A Characterization and Evaluation of Coal Liquefaction Process Streams

Status Assessment

S. D. Brandes

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CONSOL Inc.
Research & Development
4000 Brownsville Road
Liberty, PA 15129

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SUMMARY AND CONCLUSIONS

A review of the literature dealing with the modelling of fossil-fuel resid conversion to product oils and an updated assessment of the physico-chemical analytical methodology applicable to coal-liquefaction product streams is presented in this document. In addition, a review of the Participants Program and a brief description of the Base Program conducted under DOE Contract No. DE-AC22-89PC89883 is provided. Analytical methods which were addressed under Contract DE-AC22-89PC89883 and found to be potential candidates for this contract are briefly described. A sampling plan for the work on resid reactivity to be performed under this contract by the University of Delaware also is included.

Analytical methodologies included here are either those which are different than those previously surveyed^{1,2} or are improvements on, or significantly different applications of methods previously surveyed. The literature cited spans the time period from 1991 to the present. This survey can be considered as an addendum to the Analytical Needs Assessment¹ and Literature Survey² produced under DOE Contract DE-AC22-89PC89883.

The literature dealing with fossil-fuel resid conversion kinetic models was surveyed. The literature was examined from the 1960s through the present. When possible, for each model described, the methodology for deriving the model and the relative quality of the kinetic parameters derived is discussed. Many of the models are similar; however, no attempt to compare them is made here. Proposed reaction schemes used for constructing coal-conversion models, in many cases, include the conversion of a 'resid' intermediate to light products. These models are, therefore, also of interest, and are included here.

The kinetic models are grouped into two general approaches. One approach entails the choice of pseudo components (or lumps). Each lump represents a characteristic of many chemical compounds of the reactants and products. Reaction kinetics are then derived for reactions of these lumps. The derived kinetic models in many cases fit the experimental data quite well. However, each model is dependent on the choice of the pseudo components and the similarity of the species which comprise it. If the lump is made up of species that vary widely in their kinetic behavior, the generalized behavior of the lump will not fit the experimental behavior.

An extension of the lumped modeling approach is to recognize that the lumps are actually representations of a continuum of properties, and thus, the kinetic model attempts to describe a continuum of reactions. Continuous distribution mathematical representations are thus applied to the description of the lumps and are used to describe the reactions. This approach requires the choice of some variable (or variables) to represent the distribution; molecular weight and carbon atom content are two variables often chosen.

A second approach to modeling the kinetics of resid conversion is the construction of a structural model. These can be "built" using Monte Carlo techniques or other structure-building methods such as the assignment of vector descriptions to individual organic compounds. In these techniques, structures are built based on the probability distribution that is predicted for their existence. These structures are then "reacted" based on the probability that they will undergo certain molecular scission and combination reactions. The properties of the "reacted" system are then checked against measured properties of the materials being modeled. An iterative procedure is used to cause the computer simulated model to conform to the experimental data. The kinetic parameters, such as rate constants, pre-exponential factors, and activation energies are derived from the computer-generated reaction networks. The availability of increasingly powerful computing technology has made this kinetic modeling approach more prevalent.

State-of-the-art modeling techniques, when applied to complex systems such as coal-derived resids, deal with the structural components of the material. In doing so they represent the detail and complexity of these multi-component hydrocarbon mixtures. These models can incorporate fundamental physico-organic chemical information of the system. Thus, the model provides a means for this fundamental information to be directly connected to properties of the material and to predict the material's behavior in various circumstances and applications (for example, as a refinery feedstock).

The major obstacle to the application of state-of-the-art modeling techniques to a system such as coal-derived resid is the tremendous molecular diversity of the materials to be modeled. There are an estimated 10^5 different molecules in the resid with extensive molecular connectivities. The sheer size of the system to be modeled precludes the use of single-species (pure-compound) rate equations.

Therefore, simplifying assumptions must be made. The quality of the model is dependent on the quality of these assumptions.

The kinetic models which will be constructed under this Contract will use the state-of-the-art modeling techniques. An integrated system of both lumped techniques and Monte Carlo statistical design methods will be used. This will allow for both the use of molecularly explicit physico-chemical information and information on lumped classes of compounds. The use of the data on lumped groups of materials will result in time savings in the analytical chemical investigation of the materials and will result in a model that can be easily applied. The Monte Carlo technique will be a check on the quality of the assumptions made in designing the lumps. The kinetic model generated will not be static, but can be augmented, reduced, or otherwise altered to reflect additional or inconsistent data as additional data are made available. The model generated will rely on data from a broad range of resid materials, produced under various reaction conditions. This will provide depth to the model and will assure that it be generally applicable to coal-derived resids produced in modern processes.

INTRODUCTION

The characterization of the non-distillable resid portion of liquefaction oils is important because of the role this material has in the liquefaction process. In current direct liquefaction technology, the heaviest soluble materials produced from coal are recycled to near extinction. These heavy soluble materials (850 °F+ resids) typically account for about 50% of the recycle stream fed to the first reactor stage in modern two-stage liquefaction technology. At a 2:1 recycle-to-coal ratio, the principal component of the feed to the first reactor is, therefore, not coal, but this recycled resid. Understanding the formation, composition, and reactivity of this heavy material will lead to an improved understanding of the direct coal liquefaction process, and enhance our ability to identify and prioritize cost-reduction options and evaluate the results of process development experiments. A quantitative model of resid conversion reactions should allow quantification of the effects of process variables that most greatly impact capital costs such as space velocity (reactor size), hydrogen pressure, catalyst activity, and reaction selectivity.

The reaction of coal to light products is often modeled as a multi-step process in which coal dissolution to heavy materials (resids) occurs first and then the heavy materials convert to distillate (final) products. The kinetics of direct hydrogenation of coal to produce liquid fuels is not completely understood; neither are the presumed mechanisms of the two steps of conversion of coal to resid, and resid to lighter products. Furthermore, there is incomplete chemical information on the feedstock (coal), the products, and reaction intermediates (recycled distillate and resid). The resid (operationally defined to be material boiling above a set temperature, usually between 800 °F and 1050 °F) poses a significant analytical problem since it is a high-molecular-weight material, is limited in solvent solubility, and contains a significant concentration of heteroatomic functional groups. In an effort to determine appropriate methods to obtain physico-chemical information on the resids, application of analytical techniques for the analysis of the distillation resid was undertaken.³ A summary of that survey is presented in Part III of this report. Analytical methods which previously were not addressed, or recent significant advancement of techniques which were investigated, are described in Part IV of this report.

Resid reactivity can be defined as the rate and extent of conversion of resid to lower molecular weight products with concomitant reactivity toward retrograde reactions. A straightforward measure of resid reactivity might be the disappearance of resid under some particular set of reaction conditions. It is recognized that the retrograde reactions are one of the controlling factors in the rate of production and ultimate yield of net liquid products. When the reaction conditions span a range of temperatures, residence times, concentrations, etc., reactivity can be generalized into a kinetic model. No standardized empirical test presently exists for measuring the relative reactivity of resids. However, a variety of analytical methods previously were used to produce data to construct models of the conversion behavior of fossil fuel derived materials, including coal-derived resids. Part IV of this report is a survey of the literature dealing with the construction of empirical models of the conversion of coals and fossil-fuel-derived resids.

REVIEW OF CONTRACT DE-AC22-89PC89883

PARTICIPANTS PROGRAM DESCRIPTION

The Participants Program was conducted under DOE Contract DE-AC22-89PC89883 by subcontract from CONSOL with research groups of U.S. industry, academia, and government-sponsored laboratories. In total, 24 groups were participants in the program. The projects examined the chemical and physical properties of over 100 samples utilizing 30 different analytical techniques. The primary goal of the program was to bring about a concerted effort of analytical researchers and direct coal-liquefaction process developers through the use of novel analytical methods for the achievement of improved process design, development, and operational economics. Emphasis in the program was placed on the resid component of the process streams for two reasons: on a single-pass basis, it is the major reactor feedstock and product; and it is more difficult to analyze than the light distillate products, and thus less well-defined

SUMMARY OF FINDINGS FROM PARTICIPANTS PROGRAM

An extensive survey was made by CONSOL in 1991 of the status of analytical methodology associated with direct coal liquefaction technology.¹ Sources of information for the survey included the scientific and technical literature and the coal liquefaction community, including process developers, process engineers and analytical chemists from government, industry and academia. CONSOL's participation in preparation of the U.S. DOE-sponsored Coal Liquefaction Research Needs Assessment (COLIRN)⁴ provided a foundation for this survey. The survey identified a number of broadly characterizable process-development needs. Specific methodologies (or techniques) potentially relevant to addressing most of these needs and research groups who were employing those techniques were identified. Many of the methods identified were well-developed and were new only in that they were not fully demonstrated for their applicability to coal liquids. Other techniques were "cutting edge" and were under development for a number of applications, including natural product analyses.

In addition to the Analytical Needs Assessment, a literature survey was made to identify analytical methods and techniques for application to the analysis of coal-derived resids.² Analytical methods and techniques chosen for inclusion in the review 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. That review primarily was limited to literature published between 1980 and 1991.

Using the Analytical Needs Assessment and the literature survey as a guide, 30 techniques were chosen for evaluation in the program. The criteria by which those techniques were evaluated included: demonstration of the ability to clearly delineate process-induced differences in the samples; the relative ease of use of the technique; the cost of equipment to perform the analysis; ease of data interpretation; and, most importantly, the expected impact of the use of the method on process economics. Based on these criteria, a few of the techniques surveyed were found to have a high potential for immediate application to process development for improved economics. Those techniques which were considered to have high potential for application to process development include ^{13}C -nuclear magnetic resonance (NMR) spectroscopy to produce a set of chemical structural descriptors, field ionization mass spectrometry (FIMS) to determine the molecular weight profile of the complex mixtures of which coal liquids are comprised, and to speciate a number of individual compounds, and electron spin resonance (ESR) spectroscopy combined with thermogravimetric analysis (TGA) to profile the free radical content of the coal-derived materials. Another important aspect of the program was analysis of the product oils. A set of petroleum inspection tests, routinely used to evaluate petroleum refinery feedstocks, was found to provide important information on coal-derived product oils.

A complete list of analytical techniques that were evaluated in the Participants Program and research groups that provided them are given in Table 1. In Table 2, the methods are grouped as follows: 1) methods with a high potential for immediate use, 2) methods which have potential for application, but which, because of issues of cost, complexity, or status of development, are not presently applicable to coal-derived materials, and 3) methods which were surveyed, but are not presently recommended for the analysis of coal-derived materials, especially the resids.

BASE PROGRAM DESCRIPTION

In support of the DOE direct liquefaction process development program, process samples are routinely analyzed by CONSOL. Such analyses include (when appropriate): elemental analysis, ash content, ash elemental analysis, fractional distillation, solubility fractionation, phenolic -OH concentration by FTIR

spectroscopy, calorific value, hydrogen classes by ^1H -NMR spectroscopy, and solvent quality testing. In addition, CONSOL documented the full history of the samples (plant, process conditions, age, storage conditions, hydrogen consumption, and yield data for the associated run). Kinetic parameters were often calculated for coal liquefaction runs.

LITERATURE REVIEW

ANALYTICAL TECHNIQUES FOR RESID ANALYSIS

The following is a literature review of analytical methods and techniques potentially useful for the analysis of heavy fossil fuels. It covers the period from 1991 to the present and can be considered an addendum to Reference 2. Many techniques currently in use were described previously in Reference 2; only new techniques and/or significant improvements in previously described techniques are included here.

MOLECULAR WEIGHT DETERMINATION

Mass Spectrometry

A comparison was recently made of three contemporary ionization/mass analyzer techniques useful for the analysis of complex fossil-fuel materials.⁵ The three methods are laser desorption (LD), desorption chemical ionization (DCI), and laser desorption electron ionization (DEI) high resolution mass spectrometry (HRMS). These methods were applied to pyrolysis tars and pyridine extracts derived from Argonne premium coal samples. There is good agreement in mass, if not peak intensity, for the spectra obtained by LD and DCI methods. The ion series obtained by each of the two techniques also are similar. The DEI technique also was compared to the LD technique. In general the LD mass spectra favor the aromatic compounds over the aliphatic compounds. This results in a less complex, but one with less information content. The authors describe briefly an experimental method to enhance the intensity of aliphatic component of the spectrum. In all three techniques there is an absence of ion intensity below 200 amu indicative of limited molecular fragmentation. In all three techniques, no ion peaks were observed at masses higher than 1500 amu.

Matrix-assisted laser desorption mass spectrometry (MALDI-MS) is used primarily to ionize and desorb large fragile biomolecules such as proteins and DNA intact for mass spectrometric analysis. In a paper by Herod et al.,⁶ the technique was used to characterize a set of Argonne premium coals. They showed that coals of different ranks all exhibited the same features; a series of homologous peaks in the 200-500 Da range, an intense peak in the 1000-5000 Da range, and lower intensity peaks extending to large masses (>270,000) which increased with increasing coal rank. John, et al.⁷, also report that masses (with significantly intense peaks) can be detected up to 270,000 Da in coal and up to 12,000 Da in coal-derived materials with MALDI-MS. The authors imply that the identification

of materials with such high molecular weights is possible because, unlike electron-impact, chemical ionization, and field ionization mass spectroscopy, there is no dependence on the vaporization of the sample before ionization. However, the high molecular weights observed may be explained by an occurrence of ion saturation of the detector where high ion currents cause spurious peaks which are misinterpreted as ion signals of high mass.⁵

A two-dimensional Fourier-transform ion cyclotron resonance (ICR) mass spectrometry stored waveform ion modulation (SWIM) technique produces a 2-D mass spectrum in which parent-ion peaks from a sample or mixture appear on the diagonal of the plot and product-ion peaks appear off diagonal⁸. In the technique, a sinusoidal modulation is applied to the speeds of parent ions circulating in the ICR spectrometer. Varying the modulation frequency allows the parent/product connections to be elucidated. This MS/MS technique provides a simple graphical means for identifying all gas-phase ion-molecule reactions simultaneously from a single experiment. The authors believe that this technique has high potential application for complex materials containing hundreds of components and many overlapped peaks.

Gel Permeation Chromatography and Vapor-Phase Osmometry

In an effort to produce a set of calibration standards for gel permeation chromatography (GPC) that would be more applicable to fossil fuel analyses than polystyrene standards, asphaltene fractions of Cerro Negro, Morichal, and Pao 'extra-heavy' crude oils were octylated and then fractionated on the basis of solubility in n-hexane. These fractions were then analyzed by GPC and vapor-phase osmometry (VPO).⁹ However, it was found that the molecular weight calibration line obtained by using the octylated asphaltene fractions was close to that obtained for polystyrene standards in the molecular weight range examined. Thus, it is concluded by the authors, indicates that in the molecular weight range examined, differences in polystyrene and asphaltene structure are not a major consideration. Although no difference was found using the asphaltene fractions of crude petroleum oils, it is possible that synthesis of octylated fractions from coal liquefaction resids may prove to be a useful calibration method for coal liquids rather than the use of polymers such as polystyrenes.

A study of coal pyrolysis products by size exclusion chromatography (SEC) was carried out to study the effects of thermal treatment on the polycyclic aromatic compounds (PACs) present in coal samples.¹⁰ A poly(divinylbenzene) (PDVB)-phase column was used. The PACs elute in two fractions. The substituted PACs (XPAC) elute according to molecular size. The unsubstituted PACs (HPACs) do not exhibit size dependent behavior and elute beyond the totally permeated volume. Lignite pyrolysis products produced at different temperatures show a broad distribution of XPACs and HPACs. However, the chromatograms of a bituminous coal (PSOC 997) show that the low-temperature (1223 K) pyrolysis products elute completely in the XPAC region, whereas the high-temperature (1473 K) products elute sharply in the HPAC region. The technique appears to be highly sensitive and can be applied to microgram quantities of sample.

Three recent papers deal with the use of GPC to analyze asphalts.^{11,12,13} Analyses of the asphalts (and fractions of the asphalts) are performed to produce molecular size distributions (MSD) which are used to compare samples. The presence of large assemblies of smaller molecules was noted and used to characterize the asphalts and differentiate among asphalts obtained from different sources. Three-dimensional plots (elution time vs. wavelength vs. intensity) of asphalts and their strong acid and base fractions show distinct differences among a set of three asphalts.¹¹ The use of different detectors (specifically, ultra violet-visible spectroscopy with diode array detection and differential refractive index detectors) is discussed in all three papers. To address the issue of changing molar absorptivity over the entire MSD when UV detection is employed, Bishara and McReynolds¹² fractionated the asphalt into compound classes. The relative molar absorptivity was then determined for each fraction. Small time increments of the chromatogram were analyzed to mathematically correct the MSD for the changing molar absorptivity. Saturates were separately analyzed using a refractive index detector. A study of artificial aging of asphalt cements was conducted and monitored by GPC analyses.¹³ Changes in physical properties were reflected in the MSD. It was clearly shown that the changes of MSD depicted in the GPC chromatograms could reflect the effects of aging. A regression analysis was applied to correlate the physical properties (viscosity and hardness) with the different segments of the MSD chromatogram; division of the chromatogram into 10 equal "slices" showed better resolution than fewer divisions. A good fit was obtained for the regression models with data from a variety of asphalts. The authors believe that

this demonstrates the general applicability of GPC analysis to characterize asphalt cements, predict their physical properties, and identify aging in the asphalts.

A paper dealing with the planar size exclusion chromatography (PSEC) of bitumen¹⁴ describes work done to determine the optimum conditions for analysis, make the technique quantitative in terms of molecular mass distribution (MMD), and distinguish between bitumens from different sources. PSEC can be described as thin layer chromatography using size exclusion chromatography substrates. Several substrates of various pore size were evaluated; 60 Å and 120 Å pore-size silica gel were each found to have merit in the analysis of the MMD of the bitumen. Ultraviolet detection was used; however, response factors for some of the bitumen components are significantly different than other components of the material. Polystyrene calibration standards were found to be inadequate for the bitumens. For these reasons, quantitation of results was not possible. Qualitatively different MMD profiles were obtained for bitumens of different grades and from different sources. The method also was used successfully to monitor qualitative changes in oxidation of the bitumen.

ELECTRON SPIN RESONANCE OR ELECTRON PARAMETRIC RESONANCE

Researchers at West Virginia University (WVU) have explored the use of a novel high temperature/high pressure ESR apparatus to obtain in situ ESR spectroscopy data from the hydrogenation of Blind Canyon coal at 440 °C at hydrogen pressure of 600 psi, with and without catalyst.¹⁵ In this system, the pressure can be varied as a function of time and/or temperature. The equipment has an operating temperature range of ambient to 500 °C, and the pressure range is atmospheric to 800 psi. These ranges are limited by the properties of the Pyrex ESR tube. The studies reported by WVU with Blind Canyon coal clearly show changes in free radical density (N) as a function of time, temperature, atmosphere (H₂ or N₂), and catalyst.

INFRARED SPECTROSCOPY

The in situ analysis of pyrolysis products of kerogen (extracted from Kimmeridge sediment sample) and asphaltenes (extracted from Magara, Egypt, low-rank coal) by diffuse reflectance Fourier transform infrared (DR-FTIR) spectroscopy was recently reported.¹⁶ The experimental apparatus consists of a porcelain sample cup which is placed in a zinc selenide dome. The chamber can be heated to 900 °C

and pressurized to 6.9 MPa. The chamber also can be used with various gaseous atmospheres, or evacuated and operated under vacuum conditions. Progressive variations in the DR-IR spectra of the solid samples were obtained as the temperature of the chamber was increased. Taulbee et al.¹⁷ reported on experiments designed to assess organic functional group changes in demineralized kerogens and lignite in situ during pyrolysis. These experiments were performed by coupling an optical microscope heating stage with a reflectance FTIR. The technique is not amenable to quantitative analysis and is considered by the authors to be "...a rapid and convenient qualitative tool for monitoring structural changes that can be attributed to thermal alteration". Plots of functional group intensities obtained by integrating the absorption bands in the reflectance spectra, normalizing, and plotting versus temperature show relative intensity for a given absorption band as a function of treatment temperature. It was found that variations of absorption with temperature are similar for all samples studied.

A paper describing the use of on-line infrared (IR) measurements¹⁸ for quality control of molten polymers in the manufacture of plastics may have application to the control of high-pressure, high-temperature coal liquefaction systems. The on-line IR equipment allows for visualization of the process stream in a continuous, non-intrusive manner which provides information about the stream rapidly and in a format useful for control of the process. The molten polymer stream is maintained at 400 °C and 270 bar. Therefore, FTIR equipment was designed with a high-pressure, high-temperature flow cell. Heated transfer lines convey the molten polymer to the cell. Spectral information (in the mid-IR energy range, 4400 to 400 cm^{-1}) is processed with a monitoring computer and relayed to the process control system. The cell pathlength is adjustable for a sample thickness between 2 mm and 25 μm . In order to withstand the elevated pressures, the windows are manufactured from either zinc selenide or natural diamond.

Another application of on-line FTIR is described in a paper by Solomon et al.¹⁹ This paper describes the use of a thermogravimetric analyzer coupled with an FTIR spectrometer to obtain an analysis of the decomposition products from coal pyrolysis. According to the authors, this technique is more rapid than gas chromatography. The authors also claim that the technique has an advantage over mass spectrometry in its enhanced ability to analyze very heavy products;

however, the authors do not specify the mass range which they anticipate analyzing. From this technique, a quantitative analysis of the evolved gases and tars is possible. Kinetic rates of species evolved in coal pyrolysis also were obtained by employing several heating rates. The kinetic rates thus obtained are used to extrapolate the conversion behavior expected from pyrolysis at higher heating rates.

UV-FLUORESCENCE SPECTROSCOPY

Li et al.²⁰ indicate that UV-fluorescence (UV-F) spectroscopy is a promising technique for providing information on the relative concentrations and sizes of fused ring aromatic systems in coal-derived materials. The authors acknowledge that there are a number of complications which arise in interpretation of the UV-F analyses of complex systems, such as coal-derived products. In an effort to minimize these complications, Li diluted pyrolysis tar samples and the size exclusion chromatography fractions of the whole tars, obtained from 8 different coals, in CH₃OH to 1.0×10^{-6} g/mL. The dilution of the samples was done to minimize the effects due to self-absorption, intermolecular energy transfer, and excimer formation. Correlations were made between coal rank, pyrolysis pressure, and maceral content and the excitation and emission spectra. It was found, for example, that as coal rank increased, the aromaticity of the tar increased as determined by the increasing relative intensities of the excitation spectra. A number of conclusions were drawn that the authors describe in the context of both the parent-coal and the pyrolysis-tar structure.

X-RAY TECHNIQUES

In an effort to understand the structure of coals and how processes such as liquefaction affect that structure, three X-ray characterization methods were applied to the study of Wilsonville 850 °F⁺ resids and the THF-insoluble portion of the resids.²¹ Diffraction experiments, absorption experiments, and X-ray fluorescence experiments were performed with the resids and the THF-insolubles. The X-ray fluorescence spectra exhibit peaks identified as iron, calcium, titanium, potassium, sulfur, and silicon. From the mass absorption experiments, a mass absorption coefficient was calculated for each sample. The values obtained indicate that the resid is a weak absorber whereas the mineral-rich insoluble portion is a much stronger absorber. The absorption coefficients were used to calculate the absorption-corrected intensities from the diffraction experiments. The diffraction experiment allows for differentiation of the

crystalline minerals and the broad peaks associated with stacked polyaromatic hydrocarbons in the sample.

Mitra-Kirtley and co-authors reported on the application of X-ray absorption near-edge spectroscopy (XANES) to determine the major nitrogen-containing chemical structures in coals and other fossil-fuel materials (specifically, oil shale kerogen and bitumen).^{22,23,24} The extension of XANES technology to the study of nitrogen compounds has come about because of the recent availability of high resolution soft X-ray beam lines and of efficient fluorescence detectors. The authors did their studies using the 'Dragon' beam line at the National Synchrotron Light Source at Brookhaven National Laboratories. In their studies they detect pyridines, pyridones, pyrroles, and aromatic nitrogens. No saturated amines were detected. Pyridine and pyrrole are the most abundant of the nitrogen structures. They report that there is a detectable shift of the ratio of pyridone to pyridine as a function of increasing coal rank. The authors generally conclude that nitrogen XANES is among the best methods for differentiating nitrogen chemical forms in fossil fuels because of the high degree of specificity coupled with the well-resolved resonances inherent in the method.

¹H NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Gerstein, Pruski, and Michel²⁵ reviewed the use of pulse and Fourier transform ¹H-NMR for the analysis of coal, cokes, and coal-derived liquids. They describe methods for quantitative analysis of both solids and liquids, obtaining and interpreting spin-lattice relaxation times (T_1) for solid fossil fuels, the use of high resolution methods for analysis of solids, and techniques for analysis of liquid extracts of coal. Many applications of the combined rotation and multiple pulse spectroscopy (CRAMPS) technique for the analysis of solid coal samples are described. All references cited in this review were published prior to 1990, as such, a number of them were included in References 2 and 3. However, a section of the Gerstein review is devoted to fossil hydrocarbons and contains references to several interesting applications of ¹H-NMR to coal-derived materials.

The technique of proton magnetic resonance thermal analysis (PMRTA) was applied to the study of eight Argonne premium coal samples.²⁶ In this method (originally described in 1988²⁷), the ¹H-NMR measurement is made in situ during heating of

the samples to pyrolysis temperatures. In the study described, use is made of the fact that the uncoupled proton magnetic resonance is sensitive to the molecular structure and dynamics of the solid coals. Transient phenomena are monitored as the coal is heated and the resulting data are correlated with fluidity, plasticity, and other physical and some chemical properties, including H/C ratio and sulfur content of the coal.

¹³C NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Magic angle turning (MAT) ¹³C-NMR experiments were shown to have advantages over the older technique of magic angle spinning ¹³C-NMR.²⁸ The MAT technique eliminates the necessity of using very high spinning speeds required to suppress or separate sidebands and the consequent difficulty in uniformly polarizing all spins. In MAT spinning, the rotational speed is <50 Hz which favors quantitative polarization of all carbons. The technique can be applied to complex powdered solids, for which it can separate tensor powder patterns according to their isotropic shifts. The resolution of the method, in terms of the chemical isotropic shift, is comparable to that of the conventional cross polarization/magic angle spinning (CP/MAS) experiment.

A study of pyridine-extracted Argonne Premium coals and the extracts was made using CP/MAS ¹³C-NMR.^{29,30} From the spectra of these materials, the authors assigned values to structural parameters and molecular descriptors (these have been described previously²). It was found that the number of cross-links and number of substituents on aromatic rings is lower for the extracts than the residues. The authors conclude that the extracts have fewer covalent bonds to the coal macromolecular structure and that this difference is why these materials are extractable.

CP-MAS and dipolar dephasing (DD)-MAS ¹³C-NMR analysis of two coals (a Montana subbituminous coal and a Wyodak subbituminous coal), the THF extracts of these coals, and the THF-insoluble portion of coal-liquefaction residues obtained from these coals is described in a paper by Song et al.³¹ A quantitative CPMAS-NMR analysis of the Montana coal showed it to have 63-64% aromatic carbon. From the DDMA- and CPMAS-NMR data, it was determined that 34-35% of the aromatic carbons of the Montana coal are protonated, 23-24% are chemically bound to oxygen atoms, and the remaining 31-33% are bound to other carbon atoms, nitrogen, and sulfur. The Wyodak coal was found by CPMAS to have a lower aromaticity (57%). The

CPMAS- and DDMS-NMR data of the liquefaction residues obtained from a non-catalytic liquefaction of the two coals at 350-425 °C for 30 min, and the THF-extracts of the coals were compared. It was found that reaction temperature has the most significant impact on the spectral characteristics of the liquefaction residues. Oxygen functionalities decreased and carbon aromaticity increased with increasing liquefaction temperature.

Single pulse excitation (SPE) and associated ^{13}C -NMR relaxation techniques were used to analyze coal-derived pitches and their toluene-insoluble fractions.³² Thermal relaxation times of the quaternary aromatic carbon present in the pitch were determined using variable delay, dipolar dephasing (DD) SPE measurements. Over 90% of the carbon is observed in the measurement. It was determined by DD-SPE ^{13}C -NMR that 60 to 70 % of the aliphatic carbon in toluene-insoluble pitch is present as CH_3 . CP-NMR can "vastly underestimate quaternary aromatic carbon concentration". The carbon concentrations which can be determined by DD-SPE are higher than those obtained by CP ^{13}C -NMR, even at long contact times; thus, the SPE method is considered by the authors to be in this application the superior technique.

SEPARATIONS AND CHROMATOGRAPHY

Three 650-1000 °F distillation fractions from the Wilsonville two-stage direct liquefaction unit were separated into aromatic ring number fractions using a dinitroaniline stationary-phase liquid chromatography column.³³ Necessary preliminary steps included first separating the materials on ion exchange resin to remove polar materials (phenols). Aromatics were then isolated from the polar- compound-free material by silica gel chromatography. This aromatic material was then separated by ring number on the DNAP column using a hexane/tert-butyl methyl ether gradient. A UV absorption spectra was obtained for each eluting fraction. Little overlap was observed in the fractions and fractions corresponded to the same separation that had been obtained for model compounds. Five fractions were obtained of corresponding aromatic rings numbers 1-5. Gas chromatography (GC) and GC-mass spectroscopy were used to confirm some compound identifications.

Green and co-workers fractionated petroleum resids into nine fractions.³⁴ These fractions were used to determine whether microcarbon residue (MCR) yield from a single resid was additive within compound types and to determine the relative

coking tendencies of the resid. In addition, the behavior of nitrogen, nickel, and vanadium partitioning (between volatiles and solids) of each compound type was studied. The first five fractions were separated by nonaqueous ion exchange chromatography. They are: 1) strong acids, 2) weak acids, 3) strong bases, 4) weak bases, and 5) neutrals. The neutrals then were separated into polar neutrals, sulfides, saturated hydrocarbons, and neutral aromatics by high performance liquid chromatography.

Slurry oil from the Tianjing refinery and heavy aromatic oil from the Lusyang refinery (China) were separated using a number of techniques to evaluate these materials for use as potential raw materials for the production of carbon fibers.³⁵ Saturated hydrocarbons were separated by normal-phase HPLC, polycyclic aromatic compounds were separated by reversed-phase HPLC. Fractions were characterized by mass spectroscopy. Average molecular weights of these materials and their fractions was determined by high performance gel permeation chromatography (HP-GPC).

MICROSCOPY

Scanning tunneling microscopy (STM) of coals and pyridine extracts of coals was attempted by researchers at Southern Illinois University.³⁶ Resolutions of 0.01 nm for lateral and 0.001 nm for vertical measurements can be obtained with this technology. Scan size can be as big as 14 x 14 μm and as little as 2 x 2 nm. Illinois No. 6 coal from the Illinois Basin Coal Sample Program (IBCSP 101) was used in this study. Sample preparation for coals was an obstacle to obtaining good nanographs. Attempts were made to scan polished coal particles, scattered coal particles, coal powders on steel slides coated with conducting paint, and coal macerals pressed into a thin wafer. Success was achieved with both coal dust deposited on conducting paint and the pressed wafers. A tetrahydrofuran (THF) extract of the Illinois No. 6 coal, diluted to 100,00:1, was deposited on the surface of highly oriented pyrolytic graphite (HOPG). A monolayer of this material gave clear images of various aromatic compounds. The images were easily differentiated from the HOPG basal plane surface.

MODELING REACTION KINETICS, THERMODYNAMICS AND MECHANISMS OF RESID REACTIONS

INTRODUCTION

Kinetic modeling of complex chemical processes requires four components³⁷. These include: 1) a complete knowledge of the elementary kinetic steps (a mechanism or reaction scheme); 2) accurate thermochemical data on all of the species involved; 3) accurate kinetic data for each step; and 4) an understanding of surface processes, which may be of importance. It can be inferred from this list of requirements that the construction of kinetic models and the determination of the kinetic parameters of reactions of complex mixtures, such as coal-derived resids, is not a trivial matter. To simplify the task, many strategies have been devised. The most prevalent of these strategies is the use of lumped kinetics. In this approach, similar chemical species are grouped together into defined classes. These classes are then manipulated in the same manner that individual reacting species would be dealt with in simpler systems. The definition of what constitutes a class, and the relationship of classes to one another varies with the degree of simplification of the possible reaction paths, number of experiments, and amount of analytical work required to define the kinetic behavior of the reacting mixture.

Construction of many of the kinetic models described in this review follows a similar scenario. Each modelling effort begins by defining the classes or lumps. An assumption is made (based on any of a number of factors) of what the reaction orders are for the reactions of conversion of one lump to another. Mass balance equations then are written for ideal reactors (batch, back-mixed, plug flow, etc.). Reaction rate constants are defined, the mass balance equations are solved, experimental data are accumulated, and the rate constants are fit to Arrhenius-type plots. The theoretical data are compared to the experimental data and the model is subsequently revised. This approach to constructing kinetic models, as will be seen below, can do a good job of describing experimental data. However, each model is often limited in scope and is applicable only to the specific conditions it was developed to model.

Luss, and Golikeri³⁸ strongly caution against indiscriminate lumping in their paper ("Grouping of Many Species Each Consumed by Two Parallel First-Order Reactions"). In their paper, they describe the pitfalls which may be encountered in grouping together various species to model complex mixtures with many components. They state that, in order to enhance the reliability of the kinetic

model, it is desirable to form pseudo components which contain only species with similar kinetic behavior. They believe that, in general, it is desirable to group together species which have about the same reactivities. A properly grouped model has to accomplish an adequate balance between the required predictive capabilities and the experimental and computational effort required to determine the corresponding kinetic parameters. If..."the pseudo component contains species with rather different kinetic behavior, the kinetic expression obtained in one reaction may not be suitable for predicting the conversion or the selectivity in a reactor with a different residence time distribution." They demonstrate these cautions with a series of extreme cases.

The increasing computational power available is (in some ways) changing the approach to deriving kinetic models. Turpin, in a paper entitled "Cut Benzene Out of Reformate"³⁹ provides a general primer for the use of computer calculations to produce reaction models for plant-scale processes. The specific case described in this paper, modeling techniques which demonstrate the effectiveness of a prefractionator to reduce benzene in gasoline production, can be applied to all modeling efforts. His six-step approach is to 1) define the modeling objective, 2) identify the process, 3) select the appropriate model, 4) collect data, 5) validate data, and 6) calibrate and verify the model's use. He cautions that before initiation of these six steps, a base relationship between process modeling software and measured plant test data must be established. Based on the users expectation of the modeling results, the computer model should include: 1) questions to be answered, 2) the degree of accuracy required, and 3) which process is the starting point for the model. For example, identification of something as seemingly straightforward as whether the model is dealing with a reaction process or a separation/mixing process for the components of the reaction streams of interest should be clearly defined. Turpin provides two categories of software for selection. The choice can be made between correlation models and pseudo-kinetic models. Correlation models are regressions of observed data formatted to allow the user to estimate changes in certain process variables. Correlation models are neither in heat nor material balance. Pseudo-kinetic models are used to calculate bulk reactions (such as total aromatics production). Pseudo-kinetic models handle interdependent and forward/reverse reactions and are excellent tools for predicting individual component yields as well as yield patterns (such as C_5^+ in a reformer). Turpin notes that there may be several reaction mechanisms, but because of limited data, one mechanism is

selected to match observed data to produce the model. The kinetic model is designed to be both flexible on some points and rigorous on others. Turpin recommends that data collection be optimized for best-collection conditions and data quality. Deviations in material balances that are acceptable (for example, 1 wt %) must be established; the same holds for H_2 balances, etc. Other criteria used to test data quality must be determined. Process modelling requires "calibration". The calibration cases use plant data to test and adjust the model to give correct responses of dependent variables to changes of independent variables. Model verification is performed by comparing alternate plant test data with model predictions. A properly designed and tuned model will predict the dependent variables within the accuracy of the measuring equipment and the model limitations.

A number of papers reviewed here do not advocate a lumping approach, but instead deal (statistically) with all the compounds in the mixture. These models 'build' a reaction network, apply a set of reaction rules, and describe the products of the 'reactions' to conform with experimental data. Iterative procedures are usually performed to hone the models. These 'structure-oriented' models are proving to be applicable to complex mixtures such as coal-derived materials.

The conversion of coal to light products is often postulated as a many-step process which includes conversion of coal to an intermediate heavy material. The intermediate material then simultaneously or sequentially decomposes into mid- and light-weight oils. For this reason, models which describe the conversion of coal via this intermediate-forming route are included in this survey. They are presented separately, following reviews of the models which describe the conversion of heavy oils or resids.

LUMPED KINETIC MODELS

Resid Conversion

In a paper by Gray,⁴⁰ data from the catalytic and thermal hydrotreating of syncrude coker gas oil (SCGO) are used to produce a reaction model by lumping of reaction kinetics based on structural groups. The groups on which the model is based are aliphatic and aromatic carbon groups. Reactions are modelled for a continuous stirred tank reactor (CSTR).

Feed and product sample were separated into saturate, aromatic, and resin fractions on a silica gel column. ^1H -NMR and ^{13}C -NMR spectroscopy, elemental analyses, and IR spectroscopy data are combined to give concentrations of a set of structural groups representing each fraction. "Analytical data were used to formulate a constrained optimization problem. Balanced equations relating the concentration of structural groups to data from elemental analysis and ^1H -NMR and IR spectroscopies constituted the linear constraints, while ^{13}C -NMR data were used to formulate a quadratic objective function. The structural profiles were obtained as the optimum solution to the objective function, subject to linear constraints." Estimated group concentrations were lumped to simplify kinetic analyses and reduce error. Lumps consisted of (1) groups α to aromatic ring, (2) total naphthenic carbon, (3) all groups β or further from aromatic ring, (4) paraffinic $\text{CH}_2 + \text{CH}$ (C-6 or longer).

Rates of reactions of each group for the catalytic case were calculated by using:

$$r_i = \frac{M_{i,\text{in}}Q_{\text{in}}\rho_f - M_{i,\text{out}}Q_{\text{out}}\rho_p}{W_c}$$

where:

$M_{i,\text{in}}$ = molality of group i in feed, mol of group/kg

$M_{i,\text{out}}$ = molality of group i in product, mol of group/kg

Q = volumetric flow rate

ρ = density

W_c = weight of catalyst

For the thermal case, rates of reaction were calculated by using:

$$r_i = \frac{m_{i,\text{in}}Q_{\text{in}}\rho_f - M_{i,\text{out}}Q_{\text{out}}\rho_p}{V_r(\rho_p/\rho_{p,r})}$$

where:

V_r = volume of liquid in reaction

Eliminated from consideration were groups which did not show significant changes in the reaction.

Molal conversions were calculated by using:

$$X_i = \left| \frac{M_{i,in} Q_{in} \rho_f - M_{i,out} Q_{out} \rho_p}{M_{i,in} Q_{in} \rho_f} \right|$$

(Absolute values are used here because some components increased while others decreased.) When all the rates of reaction were positive (indicating net removal), the pseudo-first-order rate constants were calculated by using:

$$k_i = \frac{r_i}{m_{i,out} \rho_{p,r}}$$

Arrhenius plots of $\ln(k_i)$ vs $1/T$ were used to determine which groups followed first-order kinetics. It was found that removal of heteroatoms and a decrease of aromatic carbons by catalytic hydrogenation followed first-order kinetics. Neither removal of β -CH₃ groups nor removal of C_{ar}-(C_{ar})₃ groups followed first-order kinetics.

Rates of reaction for the groups at steady state were used to identify those groups which reacted under pseudo-first-order kinetics, and those groups which were related by stoichiometric constants over a range of reaction temperatures and liquid hourly space velocities (LHSV). It is the intent of the author to use these stoichiometric relationships to construct models for SCGO hydroprocessing that link reactions that have been previously analyzed as if they were independent. The rates of reaction of groups can be linked if a stoichiometric relationship can be established. Gray proceeds to establish a relationship by first defining a stoichiometric coefficient for species i in reaction j as:

$$\sigma = \frac{r_i}{\zeta_j}$$

where: ζ_j is the molar extent of reaction j .

If instead of an individual species, i represents a group and a single reaction dominates the behavior of the group, then an estimate of a true stoichiometric coefficient can be obtained from:

$$S_i = \frac{r_i}{r_j}$$

where: r_i is the rate of reaction of a basis group.

A plot of r_i versus r_j should be linear with an intercept at the origin if the groups participating in the reaction in question are correlated. Plots were made of the data collected on certain groups (Total C_{ar} , $C_{ar}-(O,N,S)$, $\beta-CH_3$, and Naphthenic C) of reaction rate (r_i) vs the rate of heteroatom removal ($r_{O,N,S}$ (removal)). Straight lines with intercepts at the origin were achieved. From this, it was concluded by the author that changes in the concentration of the structural groups are driven by the removal of heteroatoms. It generally is observed that stoichiometric relationships between groups can be deduced from raw data using these analyses, even in complex mixtures.

Eccles described a single equation model for petroleum residue hydroprocessing in ebullated-bed reactors.⁴¹ The kinetics of residue hydroprocessing were successfully modeled by application of the law of mass action to hydrogenation in the ebullated-bed reactor's back-mixed liquid phase. From the model, an estimation of frequency factor or pre-exponential factor can be obtained. In this paper, correlations of the pre-exponential factor and various reactor independent variables (such as temperature, H_2 pressure, and weight hourly space velocity) was demonstrated.

The construction of the kinetic model is described as follows: In the ebullated-bed hydrogenation reactions occur in the liquid phase, products leave as vapor. Using this description of the physical reaction environment, the kinetic model is built by first assuming that the reactions are irreversible:

where: A_p is the frequency or pre-exponential factor
 R_g is the gas constant

Secondly, the flow through a stirred tank or back-mixed reactor is represented by:

$$r_A = X_A F_A / V$$

where: X_A = mole fraction of A converted

F_A = rate of introduction of A to reactor

V = reactor volume occupied by liquid

$(WHSV)_A$ = weight hourly space velocity of A (weight per hour of A introduced to the reactor divided by the volume of liquid in the reactor)

Thus: $r_A = X_A (WHSV)_A$

Therefore:

$$X_A (WHSV)_A = A_p \exp (-E/R_g T) C_A^\alpha C_B^\beta$$

The reaction model is thus expressed as:

$$A_p = X_A (WHSV)_A \exp (+E/R_g T) C_A^{-\alpha} C_B^{-\beta}$$

where: A = residue or one of the components of the residue (expressed as a weight fraction)

B = hydrogen; and by Henry's Law $[B]_{liq} \propto p_{B \text{ gas}}$ (Henry's law)

A_p is independent of the process variables in the equation, therefore, once a value for A_p is established for a given feed, catalyst, and catalyst activity, that value of A_p permits prediction of conversion as a function of temperature, hydrogen pressure, and space velocity.

Eccles applies the model to back-mixed reactors. (C_A in the reactor is essentially same as $C_{A \text{ out}}$). Taken into consideration are series (concentrations of stream composites) of reactors and liquid hold-up, gas hold-up, solid hold-up, and catalyst concentration effects. Frequency factors (A_p) are obtained from lab data by varying WHSV, pressure, temperature, and obtaining conversions of resid and Conradson carbon numbers.

In ebullated bed reactors, it is possible to add and withdraw catalyst. Therefore, catalyst aging, and replacement rates were studied and correlated with pre-exponential factors. Three kinds of laboratory-scale reactors were used in the study: ebullated bed reactor (EBR) with catalyst addition and withdrawal; fixed catalyst inventory; and stirred-basket. From these studies correlations were made which include effects of catalyst replacement rates, catalyst pore volume and ratio of thermal to catalytic zones in the reactor. A scale-up study using the laboratory-generated frequency factors A_p was done and A_p 's were found to be essentially the same for stirred-basket, bench-scale EBR, and full-scale EBR reactors. The author concludes from this that the model can be used to monitor plant-scale operations. Plots of $\log A_p$ vs time will show if there are reactor problems such as deposition of coke or an increase in gas hold-up.

In a paper by Del Bianco et al.,⁴² an attempt was made to develop a kinetic and mechanistic understanding of the thermal cracking of petroleum residues alone and in the presence of hydrogen-donor compounds. Experiments were performed with an Egyptian petroleum (Belaym) vacuum resid in 30 mL microautoclaves. As a preliminary step to studying the H-donor visbreaking system, a kinetic analysis of the thermal cracking at the temperatures used for visbreaking was performed. Conversion experiments were performed at 410, 430, 450, and 470 °C and times of 1-120 min.

Three pseudo-components were defined as: (1) Vacuum residue (VR): THF soluble, but not distillable; (2) Distillate (D): Volatile material (bp < 530 °C); (3) Coke (C): THF-insoluble material.

Experimental data show that VR yield goes down with reaction time. Distillate yield goes up immediately and levels off in time. Coke yield slowly rises (through an induction period which decreases at elevated temperature. This suggests that coke (C) is generated through a reaction intermediate as depicted in the following scheme:

At any time: $VR' + I = VR$

The authors consider only first-order reactions in construction of the model. Therefore:

$$\begin{aligned}\frac{dVR'}{dt} &= -(k_1 + k_2) VR' \\ \frac{dI}{dt} &= k_2 VR' - k_3 I \\ \frac{dC}{dt} &= k_3 I \\ \frac{dD}{dt} &= k_1 VR'\end{aligned}$$

Integrated differential equations were used to calculate the amount of each component at any time:

$$VR' = VR_o e^{-kt}$$

$$I = \left[\frac{k_2}{k_3 - k} \right] VR_o (e^{-kt} - e^{-k_3 t})$$

$$C = \frac{k_2}{k} \{ VR_o [1 - (k_3 e^{-kt} - k e^{-k_3 t}) / (k_3 - k)] \}$$

$$D = VR_o - VR' - I - C$$

where: $k = k_1 + k_2$

VR_o = initial amount of VR

In order to model distillate formation, kinetic coefficients were obtained by linear regression. The activation energies for reaction to C and D (E_1 and E_2) were obtained by use of the Arrhenius law. Activation energy for the reaction:

was calculated from $E_1 - E_2$, which was obtained for the relation that holds for parallel reactions:

$$\ln \left(\frac{k_1}{k_2} \right) = \ln \left[\frac{\%D_{\infty}}{(100 - D_{\infty})} \right] = \ln \frac{A_1}{A_2} - \left(\frac{E_1 - E_2}{RT} \right)$$

The frequency factors (A_1 , A_2 , A_3), and E_3 were estimated using a computer program (OPTNOV). Rate constants and Arrhenius parameters were obtained for the conversion of the vacuum resid (VR) to coke (C) and distillate (D). They are tabulated here:

<u>T (°C)</u>	<u>Rate Constants (10² min⁻¹)</u>		
	<u>k₁</u>	<u>k₂</u>	<u>k₃</u>
410	1.19	0.91	0.21
430	3.36	2.17	0.80
450	8.95	4.93	2.84
470	22.58	10.71	9.40
E (kcal/mole)	49.4	41.4	63.9
Ln A (min ⁻¹)	31.973	25.808	40.921

It is apparent from the table that the activation energy for formation of coke (the reaction governed by rate constant k_3) is higher than those for the competing reactions. This information is used to correct "...the conventional approximation of considering time and temperature as interchangeable operating variables in thermal cracking".

In another paper by Del Bianco et al. entitled "Thermal Cracking of Petroleum Residues. 2. Hydrogen-Donor Solvent Addition",⁴³ studies of the thermal cracking of resid from Belaym crude (Egypt) are further described (see Reference 38). The thermal cracking reactions were carried out at 390-450 °C in the presence of a hydrogen-donor model-compound solvent dihydrophenanthrene (DHP). DHP was chosen over tetralin because its higher boiling point keeps it in liquid phase during reactions. Reactions were performed in 30 mL reactors for 240 min, at an 80:20 crude:DHP ratio. The percent of H₂ uptake was calculated from: ((H₂ generation - H₂ gas)/H₂ generation) x 100. The same three pseudo-components were used as in the paper discussed above:³⁸ vacuum resid (VR); distillate (D) and coke (C).

The presence of DHP decreases the rate of VR conversion by reducing the reaction rates of both distillate and coke formation, but at longer times VR conversion is enhanced by the presence of DHP. Free radical mechanisms are proposed, based

on these findings. The free radicals are postulated to form by thermal bond scission;

Both pathways are inhibited by H-transfer reactions.

Based on experimental data, the following reaction scheme is proposed:

With the addition of DHP, $\text{VR} \rightarrow \text{VRH}'$. This is dependent on:

$\text{DHP} \xrightarrow{k_8} \text{Ph} + 2\text{H}$ which follows first order kinetics.

This proposed model involves the following set of differential equations:

$$\frac{dVR'}{dt} = - (k_1 + k_2) VR' - k_4 [DHP] VR'$$

$$\frac{dI}{dt} = k_2 VR' - k_3 I$$

$$\frac{dC}{dt} = k_3 I + k_7 IH$$

$$\frac{dVRH'}{dt} = k_4 [DHP] VR' - (k_5 + k_6) VRH'$$

$$\frac{dIH}{dt} = k_6 VRH' - k_7 IH$$

$$\frac{dDHP}{dt} = k_8 [DHP]$$

A mass balance provides D: $D = VR_0 - VR' - VRH' - I - IH - C$

The authors adopt values for the coefficients k_1 , k_2 , k_3 from the thermal cracking case. They assume k_3 and k_2 are about equal. Values for k_4 , k_5 , and k_6 are obtained from a computer optimization program (OPTNOV). The set of differentials was integrated by a fourth-order Runge-Kutta numerical method. The magnitude of the rate constant k_4 indicates that the reaction of hydrogen transfer from DHP to VR' is very rapid. Comparisons between the experimental data and calculated kinetic curves for the three pseudo-components show the model to be in good agreement with the data.

Dave, Duffy, and Udaja⁴⁴ describe the development of a four-lump kinetic model for the cracking/coking of recycled heavy shale oil. The heavy fraction of the shale oil is produced by retorting processes and is then recycled to a retort where cracking reactions, catalyzed by the minerals in the shale, reduce the fraction to lighter products. The kinetic model considers both vapor-phase cracking reactions and catalytic cracking reactions which lead to coke deposition when the heavy oil is contacted by the shale minerals.

A four-lump model is proposed: Lump 1) heavy oil; Lump 2) light oil; Lump 3) solid residue (coke); Lump 4) C_1-C_4 gases. The overall reaction scheme presumed by the authors is as follows:

Reaction orders were chosen based on intuitive assumptions that the transformation of light oil to coke would entail fewer different rates of catalytic cracking than the heavy oil which would have considerable changes in reactivity as the composition changes. Therefore, a pseudo second-order rate should give a better approximation to the non-linearity of heavy oil coking. It also is assumed that active acidic sites on spent shale ash follow an exponential first-order decay. The rate of reaction of heavy oil is given as:

$$\frac{dy_1}{dt} = k \Phi_1 y_1^2$$

where:

y_1 = [heavy oil]

k = intrinsic rate constant for formation of light oil from heavy oil

$\Phi = e^{(-\alpha t)}$ catalyst decay function where t = time for catalyst exposure to oil

α = catalyst decay coefficient.

Assuming ideal plug-flow conditions, the mass balance for the heavy oil is given as:

$$\frac{\delta y_1}{\delta t} + u \frac{\delta y_1}{\delta z} = -R(y_1, t)$$

where:

u = vapor velocity

z = distance along reactor

R_1 = reaction rate for the heavy oil

The mass balance for cracking of the light oil is given as:

$$\frac{\delta y_2}{\delta t} + u \frac{\delta y_2}{\delta z} = a_1 R_1(y_1, t) - R_2(y_2, t)$$

where:

a_1 = kg of light oil produced

R_2 = reaction rate for the light oil

At steady state:

$$\frac{\delta y_1}{\delta t} = \frac{\delta y_2}{\delta t} = 0$$

Assume Φ = same for all reaction paths. Therefore:

$$\frac{dy_1}{dx} = -\frac{K_0}{s} \Phi y_1^2$$

$$\frac{dy_2}{dx} = a_1 \frac{K_0}{s} \Phi y_1^2 - \frac{K_1}{s} \Phi y_2$$

where:

s = vapor hourly space velocity

K_0 and K_1 are the rate constants for the reactions of heavy oil to coke and light oil to coke, respectively.

x = dimensionless reactor length

Similar equations are written for gas production. The equations are solved to give quantities of various product lumps formed during the cracking/coking reactions. The parameters α , K_0 , K_1 , $a_1 K_0$, $a_2 K_0$, $a_3 K_0$, $a_4 K_1$ and $a_5 K_1$ all have an Arrhenius-type relationship with temperature. Thus, values can be derived for these parameters, as well as frequency factors and activation energies.

Data from moving packed-bed experiments provided values of yields (y_1, y_2, y_3 , and y_4) of the different lumps. The theoretical values for heavy oil conversion were within 10% (absolute) of experimental data over a wide range of temperatures and pressures. Prediction of coke formation was in close agreement with measured values.

Köseoglu and Phillips⁴⁵ describe how the kinetics and product yield distributions of the non-catalytic hydrocracking of Athabasca bitumen were studied to construct a kinetic model. The model is initially based on four pseudo components: coke, asphaltenes, maltenes, and gases. Mechanisms (or reaction models) are proposed. By eliminating unlikely or low-probability reactions from each mechanism, six reaction models were proposed. Each model incorporates more pseudo components as the model becomes more exact (i.e., the initial four "lumps" are divided to provide more specificity). The final forms of the reaction models derived are the following:

Rate constants and Arrhenius parameters were determined for each of these models. The model prediction was compared with experimental data in each case.

These reaction models provide insight into the reaction mechanisms and homogeneity of the bitumen fractions. By comparing the activation energies of the reactions of different pseudo components to products, assumptions can be made about the similarities or dissimilarities of the reactivities of the components of the initial four "lumps". If the activation energies are similar, the authors

believe that this is justification for the simpler model and there is no need to break down the all-encompassing pseudo component into sub-components.

Parnas and Allen⁴⁶ describe a method to do compound class modeling of the thermal hydropyrolysis of mixtures of hydrocarbons which are expected to be found in heavy oils. The model differs from other models in two ways. 1) In addition to total concentration of each lump, the model computes statistical quantities (such as average C number for each compound class). 2) The model uses a fundamental rate parameter to describe the chemical reactions of compound classes. Ten compound classes were chosen: 1) paraffins, 2) olefins, 3) cycloparaffins, 4) cycloolefins, 5) cyclodiolefins, 6) benzenes, 7) tetrahydronaphthalenes, 8) dihydronaphthalenes, 9) naphthalenes, and 10) diolefins.

The model consists of 29 reactions interconnecting the 10 compound classes. All reactions are free radical and include initiation, propagation and termination steps. The total concentration of radicals is calculated using the pseudo-steady state approximation. The total radical concentration is given by:

$$[R^*] = (K_{Eq}[R])^{1/2}$$

where K_{Eq} is the equilibrium constant for the appropriate initiation and termination reactions and $[R]$ is the total concentration of the reacting species. The value of K_{Eq} was based on appropriate values reported in the literature for initiation and termination reactions. The value chosen for K_{Eq} is constant and for this model is:

$$K_{Eq} = \frac{k_i}{k_t} = 10^6 \exp(-60,000/RT)$$

To make the model useful, the average number of carbon atoms per compound class and the average length of the substituents are used to provide more detail than is obtained from just the concentrations of each compound class in the mixture. Each reaction is considered to transfer carbon from one compound class to another. This is expressed by a series of algebraic equations:

$$C_j|_{t+\Delta t} = C_j|_t + \sum_{i=1}^{N_{rxn}} M_{ij} CT_{ij}$$

where M_{ij} is the number of molecules in the class j transferred to another class in a small increment of time Δt by reaction i ; CT_{ij} is the number of carbon atoms per molecule transferred by reaction i .

A relation is found between the number of carbons transferred and the concentration of each compound class in the mixture. Numerical simulations were found to agree well with results of hydrolysis experiments.

Trauth et al.⁴⁷ used a lumped kinetic model to investigate differences in the pyrolytic reactivity of two petroleum vacuum resids (Hondo and Maya) and the asphaltene portions of the two resids. Pyrolysis of the resids and isolated asphaltenes was carried out at different reaction temperatures and residence times to determine if the asphaltenic component of the resid reacts differently when in the resid versus in isolation. Products were separated by solubility classes into maltenes (n-heptane solubles), asphaltenes (n-heptane insoluble, toluene soluble), and coke. Gas formation was determined gravimetrically. These solubility fractions (and the gas) were used as the "lumps" for modeling. The model proposed to describe the asphaltene and coke formation from maltenes is the following:

It was found that both isolated asphaltene samples reacted faster than the samples of asphaltene in the resid. The time dependence found experimentally for the product yields was used to find optimized rate constants (k_1 - k_7) for the proposed model. A set of best-fit parameters, (K), was found by minimizing:

$$\chi_M^2 = \sum_{i=1}^N [Y_{Ei} - Y_M(K)_i / \sigma_i]^2$$

where:

Y_{Ei} = experimental data

$Y_M(K)_i$ = model predictions

N = number of data points

σ_i = standard deviation

The cases of first- and second-order kinetics were considered. In either case, k_4 and k_5 were negligible. Above 450 °C, k_7 became unimportant and at 450 °C, k_4 became significant. k_1 , k_2 , and k_3 and k_5 all increased with reaction temperature for resid reactions. However, for isolated asphaltene reactions, k_5 was negligible.

The apparent first- and second-order rate constants for asphaltene disappearance were found to be effective measures of the effects of reaction environment. These rate constants were used to determine activation energies. The activation energies for asphaltene disappearance were higher for the asphaltene as a component of the resid than for the isolated asphaltenes. It was concluded that the maltenes inhibited the reaction of the asphaltenes for both resids studied.

A study is described in a report by Baldwin⁴⁸ of the effect of operating conditions (temperature, added catalysts, and pressure) on the thermal rate of hydrogenation of coal-derived preasphaltenes and asphaltenes. Reactions were run in a CSTR with asphaltenes isolated from SRC-I. The SRC was produced at the Wilsonville direct coal liquefaction pilot plant (11/74; Run 13); the feed coal was from the Illinois No. 6 seam, Burning Star 2 mine. Asphaltenes were hydrogenated at a range of conditions. Various space times (7.5-90 min), two temperatures (375 °C and 400 °C), a total pressure of 1500 psig, and a 20:1 tetralin:asphaltenes ratio were used. The products of the reaction were analyzed for conversion to oil or preasphaltenes using selective solvent fractionation (using pentane followed by toluene, and then THF). The amount of asphaltenes that did not solubilize in the tetralin (about 45% did not dissolve) was accounted for in the conversion calculations. Very little preasphaltenes was

produced in any of the runs (<1% of feed). Gases were analyzed by GC and were found to be negligible.

The kinetic modeling of the results of the hydrogenation of the asphaltenes was thus based on the 'oil' fraction as the primary product. A mass balance for the asphaltene component was written as:

$$\begin{array}{ccccccc} \text{rate of} & & \text{rate of mass} & & \text{rate of mass} & & \text{net rate of} \\ \text{asphaltene} & = & \text{flow of} & - & \text{flow of} & + & \text{asphaltene} \\ \text{accumulation} & & \text{asphaltene into} & & \text{asphaltene out} & & \text{generation} \\ & & \text{system} & & \text{of system} & & \end{array}$$

this reduces to:

$$0 = M_{Ao}Q_{in} - M_AQ_{out} + (\text{rate of reaction}) \times (\text{volume of reactor})$$

where:

M_A = mass concentration of asphaltenes (g/L)

Q = volumetric flowrate (L/h)

however: $Q_{in} = Q_{out}$

therefore: $-r(V/Q) = M_{Ao} - M_A$

where: $V/Q = \tau$, and $X = (M_{Ao} - M_A)/M_{Ao}$

therefore: $M_{Ao}X/\tau = -r$

Three kinetic models were proposed to fit the experimental results. The first of these is a first order reversible reaction model:

The rate expression for this model is: $-r = k_f M_A - k_r M_o$. The second model is a second order reversible reaction model and the rate expression for it is: $-r = k_f M_A^2 - k_r M_o^2$. The third model is a first order reversible reaction model and the rate expression is expressed as; $-r = k_f M_{Ao}(a-x)$.

The first two models better predict the expected Arrhenius dependence of the forward rate constants than the third model. However, none of the three models

gave very linear plots. This is explained by the authors as due to the "fairly low" conversions of asphaltenes in the reaction system, which at the same time, had "fairly large" error inherent in the system (sampling, etc.) as compared to the observed conversions. Secondly, because of the heterogeneous nature of the asphaltenes with the probable variation in the hydrogenation activation energies of the different chemical compounds that make up the asphaltenes, the Arrhenius plots may be expected to be non-linear. Additionally, the main reactions which are taking place are actually thermal and little hydrogenation takes place, therefore the plots would not necessarily be linear.

It was concluded that the modeling of the kinetics must include some form of reversibility since the conversion of asphaltenes to oils is incomplete. First and second order rate constants predict increasing forward rate constants at increasing temperatures. The equilibrium constants predicted from first and second order reversible models describe accurately the maximum conversions obtained.

Coal Conversion

Shalabi et al.⁴⁹ explored noncatalytic coal liquefaction in a donor solvent. The rates of formation of oils, asphaltenes and preasphaltenes during solvent extraction were experimentally determined. A mathematical model that describes the observed data was constructed.

Experiments were conducted in a 300 mL stirred batch reactor. The coal used was a high volatile A bituminous coal, Madisonville No. 9 seam, Fies, KY (Island Creek Coal). Experiments were run with a coal:tetralin (1:1 on 1:1.2 by wt) mixture which was injected into additional tetralin. The liquefaction was carried out at reaction temperatures of 350, 375, or 400 °C. Reaction pressure was maintained at 2000 psig, total, (at temperature).

Reactions of dissolution and conversion were assumed to be first order and irreversible. Temperature regimes where regressive reactions become important were avoided. Three models were investigated and compared to experimental data. In each case, coal is converted to asphaltenes and then either sequentially or simultaneously converted to preasphaltenes and/or oils.

Model 1 is described as follows:

The following differential equations represent the rate of disappearance and formation of reactants and products for Model 1:

$$dA/dt = -k_1 A$$

$$dB/dt = k_2 C - k_3 B$$

$$dC/dt = k_1 A - k_2 C$$

$$dD/dt = k_3 B$$

at $t = 0$; $A = a$ (dmmf basis); $B = C = D = 0$

at $t = t$; $A' = 1 - a + A$

A' = unreacted coal; $1 - a$ = unreactive fraction of coal

a = reactive fraction of coal at $t = 0$; a = reactive fraction at $t = t$

$(1 - a)$ is a necessary concept since not all A will react at $t = \infty$;

$(1 - a)$ is found experimentally at long reaction time.

Solutions of the differential equations give (after subbing in $(1 - a)$):

$$A' = 1 - a + ae^{-k_1 t}$$

$$B = \frac{ak_1 k_2}{k_2 - k_1} \left[\frac{(e^{-k_1 t} - e^{-k_3 t})}{(k_3 - k_1)} + \frac{(e^{k_3 t} - e^{k_2 t})}{(k_3 - k_2)} \right]$$

$$C = \frac{ak_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$D = 1.0 - (A' + B + C)$$

Model 2 is postulated as the following:

The differential equations for this model are:

$$dA/dt = -k_1 A$$

$$dB/dt = k_2 C - k_4 B$$

$$dC/dt = k_1 A - (k_2 + k_3) C$$

$$dD/dt = k_3 C - k_4 B$$

Solutions of these differentials for Model 2 are:

$$A' = 1 - a + a e^{-k_1 t}$$

$$C = \frac{k_1 a}{k_2 + k_3 - k_1} [e^{-k_1 t} - e^{-(k_2 + k_3) t}]$$

$$B = \frac{k_1 k_2 a}{k_2 + k_3 - k_1} \left[\frac{(e^{-k_1 t} - e^{-k_4 t})}{(k_4 - k_1)} + \frac{(e^{-k_4 t} - e^{-(k_2 + k_3) t})}{(k_4 - k_2 - k_3)} \right]$$

$$D = 1.0 - (A' + B + C)$$

Model 3 is defined as follows:

The rates of disappearance and formation are given by:

$$dA/dt = -(k_1 + k_2 + k_3) A$$

$$dB/dt = (k_1 A) + k_6 C - k_4 B$$

$$dC/dt = k_2 A - (k_6 + k_5) C$$

$$dD/dt = k_3 A + k_4 B + k_5 C$$

define

$$k_1 + k_2 + k_3 = \beta$$

$$k_5 + k_6 = \gamma$$

Solutions to the differentials for Model 3 are:

$$A' = 1 - a + ae^{-\beta t}$$

$$C = \frac{k_2 a}{\gamma - \beta} (e^{-\beta t} - e^{-\gamma t})$$

$$B = \frac{a}{k_4 - \beta} \left(k_1 + \frac{k_2 k_6}{\gamma - \beta} \right) (e^{-\beta t} - e^{-k_4 t}) + \frac{a k_2 k_6}{(\beta - \gamma)(k_4 - \gamma)} (e^{-\gamma t} - e^{-k_4 t})$$

$$D = 1.0 - (A' + B + C)$$

The rate constants were obtained by regression analysis using a computer. These estimated values then were substituted into the analytical solutions and curves were generated to represent the theoretical trends for oils, asphaltenes and preasphaltenes, and unreacted coal. Experimental data then were superimposed on these plots.

Model 3 best fits the experimental data. The data show a rapid conversion of the reactive fraction of the coal to liquid products and indicate that stable asphaltenes and preasphaltenes are present in the reactor for long periods of time. The authors caution, however, that this model only approximates the true mechanism. They believe that a more adequate model can be constructed based on fundamental chemistry, incorporating pseudo-reversibility in the reaction steps, and incorporating initial second-order pyrolysis followed by first-order hydrogenation.

A combination of kinetic modelling and statistical analyses was applied by König and Jancke⁵⁰ to find which coal characteristics most influence coal reactivity. The proposed reaction scheme for the hydrogenation of brown coal is

where: IOM, PAS, ASP, OIL, and GAS are the pseudocomponents: insoluble organic material, preasphaltenes, asphaltenes, oil, gas, and coke, respectively. The coke (C*) is not accounted for in the proposed model.

Twenty-two brown coals with similar elemental analyses, varying significantly only in S content, were reacted in a 0.1 L microautoclave at 450 °C for 30 min under H₂ pressure of 10 MPa (at 20 °C) in tetralin. Hydrogenation kinetic measurements with these coals confirmed that the proposed reaction scheme describes the reaction adequately. Computer sensitivity tests and mechanistic investigations of the influence of the tetralin to coal ratio on the reaction kinetics led to the conclusion that the reaction of direct oil formation (reaction 9) is second order; all other reactions are assumed to be first order.

Integration of the mass balance equations was performed, and rate constants (k_1 - k_9) for different coals were found to vary widely. A forced method of correlation analysis using the computer software package STATGRAFICS was applied to determine which coal characteristics were responsible for the differences.

In order to investigate the effect of coal characteristics on the conversion of the coal to the different pseudocomponents, "dry" hydrogenation experiments were performed in which tetrahydrofuran (THF) was substituted for tetralin. The authors believe that the THF does not influence the composition of the product oils. Data from these experiments then were analyzed first by use of a simple regression analysis. Data obtained by ¹H-NMR spectroscopy were used to calculate structural parameters for the oil products of these "dry" reactions. These parameters are aromaticity, hydroaromaticity, and aliphaticity; they were used as independent variables in the development of the statistical model. It was found that direct oil formation via reaction 9 may be dependent on the presence of aromatic compounds in the oil. The authors predict that the ability of condensed aromatic compounds to transfer hydrogen from the gas phase to reaction intermediates will increase oil yields. It also was found that there is a dependence of the coal degradation reactions (1, 2, and 3) on the sulfur content of the coal.

To confirm the results of the simple regressive analysis, the authors used a multivariate statistical method. Factor analysis of the independent and dependent variables confirmed the results from the regression analysis. The

properties examined were coal sulfur concentration, bitumen (defined as the toluene-soluble portion of coal) content, coal ash content, tar content, coal oil aromaticity (ARN), coal oil hydroaromaticity (HAN), coal oil aliphaticity (PAN). The two findings (discussed above) from the regression analysis were confirmed. In addition, a positive effect of ash content was found on the rate constant k_3 . However, previous experience shows that an increased ash content decreases oil yield. The authors explain this apparent contradiction by speculating that a positive effect of enhancement of asphaltene conversion to oil is accompanied by the catalysis of oil gasification to hydrocarbons which would result in a decrease in oil yield.

The kinetic model developed in a paper by Singh and Carr⁵¹ is based on previous work by the authors which produced a kinetic model limited to the liquefaction of bituminous coals by the SRC II process.⁵² In the model developed here, the previous model was extended to include the effects on coal liquefaction of added sulfided iron catalysts (iron pyrite) and the catalytic activity of the coal minerals. The model requires that the products of reaction from the SRC II process be classified into lumps. These lumps are: 1) inorganic matter (ASH), 2) pyridine-insoluble organic matter (IOM), 3) solvent-refined coal (SRC), 4) heavy distillate (HD) (288-482 °C), 5) middle distillate (MD) (193-288 °C), 6) light distillate (LD) (C_5^+ -193 °C), 7) water, 8) by-product gases (NH_3 , H_2S , CO , CO_2), 9) C_1 - C_4 hydrocarbon gases, 10) hydrogen.

The reaction pathway for SRC II coal liquefaction is given by:

In this scheme, coal is considered to be instantaneously dissolved. The SRC product of the dissolution is then further converted to yield lighter products. The rate of reaction of SRC as derived in the previous model is given by:

$$r_{\text{SRC}} = -1.567 \times 10^5 \exp\left(-\frac{79160}{RT}\right) P_{\text{H}_2}^{0.28} g_{\text{ASH}} \text{ kg}/(\text{L}\cdot\text{h})$$

where P_{H_2} is partial pressure of hydrogen and g_{ASH} is the mass fraction of ASH in the reactor, R is the gas constant (kJ/kmole K); T is in K.

Extension of this model to include the catalytic effects of the added sulfided iron and the mineral content of the coal result in a rate expression of the following form:

$$r_{\text{SRC}} = \frac{a \exp(-79160/RT) p_{\text{H}_2} g_{\text{I}}}{1 + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{H}_2\text{S}} p_{\text{H}_2\text{S}}}$$

where:

g_{I} is the mass fraction of iron.

a is the pre-exponential factor

A series of experiments was made in a one-stage SRC recycle system. Mass balance equations were written around the single-stage reactor. With a set of assumed values for rate constants for formation of H_2 , H_2S and an assumed value for a , the mass balance equations were simultaneously solved to obtain the yields of the different component lumps. An optimization program was used to find the best-fit values for a , K_{H_2} , and $K_{\text{H}_2\text{S}}$. The resultant rate expression is different from the previously derived expression in that it includes a representation of the catalyst concentration and partial pressure of H_2 , and the inclusion of the H_2S partial pressure effect.

The modified rate expression has the form:

$$r_{\text{SRC}} = -9.85 \times 10^5 \exp(-79160/RT) P_{\text{H}_2} g_{\text{I}} / (1 + 30 P_{\text{H}_2\text{S}})$$

where g_{I} is the mass fraction of iron (derived from coal minerals and added iron pyrite in the reactor, and $P_{\text{H}_2\text{S}}$ is the partial pressure of H_2S .

Testing of this reaction model by liquefaction of widely different coals catalyzed by iron-sulfur catalysts showed that there was good agreement between the final model results and the yield data. It also was found that the source

of the iron-sulfur catalyst (native in the coal minerals or added pyrite) had no effect, whereas H_2S has a strong inhibitive effect on the rate of hydrogenation reactions.

Abusleme et al.⁵³ proposed a lumped kinetic model for the catalytic liquefaction of two Chilean subbituminous coals (Pecket and Catamutan). Liquefaction experiments were conducted in a 1 L autoclave at 300-400 °C, 10 MPa of H_2 , using a coal-derived liquid as solvent and Co-Mo/ γAl_2O_3 as catalyst. Components were separated into oils, asphaltenes, preasphaltenes, and unreacted coal.

Starting with all possible routes, a general model accounting for the products was proposed:

It was found by imposing Arrhenius law temperature dependency, and testing each possible route against experimental data that the following mechanism fit the experimental data for the two coals under different reaction conditions, 300-400 °C for the Pecket coal, and 350-450 °C for the Catamutun coal.

A different model was derived for Pecket coal at 450 °C.

The formation of asphaltene 2 is described as a retrogressive reaction occurring at long reaction time in the form of polycondensation of free radicals in the oil which were not hydrogenated because of poisoning of the catalyst. At short time, the formation of asphaltene 2 is explained by the rapid formation of free radicals which cannot be hydrogenated before they polymerize.

The authors show that the model does a good job of fitting the experimental values. However, the liquefaction behavior is shown to be different for the two coals studied. The derived kinetic parameters have different values for each of the coals. The authors attribute this to differences in the maceral structure of the two coals.

A kinetic model was proposed⁵⁴ for the liquefaction of Illinois No. 6 coal in the NEDOL process. The model is:

The key to this model is that all conversion of asphaltenes to the different oil fractions occurs simultaneously.

Two coals were liquefied in the NEDOL process (Illinois No.6 and Wandoan coal). Base liquefaction conditions were: 450 °C, 170 kg/cm²G, 3 wt % iron sulfide catalyst; gas slurry ratio (G/L) 700 NL/kg. Each experiment was conducted by changing only one factor at a time from these base conditions.

Rate constants of all reactions were determined from experimental data. An experimental formula for each rate constant was obtained by means of regression analysis. Each reaction was assumed to be first order irreversible. Each rate constant was calculated by material balance data on every operating condition. The following empirical formula for each rate constant was obtained by the regression analysis methods.

$$K_i = A_i \cdot [C_{cat}]^x \cdot [P_{H_2}]^y \cdot [\epsilon_g]^z \cdot \exp(-E/RT)$$

where:

K_i = reaction rate constant of composition i (L/min)

C_{cat} = amount of catalyst addition (wt%)

P_{H_2} = partial pressure of hydrogen (kg/cm₂)

ϵ_g = gas hold up

R = gas constant (cal/mol·K)

E = activation energy (cal/mol)

Calculated and experimental data agree well. Comparison of this model and one in which sequential steps of asphaltenes to heavy oil to mid-oil to light oil show that the new model fits Illinois No. 6 coal liquefaction data, but the sequential model fits better the data from liquefaction of Wandoan coal. The authors believe that the Wandoan coal first rapidly decomposes to heavy distillates, and that these heavy distillates convert to light material, whereas the Illinois No. 6 coal decomposes to a primary product of asphaltenes which then undergo the conversion to oil fractions. They further state that because of the different behaviors of the different coals it is necessary to choose a kinetic model specific to the kind of coal (at least when dealing with such simplified kinetic models).

Curran, Struck, and Gorin described kinetic equations which were developed to obtain a correlation useful in predicting and interpreting results of coal conversion via a hydrogen-donating mechanism from continuous bench- and pilot-scale units.⁵⁵ Experimental data were obtained with shaker-bombs (microautoclaves) in batch experiments. Pittsburgh seam Ireland Mine coal and pure tetralin as a hydrogen-donor solvent were used. Xylenol-solubles at 220 °F were used as a measure of "depth of extraction". Experiments also were conducted with a "shallow extract" obtained from coal with decalin at 650 °F in a stirred autoclave for 1 hr. This shallow extract yield was about 23 wt % MAF coal. Thus, in terms of a lump model, it can be considered that the "lumps" which Curran et al. consider are simply the coal, the decalin coal extract, or the xylene coal extract.

The authors found that the rate of thermal decomposition of the coal determines the extent of H transfer from the hydrogen donor. This observation points to a free-radical mechanism:

where coal-H are stable, soluble in cresol molecules

It was found that the hydrogen-donor extraction process is a first-order reaction if a high hydrogen-donor concentration is used so that there is negligible change in its concentration as the reaction proceeds. At long-times, a straight line correspondence between time and $\log \frac{1}{1-\alpha}$ exists.

where:

α = fraction of ultimate conversion

It was assumed that there are two or more decomposition processes occurring simultaneously with different rate constants. The rate of coal pyrolysis in this model is given by:

$$C_T - C = \sum_{i=1}^n C_i e^{K_i t}$$

where C_i is the weight percent of the coal which decomposes with the characteristic rate constant K_i .

Assuming that only two first-order reactions occur in parallel, this can be rewritten as

$$C_T - C = \gamma C_T e^{-K_1 t} + (1 - \gamma) C_T e^{-K_2 t}$$

where γ represents the fraction of coal which decomposes by the faster of the two rates.

Solutions to this are obtained by iteration to get K_1 and K_2 and γ . From Arrhenius plots (equations), at initial conditions, A_1 , E_1 , γ , A_2 and E_2 are obtained.

Hydrogen transfer is treated kinetically the same way as coal conversion (hydrogen transfer maximum value, determined experimentally, of $H_T = 2.6\%$). However, the rate equation is not just a simple first-order rate equation, but a sum of first-order reactions:

$$H_T - H = \sum_{i=1}^n h_n e^{-K_n t}$$

The model derived is based on two types of bonds: strong and weak. They are solved as the conversion equations were solved.

Curran et al. found that the fast hydrogen-transfer rate is the same order of magnitude as the slow coal (extract) conversion rate, but greater by a factor of two. This is considered reasonable by the authors because the fast coal-conversion rate is associated with little or no hydrogen transfer. The fast H_2 -transfer rate takes over in the coal conversion range of 50-90%, which corresponds to the slow coal-conversion rate. "The slow H_2 -transfer rate corresponds in all likelihood to continued transfer of hydrogen to coal extract".

The effect of solvent to coal (or extract) ratio was considered. A model was chosen, because of its simplicity, which considers that the extract or MAF coal has built-in H-donor structures, which compete for the free radicals (R) produced in the thermal dissociation.

The model consists of the following steps:

	<u>Rate Constant</u>
$M \rightarrow 2R$	k_0
$R+D \rightarrow RH+D^\cdot$	k_1
$R+M \rightarrow RH+M^\cdot$	k_2
$R\&D^\cdot \rightarrow RH+(D-H_2)$	k_3
$R\&M^\cdot \rightarrow RH+(M-H_2)$	k_4

$M^\cdot$: free radicals formed from extract

$D^\cdot$: free radicals formed from tetralin

$D-H_2$: dihydronaphthalene (formed from tetralin)

$M-H_2$: corresponding dehydrogenated structure derived from extract

An expression was derived which related the amount of H transferred from tetralin (H_1) and total amount H (H) transferred by all mechanisms. After manipulation of equations, the authors obtained:

$$\frac{1}{H_1} = \frac{1}{H} \left[1 + C \left(\frac{M}{D} \right) \right]$$

$$C = kH_E^\circ \left(\frac{132}{400} \right)$$

H_E° : hydrogen transfer capacity of tetralin ($g_{atoms}/100g$ extract or MAF coal)

Plots of $1/H_1$, vs M/D lie on a straight line with slope C/H and intercept $1/H$. Fits for experimental data were good for high tetralin/coal ratios.

Chen and Schindler, in a paper entitled "A Lumped Kinetic Model for Hydroprocessing Coal Extract",⁵⁶ develop a kinetic model which distinguishes between hydrogenation and cracking of 850 °F⁺ coal extracts. From this model, the effects of hydrotreating temperature, space velocity, feed properties, and catalyst aging on 850 °F⁺ product properties and reactor performance are determined.

The authors propose that the 850 °F⁺ feed is composed of compounds which can be lumped together in groups; aromatic (AR), cyclic (CY), and alkyl (AL) components.

The following scheme is postulated for the process of catalytic hydroprocessing:

$$m = x + y = x + z + t$$

In this scheme, the $850^\circ F$ material is composed of all three lumped compounds (AR_m , $AR_x CY_y$, and $AR_x CY_z AL_t$). The authors presume that each compound consists of the same number of carbons. Using proton NMR data, they express the relative contents of each lump and thus transform the above reaction scheme in the following way: ARH = condensed + uncondensed aromatic hydrogen, CYH = cyclic α + cyclic β hydrogen; ALH = alkyl α + alkyl β + γ hydrogen.

Thus:

Doing this limits the reaction system to only carbons attached to hydrogens. The concentration of carbons are given by:

$$C_i = W x_h x_i / n_i$$

Therefore conversion is given by:

$$X = 1 - \Sigma C_i / (\Sigma C_i)_0$$

C_i : feed concentration

i : AR, CY, and AL

The assumption is made to use a first-order reaction for a back-mixed, single reactor:

$$-C_{AR} k_1 + C_{CY} k_2 = (C_{AR} - C_{AR,0}) SV$$

$$-C_{AR} k_1 - C_{CY} k_2 - C_{CY} (k_3 + k_4) = (C_{CY} - C_{CY,0}) SV$$

$$C_{CY} k_4 - C_{AL} k_5 = (C_{AL} - C_{AL,0}) SV$$

The use of first-order kinetics is validated by 1) the fact that near-constant values are obtained for rate constants found over a wide range of conversions, and 2) when the effect of the concentration of 850 °F⁺ resid in the feed was tested by modeling the case of multiple reactors in series, the calculated interstage conversions compare well with first-order predictions.

The authors assume that hydrogenation adds hydrogen only to carbons originally attached to hydrogen. Therefore, the content of these carbons is unchanged during reaction. Thus, conversion is determined by the loss of these carbons (see equation 4, above). Experimentally, this assumption seems to hold for most data.

Both conversion of 850 °F⁺ coal extract in a catalytic hydrocracker and the proton distribution of the unconverted feed can be predicted from the proton distribution of the feed and the reaction conditions.

It was determined that the hydrogenation reactions have lower activation energies than the cracking reactions. Because cracking and hydrogenation reactions can be distinguished, the authors believe the model is a useful tool for catalyst evaluation and development.

The development of a kinetic model of coal liquefaction was recently explored by Douglas et al.⁵⁷ Experimental data was obtained from the liquefaction of a Wyodak (Clovis Point) subbituminous coal at the Wilsonville liquefaction facility in Wilsonville, Alabama. Reactions were run in the variable submergence temperature control (VaSTeC) autoclave.

In the model, components and groups of compounds are selected. These groups are: (1) hydrogen, (2) water, (3) CO, CO₂ and H₂S, (4) C₁-C₃ gases, (5) C₄-822 K distillate (549 °C, 1020 °F), (6) thermal resid, (7) unconverted coal (UC), (8) MAF coal. Conversion of the distillate was not considered in the kinetic model. Neither was the ash, since any effect it had on conversion was outweighed by disposable Fe₂O₃ catalyst added to the Wyodak coal.

Reaction variables which were studied are: 1) reaction time, 2) temperature, 3) pressure, 4) amount of Fe₂O₃ catalyst in feed, 5) amount of (CH₃)₂S (DMDS) in

feed, 6) amount of resid in recycle oil feed, and 7) solvent-to-coal ratio in feed.

Liquefaction is assumed to occur in two distinct stages. In the first stage, coal is assumed to dissolve instantaneously with the formation of a wide variety of products. The product distribution was assumed to be unaffected by reaction conditions and a function of the feed coal only. So, for each compound i , a distribution coefficient f_i^{coal} was assigned to represent the fraction of MAF coal which would form that compound.

In the second stage, a rate controlled reaction of unconverted coal (UC) and thermal resid (TR) was assumed to occur. But, the model was set up where UC only went to resid and then resid to other products. The authors define

$$f_i^{\text{UC}} \text{ and } f_i^{\text{TR}}$$

Mass balance equations are written for each compound group.

r_{UC} = rate of conversion of unconverted coal

τ = reaction time

r_{TR} = rate of conversion of thermal resid

$$1. \quad x_{\text{UC}}^{\text{out}} = x_{\text{UC}}^{\text{in}} + f_{\text{UC}}^{\text{coal}} x_{\text{coal}}^{\text{in}} - r_{\text{UC}} \tau$$

$$2. \quad x_{\text{TR}}^{\text{out}} = x_{\text{TR}}^{\text{in}} + f_{\text{TR}}^{\text{coal}} x_{\text{coal}}^{\text{in}} + f_{\text{TR}}^{\text{UC}} r_{\text{UC}} \tau - r_{\text{TR}} \tau$$

$$3. \quad x_{\text{C}_4-822\text{K}}^{\text{out}} = x_{\text{C}_4-822\text{K}}^{\text{in}} + f_{\text{C}_4-822\text{K}}^{\text{coal}} x_{\text{coal}}^{\text{in}} + f_{\text{C}_4-822\text{K}}^{\text{TR}} r_{\text{TR}} \tau$$

$$4. \quad x_{\text{C}_1-\text{C}_3}^{\text{out}} = x_{\text{C}_1-\text{C}_3}^{\text{in}} + f_{\text{C}_1-\text{C}_3}^{\text{coal}} x_{\text{coal}}^{\text{in}} + f_{\text{C}_1-\text{C}_3}^{\text{TR}} r_{\text{TR}} \tau$$

$$5. \quad x_{C_o-H_2S}^{out} = x_{C_o-H_2S}^{in} + f_{C_o-H_2S}^{coal} x_{coal}^{in} + f_{C_o-H_2S}^{TR} r_{TR} \tau$$

$$6. \quad x_{H_2}^{out} = x_{H_2}^{in} + f_{H_2}^{coal} x_{coal}^{in} + f_{H_2}^{uc} r_{uc} \tau + f_{H_2}^{TR} r_{TR} \tau$$

$$7. \quad x_{H_2O}^{out} = x_{H_2O}^{in} + f_{H_2O}^{coal} x_{coal}^{in} + f_{H_2O}^{TR} r_{TR} \tau$$

$$\text{constraints: } \sum f_i^{coal} = \sum f_i^{uc} = \sum f_i^{TR} = 1$$

It is assumed that the rate expressions for the conversion of unconverted coal and thermal resid is zero order with respect to the mass fraction of SRC in the reaction, this allows the mass balance equations to be directly applied to the VaSTeC autoclave data. Rate expressions are, thus, functions of reaction variables only (numbers 2-7 above). Even though, experimentally, it was found that not all of these variables have an effect, they all were assumed to have a positive influence on rates of reaction (conversion). The intent of this was to determine if a correlation exists between reaction rates and combinations of reaction variables. For both rate expressions, the nature of the dependence on each variable was assumed to be identical.

Modeling steps and assumptions include:

- Temperature dependence - use Arrhenius expression.
- Total reaction pressure used for p_{H_2} , since this is not determined experimentally
- Assume first order with respect to H_2 pressure.
- The concentration of Fe_2O_3 catalyst was varied in the experiments described; at $[Fe_2O_3] = 0$ the rate expression goes to zero. Therefore, the authors explored three forms of dependence: a) Fe_2O_3 ; b) $1 + Fe_2O_3 / (\overline{Fe_2O_3})$, where $\overline{Fe_2O_3}$ is mean value over all runs, and c) $1 + b_1 Fe_2O_3$.
- The required amount of DMDS also was varied experimentally, and three forms for dependence of the reaction rates on DMDS concentration were tested: a) DMDS, b) $1 + DMDS / \overline{DMDS}$, where $\overline{DMDS}$ is the mean value of the amount of DMDS; and c) $1 + c_1 DMDS$.

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- First-order relationships were adopted for the amount of thermal resid and the solvent:coal ratio.

From the above expressions, rates of conversion of UC and TR are obtained. The final, complete kinetic model, therefore, consists of seven mass balance equations and two rate expressions.

$$r_{uc} = 2.0460 \times 10^{10} e^{\left(\frac{-1.784 \times 10^5}{RT}\right)} P (1 + Fe_2O_3)$$

r_{uc} is assumed to be invariant with composition and to be only a function of conditions.

$$r_{TR} = 2.4295 \times 10^{10} e^{\left(\frac{-2.3463 \times 10^5}{RT}\right)} (1 + Fe_2O_3) TR_f$$

r_{TR} is a function of reaction conditions only.

A study⁵⁸ was undertaken to quantitatively assess the effect of novel catalysts for coal liquefaction. The catalysts are finely divided iron oxides, Fe_2O_3/SO_4 , and $Mo/Fe_2O_3/SO_4$.

A single lumped component model was used to evaluate the liquefaction of Wyodak and Anderson seam subbituminous coal using the three different catalysts. The lumps are oil, asphaltenes, and gases. The total conversion of coal and conversions to product fractions were defined as follows:

$$\begin{aligned} \text{fractional coal conversion} \quad Y_T &= (1 - Y) \\ \text{unreacted coal fraction} \quad Y &= (W_i - W_c - W_{ash})/W_{maf} \\ \text{asphaltene fraction} \quad Y_A &= (W_A/W_{maf}) \\ \text{gas fraction} \quad Y_G &= Y_T - Y_m; \text{ where } Y_m = W_m/W_{maf} \\ \text{oil fraction} \quad Y_o &= Y_m - Y_A \end{aligned}$$

where W_i , W_c , W_{ash} , W_{maf} , W_A , and W_m are masses of methylene chloride insolubles, catalyst, ash, maf coal, pentane insolubles, and methylene chloride solubles, respectively.

The kinetic model chosen has both series and parallel conversion of coals into oils:

All reactions are assumed to be first order and rate constants are described by:

$$K_i = A_i \exp(-E_i/RT)$$

Both thermal and catalytic pathways are allowed for reactions 1, 2, and 3. Additional assumptions include: no dependence on coal particle size, no dependence on hydrogen pressure, and the rate of conversion is proportional to the amount of catalyst. It also is assumed that the ultimate coal conversion (C^*) always will be less than 100%.

Reactions were carried out at 3 different temperatures (648, 673, 698 K) for 3 hr; total coal conversions (defined above) of 76%, 87%, and 93% on a MAF basis were obtained, respectively.

Thermal and catalytic reaction pathways were assumed to occur in parallel. Therefore,

$$K_x = K_{xT} + m_c K_{xc}$$

where:

K_x is the overall rate constant for the reaction

K_{xT} is the thermal rate constant

K_{xc} is the catalytic rate constant

m_i = mass of catalyst used

Experimental data for the fraction of coal remaining, the fraction converted to oil, and the fraction converted to asphaltenes were included in the model correlation (f); (the gas fraction was determined by difference and was not used).

The following equation for f was minimized by determination of the best-fit rate constants.

$$f = \sum_{i=1}^N [w_c (Y_{c,i} - \hat{Y}_{c,i})^2 + w_A (Y_{A,i} - \hat{Y}_{A,i})^2 + w_o (Y_{o,i} - \hat{Y}_{o,i})^2]$$

where: w_i s are weighing factors

Solution of the differential equations gives:

$$\hat{Y}_c(t) = (1 - C^*) + C^* \exp[-(K_{CA} + K_{CO} + K_{AO})t]$$

$$\hat{Y}_A(t) = \frac{C^* K_{CA}}{(K_{AO} - K_{CA} - K_{CO} - K_{CG})} (\exp[-(K_{CA} + K_{CO} + K_{CA})t] - \exp[-K_{AO}t])$$

$$\hat{Y}_o(t) = \frac{C^*}{(K_{CA} + K_{CO} + K_{CG})} (K_{CA} + K_{CO} - K_{CO} \exp[-(K_{CA} + K_{CO} + K_{CG})t])$$

$$+ \frac{C^* K_{CA} \exp[-K_{AO}t]}{K_{AO} - K_{CA} - K_{CO} - K_{CG}} - \frac{C^* K_{CA} K_{AO} \exp[-(K_{CA} + K_{CO} + K_{CG})t]}{(K_{CA} + K_{CO} + K_{CG})(K_{AO} - K_{CA} - K_{CO} - K_{CG})}$$

$$\hat{Y}_g(t) = 1 - [\hat{Y}_T(t) + Y_A(t) + \hat{Y}_o(t)]$$

The best-fit rate constants were determined by a derivative-free nonlinear regression program. There are four thermal rate constants and three catalytic rate constants for each of three catalysts. In order to determine which catalytic effects were important, regressions were made using different sets of rate constants. The significance of the constants then was ranked. This allowed for identification of the pathways which were significant.

It was found that the asphaltenes to oils pathway is exclusively catalytic in nature, and is strongly influenced by the type of catalyst used. However, the production of asphaltenes from coal was primarily thermal in nature.

The Delplot technique is not a kinetic model, but a way to synthesize the information from a lumped kinetic model into a network of reactions. Bhole, Klein, and Bischoff^{59,60} describe the Delplot procedure for determination of the rank (primary, secondary, etc.) of reaction product pathways as a first step in independent deduction of a reaction network. Plots of selectivity (molar yield of P, y_p), divided by conversion of reactant A, (x_A), vs conversion (x_A) can be used to discriminate between primary and nonprimary products. For first-rank Delplots, as $x \rightarrow 0$, the intercept is used to determine if the product is primary (the intercept is finite) or nonprimary (intercept is zero). For higher rank Delplots, products can be sorted by rank. In the higher rank Delplot method (y/x_r vs x for integer values of r ; where r is the rank of the Delplot) for first order kinetics, secondary products have non-zero intercept with $r = 2$, tertiary products have non-zero intercept with $r = 3$, and so on. However, for non-first order kinetics, the higher rank Delplot intercepts can be dependent on the reaction rate order. So, the method is really only completely decoupled from reaction kinetics for $r = 1$. Once the network is derived and quantitative rate laws are determined for each step, quantitative parameter estimation that assigns rate parameters (k , E^* , A , and order) to each step in the network are made. Network predictions are then compared with the experimental data.

The complexity of fossil fuel feedstocks, which can be comprised of on the order of 10^5 distinct molecular species, is attributable to the number and arrangement of substituents, ring sizes, and other structural attributes⁶¹. The complexity can be diminished by lumping the reaction types. (In this case, for pyrolysis, into four classes: 1) classic bond fission, 2) H-transfer, 3) β -scission, and 4) radical recombination disproportionation). To develop this approach, model

compound data for structure classes (paraffin, alkyl benzene, and alkyl naphthalene classes) were organized according to the four reaction lumps. The kinetics of the reaction families (lumps) were described by a quantitative structure-reactivity relationship (QSRR).

The literature on the reactions of each family was explored and a summary of structure-reactivity relationships was made. These relationships were based on thermochemical properties (ΔH_f° , S_f , C_p°) for estimation of the kinetic parameters (A , E^*). They are summarized for pyrolysis reactions in the following table for each reaction family in the following table.

Reaction Family	$\log (A)$	E^* (Activation Energy)
bond homolysis	16.0	Δd°
H abstraction	8.5	$E^* = E_\alpha^* - \alpha q$ (exo) $E^* = E_\alpha^* - (1 - \alpha) q$ (endo)
β scission	13.0	$E^* = E_\beta^* - \beta q$
Recombination	9.0	0.0

Δd° = bond strength of weakest C-C bond
 E_α^* and α are Polanyi parameters
 $q = -\Delta H_\alpha$

From the model compound experimental data base, a logic was established for deducing QSRR parameters. This logic first considers an experimentally observed rate constant (k_{obs}) for pseudo first order reactions. These values were compared against the predicted values to determine the quality of the prediction. Molecular (and radical intermediate) structures, and their associated heats of formation serve as the basic data base. These would be used to provide rate constants, k , of the steps of the reaction mechanism. With these rate constants, the model could be solved to predict rates and, thus, k_{pred} s. Calculation of the objective function X , yields an optimal set of QSRR parameters $X = (K_{obs} - k_{pred} (QSRR)^2 / \sigma^2)$ (X is optimized by the SIMPLEX program). This system was applied to a pyrolysis reaction model. It was concluded that the optimized set of structure-reactivity parameters can summarize the entire model-compound data base. This system provides for extrapolation in terms of only a few parameters.

In another approach⁶² which considers the lumps as a class of species with continuous properties, the chemical species which are produced from coal liquefaction are represented by a concentration distribution function. This approximation thus requires that there be also a continuum of chemical reactions of these species.

In a continuum of reactions, the rate of a reaction between given differential reactant and product species can be expressed in terms of a reaction rate function (called the "rate kernel") which will, in general, depend on all species involved in the differential reaction.

The authors believe that the most important variable describing any species is its molecular weight. They consequently choose molecular weight as the only "state variable" to formulate and study a simple continuous mixture model. State variables are those variables which completely describe all the product species and their properties. By using only one state variable (molecular weight) the authors actually do lump together several isomers into one species. However, they view coal itself as a continuum of molecular weights distributed about a statistical average value (u).

Two types of reactions are assumed to take place in the liquefaction process: 1) coal to products and 2) heavier products to lighter products. The reactions are assumed to be first order with respect to reactants and there is assumed to be an excess of hydrogen to prevent reverse reactions; stabilization by hydrogen is assumed to be fast.

In this 'fission' model, each differential reaction can be characterized by only single reactant species and a single product species; therefore, the rate kernel is a function of the molecular weight of the reactant and product.

The reactions are written as:

$$A(x) \xrightarrow{\bar{k}_1(x, x')} A(x-x') + A(x'); (0 \leq x' \leq x \leq u)$$

The rate kernels satisfy the following symmetry relations:

$$\bar{k}_s(x) = \bar{k}_s(u-x)$$

where:

$\bar{k}_s$ describes the reactivity of coal

$$\bar{k}_1(x, x') = \bar{k}(x, x-x')$$

where:

$\bar{k}_1$ describes the reactions between the product species.

u is the molecular weight of coal represented as a lumped species.

Using an assumed concentration C_s for coal, and making a differential mole balance, the authors obtain the following set of equations:

$$\frac{dC_s}{dt} = - \int_0^{u/2} \bar{k}_s(x') C_s dx'$$

$$\frac{\partial C}{\partial t} = \bar{k}_s C_s + \int_x^u \bar{k}_1(x', x) C(x', t) dx' - \int_0^{x/2} \bar{k}_1(x, x') C(x, t) dx'$$

where initial conditions are:

$$C_s(0) = C_o = \frac{W_o}{u}$$

$$C(x, 0) = 0$$

The first term on the right side of the partial differential equation represents the rate of generation of species from coal, the second term accounts for the rate of generation from heavier products, and the last term accounts for the rate of consumption to form all the lighter products.

These equations are rigorously solved via a numerical solution. To check the numerical solution, an analytical solution, obtained by considering a specific and simple rate kernel, was derived. The characteristics of the rate kernel (and thus the kinetics reactions) can be linked quantitatively to the coal structure. Since the rate kernel $\bar{k}_s$ describes the initial bond breaking of the coal, it can be expressed in dimensionless form as:

$$\int_0^{1/2} k_s(y) dy = \frac{1}{u}$$

The form this function takes is bounded by two extremes. In one case, the coal equally splits into two parts. In the other extreme, the coal splits apart at multiple weak links. This picture gives, effectively, two curves; one equally distributed around $y = 0.5$ and the other with a bimodal distribution with peaks at $1.0 = y$ and $0 = y$.

The choice of k_1 depends, also, on the reactivity of the structural units. Whenever extremely stable compounds or impossible reactions are involved, k_1 will tend to zero.

Functions which express both of the extreme cases for k_s and the properties for k_1 are the following:

$$\begin{aligned} k_s &= 0.002 y (1 - y) \\ k_s &= 21.1 z^3 (1 - z)^{30} \\ k_1 &= my' (y - y') \\ k_1 &= nyy' (y - y') \end{aligned}$$

where:

$$\begin{aligned} y &= \frac{x}{u} \\ y' &= \frac{x'}{u} \end{aligned}$$

m and n are adjustable constants

$$z = y (1 - y)$$

Comparisons with experimental data show that if k_1 is restricted at certain values corresponding to specific molecular weights, the form of the function approaches a fit to the experimental values. These specific molecular weights are described by the authors as those which represent stable compounds which build in concentration as the reaction proceeds. The molecular weight curves are shown to be insensitive to the rate kernel k_s , even at times as short as 10 min. It was shown that the overall reactivity of the reactant species falls off as the cube of their molecular weight. Thus, this method of kinetic analysis can give an account of the chemical processes in the reacting system.

STRUCTURE/KINETIC MODELS

The premise of a paper by Trauth et al.⁶³ is that even though light fractions and gas oil can be fully characterized by analytical chemistry, it is not possible to do the same with resids. Additionally, in order to produce molecular reaction models for feedstocks with such high complexity as resids, the computational power which is required is tremendous. Because of this chemical complexity of resids, a statistical representation of a resid structure was obtained through Monte Carlo methods. This approach estimates a resid structure. This statistical representation is then used to produce molecular models of resid upgrading.

Two extremes bracket the protocol: (1) Detailed molecular structure is first derived from separations and analyses. In the work described in this paper, those analyses were used to provide probability density functions (pdf) of the distribution of the resid molecules. (2) A few global measurements (e.g. $^1\text{H-NMR}$; molecular weight, and elemental analysis) were made. Combining pdf and these global measurements gave estimates of molecular distributions, but the authors note that this description is "generally under-specified". Therefore, to compromise they "sought to define and characterize the 'attributes' of resid molecules that would allow for the assembly of a statistical representation of a given feedstock".

The approach the authors take in doing this is to consider resid molecules as the simultaneous occurrence of structural attributes, such as aromatic and naphthenic rings substituted with alkyl chains. The resid molecules are determined in the model by random generation within a set of predetermined groups (saturates, which are comprised of paraffins and naphthenics, which are further broken down by

chain length and number of rings, number of side chains, and length of side chains (respectively); aromatics and resins; and asphaltenes which in the model are represented by a number of unit sheets. Stochastic sampling of the features (such as number of rings) is used to build the molecules.

In this model, the pdfs are approximated by the chi-square distribution:

$$p = \frac{(x-\min)^{(\frac{r}{2} - 1)} \cdot e^{(-\frac{x-\min}{2})}}{\Gamma(\frac{r}{2}) \cdot 2^{(\frac{r}{2})}}$$

$$r = \mu = \frac{\sigma^2}{2}$$

where:

p = probability

x = attribute value

min = minimum value of x

r = degrees of freedom

Γ = gamma function

μ = mean

σ = standard deviation

Starting with an estimate for pdf parameters, the model generates 10,000 molecules. The attributes are compared to experimental data and estimates are altered until a best fit is achieved.

Application of the model to a single example shows that five of seven attributes used to construct the resid affect the average physical properties enough to warrant optimization. Results for the real resid show that the solution fits experimental data well and, in terms of pdf parameters, is "tightly focused". The experimental and predicted data are presented in the following table:

Analytical Test	Experimental Results	Simulation Results
Number average MW	622	689
H/C ratio	1.60	1.57
Alpha proton, %	11.2	9.9
Saturate, %	27	28
Aromatic and Resin, %	71	71
Asphaltene, %	2	1
Simulated Distillation, wt %		
610-800 °F	2	3
800-1000 °F	9	20
1000 °F ⁺	89	76

The general concept set forth in a paper by Petti et al.⁶⁴ is that a statistical model can be built to construct a representation of resid molecules from measurements of resid attributes because individual, specific molecules are not identified in the resid. Thus, resid-reaction behavior can assist in determination of resid structure.

In this case, resid reactivity is considered just another measurable resid property (like proton environment (NMR) or molecular weight (which here is obtained by vapor phase osmometry (VPO))). A reaction model (pyrolysis model based on four model compounds) was used to obtain predicted resid reactivity. This was used as additional information in the optimization objective function that provides the optimal pdf parameters (see Ref 47).

It was determined that "...the reaction model did not prove useful for pdf parameter optimization, [but] the fact that the predicted reaction behavior did not adversely affect the optimization offers a validation of the reaction model. This model can therefore be used in studying the reaction behavior of the resids that have been previously characterized in terms of structural attribute pdfs.

Quann and Jaffe⁶⁵ undertook the task of describing the chemistry of complex hydrocarbon mixtures using the technique of Structure-Oriented Lumping (SOL). They believe this technique is not subject to the limits that are placed on a lumped kinetic modeling approach. They state that there are four limitations on lumping thousands of individual constituents in a complex feedstock into broad, but measurable, categories. These four limitations are: 1) the approach often fails to extrapolate to different feedstocks because of composition differences

within the same defined lump; 2) the actual composition of lumps in terms of molecular components may change with overall conversion of the system and mask the true kinetics; 3) coarsely lumped models cannot be utilized to interpret the effects of catalyst properties on the phenomenological aspects of catalytic chemistry because fundamental catalytic reaction mechanisms are not incorporated into the kinetic scheme; and 4) insufficient detail exists in the lumped models to predict subtle changes in product properties - the main limitation."

In the structure-oriented lumping method, hydrocarbon molecules are described as vectors. The elements of each vector represent structural features. Therefore, each molecule in any mixture is represented by a structure vector. In essence, this method is a lumping approach, but on a molecular level. Different molecules with the same set of structural groups (i.e., isomers) are lumped and represented by the same vector. LC-FIMS and GC/MS are used to determine carbon number distributions of homologous series. This information is used to construct the hydrocarbon structure vectors 'a' and a stoichiometric matrix 'S'. Columns of the matrix contain C, H, S, N, and O atomic stoichiometry contributions of each element or structural group of the vector. The structural groups have the stoichiometry to construct a molecule incrementally. The authors refer to the groups as "structural increments". These structural increments can be better understood by the following example of a single six-carbon aromatic ring (A6: a six-carbon aromatic ring present in all aromatic molecules). The A6 element of the vector is a group that can exist by itself as benzene when all other incremental structures are absent (zero). The A6 group has 6 carbons and 6 hydrogens, (the proper C and H stoichiometry for benzene). All multi-ring aromatic compounds must contain one A6 ring and are built with the addition of other incremental ring structures to the A6 ring.

This can be seen in the following stoichiometric matrix for benzene:

A6	A4	A2	N6	N5	N4	N1	R	br	me	H	AA	NS	RS	AN	NN	RN	NO	RO	OO
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

The columns of the matrix are the atomic stoichiometry contribution of each element or structural group of the vector. A4: 4C ring; A2: 2C aromatic increment; N6 and N5: 6 and 5 carbon naphthenic ring increments; N4, N3, N2, N1: addition of 4, 3, 2, 1 carbon naphthenic ring increments that must be attached

to other naphthene or aromatic ring structures; R: carbon number of total alkyl-group on ring or carbon number of aliphatic molecules; IH: incremental hydrogen to specify degree of unsaturation (in addition to that from aromatic rings); br: number of branch points on alkyl side chain R; me: number of carbons of total alkyl structure R which are $-CH_3$ groups; AA: biphenyl bridge; NS, NN, NO: a S, N ($-NH-$), or O inserted between a C and H to form a mercaptan, amine, or alcohol; AN: N in aromatic ring; and KO: ketone or aldehyde group.

The authors demonstrate that they can apply these structural increments to any molecule. But to use these matrices, they invoke a set of reaction rules. In these rules, chemical reactions are treated as transformations of the reactant-structural increments to the product-structural increments. Specific transformations that reflect fundamental reaction chemistry are termed reaction classes which are determined by a set of reaction rules. There are a limited number of these reaction rules. A single reaction rule is applied to all molecules which undergo a particular transformation. A reaction rule has two components: 1) a reactant selection rule to determine if a reactant has a proper structural increment for that reaction, and 2) a product generation rule. Six rules are given here as examples: 1) A6 Saturation, 2) A4 Saturation, 3) N4 Ring Opening on Aromatics, 4) Paraffin Isomerization, 5) Aromatic Dealkylation, and 6) Paraffin Hydrocracking.

The authors indicate that the SOL approach simplifies the solution of the kinetic rate equation $y' = Ky$, where y is the composition vector, y' is the derivative of y with respect to time or distance through the reactor, and K is a square matrix whose elements are the rate constants for the reactions which take place in a mixture of variously reacting components. For a small number of components and reactions, the K matrix can be constructed; however, for large complicated systems construction of the entire matrix is very complicated. Use of the reaction rules (described above) and the SOL technique allows for computer-generation of large complex reaction network and the rate equations. The reactant-selection rules and the corresponding product-generation rules identify reactant-product pairs in terms of the column-row positions of the rate constants in the matrix K , as well as the position of the composition vector y . Integration of the rate equation yields the composition of the mixture for all components as a function of time (or position in the reactor).

ANALYTICAL METHODS FOR POTENTIAL USE IN THE CONTRACT

In DOE Contract DE-AC22-89PC89883, analytical techniques were identified that were shown to be useful for providing physico-chemical information of coal-liquefaction resids. These techniques are nuclear magnetic resonance spectroscopy, mass spectrometry (especially the technique of field ionization mass spectrometry), electron spin resonance spectroscopy coupled to thermogravimetric analysis, and a suite of petroleum inspection tests. It is recommended that these techniques be used in the present contract.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY^{66,67}

Among the methods which are considered for potential use in this contract is cross polarization/magic angle spinning (CP/MAS) ^{13}C -nuclear magnetic resonance (NMR) spectroscopy. The method can provide data for the derivation of a number of carbon structural parameters and molecular structural descriptors for coal and coal-liquefaction resids. Carbon structural parameters which are obtained from these analyses include the fraction of aromatic and aliphatic carbon present in different forms in the sample (Table 3). Molecular structural parameters which can be derived (Table 4) include such values as the ring cluster size, the number of clusters per molecule, the degree of ring substitution, and the number of bridges between clusters. The information produced by this method can be used to form the basis for a mechanistic model of coal conversion to liquid products. The process-induced changes discernable by the ^{13}C -NMR method in the coal liquefaction samples can be used to guide process operations to optimize the chemical properties of the liquefaction streams.

Another use of NMR techniques is to directly monitor the process streams for aromaticity of the coal liquefaction materials, especially the resid, which is comprised of condensed aromatic structures. Solid-state ^1H - and ^{13}C -NMR can provide the aromaticity values of the solid resid portion of process stream samples. These data, combined with the mass balances and the elemental analyses of the materials analyzed, can provide information on the degree of hydrogenation and modes of hydrogen utilization during coal liquefaction. Additionally, the extent of condensation or retrograde reaction that has occurred in the various product streams can be inferred from these measurements. Thus, the information obtainable with the solid-state NMR techniques can be used to develop a lumped

kinetic model for coal liquefaction such as those described in Part V of this report.

MASS SPECTROMETRY^{68,69,70}

Molecular weight distributions and speciation of high-mass compounds in coal-derived materials determined by field ionization mass spectroscopy (FIMS) are recommended. The FIMS profile of resid samples previously studied consists of a broad distribution of molecular weights ranging from 200 to 1000 Da. (Figure 1). A simple data analysis method which deconvolutes the mass profile into two principal groups was applied to the FIMS profiles generated in that study (Figure 1). The use of this simplifying double-lump model to handle the complex FIMS profiles was highly effective. The two pseudo-components, centered at approximately 350 and 600 Da, were modeled by use of a non-linear regression routine based on fitting an expression to the general form of the peaks and deriving fitting parameters from a few sample spectra. Changes in the relative weight percent of these components could be attributed to changes in process parameters. This simple scheme holds great potential for process development application. In addition to the broad molecular weight profiles obtainable by FIMS, structural identification can be made of some molecular components in the 160 to 320 Da range of the FIMS spectrum (Figure 1). Identification of these compounds can yield information of the mechanisms (and possibly kinetics) of resid conversion.

ELECTRON SPIN RESONANCE SPECTROSCOPY/THERMOGRAVIMETRIC ANALYSIS⁷¹

Temperature-programmed electron spin resonance (ESR) spectroscopy coupled with thermogravimetric analysis (TGA) techniques have shown potential for the analysis of direct coal liquefaction resid samples, and, thus, for providing direction for process development. The free radical density (N) determined by ESR may be a good indicator of resid reactivity. The resids with lower N values were found to be more hydrogenated and, therefore, presumably more reactive to cracking. This is supported by the TGA data, which also shows that samples with a lower N value are more volatile, and therefore, presumably more reactive.

PETROLEUM INSPECTION TESTS^{72,73,74}

Standard petroleum inspection tests are recommended for use in this contract to evaluate the quality of the net product oils from the direct coal conversion processes. These analyses are comprised of over 30 individual tests (Table 5). Previous experience in application of these tests to coal-derived net product

oils has shown them to be useful tools for evaluation of the quality and potential commercial value of the materials.⁷⁵

RESID REACTIVITY STUDIES⁷⁶

Included in the Participants Program, described above, was a project conducted by the University of Delaware designed to evaluate a laboratory method to measure resid conversion reactivity. A laboratory-scale batch reactor (Short Time Batch Reactor, STBR) (Figure 2) was used in this study. The project goals were to investigate the feasibility of using this reactor to determine the reactivity of coal-derived resids to form lower boiling products and to develop and verify an experimental protocol for measuring the relative reactivity of resids to transform into lower boiling products. Tetralin was used as a solvent, a commercial catalyst was used, and reactions were carried out at conditions relevant to coal liquefaction (about 400 °C, 1500 psi H₂ (cold), 3:1 solvent to resid ratio).

It was recognized that an essential part of the study of resid conversion is an analytical system for measuring the changes in the resid resulting from processing it under various conditions. Several analytical techniques including Thermal Gravimetric Analysis (TGA), Gas Chromatography/Mass Spectrometry (GC/MS) and Gas Chromatography (GC) were used for this purpose. Changes in the boiling ranges of the liquefaction products, as a function of process conditions in tetralin donor solvent, with and without catalysts, were monitored. An experimental protocol was developed which could be used to determine the relative amount of resid conversion, unhindered by the catalyst content of the reaction mixture. Reproducible data were obtained over a large matrix of reaction conditions. The work under this contract will greatly expand on the earlier work.

SAMPLING PLAN - UNIVERSITY OF DELAWARE

A number of different kinds of samples will be used in the University of Delaware experimental program to investigate resid reactivity. To calibrate the thermogravimetric method that will be used to define conversion, several pure organic compounds will be used by Delaware. These materials have boiling points close to 850 °F. Additionally, Delaware will use recomposited mixtures of direct

coal-liquefaction 850 °F+ distillation resids and direct coal liquefaction 850 °F- distillates made in known proportions to use for calibration standards.

One catalyst chosen for the experimental program is a Shell 324 Ni/Mo on alumina unimodal catalyst that was presulfided in oil for Wilsonville Run 260. The oil was stripped from the catalyst by Soxhlet extraction in tetrahydrofuran, the catalyst was ground under N₂ and packaged in 150 g batches to protect it from oxidation. A second catalyst that is proposed for use in the program is a homogeneous molybdenum catalyst. The catalyst will be chosen by Delaware and CONSOL, based on preliminary experimental results.

The study of resid reactivity will be made with a number of different direct coal liquefaction 850 °F+ distillation resids. Fifteen resids were chosen on the basis of CONSOL's previous experience and the Statement of Work. Resid samples were chosen to represent a wide range of feed coal properties and liquefaction process conditions at the Wilsonville and HRI facilities. The resid samples are composites of 850 °F+ resid samples from individual run periods. The solvent which will be used for the majority of the Delaware work will be tetralin (tetramethylnaphthalene). However, some studies will be conducted using process derived oil as solvent. The solvent samples chosen were obtained from two different Wilsonville liquefaction runs. One solvent sample was produced from a Wyodak and Anderson seam, subbituminous coal. The other solvent sample was produced from an Illinois No.6 seam, bituminous coal. Both samples are the composites of the 850 °F- distillate fractions of samples obtained from the recycle stream over the course of the run. A list of all samples is given in Table 6.

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TABLE 1
PARTICIPANTS PROGRAM - PHASE 1

<u>Participating Organization</u>	<u>Project Title</u>	<u>Methods</u>	<u>Principal Investigators</u>
University of Kentucky/ Center for Applied Research	Novel Analytical Techniques for Coal Liquefaction: Fluorescence Microscopy	Fluorescence Microscopy	F. Derbyshire R. Rathbone
Virginia Polytechnic Institute and State University	Analysis of Coal Liquefaction Process Streams by Chromatographic and Spectroscopic Techniques	SFE SFC Liquid Chromatography-FTIR	L. Taylor
Western Research Institute	Solid-State NMR Characterization of Coal Liquefaction Products	Solid State $^1\text{H}/^{13}\text{C}$ -NMR	F. Miknis D. Netzel
The Pennsylvania State University	Gold Tube Carbonization and Reflectance Microscopy	Reflectance Microscopy Gold Tube Carbonization - Microscopy	A. Davis G. Mitchell
SRI International	Characterization of Coal Liquids by Field Ionization Mass Spectrometry and Iodotrimethylsilane Derivatization	FIMS Oxygen Speciation by Derivatization	R. Malhotra D. McMillen
Advanced Fuel Research	FT-IR Methods for Characterization of Coal Liquefaction Products Advanced Fuel Research	FTIR TG-FTIR	M. Serio
National Institute for Petroleum and Energy Research	Application of Liquid Chromatographic Separation Methods to THF-Soluble Portions of Integrated Two-Stage Coal Liquefaction Resids	Acid/Base/Neutral Separation	R. Anderson J. Green
Battelle, Pacific Northwest Laboratories	Application of Liquid Chromatographic Separation Methods to THF-Soluble Portions of Integrated Two-Stage Coal Liquefaction Resids	FDMS 2-D NMR ^{13}C NMR HPLC	J. Campbell
Conoco Inc. Petroleum Products Research Division	Inspection of Integrated Two-Stage Liquefaction Products by Petroleum Assay	ASTM Petroleum Inspection Tests	R. Kramer

TABLE 1 (Continued)
PARTICIPANTS PROGRAM - PHASE 2

<u>Participating Organization</u>	<u>Project Title</u>	<u>Methods</u>	<u>Principal Investigators</u>
Lehigh University	Application of ^{252}Cf -Plasma Desorption Mass Spectrometry to the Analysis of Direct Coal Liquefaction Heavy Products	^{252}Cf -PDMS	J. Larsen
University of Pittsburgh	UV Resonance Raman Studies of Coal Liquid Residuals	UV Resonance Raman Spectroscopy	S. Asher
University of Kentucky/CFFLS	Investigation of the Forms of Sulfur in Five Wilsonville Resid Samples by XAFS and Mössbauer Spectroscopy	XANES (S Speciation)	G. Huffman
University of Chicago	The Use of Selective Chemical Reactions and Carbon NMR Spectroscopy in the Speciation and Quantification of Oxygen Functional Groups in Coal Resids	Oxygen Derivatization/ ^{13}C -NMR	L. Stock
University of Utah	^{13}C -NMR Analysis of CONSOL THF-Soluble Residual Materials from the Wilsonville Coal Liquefaction Process	^{13}C -NMR/Structural Description	R. Pugmire M. Solum
Vander Sande Associates	Electron Microscopy Observations of Resids Obtained from Coal Liquefaction Experiments Advanced Fuel Research	Scanning Transmission Electron Microscopy	J. Vander Sande
Iowa State University	Estimation of Total Phenol Concentrations in Coal Liquefaction Resids by ^{31}P -NMR Spectroscopy	Phospholane Derivatization/ ^{31}P -NMR	J. Verkade
West Virginia University	Characterization of Coal Liquefaction Resids Employing Thermogravimetric Analysis and Electron Spin Resonance Spectroscopy	ESR/TGA 2-D NMR ^{13}C NMR HPLC	M. Seehra M. Ibrahim

TABLE 1 (continued)
PARTICIPANTS PROGRAM - PHASE 3

<u>Participating Organization</u>	<u>Project Title</u>	<u>Methods</u>	<u>Principal Investigators</u>
University of Utah	Analysis of Black Thunder Coal and Liquefaction Products from HRI Bench Unit Run CC-15	¹³ C-NMR/Structural Description	R. Pugmire
SRI International	FIMS Analysis of Direct Coal Liquefaction Process Streams	FIMS	R. Malhotra D. McMillen
University of Pittsburgh	Assessment of Hydroaromatic Content and Hydrogen Donor Ability of Coal Liquefaction Intermediates by Means of Catalytic Dehydrogenation	Catalytic Dehydrogenation	I. Wender
The Pennsylvania State University	High Performance Liquid Chromatography (HPLC) of Coal Liquefaction Process Streams Using Normal-Phase Separation with UV Diode Array Detection	2-D HPLC	P. Hatcher
University of Delaware	Preliminary Evaluation of the Kinetics of Coal Liquefaction Distillation Resid Conversion	Resid Reactivity	W. Calkins
NIPER	Analysis of Coal-Derived Synthetic Crude; Part I: from HRI CTSL Run CC-15, Part II: from HRI Run CMSL-2	Petroleum Inspection Tests	G. Sturm

TABLE 2

ANALYTICAL METHODS EVALUATED UNDER
DOE CONTRACT DE-AC22-89PC89883

METHODS WITH HIGH POTENTIAL

- Nuclear Magnetic Resonance Spectroscopy
- Field Ionization Mass Spectrometry
- Electron Spin Resonance Spectroscopy/Thermogravimetric Analysis
- Petroleum Inspection Tests

METHODS WITH MODERATE POTENTIAL

- X-ray Absorption Near Edge Structure Spectroscopy
- Mössbauer Spectroscopy
- Fluorescence Microscopy
- Molecular Weight Determination
  - ^{252}Cf -Plasma Desorption Mass Spectrometry
  - Field Desorption Mass Spectrometry
  - Gel Permeation Chromatography
- Acid/Base/Neutral Separation
- Fourier Transform Infrared Spectroscopy
- Scanning Transmission Electron Microscopy
- Reflectance Microscopy
- Liquid Chromatography
- Two-Dimensional, High Performance Liquid Chromatography

METHODS WHICH ARE PRESENTLY NOT RECOMMENDED

- Catalytic Dehydrogenation
- Iodotrimethylsilane Derivatization for Oxygen Analysis
- Gold Tube Characterization
- ^{31}P -Nuclear Magnetic Resonance Spectroscopy
- Two-Dimensional Nuclear Magnetic Resonance Spectroscopy
- Oxygen Speciation by Selective Chemical Reactions
- Ultra Violet Resonance Raman Spectroscopy
- Liquid Chromatography-Fourier Transform Infrared Spectroscopy
- Supercritical Fluid Extraction

TABLE 3
CARBON STRUCTURAL PARAMETERS
DETERMINED BY ^{13}C -NMR

Symbol	Fractions of sp^2 -hybridized Carbon	Symbol	Fractions of sp^3 -hybridized Carbon
f_a	total carbon	f_{al}	total carbon
f_a^H	in an aromatic ring	f_{al}^H	CH or CH_2
f_a^C	carbonyl	f_{al}^*	CH_3 or nonprotonated
f_a^H	protonated and aromatic	f_{al}^O	bonded to oxygen
f_a^N	nonprotonated and aromatic		
f_a^P	phenolic or phenolic ether		
f_a^S	alkylated aromatic		
f_a^B	aromatic bridgehead		

TABLE 4
AVERAGE MOLECULAR STRUCTURAL DESCRIPTORS
(LATTICE PARAMETERS)
DETERMINED BY ^{13}C -NMR

Symbol	Description	Symbol	Description
x_b	mole fraction of condensed carbons; $x_b = f_a^B / f_a$	B.L.	bridges and loops per cluster; $\text{BL} = (\sigma + 1) \times P_O$
C	average aromatic cluster size	S.C.	side chains per cluster; $\text{SC} = (\sigma + 1) - \text{BL}$
$\sigma + 1$	number of attachments per cluster	MW	total molecular weight; $\text{MW} = (\text{Cx}12.01) / (f_a \cdot x\% \text{C} / 100)$
P_O	fraction of intact bridges; $P_O = \{f_a^P + f_a^S - f_{al}^*\} / \{f_a^P + f_a^S\}$	M_δ	average molecular weight per attachment

TABLE 5
PETROLEUM INSPECTION TESTS

Properties Examined

- Specific Gravity @ 60°F (D4052)
- API Gravity
- Elemental Analysis
  - Carbon
  - Hydrogen
  - Sulfur
  - Nitrogen
  - Oxygen (by diff)
  - Basic Nitrogen (UOP269)
  - Mercaptan Sulfur (D3227)
- Trace Metals, (D5185), Vanadium, ppm
  - Nickel, ppm
  - Iron, ppm
  - Copper, ppm
- Ash (D482), wt %
- Viscosity (D445) cSt
  - @70 °F
  - @100°F
  - @-20°C
- Refractive Index (D1218), 20 °C
- Freezing Point (D2386), °F
- Cloud Point (D2500), °F
- Pour Point (D97), °F
- Reid Vapor Pressure (D323), psi
- Microcarbon Residue (D4530), wt %
- Flash Point (D56, D93)², °C
- Heptane Insolubles (D3279), wt %
- Group Analysis³
  - Paraffins, vol %
  - Naphthenes, vol %
  - Aromatics, vol %
  - Olefins, vol %
  - Benzene (PIANO, mod D6134)³
  - Naphthalene (D1840), vol %
- Bromine Number (D1159)
- Aniline Point (D611), °F
- Smoke Point (D1322), mm
- Acidity (D3242), mg KOH/g
- Copper Corrosion (D130)
- Existent Gum (D381), mg/100 mL
- Oxidation Stability (D525), min
- Oxidation Stability (D2274), mg/100 mL
- Thermal Stability (JFTOT)(D3341)
- Distillation (ASTM D2892), wt %
- Octane Number Motor Method (D2700)
- Octane Number Research Method (D2699)
- Cetane Index (D976)

TABLE 6
SAMPLES FOR UNIVERSITY OF DELAWARE EXPERIMENTAL PROGRAM

Model Compounds for TGA Calibration, Boiling Point (°F)			
n-dotriacotane, 872.6		n-tetracosane, 735.8	
pyrene, 739.4		1,2 benzanthracene, 818.6	
chrysene, 838.4		triphenylmethane, 678.2	
n-hexacosane, 773.6			
Resid/Distillate Samples for TGA Calibration			
Wilsonville 261 Period A, Recycle Stream			
HRI POC-2, Second Stage Product Stream			
850°F ⁺ Distillation Resid Samples ^a			
Run	Stream ^b	Feed Coal (seam/mine)	Comments
Wilsonville 258	V 131B	Wyodak and Anderson/ Black Thunder	
Wilsonville 259	V 1067	Pittsburgh/Ireland	Catalytic/Catalytic
	R 1235		
	V 131B		
Wilsonville 260	V 1067	Wyodak and Anderson/ Black Thunder	Thermal/Catalytic and High/Low temperature & Catalytic/Thermal and Low/High temperature
	R 1235		
	V 131B		
Wilsonville 261	V 1067	Illinois No. 6/Burning Star No. 2	Catalytic/Catalytic with ash recycle
	R 1235		
	V 131B		
Wilsonville 262	V 1067	Wyodak and Anderson/ Black Thunder	Slurry (Dispersed) Molybdenum catalyst - first stage, Supported catalyst - second stage
	R 1235		
	V 131B		
HRI POC-1	O-43	Illinois No. 6/ Burning Star No. 2	
HRI POC-2	O-43	Wyodak and Anderson/ Black Thunder	
Solvent Samples			
Wilsonville 261	V 131B	Illinois No. 6/Burning Star No.2	850°F ⁻ distillate
Wilsonville 262	V 131B	Wyodak and Anderson/ Black Thunder	850°F ⁻ distillate

a. resid samples are composites made of the 850 °F⁺ resid samples from individual run periods

b. R 1235 = interstage steam; V 1067 = 2nd stage product stream; V 131B = recycle stream; O-43 = recycle stream

Figure 1. FIMS of the Pittsburgh (Run 259) Recycle Oil Showing the Prominent PCAH Structures in the 200-350 Da Range.