and several with the extended technology that included GC/MS and NMR.

Availability of the very detailed and summarizable data was demonstrably of great use in the planning, development, and evaluation of coal liquefaction and upgrading processes including very small to large scale efforts.

Table I

MAJOR COMPOUND CLASSES IN COAL LIQUIDS

Class	Type
• SATURATES	• n-paraffins, iso-paraffins, cyclopentanes, cyclohexanes, 1-8 ring condensed cycloparaffins; biological residuals (biomarkers) such as isoprenoid paraffins, steranes, hopanes, etc.
• AROMATICS	• One to eight ring aromatics, such as benzenes, naphthalenes, acenaphthenes, fluorenes, phenanthrenes, pyrenes, chrysenes, benz-pyrenes, benz-perylenes, coronenes, etc.; and the corresponding aromatic thiophenes, dithiophenes, furans, difurans, thiophenfurans.
• NAPHTHENOAROMATICS	• One to eight ring aromatics as above associated with one or more six membered naphthenic rings (hydroaromatics) and/or one or more five membered naphthenic rings. Typical hydroaromatics are tetralins, tetra and octa hydrophenanthrenes, the various hydropyrenes; typical naphtheno-aromatics are indans, benzindans, etc.
• POLAR AROMATICS	• Mono, di- and trihydroxyl-aromatics and naphtheno-aromatics; pyrroles and pyridines associated with aromatics; dinitrogen compounds (probably dipyridine types); nitrogen-oxygen compounds such as hydroxy pyridines and hydroxy pyrroles.
• ASPHALTENES	• Polar aromatics with increased amounts of poly-functional types, such as di-oxygen compounds.

Table II

MS TYPE ANALYSES ARE IN GOOD AGREEMENT WITH CHROMATOGRAPHIC SEPARATIONS

A. Accuracy

Sample	Weight Percent					
	Saturates		Aromatics		Polars	
	MS	Sepn.	MS	Sepn.	MS	Sepn.
A	17	19	44	47	39	34
B	8	8	65	63	27	29
C	4	4	51	55	39	36

B. Reproducibility

Replicate runs	Weight Percent	
	Saturates	Aromatics & Polars
1	27.69	72.31
2	27.66	72.34
3	27.71	72.29
4	27.92	72.08
5	27.68	72.32
6	27.54	72.46
Average standard deviation on 16 runs in one month	0.081	0.081

Table III

SEPARATION PLUS HIGH RES MS DETECTS PPB COMPONENTS

Example: Acidic Fraction of a Coal Liquid

Carbon No.	Concentration, parts per billion			
	Phenols	Indanols	Hydroxy-Indenes	Naphthols
6	4389	---	---	---
7	28400	---	---	---
8	16875	---	---	---
9	1715	301	62	---
10	450	142	43	0
11	287	58	35	15
12	21	44	30	5
13	8	49	14	0
14	0	36	0	0
15	34	18	3	0

- Separation enrichment : ~4,200-fold
- Dynamic range in high res MS run : ~18,000

Table IV

TYPICAL MULTIPLET SITUATIONS IN COAL LIQUIDS

Component Class	Example	Delta Mass	Resolving Power Required Mass 300	Resolving Power Required Mass 600
Non Condensed/Condensed Hydrocarbons	$C_{22}H_{36}/C_{23}H_{24}$	0.0939	3200	6400
Non Condensed Hydrocarbons/ Aromatic Thiophenes	$C_{22}/H_{36}/C_{20}H_{28}S$	0.0905	3300	6600
Non Condensed Hydrocarbons/ Mono-Oxygen Compounds	$C_{22}H_{36}/C_{21}H_{32}O$	0.0364	8300	16600
^{13}C isotopes of Hydro-carbons/N compounds	$^{13}C^{12}C_{21}H_{36}/C_{21}H_{35}N$	0.0082	37000	64000
Aromatic Thiophenes/ condensed Hydrocarbons	$C_{20}H_{28}S/C_{23}H_{24}$	0.0034	88000	176000

Table VI

PARAMETERS CALCULATED BY HIGH RESOLUTION, LOW VOLTAGE MS ANALYSIS

Composition

• Each component (carbon no. homolog)	+ weight percent
• Each homologous series	+ weight percent + Avg. C no. + Avg. MW
• Overall sample	+ Aromatic ring distribution by chemical class + Avg. MW + Avg. carbon no. + Avg. hydrogen deficiency + Weight fraction in aromatic nuclei, sidechains, saturate rings

Physical Properties

• Overall sample	+ Atomic C, H, O, N, S, H/C + C, H types as measured by NMR
• Selected classes, homologous series for suitable properties	+ Distillation curve + Density, refractive index + Predicted composition of potential distillation cuts

Process Related Parameters

• Overall sample	+ Solvent quality index in Exxon Donor Solvent process + Several others

Table V

MS ANALYSIS DETERMINES VERY LARGE NUMBER OF COMPONENTS

Chemical Class	List of Components Determined Range in Homologous Series			Appr. No. of Components
Hydrocarbons	C_nH_{2n+2}	through	C_nH_{2n-50}	700
Thiophenes	$C_nH_{2n-2}S$	"	$C_nH_{2n-50}S$	550
Dithiophenes	$C_nH_{2n-6}S_2$	"	$C_nH_{2n-44}S_2$	550
Furans/Phenolics	$C_nH_{2n-2}O$	"	$C_nH_{2n-50}O$	1100
	$C_nH_{2n-6}O_2$	"	$C_nH_{2n-40}O_2$	650
	$C_nH_{2n-6}O_3$	"	$C_nH_{2n-28}O_3$	600
	$C_nH_{2n-6}O_4$	"	$C_nH_{2n-28}O_4$	600
Nitrogen Cpds	$C_nH_{2n-3}N$	"	$C_nH_{2n-41}N$	500
Nitrogen Oxygen Cpds	$C_nH_{2n-3}NO$	"	$C_nH_{2n-41}NO$	500
Sulfur-Oxygen, Sulfur-dioxygen Cpds	$C_nH_{2n-10}SO_x$	"	$C_nH_{2n-40}SO_x$	1000
DiNitrogen, Nitrogen Di-oxygen Cpds	$C_nH_{2n-6}N_xO_x$	"	$C_nH_{2n-40}N_xO_x$	500
Miscellaneous highly condensed, poly-functional compounds	--------			600
			Total	7250

Table VII

COMPARISON OF ELEMENTAL ANALYSES BY MS AND CHEMICAL TECHNIQUES

A. Individual Samples

Weight Percent					
Atomic H/C		Elemental N		Elemental O	
MS	Chem.	MS	Chem.	MS	Chem.
0.93	0.96	0.10	0.12	0.02	0.10
1.12	1.14	0.90	0.70	0.71	0.76
1.70	1.69	2.30	2.52	2.40	2.63
2.17	2.17	5.92	6.00	3.68	3.22

B. Composite Data on Separated Classes

	Weight Percent				
	MS on Separated Classes				
Element	Saturates	Aromatics	Polars	MS Composite	Chemical
C	86.10	91.34	84.68	88.60	88.84
H	13.90	7.68	7.37	7.84	7.82
O	---	0.40	5.43	2.28	1.83
N	---	---	2.52	0.95	1.17
S	---	0.58	---	0.33	0.33

Table VIII

COMPARISON OF MS AND GC DISTILLATIONS

Temperature, °F	Percent Off			
	Sample A		Sample B	
	MS	GCD	MS	GCD
400	0.9	0.1	13.4	12.8
500	5.5	3.6	52.5	48.3
600	15.0	14.0	83.6	86.5
700	37.0	34.4	96.7	98.2
800	63.1	65.8	99.2	99.8
900	86.0	88.5	99.7	100.0
1000	76.8	98.3	99.9	100.0

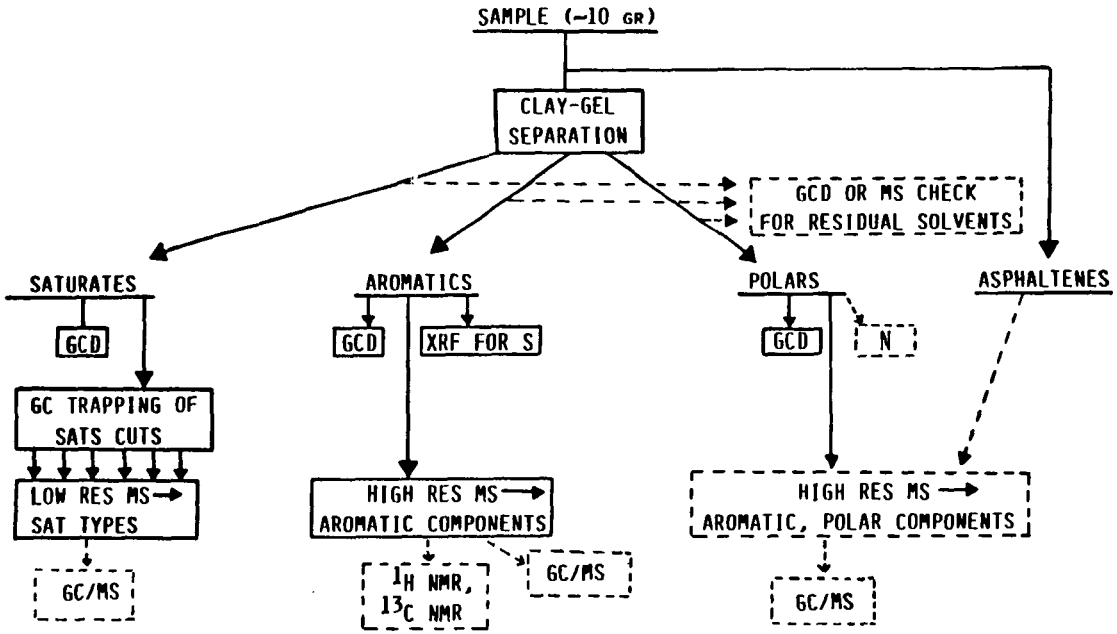
Table IX

COMPARISON OF CARBON TYPES BY MS AND NMR

Carbon Type	Mole Percent	
	MS	NMR
Saturate	37.1	38.7
Naphthenic	18.2	19.5
Linear	18.9	19.2
Olefinic	0.0	0.0
Aromatic	62.9	61.3

Figure 1

ANALYTICAL PROCEDURE FOR COAL LIQUIDS



LEGEND: ☐ : STANDARD
⬚ : OCCASIONAL; ON REQUEST

LEGEND: GCD : GAS CHROMATOGRAPHIC DISTILLATION
MS : MASS SPECTROMETRY
RES : RESOLUTION
S : SULFUR
N : NITROGEN (DETERMINATION OF)
NMR : NUCLEAR MAGNETIC RESONANCE