A Characterization and Evaluation of Coal Liquefaction Process Streams

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P.O. Box 880
Morgantown, West Virginia 26507-0880

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By
CONSOL Inc.
Research and Development
4000 Brownsville Road
Library, Pennsylvania 15129

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ABSTRACT

An updated assessment of the physico-chemical analytical methodology applicable to coal-liquefaction product streams and a review of the literature dealing with the modeling of fossil-fuel resid conversion to product oils are presented in this document. In addition, a summary is provided for the University of Delaware program conducted under this contract to develop an empirical test to determine relative resid reactivity and to construct a computer model to describe resid structure and predict reactivity.

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Section 1

SUMMARY

An updated assessment of the physico-chemical analytical methodology applicable to coal-liquefaction product streams and a review of the literature dealing with the modeling of fossil-fuel resid conversion to product oils are presented in this document. In addition, a summary is provided for the University of Delaware program conducted under this contract to develop an empirical test to determine relative resid reactivity and to construct a computer model to describe resid structure and predict reactivity.

Analytical methodologies included here are either those that are different than those previously surveyed,^{1,2,3} or are improvements to or significantly different applications of methods previously surveyed. The literature cited spans the time period from 1994 to the present. This survey can be considered as an addendum to the Analytical Needs Assessment,¹ the Literature Survey produced under DOE Contract DE-AC22-89PC89883,² and the Task 1.1 Status Assessment produced under this contract (DE-AC22-93PC94054).³

The literature dealing with fossil-fuel resid conversion kinetic models was surveyed extensively for the Task 1.1 Status Assessment.³ The literature cited in this report was published between 1994 and 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.

The kinetic models described in the previous report³ were grouped into two general approaches. One approach entails the choice of pseudo components (or lumps) and an extension of the lumped modeling approach which utilizes continuous distribution mathematical representations of the lumps. The second approach is the construction of a structural model "built" using Monte Carlo techniques or other structure-building methods. 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 then are checked against measured properties of the materials being modeled. The distinction between the two approaches is maintained in this Status Assessment.

Section 2

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 in the feed, a principal component of the feed to the first reactor is 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 improve our ability to evaluate the results of process development experiments and identify and prioritize cost-reduction options. 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 material converts to light (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 the effectiveness of appropriate methods and to obtain physico-chemical information on the resids, analytical techniques for the analysis of the distillation resids were undertaken.⁴ The summarized findings of that survey were presented previously.³ Analytical methods which previously were not addressed, or recent significant advancement of techniques which were previously examined, are described in Section 3 of this report.

Resid reactivity can be defined as the ease of conversion of resid to lower molecular weight products or 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 retrograde reactions are one of the controlling factors in the rate of production and ultimate yield of net liquid products. When the conditions are broad and represent a range of temperatures, residence times, concentrations, etc. the empirical reactivity can be generalized into a kinetic model. If the empirical model is tied to the chemical characteristics of coal it can be applicable to a *priori* prediction of feedstock behavior. A standardized empirical test for measuring the relative reactivity of resids was recently developed by the University of Delaware under subcontract to CONSOL. A computer model of the structure and conversion behavior of coal-derived resids also was developed. Section 4 of this report is a brief overview of the work performed at the University of Delaware. A report of the entire University of Delaware project can be found in Reference 5.

Section 3

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. This review covers the period from 1994 to the present. It can be considered an addendum to References 1-3.

Molecular Weight Determination

High resolution mass spectrometry (HRMS) was used to analyze the isolated asphaltene fraction from Maya crude oil and to compare compositions of asphaltenes which had been hydrotreated to different extents of reaction (30%, 70% and 85% conversion).⁶ Ion spectra of the hydrotreated asphaltene fraction showed ion intensities from 100 to 850 amu. These data suggest structures with as many as ten rings. The elemental analyses calculated from the mass spectra were in good agreement with those from traditional techniques; however, the aromaticity values, based on the mass spectral data, were slightly lower.

Matrix assisted laser desorption/ionization mass spectrometry (MALDI) is used to detect intact molecular species with masses from 1000 to 100,000 amu. Pindori et. al. examined residual tar from coal gasification, coke oven tar, and crude oil flash-column residue by MALDI.⁷ For all three samples, mass spectra showed signal masses >20,000 amu, with the gasification residue showing the narrowest range of molecular masses. Hunt and Winans state that in coal and coal extracts, there are no ion intensities over mass 2000 detected by a MALDI analysis.⁸ Hunt and Winans caution that the reporting of high masses from coal and coal-derived extracts is, in some cases, a result of sample preparation. Additionally, ion intensities from mixtures rarely show true abundances and the lowest-concentration species in the mixture may not be observed because of high background noise levels.

IR Spectroscopy

A method was developed to determine the moisture content of coal/oil slurries using Fourier transform infrared (FTIR) spectroscopy.⁹ The method was based on one previously developed

for the analysis of phenolic -OH in coal liquids.¹⁰ A series of coal/oil/water standards was used to calibrate the measurement. The mass of water in each sample can be calculated from:

$$\text{absorbance} \times 0.1060 = g_{\text{H}_2\text{O}}$$

FTIR was used to characterize isotropic pitches derived from heavy crude oil and asphaltites.¹¹ The pitches have value for the production of carbon fibers. The analyses were made on solid samples prepared as KBr pellets. A relationship was found between the softening point of the pitches and the intensity of the absorption peaks at 3050, 1600, 2960-2855, and 1450 cm^{-1} . The peak intensities increased at 3050 and 1600 cm^{-1} and decreased for the other peaks as the softening point increased, confirming that the aromaticity of the pitches increases with increasing softening point.

Near-infrared diffuse reflectance (NIRDR) spectroscopy was used to estimate the bitumen content of Athabasca oil sand cores.¹² The NIRDR method was calibrated by extracting the oil from numerous samples taken from a 20 m long 7 cm in diameter oil sand core. Bitumen content ranged from 1 to 6 wt %. IR scanning of the core along its length provided a detailed pattern of variability of bitumen content. Greater heterogeneity (found at the top of the section of oil sand field represented by the core) indicated that more closely spaced sampling and analysis at the top of the cores would be required to assess the bitumen content. The effect of sample surface roughness also was evaluated.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) has been used to determine the boiling point distributions for heavy coal-derived liquids.¹³⁻¹⁴ The method has proved useful for mixtures which are not amenable to distillation or simulated distillation techniques because of the high boiling points and low volatility of the materials. In work by Zhang et al.¹³ boiling point distributions of 450 °C+ materials were determined after calibration of the TGA with model compounds. The maximum rate of change in the mass-loss curve from the TGA was taken to correspond to the boiling point of a standard compound. In work of Huang et al.,¹⁴ coal-liquefaction resid conversions were determined via TGA. A three-phase analysis (ramp to 600 °C in nitrogen, oxidation at 600 °C, and ramp to 900 °C in oxygen) provided measurements of volatile matter (VM), fixed carbon (FC), and ash, respectively.

UV Fluorescence Spectroscopy

Fluorescence spectroscopy was used to examine the products of supercritically extracted coal and coal-heavy oil mixtures.¹⁵ The analyses were performed on the solubility fractions of the THF soluble products of coal; coal and heavy oil; coal and the acetone-soluble or acetone-insoluble portion of the heavy oil; coal and anthracene oil; and coal, heavy oil and anthracene oil. The saturates and aromatics fractions gave spectra with a maximum fluorescence emission at 463 nm. Thus, the authors claim that the quality of the "liquefaction" products is related to this intensity. They find that mixtures of coal, heavy oil and anthracene oil give the highest intensity peak.

X-ray Techniques

Particle induced gamma emission (PIGE) and particle induced X-ray emission (PIXE) analyses were performed on Nigerian tar sands¹⁶ to determine major elements in the tar sands. The PIGE method is based on the detection of γ -rays from de-excitation of a sample bombarded with protons of sufficient energy to cause (p,p' γ), (p, γ), and (p, $\alpha\gamma$) reactions. PIXE is a complimentary technique which causes X-rays to be emitted. PIGE is adequate for the detection of light elements and PIXE for mid to high Z elements. Both techniques are suitable for bulk materials and neither requires sample preparation except for grinding and pelletizing solids. The analyses presented include values for directly determined oxygen, a value obtainable only by difference using ASTM elemental analyses.

¹³C-NMR Spectroscopy

The aromatic cluster sizes in model compound mixtures and coal-derived liquids were determined by the ratio of protonated to nonprotonated carbon (X_p/X_Q).¹⁷ This ratio was determined experimentally from the differential proton-induced dipolar relaxation rates. This can be done even when the complexity of the mixture prevents resolution of individual resonance lines. Differences noted between the model compound mixtures and the authentic coal-derived liquids include the higher viscosity of the coal liquids which may account for the slower relaxation times and the possible presence of free radicals which, also, may decrease spin-lattice relaxation times.

Solid-state ¹³C-NMR techniques were used to determine the effects of different coal-drying techniques on the structure and reactivity of coal.¹⁸ Thermal drying, microwave drying, and chemical drying were investigated. Changes in coal structure were noted in the carboxyl region (~180 ppm) for coals dried thermally. Coals dried by microwave showed small changes in the

phenolic groups (~155 ppm), and coals dried chemically showed little or no effect on the organic composition of the coals.

Separation and Chromatography

High performance liquid chromatography was used to fractionate organic extracts of bottoms sediments, coal tar-contaminated sediments, zebra mussels,¹⁹ coal-derived liquids,²⁰ phenols in coal liquids,^{21, 22} and heavy petroleum oils.²³

Polycyclic aromatic hydrocarbons (PAHs) ranging in molecular mass from 300 amu to 600 amu were fractionated using normal phase HPLC and further characterized by atmospheric pressure chemical ionization liquid chromatography-mass spectrometry (APCI LC-MS).¹⁸ Samples derived from various environmental matrices (bottom sediments and living-organism (mussel) extracts) were examined and compared. Similar PAH profiles were observed for all samples collected from the same ecological environment (Hamilton Harbour, Hamilton, Canada).

HPLC was used to separate coal-derived liquids into six classes (aliphatics, 1-, 2-, 3-, and 4-ring aromatics, and polars).¹⁹ The separation was effected by use of three columns (a PAC 25 x 0.46 cm column from Whatman, a DNAP-silica 30 x 0.46 cm column from ES Industries, and a DIOL-silica 25 x 0.46 cm column from SUPELCO). A UV photo-diode-array detector was used for compound class identification of materials with boiling point <315 °C. Quantitative analyses were obtained with an evaporative-light-scattering detector for higher-boiling material. The major drawback of this method is that samples must be soluble in a nonpolar solvent.

A Wandoan coal-derived liquid was separated by HPLC into compound classes.²⁰ The polar class was further divided into three fractions. Each of the three fractions was analyzed by electron impact mass spectrometry (EI-MS). The EI-MS spectra were divided into boiling ranges. An average total carbon number was determined for each range. The boiling ranges were adjusted for the presence of hydroxyl functional groups and a correlation was developed for boiling point of various oxygen compounds in mixtures.

HPLC and ³¹P-NMR spectroscopy were used to analyze coal liquids for phenols.²¹ The coal liquids were separated into polar and non-polar fractions and the polar fraction was analyzed by reversed-phase HPLC. The retention times and response factors were compared with model compounds. ³¹P-NMR spectra of the polar fraction derivatized with ClPOCMe₂CMe₂O were

obtained and compared to phenolic model compound mixtures. Individual phenols could not be quantitated. However, the total phenolic oxygen content for the coal liquids was determined and this value compared well with values obtained by FTIR spectroscopy.

HPLC with an evaporative light scattering detector (ELSD) was used to develop a rapid method to determine the content of vacuum gas oil and residua in heavy petroleum oils.²² The ELSD, also called an evaporative mass detector, nebulizes the HPLC output with an inert gas and vaporizes the solvent. High-boiling components are left in the vaporization tube in micrometer-size "packets". At the bottom of the vaporization tube, these packets scatter light from a laser beam to produce the detector signal. The temperature of the ELSD can be varied to deposit materials boiling above a given temperature. In this study, the lower boiling point detection limit was set to correspond to various distillation cuts used in the petroleum industry. The ELSD response is sensitive to many operating parameters. Analyses in this study were all run under the same conditions. Results are comparable to those obtained by gas chromatography-simulated distillation, but, unlike GC-SD, the method can measure nondistillable materials directly rather than by using internal standards.

Microscopy

Two Turkish coals were extracted with supercritical toluene.²⁴ The unextracted solid products of the extraction were imbedded in epoxy resin and examined by optical microscopy under oil immersion. The authors found disappearance of liptinites, production of a high-reflecting vitroplast, increase in the concentration of inertinite macerals and had an increased reflectance.

Confocal scanning laser microscopy (CSLM) was used to observe the number and size of water droplets in an oil-water emulsions.²⁵ CSLM can be used to produce sharply focused two-dimensional layers of objects which can then be assembled into a three-dimensional representation. It can operate in a reflected light mode or fluorescent incident/emitted light mode. In the case of water-oil emulsions the addition of florescent dyes enhanced the image; however, the water-soluble dye was also partially oil soluble and the enhancement was of the oil. This resulted in a negative water image. Inverting the negative allowed for analysis of the water droplets. The two-dimensional slices were stacked to provide a 3D image.

Electrochemical Analysis

Electrochemical analysis of dissolved polycyclic aromatic molecules allowed for the direct identification of aromatic groups from the half-wave potentials ($E_{1/2}$) at which they are reduced. $E_{1/2}$ values of a large number of model compounds were accumulated and used to determine the distribution of structures in coal-derived liquids. 'Hard mercury' electrodes (HME) and an aqueous electrolyte solutions were used for this work.²⁶ Consequently, introduction of the coal-derived samples (anthracene oil, coal tar, soft pitch, and recycle oils, sources not given) was in acetone solution. The identified polycyclic structures from all samples examined included fluoranthene, anthracene, pyrene, phenanthrene, chrysene, dibenzothiophene, carbazole, naphthalene, phenanthridine, and alkylated naphthalenes.

MODELING REACTION KINETICS, THERMODYNAMICS, AND MECHANISMS OF HEAVY FOSSIL-FUEL REACTIONS

Introduction

The following summaries describe reaction and kinetic models that are applied specifically to heavy fossil-fuel materials. The models described are either new modeling approaches or significantly improved versions of previously described models. The kinetic models described in the previous report³ were grouped into two general approaches. One approach entails the choice of pseudo components (or lumps) and an extension of the lumped modeling approach which utilizes continuous distribution mathematical representations of the lumps. The second approach is the construction of a structural model "built" using Monte Carlo techniques or other structure-building methods. 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. The distinction between the two approaches is maintained in this Status Assessment.

Lumped Kinetic Models

A mechanistic model for the acid catalyzed cracking of n-heptane over HZSM-5 catalyst was developed using a mechanism-based lumping scheme.²⁷ In this scheme, eleven classes of elementary steps were identified as constituting the overall mechanism for the reactions of n-heptane. These steps are paraffin adsorption, paraffin desorption, carbonium ion cracking, β -scission, hydride shift, methyl shift, isomerization, reverse isomerization, hydride transfer, deprotonation, and protonation. The bond breakage and formation which can occur for each of these reactions can be represented by a reaction matrix. For example, for paraffin adsorption:

	R ₁	R ₂	H
R ₁	0	0	1
R ₂	0	0	1
H	1	1	0

The reaction matrix is a mathematical representation of the changes in atomic bonding that occur during reaction. Each row and column corresponds to an atom participating in the reaction. To build the model, each of the reaction family matrices was applied to the n-heptane and HZSM-5 reactants and subsequent product species (which were determined experimentally). A set of reaction rules was used to guide the model building. Application of the reaction matrices with the associated reaction rules resulted in a mechanistic model with 235 possible reactions which, in turn, could be organized into the 11 reaction families. The change in concentration for each species in the model was represented by an ordinary differential equation (ODE). The full set of 70 ODEs constitutes the n-heptane cracking mechanistic model. Solution of the 70 equations required estimates of rate constants for each elementary reaction step. A linear free energy relationship (LFER) kinetic correlation was used for each reaction family. One such LFER is the Polanyi relationship. It allows the rate constants to be estimated from the standard enthalpy change of reaction. The rate constants for each reaction family were described in terms of a "family-specific" Arrhenius A-factor and the Polanyi relationship parameters that relate the activation energy to the enthalpy change of reaction. Enthalpy changes of reactions were estimated via computational quantum chemistry. The model fit the experimental points for n-heptane conversion versus space time and experimental molar yield of products from cracking. The model was then used to predict experimental results at different reaction temperatures. The predictions were a close fit to experimental data.

Ayasse et al.²⁸ constructed a lumped kinetic model to fit experimental data from single-pass and multi-pass operation of a continuous-flow bitumen hydrocracker. Their model is based on the

work of Mosby.²⁹ Data from single-pass bitumen conversion were used to test the predictions of the Mosby model (shown in a generalized form, below).

It was found that trends were well predicted, but the yield of gas oil was under-predicted and the yield of middle distillate was over-predicted. In order to adapt the Mosby model to fit the hydrocracking behavior of Athabasca bitumen, the authors wanted to develop the simplest possible lumping model to minimize the problem of determining the kinetic parameters. To do this, two types of experiments were used. In the first, the first-pass reaction products were recycled. The residue was reacted to extinction. In the second experiment, the bitumen was distilled to contain only high-boiling material ($>424^{\circ}\text{C}$). This material was reacted in a single-pass experiment. The data were used in three different models. The first model consisted of a single residue lump (under "hard residue" in the above scheme) and two gas oil lumps. The resulting six-lump model had 10 independent parameters. For single-pass experimental data, this model over-predicts the yield of middle distillate by as much as 5% and under-predicts naphtha yield at high residue conversion. The model fitted the multi-pass data well. The second model consisted of two residue lumps and a single gas-oil lump. All the gas oil, regardless of origin, was lumped as a single component. (The initial concentration of gas oil (lump 3) was zero.) This six-lump model had twelve independent parameters. The fit of experimental data to the model was almost identical to the fit of the first model. An even simpler model was evaluated. In Model 3, all the residue was lumped as "hard residue" and the initial concentration of the gas oil was zero. This five-lump model has seven independent parameters. The multi-pass experimental data were

used to determine the parameters. The best-fit stoichiometric constants and rate constants were then used to predict the proportions of naphtha, middle distillate, and gas oil. The model fitted the yields from the multi-pass experiments and the experiments with the $>424^{\circ}\text{C}$ bitumen well, and gave satisfactory predictions of yield structure. However, the model over-predicts the yield of middle distillate and gas oil. And the ability to represent the residue conversion over a range of conversions was not as good as with Model 2. It was generally concluded, however, that the models with six and seven lumps are unnecessarily complex, and the five-lump model is satisfactory to predict yields at moderate severity reaction conditions for multi-pass experiments.

A mathematical model was developed to calculate reaction rate parameters for coal weight loss during direct liquefaction.³⁰ Represented in the model are: product release during heat up, and pre- and post-covalent bond scission temperature (around 350°C) regimes. The model initially considered that all reactions occurring before significant covalent bond breaking ($<350^{\circ}\text{C}$, Stage A) and after the onset of extensive bond breaking ($>350^{\circ}\text{C}$, Stage B) could each be represented by a single, irreversible, first-order reaction.

A: Converted in tetralin prior to extensive covalent bond scission
 B: Converted in tetralin following onset of extensive bond scission
 C: Unconverted in tetralin at 450°C during 1600s hold

As the model was further developed, stages A and B were represented by multiple parallel, independent, irreversible, first-order reactions, with a Gaussian distribution of activation energies.

A: Converted in tetralin prior to extensive covalent bond scission
 B: Converted in tetralin following onset of extensive covalent bond scission
 C: Unconverted in tetralin at 450°C during 1600.s hold

The value of T_d (a threshold temperature chosen to distinguish between Stages A and B) was set at 350 °C for most coals, but it was varied as much as 25 °C. The time dependent weight loss variable for Stage A is represented by $x_A(t)$. This value has an experimentally determined ultimate (equilibrium) value of x_{mA} . Sample weight loss due to Stage B processes is defined as $x_B(t)$. Thus, overall conversion at any time t is defined as $x(t) = x_A(t) + x_B(t)$. The overall ultimate conversion for Stage B is written as $x_m = x_{mA} + x_{mB}$, where x_m is the total weight loss. Three kinetic parameters (x_m , k_0 , and E_x) needed to be determined for each stage (A and B), where E is the activation energy and k_0 is the rate constant at time = 0, $X_A = 0$, and $T = T$ at time = 0. Values for x_{mA} and x_m are determined experimentally (x_{mB} is determined by difference). An algorithm for two-dimension surface fitting was used to solve simultaneously for k_0 and E_0 .

The two-stage multiple reaction model uses a kinetic expression for any single process "i" as follows:

$$\frac{dx_i}{dt} = k_i(x_{mi} - x) = k_{oi} \exp\left(-\frac{E}{RT}\right)(x_{mi} - x_i)$$

and

$$\frac{(x_{mi} - x_i)}{x_{mi}} = \int_0^t k_{oi} \exp\left(-\frac{E}{RT}\right) dt$$

The distribution for the activation energies is given as:

$$dx_{mi} = x_{mi} f(E) dE$$

with:

$$\int_0^\infty f(E) dE = 1$$

where: k_{oi} is the rate constant for any single process "i" at time = 0, $T = T_o$, and $x_i = 0$.

The model assumes that $k_{oi} = k_o = \text{constant}$ for all i. In the multiple reaction model, the standard deviation of the distribution of activation energies (as well as k_o and E_o) must be calculated.

Experimental data were collected in a flowing-solvent reactor system. In this system, products are rapidly swept from the reaction zone. Experiments were carried out with Point of Ayr coal and a suite of Argonne Premium Coal Sample Program coals. The calculated kinetic parameters for the single reaction model were found to have a poorer fit to experimental data than the multiple reaction model. Activation energies for Stage A processes were similar, indicating that the "...number and nature of independent pathways involved in Stage A processes are probably quite limited". The activation energies calculated from the multiple reaction model for Stage B were significantly higher than those calculated for the single reaction model. This reflects the (apparent) multiplicity of parallel reactions which occur above ca. 350 °C.

Structure/Kinetic Models

Provine and Klein³¹ describe the construction of a description of Illinois No. 6 coal via Monte Carlo techniques. The constructed coal structure was then 'reacted' under the conditions of coal pyrolysis via a Monte Carlo simulation. The coal structure was designed as a "rigid and mobile phase". The basic building blocks of the coal structure are limited to eight kinds of aromatic clusters and 17 kinds of crosslinks and substituents. The relative probability (the probability density function or pdf) that each of these groups is present in the coal structure is determined. The determination is limited by analytical constraints determined from CP/MAS solid-state ¹³C-NMR, coal flash pyrolysis, elemental analyses, ¹H-NMR, and wet chemical techniques. Additional "relative" constraints which impose relationships between structural groups are applied to achieve a unique solution. Once the relationships are established, the structural groups are grouped into specific pdfs and the numerical values of the pdfs are determined. Once the structure of the coal is determined, it is reacted through free-radical mechanisms. "The free-radical chemistry dictates the rate of cleavage of the different reactive moieties which exist in the coal structure." The Monte Carlo reaction simulation provides not only an explicit physical description of the reacting molecule, but also of the free-radical intermediates. The initial coal structure was compared to the properties known by analyses. Individual structural parameters are within 30 % of the observed values. Although the authors consider this to be in good agreement, they do describe methods to improve the agreements. The results of inputting the structural representation to a "pyrolysis reaction" are followed in time. Total conversion, liquid-phase aromaticity, proton NMR distributions, solid carbon aromaticity, transformations of oxygen functional groups and sulfur functionalities are followed in time, as well as gas production and liquid production. The model predicts these properties and yields with fairly good agreement with experimental data. The initial stages of pyrolysis for Illinois No. 6 coal were shown to be controlled by initiation-hydrogen-transfer-termination chemistry. Ether groups were shown to produce liquid products and thioether products produced gas. Retrograde reactions were shown to become more important as the coal conversion neared 30%. This is the point at which the "rigid" phase of the coal was completely reacted and high molecular weight fragments had formed.

Distributed activation energy (DAE) models assume that complex materials react in a series of parallel first-order reaction with different rates. These models use continuous and discrete distributions of activation energies (E) to represent the effects of temperature on the reaction progress. The distributions of E are often taken to be Gaussian; however, this does not always

reflect real situations.³² Frequency factors (k_0) often are assumed to be constants; this also may not be valid for the conversion of coal or other complex systems where the distribution of E is broad. Two papers that address these limitations of DAE models for coal^{32, 33} and kerogen³³ present alternative distributions and variable k_0 's.

A method to estimate the distribution of activation energies ($f(E)$) and frequency factors (k_0) for the pyrolysis reactions of 19 different coals was described by Maki et al.³² Three sets of devolatilization experiments, performed with different heating profiles, were used to provide the data for the parameter estimations. The method was described in the following five steps:

1. Measure V/V^* (total volatiles/effective volatile content of the coal) versus T relationships at three different heating rates.
2. Calculate nominal rates $\bar{k} = dV/dt/(V^* - V)$ at several different heating rates.
Make Arrhenius plots of $\bar{k}$ at the same V/V^* values.
3. Determine activation energies from the Arrhenius plots at different levels of V/V^* , then plot V/V^* against the activation energy (E).
4. Differentiate the V/V^* vs E relationship by E to give $f(E)$, since the following relationship holds approximately:

$$V/V^* = 1 - \int_E^\infty f(E) dE = \int_0^E f(E) dE$$

5. Calculate k_0 corresponding to each E value at all the heating rates a_j ($j = 1, 2, 3$) using:

$$\frac{0.545a_j E}{k_0 R T^2} = e^{\frac{-E}{RT}}$$

then employ the averaged k_0 value as a true k_0 value.

For the 19 coals, it was found that the $f(E)$ curve extends over 150–400 kJ/mol and that the frequency factor increases from 10^{12} to 10^{25} s⁻¹ with the increase in E . The predicted V/V^* vs. T curves closely matched the experimental data. The shape of the $f(E)$ curves was significantly different for each of the coals. However, the k_o vs. E relationship had little dependence on coal type.

The use of a distribution known as the Weibull Distribution for the probability distribution of the activation energy ($f(E)$) was shown by Lakshmanan et al.³³ to model the weight loss by thermal decomposition of organic matter (such as shale or coal). The model assumes first-order kinetics for all chemical reactions and assumes that the activation energies for these parallel first-order reactions follow a Weibull distribution. The preexponential factor k_o also is represented by a distribution. The model takes the form:

$$R_t = \int_{\gamma}^{\infty} \exp\left[-\int_0^t k_o \exp\left(-\frac{E}{R(T_o + Pt^*)}\right) dt^*\right] f(E) dE$$

Where: R_t = the weight loss of organic matter (at $t=0$, $R_t=100\%$)

E = the activation energy

k_o = the preexponential factor

$$f(E) = \left(\frac{\beta}{\eta}\right) \left(\frac{E-\gamma}{\eta}\right)^{\beta-1} \exp\left[-\left(\frac{E-\gamma}{\eta}\right)^{\beta}\right] \quad (\text{Weibull distribution})$$

Where: η = scale parameter

β = shape parameter

γ = threshold or location parameter

The model incorporates a term (P) for the heating rate of the experimental decomposition; it is initially assumed to be linear.

A number of sets of experimental data were used to confirm the applicability of the model. These include data collected at multiple, isothermal, and nonisothermal conditions. Data were derived from sealed tube experiments, TGA experiments, and literature data of fission track annealing

experiments. (A fission track annealing experiment follows, in time, the annealing of fission tracks in the mineral matter of the sample. A measured residual length of the tracks represents the progress of the annealing process. The thermal annealing experiments show trends similar to that of thermal decomposition of organic matter.) The model developed from the experimental results at one heating rate (5 °C/min) reliably predicts the trends of thermal decomposition (percent residual weight) at different heating rates (10 and 15 °C/min).

Section 4
REVIEW OF UNIVERSITY OF DELAWARE SUBCONTRACT UNDER
CONTRACT No. DE-AC22-94PC93054

PROJECT ASSESSMENT

Introduction

Resid hydrocracking is a key reaction of modern (i.e., distillate-producing) coal liquefaction processes. Coals are readily converted to resid and lighter products in the liquefaction process. The resid is combined with fresh coal in a ratio often greater than 1:1, and some vacuum gas oil and is recycled to be further converted. Understanding the chemistry of resids and resid reactivity is, therefore, of great importance to improve direct liquefaction process design and to achieve economic objectives for direct coal liquefaction. Computer models that can predict resid conversion based on the chemical characteristics of the resids and reaction conditions would be a cost-efficient way to explore process variables. Implementation of such models could aid in the design and operation of liquefaction facilities.

Summary

Program Description

Under subcontract from CONSOL Inc. (U.S. DOE Contract No DE-AC93PC94054), the University of Delaware studied the mechanism and kinetics of coal liquefaction resid conversion. The program at Delaware was conducted between August 15, 1994, and April 30, 1997. It consisted of two primary tasks. The first task was to develop an empirical test to measure the reactivity of coal-derived distillation resids. The second task was to formulate a computer model to represent the structure of the resids and a kinetic and mechanistic model of resid reactivity based on the structural representations. The full report authored by the University of Delaware researchers is presented in Reference 5.

Both tasks described above were successfully accomplished. An empirical tests was developed for coal liquefaction resids which made use of a small, batch reactor system constructed at the University of Delaware. The reactor system allows for short reactant heat-up times and product

cool-down times. This permits the acquisition of kinetic data. To evaluate products, a boiling point distribution test was developed using thermogravimetric analysis techniques.

The reactivity test was applied to a suite of fifteen well-characterized 850 °F⁺ distillation resids. The resids were derived from the Wilsonville pilot plant and the HTI bench unit. Feed coals included Illinois 6 bituminous coal, Pittsburgh seam bituminous coal, and Wyodak and Anderson seam subbituminous coal. The resids were produced by distillation of process stream samples obtained from several sampling locations in the plants. The Delaware team subjected the resids to reaction conditions similar to those employed in direct coal liquefaction. Resid conversion values were determined for each resid under at least one set of reaction conditions. This set of conditions was chosen to produce (on average) conversions similar to those obtained on a single pass in the continuous plants from which the samples were obtained (about 30 wt %). Two of the fifteen resids were reacted at several residence times and temperatures to obtain kinetic data.

Chemical characteristics supplied to Delaware by CONSOL and the results of the reactivity tests were used to construct mathematical structural representations of the resids. The structural representations were then subjected to a set of reaction rules. The outcome of the calculations was a resid conversion value for each resid. Correlation between the model output and experimental results was good. However, the model constructed in this study is viewed as "first generation" and is now ready for further refinement and expansion.

Reactivity Tests

The relative reactivity of the resids was determined using an empirical test developed for this purpose. A short contact time batch reactor (SCTBR) was used to react the samples, and a thermogravimetric analysis (TGA) method was developed to evaluate the products of reaction and allow for derivation of a conversion value. Tests were made with and without catalyst. All tests were made in tetralin. Heat-up and cool-down times of the resid/tetralin feed mixtures are ca. 0.3 s. Agitation of the slurry is accomplished by an upflow of reacting gas (H₂ or N₂) at 1500 psi (cold). A homogeneous catalyst (molybdenum naphthenate) was chosen for catalytic tests after trials with heterogeneous catalyst (presulfided Shell 324 Ni/Mo on alumina) proved difficult to use because the required high catalyst loadings resulted in viscous reaction mixtures and poor ash balances. Dimethyldisulfide (DMDS) was used to sulfide the Mo in situ. Tests were made under a range of solvent/resid ratios, residence times, and reaction temperatures. Conversion values were determined by separating soluble and insoluble fractions of the reaction

products by filtration, and then subjecting the insoluble fraction to a simulated distillation employing thermogravimetric analysis (TGA) techniques to determine the amount of material boiling below 454 °C. The soluble fraction was distilled to remove most of the tetralin, analyzed by gas chromatography to determine the quantity of tetralin remaining, and analyzed by TGA to determine the amount of material boiling below 454 °C. Conversion was calculated as follows:

$$\text{Conversion} = \text{tetralin soluble fraction} \times \left(1 - \frac{\text{fraction boiling above } 454^{\circ}\text{C}}{\text{resid soluble fraction}}\right)$$

where the tetralin soluble fraction was determined by ash content of the insoluble resid after hydroprocessing. Resid soluble fraction is the amount of material soluble in tetralin prior to hydroprocessing. The sensitivity of the reaction system to different feeds was evident. Large differences in conversion (as much as 15 wt %, abs.) were determined for the different resid samples reacted under the same conditions.

Two of the fifteen resid samples were chosen to study the kinetics of hydroprocessing the resids. The two samples were chosen because they gave the highest and lowest conversions under the standard test conditions (420 °C, 30 min, tetralin/resid = 3/1). Tests were made at 435 °C to augment tests made at 420 °C. Reaction times selected were 5 min and 10 min in addition to the 30 min data already acquired. Conversion leveled off with time, consistent with the presence of a non-convertible component.

Results obtained with the SCTBR indicate that the resid must be soluble in the reaction solvent for hydroprocessing (conversion to 454 °C⁻ distillate) to occur. The resids contain ca. 5 to 15 wt % (ash-free basis) tetralin insolubles. This insoluble component is in part responsible for the unconvertible nature of the resid and the leveling off of conversion with time. Several resids were extracted with tetralin to obtain the insoluble fraction. These fractions were hydroprocessed under the same conditions (420 °C, 30 min, tetralin/insolubles = 3/1) as the resids. Less than 1 wt % of the insoluble fraction converted to 454 °C⁻ product.

No one-to-one correlation of conversion with product characteristics, such as elemental composition, aromatic carbon content or molecular weight was found; nor were correlations found with feed coal rank, sampling location, or other processing conditions.

Model Description

Four computer programs were developed that together comprise the structural/reactivity model. They are a structure optimization program, a structure 'once-through' program, a reaction optimization program, and a reaction 'once-through' program.

The structural model (comprised of the structural optimization and 'once-through' programs) uses a Monte Carlo construction technique in which individual molecules are constructed by random sampling of probability density functions (pdf's). The pdf's are functions that provide the quantitative probability of finding a value (or less) of any given attribute. Each pdf represents one molecular attribute. Thirty-three attributes were incorporated in the model. Structural representations were constructed for each of the fifteen resids that were reacted experimentally. Each structure was then optimized by minimizing an objective function so that the molecular representation matched the characterization data obtained experimentally. The optimization routine requires about 20 hours of processing time on the IBM RS-6000 workstation used by Delaware. However, the chemical characteristics of the computer generated structures are well matched to the experimental data.

Using the statistical representations generated from the structural model and a set of reaction rules based on laws of chemistry, Monte Carlo techniques were used to 'react' a set of reaction families which were used to represent the reactive moieties in the resids. Rate constants for all 15 resids were not available, consequently a subset of the resids (5) was used to optimize the rate constants. The output of the reaction model was a single conversion value for each resid. These conversion values were compared to the experimentally determined values and were within two experimental standard deviations.

Section 5

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