Coal Liquefaction Process Streams Characterization and Evaluation,

VOLUME II

Participants Program Final Summary Evaluation

S. D. Brandes, G. A. Robbins
R. A. Winschel, and F. P. Burke

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EXECUTIVE SUMMARY

This Executive Summary consists of two parts: 1) a brief summary of the overall contract, and 2) a comprehensive bibliographic summary of the entire contract. Each of these is presented below in a separate sub-section.

OVERALL CONTRACT

This 4.5-year project consisted of routine analytical support to DOE's direct liquefaction process development effort (the Base Program), and an extensive effort to develop, demonstrate, and apply new analytical methods for the characterization of liquefaction process streams (the Participants Program). The objective of the Base Program was to support the on-going DOE direct coal liquefaction process development program. Feed, process, and product samples were used to assess process operations, product quality, and the effects of process variables, and to direct future testing. The primary objective of the Participants Program was to identify and demonstrate analytical methods for use in support of liquefaction process development, and in so doing, provide a bridge between process design, development, and operation and analytical chemistry. To achieve this objective, novel analytical methods were evaluated for application to direct coal liquefaction-derived materials. CONSOL teamed with 24 research groups in the program. Well-defined and characterized samples of coal liquefaction process-derived materials were provided to each group. CONSOL made an evaluation of each analytical technique.

Under the Base Program, support was provided by characterizing process oils from six Wilsonville CC-ITSL runs (Runs 258 through 263), two HRI CTSL PDU runs (Runs 260-03 and POC-1), seven HRI CTSL bench unit runs (Runs CC-2, 5, 6, 8, 9, 15, and 16), one UOP coprocessing bench unit run (Run 37), and two DOE-sponsored laboratory research programs. These activities were conducted by working closely with the process developers to obtain the proper samples, obtain good background information, and to perform analyses which provided relevant information.

An analytical plan was formed in conjunction with HRI for collection of samples for CONSOL's analytical support of HRI's Proof-of-Concept Run POC-1. Under the plan, samples will be provided from feed and start-up materials, and from all major internal and product streams from each run segment. Additional frequent samples from selected streams will help ascertain effects of upsets, and observe process performance during periods of transitional and steady-state operation.

samples from selected streams will help ascertain effects of upsets, and observe process performance during periods of transitional and steady-state operation.

In addition to the routine analytical support, fifteen non-routine research projects were performed under the Base Program. Non-routine analytical support was supplied to Wilsonville on four separate occasions: 1) to examine deposited materials from Run 258; 2) to characterize different candidate Illinois feed coals; 3) to determine the reactivity of two samples of Black Thunder Mine coal; and 4) to examine the stability of Dowtherm A heat transfer fluid under liquefaction conditions. Analytical support also was supplied to the DOE projects of Alberta Research Council and the University of Pittsburgh. Supplemental analyses were provided on product oils from four liquefaction runs which were subjected to petroleum inspection tests (under the Participants Program). In one of these cases, CONSOL also conducted caustic washing tests. In-house research projects were conducted to simulate conversion in Wilsonville's preheater, to explore solvent quality of the maltenes fraction of a process oil, and to use O-methylation to explore solvent quality effects of phenols in process oils. Included in these activities were two analytical method development projects. The two projects dealt with 1) adaptation of an HRI method for determination of 975 μ F⁺ resid concentration in liquefaction samples using thermogravimetric analysis (TGA), and 2) adaptations to an FTIR method for determining phenolic -OH concentration in coal liquids. The changes in the FTIR method extend the method's versatility by accommodating moisture-containing and solids-containing samples.

The Participants Program was conducted in three phases. Phases I, II, and III surveyed a total of 30 different analytical techniques. Three of the 30 methods were found to have high potential to provide an immediate impact on process design and/or development. These three methods were applied in Phase III of the project to samples from a single coal liquefaction processing run. In addition to the survey of analytical techniques, two additional projects were carried out under the Participants Program. One project included the selection of samples (in conjunction with DOE and Burns and Roe Services Corporation) and completion of petroleum inspection tests on product fractions from two Wilsonville runs and two HRI bench unit runs. These results are important for product valuation, for determining suitability as refining feedstocks, and for evaluation of liquefaction options, such as in-line hydrotreating. This work provides important

distillation resids was undertaken by adapting a method currently used to study coal reactivity.

Under this contract (Base and Participants Programs), ten journal articles were published, and 28 formal papers and seminars were presented. In addition to the quarterly technical progress reports, 24 topical technical reports were issued under this contract. Included were two extensive general reports on analytical methodology for liquefaction process stream characterization that were issued as topical reports. The Analytical Needs Assessment identified key analytical needs of the liquefaction process developers. In the literature survey report, 92 papers published between 1980 and 1991 were reviewed to identify analytical methods for potential application to coal-derived resids. The remaining 22 reports were comprehensive evaluations and descriptions of completed Participants Program activities.

BIBLIOGRAPHIC SUMMARY OF CONTRACT

During the performance of this project, we obtained analyses on samples from numerous process development and research programs and we evaluated a variety of analytical techniques for their usefulness in supporting liquefaction process development. Because of the diverse nature of this program, we provide here an annotated bibliography of the technical reports, publications, and formal presentations that resulted from this program to serve as a comprehensive summary of contract activities.

TECHNICAL REPORTS

TECHNICAL PROGRESS REPORTS

<u>Report No.</u> <u>DOE/PC</u> <u>89883-</u>	<u>Report Period</u>	<u>Date</u> <u>Issued</u>	<u>Major Topics Addressed</u>
10	10/89-12/89	10/90	Wilsonville Run 258
16	1/90-3/90	2/91	Coal Calibration Tests Composite Oil Analyses Participants Program Status
22	4/90-6/90	7/91	Wilsonville Run 259 Wilsonville Run 258 Deposit Study Participants Program Status
23	7/90-9/90	6/91	HRI CTSL Runs CC-2, 5, 6, 8 Candidate Ill. Coals for Wilsonville Participants Program Status
24	10/90-12/90	6/91	Participants Program Status Conoco's Report on Inspection of Wilsonville Run 259G Net Product
27	1/91-3/91	9/91	HRI CTSL Run CC-9 and Delayed Coker Samples Solvent Quality of Maltenes Additional Analyses of Wilsonville Run 259G Net Products Coal Calibration Tests Participants Program Status
29	4/91-6/91	11/91	Wilsonville Run 260 Participants Program Status
34	7/91-9/91	11/91	Dowtherm A Hydrogenation Test Participants Program Status Conoco's Report on Inspection of Wilsonville Run 260D Net Products Microdistillation Procedure

<u>Report No.</u> DOE/PC 89883-	<u>Report Period</u>	<u>Date Issued</u>	<u>Major Topics Addressed</u>
43	10/91-12/91	3/92	Wilsonville Run 260 Additional Analyses on Net Products From Wilsonville Runs 259G and 260D Caustic Wash of Wilsonville Run 260D Net Product Reactivities of Two Wilsonville Black Thunder Coals Participants Program Status
50	1/92-3/92	8/92	Wilsonville Run 262 O-Methylation of Coal Liquids Participants Program Status
53	4/92-6/92	11/92	Preheater Simulation Tests Carbon Isotope Analysis of UOP Run 37 Samples Coal Calibration Wilsonville/CONSOL Resid Conversion Relationships Participants Program Status Corrections to Wilsonville Run 260 Calculations
60	7/92-9/92	11/92	Participants Program Status
76	10/92-12/92	10/93	HRI CTSL Run 260-03 Participants Program Status
77	1/93-3/93	12/93	HRI CTSL Run CC-16 Coal Calibration Participants Program Status
78	4/93-6/93	11/93	Participants Program Status
86	7/93-9/93	3/9	HRI CTSL Run CC-15 Additional Analyses on Net Products From HRI Run CC-15 TGA Method for Resid Determination Analyses for Univ. of Pittsburgh Analyses for Alberta Res. Council Participants Program Status
93	10/93-3/94	now	Wilsonville Run 263 HRI Run POC-1 Fast FTIR Method for Phenolic -OH Determination on Moist and Solids-Containing Samples Correction of Microautoclave Test Results Participants Program Status

TOPICAL REPORTS

Report No. DOE/PC 89883-	Date Issued	Topic
18	3/91	Analytical Needs Assessment
30	10/91	Novel Analytical Techniques for Coal Liquefaction: Fluorescence Microscopy (R. F. Rathbone; J. C. Hower; F. J. Derbyshire; University of Kentucky, Center for Applied Energy Research)
36	11/91	Solid-State NMR Characterization of Coal Liquefaction Products (F. P. Miknis; Western Research Institute)
37	12/91	Gold Tube Carbonization and Reflectance Microscopy (G. Mitchell; A. Davis; Energy and Fuels Research Center, The Pennsylvania State University)
39	1/92	Characterization of Coal Liquids by Field Ionization Mass Spectrometry and Iodotrimethylsilane Derivatization (R. Malhotra; D. F. McMillen; SRI International)
41	1/92	Chromatographic and Spectroscopic Techniques (L. T. Taylor; J. W. Hellgeth; A. Sequeira; Virginia Polytechnic Institute and State University, Department of Chemistry)
45	4/92	FT-IR Methods for Characterization of Coal Liquefaction Products (M. S. Serio; H. Teng; R. Bassilakis; P. R. Solomon; Advanced Fuel Research, Inc.)
47	5/92	Application of Liquid Chromatographic Separation Methods to THF-Soluble Portions of Integrated Two-Stage Coal Liquefaction Resids (J. B. Green; C. D. Pearson; L. L. Young; J. A. Green; IIT Research Institute, National Institute for Petroleum and Energy Research)
51	7/92	Characterization of Coal-Derived Materials by Field Desorption Mass Spectrometry, Two-Dimensional Nuclear Magnetic Resonance, Supercritical Fluid Extraction, and Supercritical Fluid Chromatography/mass Spectrometry (J. A. Campbell; J. C. Linehan; W. H. Robins; Battelle, Pacific Northwest Laboratory)

Report No. DOE/PC 89883-	Date Issued	Topic
57	10/92	Characterization of Coal Liquefaction Resids Employing Thermogravimetric Analysis and Electron Spin Resonance Spectroscopy (M. M. Ibrahim; M. S. Seehra; West Virginia University, Department of Physics)
58	10/92	The Application of ^{252}Cf -Plasma Desorption Mass Spectrometry to Analysis of Direct Coal Liquefaction Heavy Products (J. W. Larsen; A. R. Lapucha; Lehigh University, Department of Chemistry)
59	11/92	Electron Microscopy Observations of Resids Obtained From Coal Liquefaction Experiments (J. B. Vander Sande; Vander Sande Associates, Inc.)
62	11/92	Estimation of Total Phenol Concentrations in Coal Liquefaction Resids by ^{31}P NMR Spectroscopy (J. T. Mohan; J. G. Verkade; Ames Laboratory and Department of Chemistry, Iowa State University)
63	11/92	Investigation of the Forms of Sulfur in Five Wilsonville Resid Samples by XAFS and Mössbauer Spectroscopy (G. P. Huffman; F. E. Huggins; N. Shah; University of Kentucky, Consortium for Fossil Fuel Liquefaction Science)
64	11/92	The Use of Selective Chemical Reactions and Carbon NMR Spectroscopy in the Speciation and Quantification of Oxygen Functional Groups in Coal Resids (L. M. Stock; C. Cheng; University of Chicago, Department of Chemistry)
65	11/92	^{13}C -NMR Analysis of CONSOL THF-Soluble Residual Materials From the Wilsonville Coal Liquefaction Process (M. S. Solum; R. J. Pugmire; University of Utah, Departments of Chemistry and Fuels Engineering)
67	1/93	UV Resonance Raman Studies of Coal Liquid Residuals (S. A. Asher, University of Pittsburgh, Department of Chemistry)
70	6/93	Analytical Methods for Application to Coal-Derived Resids - A Literature Survey

<u>Report No.</u> <u>DOE/PC</u> <u>89883-</u>	<u>Date</u> <u>Issued</u>	<u>Topic</u>
85	1/94	High Performance Liquid Chromatography (HPLC) of Coal Liquefaction Process Streams Using Normal-Phase Separation with UV Diode Array Detection (D. J. Clifford; D. E. McKinney; L. Hou; P. G. Hatcher, The Pennsylvania State University)
87	2/94	Assessment of Hydroaromatic Content and Hydrogen Donor Ability fo Coal Liquefaction Intermediates by Means of Catalytic Dehydrogenation (J. W. Tierney; I. Wender, University of Pittsburgh, Dept. of Chemical and Petroleum Engineering)
89	2/94	The Preliminary Evaluation of the Kinetics for Coal Liquefaction Distillation Resid Conversion (M. T. Klein; W. H. Calkins; H. Huang, Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware)
90	2/94	Analysis of Black Thunder Coal and Liquefaction Products from HRI Bench Unit Run CC-15 (R. J. Pugmire; M. S. Solum, University of Utah, Departments of Chemical and Fuels Engineering and Chemistry)
91	3/94	FIMS Analysis fo Direct Coal Liquefaction Process Streams (R. Malhotra; D. F. McMillen, SRI International)
92	1/94	Analysis of Coal-Derived Synthetic Crude from HRI CTSL Run CC-15 and HRI Run CMSL-2 (G. P. Sturm, Jr.; J. Kim; J. Shay, IIT Research Institute, national Institute for Petroleum and Energy Research)

JOURNAL PUBLICATIONS

<u>No.</u>	<u>Appears in</u> <u>Technical</u> <u>Report No.</u> <u>DOE/PC 89883-</u>	<u>Citation</u>
1	50	Robbins, G. A.; Winschel, R. A.; Amos, C. L.; Burke, F. P. "Agglomeration of Low-Rank Coal as a Pretreatment for Direct Coal Liquefaction", <i>Fuel</i> 1992, 71, 1039-1046.
2	77	Miknis, F. P.; Netzel, D. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "N.M.R. Determination of Aromatic Carbon Balances and Hydrogen Utilization in Direct Coal Liquefaction", <i>Fuel</i> 1993, 72, 217-224.

- 3 77 Mohan, T.; Verkade, J. G. "Determination of Total Phenol Concentrations in Coal Liquefaction Resids by ^{31}P NMR Spectroscopy" *Energy and Fuels* 1993, 7, 222-226.
- 4 78 Lancet, M. S.; Winschel, R. A.; Burke, F. P. "Stable Carbon Isotope Analysis of Coprocessing Materials", *Fuel* 1993, 72, 1209-1217.
- 5 78 Rathbone, R. F.; J. C. Hower; F. J. Derbyshire "The Application of Fluorescence Microscopy to Coal-Derived Resid Characterization", *Fuel*, 1993, 72, 1177-1185.
- 6 93 Malhotra, R.; McMillen, D. F.; Watson, E. L.; Huestis, D. L. "Characterization of Coal Liquefaction Resids by Field Ionization Mass Spectrometry: Correlating Spectral Features with Processing Parameters" *Energy & Fuels*, 1993, 7, 1079-1087.
- 7 93 Larsen, J. W.; Lapucha, A. R.; Wernett, P. C.; Anderson, W. R. "Characterization of Coal liquefaction Heavy Products Using ^{252}Cf Plasma Desorption Mass Spectrometry" *Energy & Fuels*, 1994, 8, 258-265.
- 8 93 Ibrahim, M. M.; Seehra, M. S. "Thermal Conversions of Coal Liquefaction Resids: Temperature-Programmed Electron Spin Resonance and Thermogravimetric Investigations", *Catalysis Today*, accepted for publication.
- 9 93 McKinney, D. E.; Clifford, D. J.; Hou, L.; Bogdan, M. R.; Hatcher, P. G. "High Performance liquid Chromatography (HPLC) of Coal Liquefaction Products Using Normal-Phase Separation with Diode Array Detection" submitted to *Energy & Fuels*.
- 10 93 Huang, H.; Calkins, W. H.; Klein, M. T. "The Use of Thermogravimetric Analysis to Follow The Conversion of Coal Derived Resids in the Resid Recycling Process", for submission to *I&EC Research*.

PAPERS AND SEMINARS

Appears in Technical Report No.		<u>Citation</u>
<u>No.</u>	<u>DOE/PC 89883-</u>	
1	10	Burke, F. P. "The Evolution of Process Oil Characteristics in Two-Stage Coal Liquefaction Process Development", AIST-ANRE-NEDO/DOE-PETC Joint Technical Meeting on Coal Liquefaction, Tokyo, Japan, October 31 - November 2, 1989.
2	10	Burke, F. P. "Application of Coal Liquefaction Solvent Quality Measurements", Frontiers in Coal Science and Technology, Fukuoka, Japan, October 29-31, 1989.

Appears in Technical Report No.		
<u>No.</u>	<u>DOE/PC 89883-</u>	<u>Citation</u>
3	10	Burke, F. P.; Winschel, R. A.; Robbins, G. A. "Process and Recycle Oils in Two-Stage Coal Liquefaction", 1989 International Conference on Coal Science, Tokyo, Japan, 10/23-27/89.
4	10	Winschel, R. A. "Recycle Oils from Fluid Coking of Coal Liquefaction Vacuum Bottoms" 1989 Fall Information Transfer Session of the Cooperative Program in Coal Research, The Pennsylvania State University, November 20, 1989.
5	23	Winschel, R. A. "Advances in Direct Coal Liquefaction" lecture in short course "Advanced Coal Technologies for the 21st Century", Pittsburgh, PA, September 1990 (in conjunction with the Seventh Annual International Pittsburgh Coal Conference).
6	24	Robbins, G. A.; Winschel, R. A.; Amos, C. L. "Agglomeration of Low-Rank Coal as a Pretreatment for Direct Coal Liquefaction", 201st National Meeting of the American Chemical Society, Atlanta, GA, 4/14-19/91.
7	29	Burke, F. P.; Winschel, R. A.; Robbins, G. A. "Coal Cleaning for Liquefaction by Selective Agglomeration with Recycle Oils", 1991 International Conference on Coal Science, University of New Castle Upon Tyne, UK, 9/16-20/91.
8	29	Winschel, R. A.; Burke, F. P.; Zhou, P. "Inspection of Integrated Two-Stage Liquefaction Products as Petroleum Refining Feedstocks", 1991 International Conference on Coal Science, University of New Castle Upon Tyne, UK, 9/16-20/91.
9	29	Brandes, S. D.; Winschel, R. A.; Burke, F. P. "The Application of Advanced Analytical Techniques to Direct Liquefaction", Fourth Chemical Congress of North America and 202nd Fall National Meeting of the American Chemical Society, NY, NY, 8/25-30/91.
10	29	Lancet, M. S.; Winschel, R. A.; Burke, F. P. "Stable Carbon Isotope Analysis of Coprocessing Materials", Fourth Chemical Congress of North America and 202nd National Meeting of the American Chemical Society, NY, NY, 8/25-30/91.
11	29	Winschel, R. A.; Zhou, P. "Inspection of Integrated Two-Stage Liquefaction Products by Petroleum Assay", Sixteenth Annual Electric Power Research Institute Fuel Science Conference, Palo Alto, CA, 6/18-20/91.

Appears in Technical Report No. DOE/PC 89883-		Citation
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12	29	Robbins, G. A. "Agglomeration of Low-Rank Coal as a Pretreatment for Direct Coal Liquefaction", invited seminar at Ames Laboratory, Ames IA, May 1991.
13	34	Lancet, M. S.; Winschel, R. A.; Burke, F. P. "Stable Carbon Isotope Analysis of Coprocessing Materials", 1991 Summer National Meeting of the American Institute of Chemical Engineers, Pittsburgh, PA, August 1991.
14	34	Brandes, S. D.; Winschel, R. A.; Burke, F. P.; Robbins, G. A. "The Application of Advanced Analytical Techniques to Direct Liquefaction", 1991 DOE Liquefaction Contractors' Review Meeting, Pittsburgh, PA, 9/3-5/91.
15	34	Rathbone, R. F.; J. C. Hower; F. J. Derbyshire "The Application of Fluorescence Microscopy to Coal-Derived Resid Characterization", Fourth Chemical Congress of North America and 202nd National Meeting of the American Chemical Society, NY, NY, 8/25-30/91.
16	50	Malhotra, R.; McMillen, D. F.; Huestis, D. L. "Characterization of Coal Liquefaction Resids by Field Ionization Mass Spectrometry: Correlating Spectral Features with Processing Parameters", 203rd National Meeting of the American Chemical Society, San Francisco, CA, 4/5-10/92.
17	53	Lapucha, A. R.; Larsen, J. W. "Application of ²⁵² Cf-Plasma Desorption Mass Spectrometry to Analysis of Direct Coal Liquefaction Heavy Products", 204th National Meeting of the American Chemical Society, Washington, DC, 8/23-28/92.
18	53	Teng, H.; Serio, M. A.; Bassilakis, R.; Knight, K. S.; Bates, S. C.; Solomon, P. R. "The Application of FT-IR Methods to the Characterization of Coal Liquefaction Process Streams", 204th National Meeting of the American Chemical Society, Washington, DC, 8/23-28/92.
19	53	Brandes, S. D.; Winschel, R. A.; Burke, F. P. "The Chemical Nature of Coal Liquid Resids and the Implications for Process Development", 204th National Meeting of the American Chemical Society, Washington, DC, August 1992.
20	53	Robbins, G. A.; Winschel, R. A.; Burke, F. P. "Conversion of Resid Components in CC-ITSL Processing at Wilsonville", 204th National Meeting of the American Chemical Society, Washington, DC, August 1992.

		Appears in Technical Report No. <u>DOE/PC 89883-</u>	<u>Citation</u>
<u>No.</u>			
21	53		Zhou, P.-Z.; Marano, J. J.; Winschel, R. A. "Strategic Considerations of Coal Liquid Refining", 204th National Meeting of the American Chemical Society, Washington, DC, August 1992.
22	60		Brandes, S. D.; Winschel, R. A.; Robbins, G. A.; Burke, F. P. "The Chemical Nature of Coal Liquid Resids and the Implications for Process Development", 1992 DOE Liquefaction Contractors' Review Conference, Pittsburgh, PA, September, 1992.
23	86		Brandes, S. D.; Robbins, G. A.; Winschel, R. A.; Burke, F. P. "Coal Liquefaction Process Streams Characterization and Evaluation: an Analytical Case Study", 1993 DOE Coal Liquefaction and Gas Conversion Contractors' Conference, Pittsburgh, PA, September 28, 1993.
24	86		Winschel, R. A. "Economic Benefits of Process Stream Characterization", DOE Workshop "Direct Liquefaction: Focused Research for Improved Economics", Pittsburgh, PA, September 27, 1993.
25	93		Huang, H.; Calkins, W. H.; Klein, M. T. "The Use of Thermogravimetric Analysis to Follow The Conversion of Coal Derived Resids in the Resid Recycling Process", 207th National Meeting of the American Chemical Society, San Diego, CA, 3/13-18/94.
26	93		Burke, F. P. "Evaluation of Advanced Analytical Methods for Direct Liquefaction Process Development", United Kingdom/United States Technical Exchange Meeting and Liquefaction Workshop, Pittsburgh, PA, 9/24/93.
27	93		Zhou, P. -Z.; Winschel, R. A.; Klunder, E. B. "High-Quality Distillate Products from Direct Liquefaction of Coal", 208th National Meeting of the American Chemical Society, Washington, DC, 8/21-25/94.
28	93		Campbell, J. A.; Lucke, R. B.; Cody, C. D. "Characterization of Coal-Derived Materials Using Field Desorption Mass Spectrometry", 42nd Meeting of the American Society of Mass Spectrometry, Chicago, IL, June 3, 1994.

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ABSTRACT

An important aspect of CONSOL's support work under Contract DE-AC22-89PC89883 was the evaluation of analytical methods for the application to coal liquefaction process development. The goal was to identify analytical techniques that can provide data useful for an improved understanding of liquefaction process chemistry, which, in turn, will provide guidance to planning and interpreting process research to reduce process costs. When this project was begun, it was recognized that considerable analytical expertise already existed. Therefore, the approach taken was to evaluate available analytical methods through application by analytical experts to coal liquefaction process samples chosen by CONSOL, rather than to develop new methods. In all, 24 industrial, academic and government labs, employing 30 different analytical techniques, participated in this evaluation, referred to as the Participants Program.

A number of important analytical methods were found to be well advanced for application to coal liquefaction process development, in terms of both experimental protocol and data interpretation. These include ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, field ionization mass spectrometry (FIMS), and electron spin resonance (ESR) spectroscopy combined with thermogravimetric analysis (TGA). These techniques provide chemical and molecular information on coal and coal liquids, including the coal-derived resids which are important intermediates on the reaction pathway from coal to distillate liquid products. In addition to these analytical techniques, an empirical method was evaluated for measuring the reactivity of coal-derived resids for conversion to distillate products. This empirical method (utilizing a Short Time Batch Reactor) promises to be useful in establishing resid conversion kinetics and the relationship of reactivity to resid chemistry. Finally, a set of petroleum inspection tests which are routinely used to evaluate refinery feedstocks was applied to coal-derived synthetic crude oils. The information obtained is useful for valuation of the synthetic crudes tested, and indicates the limitations of the standard petroleum methods for application to coal-derived liquids.

Part 1

INTRODUCTION

Objectives of Program

Direct coal liquefaction is a complicated and ill-defined chemical process. To facilitate the development of coal liquefaction as an economically-feasible alternative-energy technology, fundamental chemical understanding of the direct liquefaction process must be obtained. There exists, however, a gap between the advanced, modern techniques of the analytical chemist and the application of those techniques by the direct coal liquefaction process developer. There are two major reasons for the existence of this gap: 1) much research in advanced analytical chemistry concentrates on instrument development and not application, and 2) appropriate direct coal liquefaction samples for method applications are frequently difficult for the analytical researcher to identify or obtain.

The Participants Program was designed to bridge the gap, advance our knowledge of the process chemistry of direct coal liquefaction, and improve the economics of producing liquid fuels from coal using direct liquefaction technology. The program was designed to provide well-documented samples to researchers who are utilizing techniques potentially useful for the analysis of coal liquefaction-derived samples. Demonstration of these techniques with liquefaction samples has begun to forge the essential bridge between direct coal liquefaction process development and analytical chemistry.

Methodology

The choice of techniques was based on an extensive survey made by CONSOL of the status of analytical methodology associated with direct coal liquefaction technology.¹ Sources of information for the survey included process developers and analytical chemists. CONSOL's participation in preparation of the U.S. DOE-sponsored Coal Liquefaction Research Needs Assessment (COLIRN)² provided a foundation for this survey.

The survey identified a number of broadly characterizable process-development needs. Specific methodologies (or techniques) having the potential to address most of these needs and research groups who were employing those techniques were identified. Many of these methods are new only in that they have not been fully

demonstrated for their applicability to coal liquids. Other techniques are "cutting edge" and are currently under development for a number of applications, including natural product analyses.

The program is structured in three phases. Phases I, II, and part of III were similar. They were designed to assess the potential of the analytical techniques identified in the survey. In Phase I, nine organizations evaluated seventeen different analytical methods (Appendix C, Table 1). These methods are, for the most part, well-established analytical techniques which are uncommon in their application to coal-derived materials. Phase II was an expansion of Phase I. An additional eight research groups utilizing eight different analytical techniques were participants in the program (Appendix C, Table 2). A number of techniques in Phases I and II were chosen to provide the same information but by different means. For example, three different mass spectrometric methods were evaluated to assess the molecular weight profile of the complex process-derived organic samples (field ionization mass spectrometry (FIMS), ^{252}Cf -plasma desorption mass spectrometry (PDMS), and field desorption mass spectrometry (FDMS)). Comparisons of methods will be presented later in this report. Phase III of the program included evaluations of additional analytical methods and application of the high-potential methods evaluated in Phases I and II. CONSOL evaluations and summaries of all Phase III projects are given in Appendix A.

CONSOL's program was designed to focus on the characterization of the non-distillable resid portion of liquefaction oils because of the importance of this material to the liquefaction process. In current direct liquefaction technology, the heaviest soluble materials produced from the coal are recycled to near extinction. These heavy soluble materials (850 °F⁺) typically account for 50% of the recycle stream fed to the first reactor stage in current U.S. two-stage liquefaction technology. At a 2:1 recycle-to-coal feed ratio, the largest component of the feed to the first reactor is recycle resid, not coal. The analysis of this resid is a much more challenging problem than analysis of the lighter distillate materials produced by coal liquefaction. It is believed that understanding the formation, composition, and behavior of this resid will lead to an improved understanding of the direct coal liquefaction process and, therefore, have the greatest impact on process economics. Whole process stream

samples and distillate materials also were included in the sample set when appropriate (Appendix B).

A key to the success of the analytical evaluation program was the proper selection of samples for examination. Evaluation of the analytical methodologies was based, in part, on the ability of the method to differentiate samples which were produced under different conditions. These diverse variables included feed coal rank, reactor temperature, catalyst type, age, or use in one or both reactors (in a two-stage system), sampling point in the direct coal liquefaction plant, and whether or not the feed coal was in some way treated before liquefaction. Initially, to evaluate any given method, sample sets were chosen with large differences in production variables. Analytical methods that could distinguish among the samples and provide information useful for characterization were considered successful techniques.

All samples in the program came from CONSOL's sample bank, which includes materials from the Wilsonville, Lummus, and HRI liquefaction programs. In addition, samples from active DOE-sponsored process development programs are continually obtained and some of these recently obtained samples were included in the program. All samples distributed in the program were analyzed by CONSOL. Such analyses included (when appropriate): elemental analysis, ash content, ash elemental analysis, solubility fractionation, phenolic -OH concentration by FTIR spectroscopy, calorific value, and hydrogen classes by ^1H -NMR spectroscopy. 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 have been calculated for a number of the coal liquefaction runs from which samples were selected for the program. All information was supplied to the program participants to aid in the evaluation of the analytical techniques. The analytical data for all samples examined in the program are given in Appendix B.

Criteria for Evaluation of Methods

Those techniques with demonstrated ability to clearly delineate process-related differences in the samples were considered to have the highest potential for application for process development work. Other factors, such as the relative ease of use of the technique, the cost of equipment to perform the analysis, ease

of data interpretation, and the expected impact on process economics, were considered in the evaluations of the techniques. Some techniques were found to have a high potential for an immediate impact on process development. Others have potential which was not fully demonstrated, or require more development than was feasible under this program. Another group of techniques could not meet all, or most, of the criteria listed above.

Extension to Application

Analytical techniques that successfully met the criteria described above, and which were considered to have a high potential for immediate application, were recommended for use in further studies. Subsequently, some of these high-potential methods were incorporated into Phase III of the program (Appendix C, Table 3). Those techniques further evaluated in Phase III include field ionization mass spectrometry and solid state ^{13}C -NMR spectroscopy. Additionally, standard petroleum inspection tests were used to evaluate the quality of the net product oils from the direct coal conversion process. The application portion of Phase III was designed to apply the techniques to a representative set of samples from a specific direct coal liquefaction run. In this way, the applicability of these methods to support coal liquefaction process development could be demonstrated.³

Also in Phase III, another aspect of analytical support for process development was investigated. In this study, a method used for studies of coal reactivity was adapted for study of the reaction chemistry of the recycle resid. As can be inferred from the discussion above, the reactivity of the resid strongly affects the economics of direct coal liquefaction. It greatly impacts the reactor costs by controlling factors such as space velocity, temperature, necessary reactor volume, catalyst loading, etc. Evaluation of the resids may also have an indirect impact on direct coal liquefaction product quality. Better understanding of the reactivity of the resid may provide strategies for better control on the costs of improving product quality. Thus, this study fit well in the scope of the work for this program. It is further described in Part 4 of this report.

Part 2

METHODS WITH HIGH POTENTIAL - PHASES I, II AND III

A number of methods surveyed in Phases I, II, and III of the program met the criteria described above. A description of these techniques follows. A select few of these methods were found to have a high potential for immediate application to the analysis of process-derived samples, and to provide from these analyses information which could be used to guide efforts toward improved process design and development. Some of these methods were further evaluated in Phase III of the program in a more in-depth investigation of the method by application to coal-derived materials. A description of this application effort is presented in Part 3 of this report.

Nuclear Magnetic Resonance Spectroscopy^{4,5}

Among the methods which have a high potential for application to the analysis of coal-derived materials is cross polarization/magic angle spinning (CP/MAS) ¹³C-nuclear magnetic resonance (NMR) spectroscopy, especially utilizing dipolar dephasing and variable contact time techniques. The method can provide data for the derivation of carbon structural parameters and molecular structural descriptors for coal and coal-liquefaction resids. Carbon structural parameters obtained from these analyses include the fraction of aromatic and aliphatic carbon present in different forms in the sample (Table 1). Molecular structural parameters derived (Table 2) include the ring cluster size, the number of clusters per molecule, the degree of ring substitution, and the number of bridges between clusters. In the study performed under Phase II of the program,⁴ structural parameters were obtained for the THF-soluble portion of 850 °F⁺ distillation resids and one whole resid which contained ash and insoluble organic material (IOM). Comparison of the structural parameters for the resids with their corresponding feed coals showed structural changes consistent with hydrogenation, deoxygenation and hydrogenolysis of the coals. Among the resid samples, the similarities were more pronounced than were the observed differences.

The information produced by this method could be used to form the basis for a mechanistic model of coal conversion to liquid products. This potential application was demonstrated in the context of pyrolytic coal decomposition.³⁸

Its extension to direct coal liquefaction is recommended. 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.

The precision of the solid-state (specifically, dipolar dephasing and variable contact time) ^{13}C -NMR techniques is high; measurements are highly reproducible. Sample preparation time is minimal, requiring only that the sample be uniformly ground and packed into the NMR tube. The experimental time required is on the order of one hour per sample. The 100 Mhz instrument used in this study costs approximately \$200,000.

NMR techniques, as demonstrated in another project,⁵ also can be used to directly monitor the process streams for aromaticity of the coal liquefaction materials, especially the resid which is comprised of condensed aromatic structures. In this Phase I study, solid-state ^1H - and ^{13}C -NMR and liquid-state ^{12}C - and ^1H -NMR techniques provided the aromaticity value of process stream samples, including the solid resid portion of a number of process stream samples. These data, combined with the mass balances and the elemental analyses of the materials analyzed, provides 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 could contribute to development of a lumped kinetic model for coal liquefaction.

The precision of the solid state ^1H - and ^{13}C -NMR techniques used (Cross Polarization Magic Angle Spinning (CP/MAS) and single pulse (SP) ^{13}C -NMR techniques and Combined Rotation and Multiple-Pulse Spectroscopy (CRAMPS) ^1H -NMR) is high. Not only are aromaticity measurements highly reproducible, there is also good agreement among various laboratories for different samples of coal from the same seam. The solid-state ^{13}C -NMR techniques can be rapid, requiring about one-half hour per sample for data acquisition to obtain adequate signal to noise ratios. The initial capital investment for a 100 Mhz instrument with the appropriate equipment for CRAMPS measurements is approximately \$200,000. The labor costs are relatively low. Sample preparation is minimal, requiring only

that the sample be uniformly ground and uniformly packed into the NMR tube. Samples need not be ground smaller than 100 mesh (150 μm). Solid-state ^1H NMR and liquid NMR require only 1-2 minutes data acquisition time. There is, however, some time required to do the set up for the CRAMPS procedure. Once the initial set up is done, the sample preparation and examination can be done by a laboratory technician. Computer integration of the sample signal provides quantitative information.

Mass Spectrometry

Molecular weight distributions and speciation of high-mass compounds in coal-derived materials were obtained by three different methods in Phases I and II of the program. The three methods are field ionization mass spectrometry (FIMS),⁶ ^{252}Cf -plasma desorption mass spectrometry (PDMS),⁷ and field desorption mass spectrometry (FDMS).⁸ The three independent studies demonstrated the feasibility of using each technique for the analysis of materials derived from direct coal liquefaction. The data generated by these techniques include the molecular weight profile of process-derived samples, number and weight average, molecular weights, and identification of some components of the sample. The FIMS method was found to have the greatest potential for immediate application. This was, in part, because it was not limited to solvent-soluble samples as was the case with FDMS. Additional studies using FIMS are described in Part 3 of this report.

FIMS experiments conducted in Phase I of the program were made with a suite of soluble resid samples from the Wilsonville pilot plant. The FIMS profile of the samples studied consists of a broad distribution of molecular weights ranging from 200 to 1000 Da. (Figure 1). The FIMS profiles were deconvoluted into two groups (Figure 2). The use of this simplifying two-lump model to handle the complex FIMS profiles was highly effective. The two pseudo-components, centered at 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 ratio 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 analysis of the bimodal distribution seen in the FIMS profiles, structural identification was made of some molecular components in the 160 to 320 Da range of the FIMS spectrum (Figure 1). Some well-known components of coal-liquefaction intermediate streams were identified, including: pyrene/fluoranthene and hexahydropyrene. However, in addition to these compounds, several less-desirable components also were identified. These include m/z 242, 276, 300, and 316. Probable structures for these components are given in Table 3; some are odd-carbon-number ring systems. Based on the work of Sullivan, Boduszynski, and Fetzer with petroleum resids,³⁵ these structures are considered probable precursors to coke formation. It is, therefore, very likely that these materials are related to the build-up of refractory materials. Using the relative concentrations of these species as a guide, it may be possible to assess the propensity of the process streams to produce desirable distillate products or undesirable retrogressive reaction products.

The use of FIMS for analysis of process-derived materials is highly recommended. There are however, a number of avenues for further development of FIMS for coal liquefaction derived resids. A better curve fitting routine could be developed using a more sophisticated mathematical function. This may provide some further insight into the nuances of shifts in the molecular weight distributions attributable to processing conditions. Additional speciation of the compounds in the lower molecular weight range of the FIMS profile will provide a better picture of the fundamental chemistry of the coal-derived resids.

The cost of FIMS equipment is approximately \$250,000; the cost for expendables is about \$40 per sample. Sample preparation and instrument time for the analysis of a single sample is about one to three hours.

Electron Spin Resonance Spectroscopy/Thermogravimetric Analysis⁹

Temperature-programmed electron spin resonance (ESR) spectroscopy coupled with thermogravimetric analysis (TGA) techniques were shown in a Phase II study to have potential for the analysis of direct coal liquefaction resid samples and, thus, for providing direction for process development. The two techniques, when employed in tandem, can be used to determine the content and nature of free radicals in the samples at temperatures approximating those used in the liquefaction process. The free radical density (N) may prove to be a good

indicator of resid reactivity. The lower the N value, the more hydrogenated was the resid, and, it is presumed, the more reactive to cracking. This was supported by the TGA data which also showed that samples with a higher N value were less volatile.

In the study, the resid was heated and the N values were monitored. Over the temperature range 100-200 °C, the N value of the resids increased with no corresponding increase in volatility. This behavior has no corollary in the ESR of the parent coals. Information provided by ESR, such as this, can give direction to process operations. For example, this information indicates that hydrogenation of the resids could occur in this low temperature range and thus, heating to these low temperatures may prove to be very effective for hydrogenation of the resids, and could be enhanced by the choice of an appropriate catalyst.

It is recommended that studies should be made of the effectiveness of different hydrogenation catalysts in the temperature range in which the ESR indicates that there is an increase in free radical content with minimal weight loss. Also, expanding the experimental program to include high-pressure ESR experiments with and without catalysts would provide more insight into the behavior of the resids under direct coal liquefaction processing conditions.

The Mettler TA3000 TGA apparatus used in this work costs approximately \$40,000. The 9.4 GHz Varian ESR hot probe accessory costs about \$250,000. ESR experiments, including raw data conversion, require approximately two days per sample. TGA experiments require approximately four hours per sample. Data interpretation requires a professional trained in ESR methods. Expendable supplies (ESR tubes, TGA sample holders, and purge gases) cost approximately \$100/sample.

Petroleum Inspection Tests^{10,11}

Standard petroleum inspection tests were used in the Participants Program to evaluate the quality of the net product oils from the direct coal conversion process. An evaluation of the direct liquefaction process requires an understanding of the refining requirements of the raw liquid product. This information will eventually provide more accurate estimations of upgrading costs to specification fuels. Although it is acknowledged that the standard petroleum

inspection tests were not developed for the analysis of coal liquids, it is believed that they are the best starting point for these analyses. Under the Participants Program of this contract, CONSOL examined four net product oils by standard petroleum inspection tests. These analyses are comprised of over 30 individual tests (Table 4). Two samples were analyzed in Phase I of the program with sufficiently good results to recommend the analysis of two more samples in Phase III of the program. The samples analyzed in Phase I were derived from Wilsonville Run 259 Period G and Wilsonville Run 260 Period D. The samples analyzed in Phase III were obtained from HRI Run CC-15 and HRI Run CMSL-2. The quality for all four products was assessed by comparison of the physical and chemical property test data of the whole crude and its distillation fractions to the specifications for gasolines, aviation turbine fuels, diesel fuels, or fuel oils.

The findings of the petroleum inspection tests for the four samples demonstrate the potential of using coal-derived liquids as refinery feedstocks. Qualitative refining requirements are clearly delineated by the test data. Continued use of this approach to evaluate the net product oils of direct liquefaction is highly recommended. Further description of the tests employed is given in Part 3 of this report.

METHODS WITH MODERATE POTENTIAL - PHASES I, II AND III

A number of methods that were evaluated were found to have potential for providing some understanding of the fundamental chemistry of direct coal liquefaction. However, these methods were unable to meet enough of the criteria used to evaluate the technique to have high potential for immediate application to aid in process design or development. For a variety of reasons, including cost, complexity, and status of development, these methods, although promising, are less suitable to extensive application at present. These limitations are identified in the following discussion, along with recommendations for further development and application.

X-ray Absorption Near Edge Structure (XANES) Spectroscopy¹²

One method examined in Phase II of the program was X-ray absorption fine structure (XAFS) spectroscopy, specifically the least-squares analysis of the X-ray absorption near edge structure (XANES) region of the sulfur K-shell XAFS

spectra. This least-squares analysis can be used to determine the sulfur forms in coal-liquefaction-derived materials. The XAFS/XANES method requires the use of a high-energy X-ray source (such as that produced in a synchrotron). Consequently, the availability of the method for routine process support is limited. However, the method has good potential for detection and speciation of heteroatomic species in the coal-derived samples. Because of the large amount of information obtainable by use of this method, this technique could have an impact on a broad spectrum of cost factors affecting coal liquefaction (see Part 5 of this report).

In the study performed under Phase II of the program, solids-containing liquefaction resids were examined for sulfur speciation. It was found that the dominant pyrrhotite peak in the XAFS spectra partially obscured the organic sulfur region and reduced confidence in the quantitative data. These experiments demonstrate that effective use of the XAFS/XANES technique to speciate the organic sulfur forms in coal-derived resids should be performed on an inorganic-free sample. The XAFS technique can also be used for the direct determination of other species, such as nitrogen compounds, and possibly oxygen compounds. Exploration of the applicability of the technique for the quantitative analysis of these heteroatomic species in coal liquids is recommended. The sulfur XAFS experiments were done at the National Synchrotron Light Source at Brookhaven National Laboratory. Approximate cost per sample is \$1000.

Mössbauer Spectroscopy¹²

Mössbauer spectroscopy was used for characterization of the iron-based sulfur-containing components in the coal derived materials in a Phase II study. The Mössbauer technique clearly showed that pyrrhotite was the most concentrated iron-bearing species present in the resids examined. However, iron oxides and ferrous sulfate, also were detected. Comparisons were made of the Mössbauer spectra of Argonne Premium Coal samples to spectra of the resids. It was surmised that the iron species observed in the coal resid derived from Wyodak coal came from the iron catalyst used in the processing run, not from the feed coal. This demonstrates that the Mössbauer technique has the potential to aid in process monitoring when iron-based catalysts are present. Further examination of the organic portion of the resid samples by Mössbauer spectroscopy may provide additional information on the organic sulfur compounds present in the resids.

It is recommended that additional evaluation of this technique be conducted with process-derived samples.

The Mössbauer instrument used in these studies cost approximately \$50,000. It requires approximately one day to prepare and collect data for a single sample by Mössbauer spectroscopy. Data acquisition and interpretation for the method require a skilled professional.

Fluorescence Microscopy¹³

A specific advantage of fluorescence microscopy for the analysis of resids is that the sample can be examined without chemical alteration. This results in a particularly important feature of the technique: the ability to observe inhomogeneity and to quantify inhomogeneous components of solid resid samples, such as unreacted macerals, mineral matter, and multiple resid phases. In addition to supplying qualitative observations, the technique can provide quantitative data. The measured fluorescence intensities can be related to the degree of molecular condensation of the sample. These values can be used to infer which resids are more refractory to upgrading. The determination of red:green quotients (Q) from the fluorescence spectra is a rapid method to assess the degree of fluorescence heterogeneity of the resids. The fluorescence microscopic technique is apparently responsive to process trends. The degree of liquefaction or upgrading of coal liquids is discernable among different samples taken at different points in the continuous liquefaction process. In addition, the relative degree of resid hydrogenation can be inferred in samples taken consecutively during a liquefaction run in which the major process change is catalyst age.

It is difficult to assess the precision of the technique due to the inherent variabilities of the samples examined. However, when a homogeneous sample, or the portion of a heterogeneous sample displaying only one fluorescence population is examined, repeatability is good.

The technique is relatively rapid, requiring about one-half hour for sample preparation and only a few minutes for sample examination. Sample preparation times can be reduced, if faster-setting epoxy resins can be found which do not

interfere with the microscopic analysis. Equipment costs are approximately \$85,000.

Molecular Weight Determinations

^{252}Cf -Plasma Desorption Mass Spectrometry (PDMS)⁷

It is possible with the ^{252}Cf -PDMS method to observe materials with molecular weights on the order of 30,000 Da. In the Phase II study, the ^{252}Cf -PDMS technique was shown to be capable of determining molecular weight distributions and average molecular weights of direct coal liquefaction resid samples. The THF-soluble coal-derived resids examined exhibited molecular weight envelopes which extended to approximately 3000 Da. It is possible that post-ionization recombination reactions account for some of the higher molecular weight material (>1400 Da). Additionally, the degree of discrimination by chemical class by the ionization process of the ^{252}Cf -PDMS technique is not well known. Samples obtained from different runs with different processing parameters could not be distinguished by the number or weight average molecular weights obtained by ^{252}Cf -PDMS. A more detailed examination of the ^{252}Cf -PDMS profiles may prove to be of some utility in discerning differences in the process-derived resid samples. It is recommended that the molecular weight profiles obtained from ^{252}Cf -PDMS be carefully examined to detect any systematic variations which can be attributed to changes in processing conditions such as those detected in the FIMS spectra (see above). The appearance of individual low-mass ions in the spectra of the oil and asphaltene fractions of the THF-soluble resids which are obscured in the THF-soluble resid spectrum should be further investigated in light of the corresponding appearance of these same mass ions in the FIMS experiments⁶ and field desorption mass spectrometry (FDMS) experiments⁸. A more extensive study of the application of the ^{252}Cf -PDMS technique to a larger selection of resid samples would be required to prove the value of this technique.

The ^{252}Cf -PDMS equipment used in this study was a Bio-ion Model 20 spectrometer; it costs about \$220,000. It requires approximately one half hour to prepare a solvent-soluble sample and approximately fifteen minutes to acquire data.

Field Desorption Mass Spectrometry (FDMS)⁸

The FDMS technique for the determination of molecular weights appears to have potential for the analysis of the coal-derived resids. However, a number of questions remain to be addressed. Primarily, the question of sample solubility is important. The sample is deposited from solution onto a specially prepared emitter, which consists of 10 μm tungsten wire on which has been grown carbon dendrites or single crystal silicon needles. After coating the emitter with sample, it is introduced into the mass spectrometer and exposed to field strengths on the order of 10^8 V/cm at the needle-like tips. An alternate mass spectral technique such as field ionization (FI) MS (see above) is, however, limited by volatility. Plasma desorption (PD) MS (a third technique, see above) is limited by the ability of the experimenter to create a thin film of material. Ionization artifacts are possible in all three methods. Which of these constraints is more restrictive is not known at this time.

The FDMS technique employed in the Phase II study requires a large capital investment for the equipment; the high-resolution mass spectrometer with FD capabilities costs approximately \$800,000. The experimental procedure requires 1-2 hours to prepare and run a sample.

Gel Permeation Chromatography (GPC)⁷

The GPC technique was shown to be useful for determining molecular weight distributions and average molecular weights of direct coal liquefaction resid samples. However, samples obtained from different runs with different processing parameters could not be distinguished by the number or weight average molecular weights obtained by GPC. The number average molecular weights of the samples determined by GPC were approximately the same as those obtained by ^{252}Cf -PDMS. The weight average molecular weights were consistently higher, by a factor of two, than those obtained by ^{252}Cf -PDMS. GPC can be expected to be a useful technique in the determination of weight average or number average molecular weights for direct coal liquefaction samples. However, it is recommended that many more coal liquefaction samples be examined to establish the reliability of the technique. The technique is relatively straight-forward and requires an appropriate column and liquid chromatograph with a mass detector.

Acid/Base/Neutral Separation¹⁴

Separation of coal-derived resids by acid, base, and neutral classification can be somewhat ambiguous, because a large portion of coal-derived resid molecules are multifunctional. The non-aqueous ion exchange liquid chromatography (NIELC) technique, however, was shown to have some potential for the analysis of direct coal liquefaction resid samples. It is projected that with full optimization for coal-derived materials, especially the high-molecular-weight and polyfunctional distillation resids, the technique can be useful to characterize process streams for process monitoring and development. High performance liquid chromatography (HPLC) can be used for a rapid analysis of neutrals or bases; however, a pre-separation with NIELC would be required to produce the base or neutral fractions from the whole material. The use of infrared spectroscopy to analyze resultant fractions is limited by sample solubility. Methods for solid sample analysis probably should be implemented for this application.

The NIELC technique is time consuming and relatively costly on a per-sample basis. Each preparative-scale analysis requires about \$70 for expendable supplies. Manpower is approximately one man-week per sample. The analytical-scale separations require approximately one-half a man-week. Nonaqueous titration also requires approximately one-half a man-week. Equipment costs for these three procedures are approximately \$35,000.

Fourier Transform Infrared (FTIR) Spectroscopy¹⁵

A quantitative FTIR technique used in a Phase I project can provide from a single analysis a number of sample properties normally obtained by multiple analytical techniques. This could make the method very useful as a process development tool. However, data quality are not consistent when compared to the values obtained by the other methods. FTIR spectroscopy can analyze gases, liquids, or solids. Consequently, the evolved gases from other instruments, such as those gases from a thermogravimetric analyzer (TGA), can be examined in the FTIR. However, gas evolution profiles from the TG-FTIR analysis of the resids in this study yielded inconclusive data because: 1) in this study, the instrument was not calibrated for NH_3 , COS , and CS_2 ; 2) CS_2 evolution mimics H_2O and can be confused with it; 3) SO_2 evolution is found in two peaks, one the result of small traces of oxygen in the helium carrier gas; and 4) CO_2 is sensitive to the state of oxidation of the sample. Only the CH_4 and CO peaks seemed to be reported with

reliability. The TG-FTIR technique, when fully optimized, should be able to provide structural information of the samples by monitoring first the evolution of the volatile species from pyrolysis, and then, the combustion gases from the char.

The potential utility of the FTIR method, because it is rapid and requires a relatively small amount of sample for analysis, is very high. The coupled TG-FTIR method also has potential for application to process streams analyses. Further evaluation of the methods for process design and development is recommended. The utility of the FTIR as an on-line analytical technique also was considered. This particular application requires demonstration with process samples at approximate operating conditions before it can be recommended for process application.

Commercially available FTIR equipment ranges in price from approximately \$20,000 to \$250,000. The TG-FTIR equipment, also commercially available, increases the cost of the FTIR instrument by about \$25,000. Consumables for the analyses, as performed under this subcontract, are on the order of \$10/sample. It requires less than one hour to prepare and run a single sample by the quantitative FTIR method. The TG-FTIR thermal program used in these experiments requires approximately three hours to complete.

Scanning Transmission Electron Microscopy (STEM)¹⁶

The THF-insoluble portion of direct coal liquefaction resid samples was examined by scanning transmission electron microscopy (STEM). The technique was used to determine the distribution, morphology, and elemental composition of dispersed catalyst components in the insoluble portion of the resids. Samples were chosen from a Wilsonville processing run in which Fe and Mo catalysts were introduced. It was shown that localized distributions of the different elements and compounds in the resid samples could be determined. The morphology of the detected elements and compounds was discernable. However, little difference was observed in the concentration or morphology of the Fe or Mo among the various samples in which Fe and Mo were detected. It is, therefore, not possible to fully assess the potential of the method for process development.

Sample preparation was minimal; the dry powdered sample was distributed on a carbon film, which was supported by a Cu mesh grid, and placed directly into the microscope. The time required to run one sample is about one day. The STEM instrumentation used in this Phase II project costs approximately \$650,000. The operation of the equipment and the interpretation of the data are most commonly performed by highly trained professional personnel. The equipment cost and the requirement for skilled personnel likely preclude the use of this technique on a routine basis. However, it may be possible to use the method as a supplementary method of sample evaluation on an as-needed basis.

Reflectance Microscopy¹⁷

The reflectance microscopy technique was shown to have some potential for the analysis of heterogeneous, solid, process-derived samples. The method had a high degree of reproducibility in determining the vitroplast reflectance (0.008%) and not quite as high for partially reacted vitrinite (0.032%). Reflectance measurements were related to processing parameters, such as reactor temperatures, the presence or absence of catalyst, and feed coal rank. In some cases, certain expected trends due to major process variable changes, such as reactor temperature or the presence or absence of catalyst were obscured by other process variables, such as residence time. A clear accountability for changes in the reflectance measurements among multiple samples produced under diverse conditions may not be possible. Reflectance microscopy is well-developed for inspection of coal macerals, but not for solid direct coal liquefaction process-derived materials. In order to utilize the full potential of the method for process development, a large number of well-documented samples will need to be examined and evaluated.

The reflectance method is relatively rapid, requiring only a few minutes for examination of the sample. Equipment costs are on the order of \$90,000.

Liquid Chromatography (LC)¹⁸

The preparative-scale liquid chromatographic (LC) technique used in a project in Phase I of this program provides a four-fraction separation of complex materials. The quantity of each fraction into which the materials were separated can be correlated to gross processing changes. This makes it a promising, simple method for use in process monitoring and development. However, the information obtained

from the LC separation must be used cautiously because the chemical nature of each fraction is dependent on the sample analyzed. For example, a coal-derived resid fraction would be chemically different from a petroleum-derived resid fraction. Nevertheless, there are a number of avenues for further development of the LC technique for process development. This may be to use the technique for preparation of fractions of process stream samples, less complex than the whole material, for analysis by other techniques. In order to make the preparatory-scale liquid chromatography procedure more useful, the total time for analysis will have to be reduced from several days to hours. It may be possible to perform the same separation under high pressure (HPLC) with a subsequent reduction in analysis time. The method is relatively inexpensive (on the order of \$300/sample for supplies) and can be executed by laboratory technicians. The LC equipment costs about \$20,000.

Two-Dimensional, High Performance Liquid Chromatography (2D-HPLC)²⁰

This Phase III study demonstrated the potential of using two-dimensional, high performance liquid chromatography (2D-HPLC) with normal-phase separation and ultraviolet (UV) diode array detection for the examination of filtered process liquids and the 850 °F distillate materials derived from direct coal liquefaction process streams. A commercially available HPLC column (Hypersil Green PAH-2) provided excellent separation of the complex mix of polynuclear aromatic hydrocarbons (PAHs) found in coal-derived process streams. Some characteristics of the samples delineated by the separation could be attributed to processing parameters. High resolution mass spectrometry (HRMS) and gas chromatography/mass spectrometry (GC/MS) were also used in this study to characterize the HPLC fractions. The use of an ultraviolet detector in the HPLC work precludes visualizing the aliphatic portion of the sample. The GC/MS allows for identification and quantification of the volatiles of that portion of the samples.

The method has a major drawback at this stage of development; less than 50% of the sample weight was detected in the case of the HRI pressure filter liquids examined, and only about 5% of the 850 °F distillate portions of the Wilsonville samples was detected. This poor mass balance is primarily attributable to the fact that the UV detection is blind to compounds which do not contain chromophores. Another reason for the poor mass balance may be that a number of compounds were retained on the PAH-2 column. Additional work will have to be

done to improve the recovery from the column and to augment the detection system with methods, such as mass spectrometry, that will detect the non-chromophoric materials. Despite this problem, which appears to be surmountable, the method is recommended for further investigation for application to direct coal-derived liquefaction samples. Expanded quantitative analysis of the HPLC data could be used to monitor the progress of forward (or retrogressive) reactions in the process streams.

The Waters 600E HPLC and Waters 991 photodiode array detector cost \$42,325. A personal computer and laser printer add about \$3,500 to that cost. The Hewlett Packard 5890 II gas chromatograph coupled with a Hewlett Packard 5971A mass selective detector used in this work costs approximately \$70,000. The Hypersil Green PAH-2 column costs \$650 and has a lifetime of approximately 300-500 analyses. Including sample preparation, separation, and data conversion, approximately 2 hr per sample is required to perform the HPLC experiments. The high resolution mass spectrometer (Kratos MS-80 RFA) costs approximately \$350,000. High resolution mass spectrometric experiments require approximately 1 hr per sample. HRMS data interpretation requires a professional trained in mass spectrometry.

METHODS WHICH PRESENTLY ARE NOT RECOMMENDED - PHASES I, II AND III

A number of methods were identified as not being apropos for the analysis of coal-derived materials, especially the resids. In some cases, these methods provided the same information already acquired by a more direct, less expensive, or more accurate method. Other techniques simply could not distinguish between samples provided for study. Still other techniques were not capable of analyzing the coal-derived materials.

Catalytic Dehydrogenation¹⁹

A study using catalytic dehydrogenation to provide an empirical measurement of the hydrogen donor properties of direct coal liquefaction process-derived materials was performed under Phase III of the program. Two quantities were measured. The first, total donatable hydrogen, is defined as the cumulative amount of hydrogen evolved from the resid samples at 150 min in a phenanthridine vehicle at 350 °C with Pd/CaCO₃ as catalyst. The rate of H₂ evolution (within 150 minutes) also was monitored. The second quantity, hydrogen donor ability,

is defined as the cumulative amount of hydrogen transferred to a hydrogen acceptor (stilbene) at 300 min at low temperature (300 °C) in quinaldine with Pd/C catalyst.

The catalytic dehydrogenation data produced in this survey project suggest that this method can be used as an empirical measurement of the amount of donatable hydrogen in the resids. Differences in samples were distinguishable and correlate with factors such as coal rank, processing facility, and ash content. The brief investigation of the effect of phenolic -OH on the hydrogen donor ability and donatable hydrogen content indicates that silylation of the phenolic -OH prior to catalytic dehydrogenation may be a useful technique to study the effect of phenolic -OH on hydrogen donor properties.

The equipment used in this study is not commercially available. The time required to perform a single experiment is approximately one day.

Iodotrimethylsilane Derivatization for Oxygen Analysis^{6a}

In an effort to derivatize and quantify the oxygen bound to alkyl carbon in coal liquefaction resids, a derivatization technique was used which employed iodotrimethylsilane in an organic solvent. The solvent of choice for the method (acetonitrile) is a poor solvent for the resid. Good resid solvents such as pyridine and tetrahydrofuran cause interference with the iodosilane reagent; consequently, chloroform (a moderately good solvent) was used. Use of an ion-selective electrode to quantify the amount of iodide ion produced from unconverted iodosilane was unsuccessful. Ion-exchange chromatography was used instead. Background reactions with the reaction solvent (chloroform) were responsible for a 10% loss of iodide ion in the analysis. Analysis of the data corrected for the 10% loss show that approximately 20% of the total oxygen in the resids is oxygen bound to aliphatic carbon. This result is consistent with phenolic oxygen contents determined by other methods, which are on the order of 50 to 75% of the total oxygen in the resid. Accuracy and precision of the method employed needs to be improved before the method could be recommended for further use.

Gold Tube Carbonization¹⁷

The gold tube carbonization test was originally developed for the examination of geologic samples and later applied to solvent refined coal (SRC) samples. The carbonization technique yields information on the amounts of gas plus distillate, pyridine-soluble, and pyridine-insoluble materials that are formed when a sample is heated to 450 °C and pressurized to 5000 psi in an inert atmosphere. It has potential for application to coal liquefaction samples, but sampling inhomogeneous materials is a problem. The presence of IOM and ash in the samples studied seemed to be responsible for poor reproducibility. The technique is labor intensive and reproducibility is not high, although trends can be detected. This indicates that the technique has potential, but would require further development and presently is not recommended.

Sample preparation time for the gold tube carbonization test is considerable requires a good deal of skill. The carbonization experiment requires roughly three hours including pressurization, heat-up, soak time, cool down, and depressurization. Sample work-up requires approximately 48 hours for pyridine extraction of the samples plus the time necessary to examine the samples by optical microscopy. The carbonization equipment is costly; gold tubing is preferred for use, since the mini reactor, and high pressures and temperatures are required for the reaction.

There are a number of ways to improve the potential of the gold tube method for process monitoring and development. For example: experimental parameters, originally established to accommodate SRC samples, may not be appropriate for work with samples from modern coal liquefaction processes; these parameters must be defined. Relationships between the amount of pyridine-insoluble material produced by the method and the phenolic -OH concentration of feed coals is one avenue of investigation which was not sufficiently explored in this survey project.

³¹P-Nuclear Magnetic Resonance (NMR) Spectroscopy²¹

The use of ³¹P-tagged reagents to quantify the labile hydrogen functionalities in coal-derived materials was demonstrated to a limited extent in a Phase II project. It was not possible to speciate the phenolic compounds in heavy coal liquids with the tagging reagent and NMR data analysis technique used. The total

phenol content determined by this method agreed with values obtained by established FTIR methods. One advantage of the ^{31}P -NMR method is that it is possible to quantify water present in the samples.

Before the method could be recommended for process support, a number of research avenues should be explored to determine the usefulness of the method. All include methods development and were, therefore, not within the scope of the Phase II project. Recommended research includes: 1) utilization of different ^{31}P -tagged reagents that will allow for better differentiation of the amine and phenol region of the spectra; 2) reduction of the free radical content of the samples (perhaps by hydrogenation) to reduce line broadening in the ^{31}P -NMR spectra; 3) further evaluation of the ^{31}P -NMR spectral groupings in the phenolic region and their apparent correspondence to sampling location.

The NMR instrument used in this study cost about \$300,000. Materials for reagent synthesis cost approximately \$2.00 per sample. Approximately one week is required to synthesize enough reagent to perform fifty reactions. The ^{31}P -NMR method is amenable to the use of a large variety of solvating agents for the samples, as long as they contain no labile hydrogen. Interpretation of the ^{31}P -NMR data requires a skilled professional.

Two-Dimensional Nuclear Magnetic Resonance (2-D NMR) Spectroscopy⁸

The potential usefulness of 2-D NMR to elucidate the chemical structure of resids was evaluated in a Phase II project. It was determined that the use of 2-D NMR techniques and various NMR spectral editing techniques for coal derived resids appears feasible only if the samples are first separated into narrow compound classes. These separations, as was demonstrated in a Phase II project, were performed fairly well by a series of techniques that include supercritical extraction in various organic fluids and liquid chromatography. The resultant information from such extensive and labor intensive work which was performed in this Phase II study on process stream samples, has not yet been evaluated. Such an evaluation is needed before the 2-D NMR method can be recommended as a process development tool. The high-resolution NMR spectrometer used in this study costs about \$300,000.

Oxygen Speciation by Selective Chemical Reactions²²

In order to speciate and quantify the oxygen functional groups in coal-derived resids, a novel phase-transfer methylation procedure was employed. Hydroxyl groups were directly reacted with the phase-transfer reagents and ether groups were preliminarily cleaved by single-electron transfer reactions and then methylated. The phase transfer methylation technique which used ^{13}C - and ^1H -NMR detection successfully derivatized the available hydroxyl species in the pyridine-soluble resid samples. The total quantity of phenolic -OH determined by this method agrees well with the value obtained by Fourier transform infrared (FTIR) spectroscopy, except in two cases in which sample solubility in chloroform (which was used for the NMR experiments) was poor. The FTIR technique is well-established and is rapid and reliable, which reduces the likelihood that the techniques explored here can be put to immediate use.

In addition to providing the total hydroxyl content, the derivatization/NMR method provides classification of the hydroxyl groups into hindered, nonhindered and carboxylic acid classes, something which is not readily attainable by the FTIR method. The presence of carboxylic acids in the samples studied in this Phase II project was determined to be an artifact of sample preparation and handling. Although not optimized for coal-derived resid samples, the use of single-electron transfer reagents for selective cleavage of ether groups in the pyridine-soluble resids was demonstrated. The use of two different reagents, one of which was effective and the other of which was not, illustrated the need for a more detailed study with these reagents.

Each derivatization experiment using phase-transfer reagent requires approximately five days per sample (two days for a duplicate reaction, two days for work-up, and one day of NMR data acquisition time). Ether cleavage reactions require an additional five days for sample preparation, reaction and work-up. All reagents are commercially available and cost approximately \$20 for each phase transfer methylation reaction and about \$50 for each single electron transfer reaction followed by phase transfer methylation. The ^{13}C -NMR spectrometer cost approximately \$350,000, and the ^1H -NMR spectrometer cost approximately \$150,000.

Ultra Violet Resonance Raman (UVR) Spectroscopy²³

Ultraviolet resonance Raman (UVR) spectroscopy was evaluated as a way to identify and quantify polyaromatic hydrocarbons (PAHs) in the THF-soluble portion of resids. The method previously was used for examination of bio-medical materials, polymer systems, and petroleum samples. In this Phase II study, a brief exploration of the UVR spectroscopy technique was made with direct coal liquefaction-derived materials. Before this method can be recommended for process support, more work is required. A number of avenues for further research are suggested based on the major findings. It was found that solid coal-derived resid materials can be examined by the UVR technique without solubilization. This would be the preferred method for any future work with this type of sample. The use of instrumentation with higher resolution would be desirable to determine the species present in the coal-derived materials. The technique of "Raman hole burning" and "saturation techniques" to increase resolution are indicated by this work. A reference library of Raman spectra assembled from suitable model compounds should be undertaken.

The Raman spectrometer used in these studies costs on the order of \$200,000, but it is not commercially available. The time required to produce a single spectrum is about five minutes.

Liquid Chromatography-Fourier Transform Infrared (LC-FTIR) Spectroscopy¹⁸

Coupling a liquid chromatography (LC) method with Fourier transform infrared (FTIR) spectroscopy can provide detailed chemical class information on complex mixtures. A 2-D contour plot can be obtained from the FTIR. Unlike gas chromatography and mass spectrometry, liquid chromatography is applicable to non-volatile species. The LC-FTIR method shows some potential usefulness as a process development tool; however, conditions must be optimized for the coal-derived samples before the method can be recommended for application for process support. More intensive interpretation should be done of the 2-D contour plots derived from the FTIR data than that which was done in this Phase II study. This may reveal more subtle changes relating to processing conditions than those which were detailed in this work. Possible on-line application of this method is indicated from this study; this aspect requires further study.

The cost of LC equipment used in the study is about \$20,000. The FTIR detection can be done with any of a number of commercially available instruments which range in cost from \$20,000 to \$250,000.

Supercritical Fluid Extraction (SFE)¹⁸

Supercritical fluid extraction (SFE) was tried as a method to separate the complex coal liquefaction process-derived materials into defined fractions. The full value of the SFE method for analysis of liquefaction materials cannot be evaluated from this study, since more SFE development is required. The Phase II study was aimed at application of established techniques for analysis of direct coal liquefaction samples and was not designed to accommodate development of methodology. The SFE conditions chosen, unfortunately, were not appropriate for these materials. Conditions for supercritical fluid extraction of coal liquefaction process materials will require considerable refinement before the technique has practical application. A multi-dimensional study of solvent/modifier/pressure/temperature/time should be undertaken to establish appropriate working conditions. Optimization of conditions and further testing of the technique is recommended before SFE can be fully dismissed as a process support tool.

The equipment cost for SFE is approximately \$50,000.

Part 3

PHASE III APPLICATION PROJECTS

The methods that were evaluated in Phases I and II of the program, and best met the criteria defined by CONSOL were found to have the highest potential for application to the advancement of direct-coal liquefaction process design and development. Those criteria include the ability to clearly delineate process-induced difference in the samples, the relative ease of use of the technique, the relative cost of equipment to perform the analysis, ease of data interpretation, and, most importantly, the expected potential impact on process development and economics. The assessment of projects from Phases I and II of the program indicated that a number of techniques have a high potential to provide analytical information useful for process development interests. Of those techniques examined in Phases I and II, three were considered to have most successfully met the criteria listed above. These are solid state ^{13}C -nuclear magnetic resonance (NMR) spectroscopy, field ionization mass spectrometry (FIMS), and petroleum inspection tests.

In Phase III, these three techniques were applied to material balance streams produced in the HRI, Inc. bench-unit Run CC-15. HRI Run CC-15 had three major operating variables, catalyst age, pretreater temperature, and the use of raw feed coal vs iron-impregnated feed coal. (For details of the run see References 3 and 33, and citations therein). Due to the relative simplicity of the run, data interpretation is comparably straightforward. This uncomplicated case study provides a good demonstration of the usefulness of the techniques employed, and lays the groundwork for application of these techniques to more complex processing runs. Analytical data from this study, designed to demonstrate in a systematic manner application of these methods to support coal liquefaction process development, are discussed and interpreted here in relation to Run CC-15 process conditions and performance.

HRI bench unit Run CC-15 was divided into four operating conditions (Table 5). Samples from Conditions 2, 3, and 4 were issued to the participants for this application study. In Conditions 2 and 4, an iron-impregnated feed coal was used; in Condition 3 the raw feed coal was used. The samples are designated as the interstage sample (or first-stage inventory sample), the pressure filter

liquid (PFL), the pressure filter cake (PFC), and a blended net product oil sample made by combining, in the proportions in which they were produced, the atmospheric still overhead (ASOH) sample and the separator overhead (SOH) sample.

Description of Methods

Solid-State ^{13}C Nuclear Magnetic Resonance (Solid-State ^{13}C -NMR) Spectroscopy and High Resolution ^{13}C -NMR Solution Spectroscopy²⁴

The solid-state ^{13}C -NMR technique was shown in Phase II to be a powerful tool for the elucidation of structural parameters in coal liquefaction resids. It was demonstrated in the Phase II project that resid samples which contained ash and IOM could be examined without further preparation. This technique was used to examine the feed coal and the PFC samples in the Phase III application project. High-resolution solution ^{13}C -NMR was used to analyze the interstage, PFL, and SOH/ASOH samples. The ^{13}C -NMR data obtained from analysis of the samples were used to calculate a set of twelve carbon skeletal-structure parameters (Table 1) and eight molecular structural descriptors (Table 2)³. This data interpretation method is of particular interest because the structural parameters developed for the process samples and coals could be used to form the basis for a mechanistic model of coal liquefaction.

Field Ionization Mass Spectrometry²⁵

The field ionization mass spectrometric (FIMS) analysis provides information on the molecular weight distribution and number average, and weight average molecular weights of the samples and provides some chemical identifications. Average molecular weights were based on data obtained from 0 to 1400 Da. In this project, it was demonstrated that very little fragmentation occurs during the FIMS analysis, and thus the distribution of molecular weights is representative of the sample. Identification of certain polyaromatic hydrocarbons (PAHs) were made from the FIMS data in the Phase I study (Table 3). These PAHs previously were recognized as precursors to the formation of high molecular weight structures, associated with the formation of coke, in petroleum vacuum gas oil. In the samples examined in this Phase III study, additional PAHs were identified.

Standard Petroleum Inspection Tests¹¹

Standard petroleum inspection tests were used to evaluate the quality of the net product oils from HRI Run CC-15. This was done because, regardless of the

specific technology used to produce transportation fuels from coal, the net product of the liquefaction process will have to undergo additional refining to make finished products. Consequently, there is a need to characterize the material that exits the liquefaction plant as net product, and enters the refinery as feed. The whole Run CC-15 product sample was a blend of the SOH and ASOH net products from Conditions 2, 3, and 4. The whole sample was inspected, then fractionated into four distillation cuts; naphtha (IBP-380 °F), kerosene (380-510 °F), diesel (510-650 °F), and resid (650 °F+). Each of the straight-run fractions was inspected using an appropriate suite of methods. The naphtha and kerosene fractions were then caustic-washed for the removal of phenolic compounds. The washed fractions were then retested. The suite of tests used to analyze the crude or distillate cuts is given in Table 4.

Analytical Results and Discussion

A summary of the analytical findings of the three methods used in this example application is presented here. An effort is made to integrate the findings from the different methods and relate them to the processing conditions. In addition to the three exploratory methods, a suite of in-house techniques was used by CONSOL to provide a base of analytical information on which to begin the evaluation of the samples. A list of these "base" methods is given in Table 6. Experimental procedures for the base methods have been published elsewhere.²⁶⁻³¹ The findings from the base method analyses and the petroleum inspection tests are given in References 3, 11, and 32. The full reports for the FIMS project and ¹³C-NMR spectroscopy project are given in References 24 and 25, respectively.

Analytical Results

The information supplied by the base analyses indicates that aging of the second-stage supported catalyst dominated most of the sample properties. This is evident in trends observed over the entire run: there were overall increases in proton aromaticity (Figure 3) and phenolic -OH concentration (Figure 4) and decreases in hydrogen donor content and paraffinic hydrogen content in the PFL, the THF-soluble portion of the PFCs, and in the product distillates (Figure 5).

The interstage samples from Conditions 2, 3, and 4 do not strictly follow the trends noted above for the other samples. The interstage sample carbon aromaticity increases by a small amount as the run proceeds (Figure 6). However,

the proton aromaticity appears to be influenced by the absence of the iron-impregnated coal in Condition 3 (Figure 3). In Condition 3, the interstage sample proton aromaticity increases by 6% and decreases in Condition 4 (by about 3%). This is consistent with the ^{13}C -NMR data, which show that the fraction of protonated aromatic carbon to total aromatic carbon (f_a^H/f_a') increases in Condition 3. This indicates that the side chains, bridges, and loops attached to the aromatic rings were cleaved, and the rings were hydrogenated. There is a small decrease in f_a^H/f_a' in the sample from Condition 4, in agreement with the proton NMR data. The interstage sample has a low number of carbons (about 2) per side chain (Figure 8), consistent with the idea that in the first-stage reactor, the coal matrix is broken apart, but without extensive ring reactions. This can be seen in the low average molecular weight of the interstage sample cluster (275 in Condition 2, 218 in Condition 3, and 195 in Condition 4 vs 346 for the feed coal). The phenolic -OH content of the interstage sample decreases in Condition 3 (from 0.6 meq/g to 0.5 meq/g) and increases again in Condition 4 (to 0.6 meq/g). It is believed that the iron catalyst in use in Conditions 2 and 4 promotes fast cracking of the low rank coal and slow dehydroxylation; thus, resulting in higher phenolic -OH content. In the thermal case (Condition 3) rates of cracking and dehydroxylation are competitive.

The fraction of aromatic carbon (f_a') in the PFL sample, as determined by ^{13}C -NMR spectroscopy, increases significantly from Condition 2 to 3 and remained high (at approximately the same concentration as the initial coal) in Condition 4 (Figure 6). The proton NMR data reflect the same behavior (Figure 3). This is presumably due to the effect of aging of the second-stage catalyst. However, the f_a^H/f_a' ratio for the PFL samples shows some effect of the discontinuation of the iron-impregnated coal in Condition 3 (Figure 7). It is speculated that when the iron catalyst is discontinued, there are fewer cracking reactions and more condensation reactions, thus increasing f_a' and lowering the f_a^H/f_a' ratio. The fraction of aromatic carbons per cluster in the PFL samples also is influenced by the absence of the iron catalyst in Condition 3. The cluster size increases in Condition 3; this is consistent with the higher carbon and proton aromaticity and the lower coal and resid conversion reported by HRI for that run condition. It also is consistent with the weight average molecular weights determined for the PFL samples by FIMS (Figure 9), which show a higher average molecular weight for the PFL sample obtained from Condition 3 than those from Conditions 2 or 4.

The earliest PFL sample shows a large increase in the number of carbons per side chain, relative to the coal, which may be indicative of ring opening reactions (Figure 8). In later run periods, this value was lower, possibly as a result of decreasing second-stage catalyst activity and the suspension of the iron catalyst in Condition 3, which, as described above, may cause the system to favor condensation reactions over cracking reactions.

Analyses of the whole PFC samples proved to be problematic in both the FIMS and ^{13}C -NMR spectroscopy studies. The PFC samples apparently contained some liquid-like oil. Under the conditions of the ^{13}C -NMR analysis, these samples released the oily component and it could not be contained in the spinning rotor. The nature of this non-solid component could not be fully elucidated because of motional averaging; however, it was determined that this component was aliphatic. This material also caused a broad background in the Bloch decay spectra. Because of the presence of the oil component in the PFC samples, the ^{13}C -NMR data can be used only for qualitative purposes. In the FIMS analysis, this same oily component was responsible for poor sampling reproducibility; thus, the FIMS data for those samples is also non-quantitative.

The ASOH/SOH blended samples from each of the three run conditions (2, 3, and 4) show almost identical properties. The proton and carbon aromaticity are fairly constant throughout the run (Figures 3 and 6). The carbon aromaticities of the ASOH/SOH samples are low (f_a' is about 20 %). Limited signal in the NMR spectral region associated with bridgehead carbon, led to the assumption that these materials contain structures with, on average, only one aromatic ring. The presence of long side chains (on the order of 6 carbons) on the ASOH/SOH samples is believed to arise from ring opening reactions (Figure 8). The phenolic -OH contents of the SOH and ASOH samples track those of the PFL samples (Figure 4). The ASOH samples are consistently higher in phenolic -OH than the corresponding whole PFLs. This arises from the concentration of alkylated phenols in this particular boiling range product.³³ This was seen previously in distillation fractions from Wilsonville Run 260,³⁴ where it was observed that phenolic compounds were more concentrated in the kerosene than in the fractions with higher or lower boiling points.

Petroleum Inspection Test Results

The coal liquid product quality was assessed by comparison of the physical and chemical property test data for the distillation fractions (IBP-380 °F, 380-510 °F, and 510-638 °F) to the corresponding specifications for gasolines, aviation turbine fuels, diesel fuels or fuel oils, respectively. The properties of the net product oil and its distillate fractions show that the coal-derived material has many desirable qualities. The whole crude has low sulfur, metals, ash and resid contents and boils below the maximum temperature allowed for the production of transportation fuels. The naphtha fraction (IBP-380 °F), which represents 40% of the net product, is highly naphthenic and has a low benzene content. The naphtha fraction appears to be amenable to mild hydrotreating to produce a good gasoline blendstock or reformer feedstock. The kerosene (380-510 °F) fraction, which represents 33% of the net product, is too cyclic for use as aviation fuel and it is recommended that this fraction be distributed into the two cuts on either end of it (diesel and gasoline feedstocks). The 510-680 °F fraction, which represents 22% of the net product, met most specifications as a diesel fuel and heating fuel, although its cetane index would need to be boosted for premium diesel fuel use. Caustic washing removed 2% and 4% phenolics from the naphtha and jet fuel fraction, respectively, and provided minor improvements in the qualities of the washed fractions.

Summary Remarks on Application Project

In summary, some of the most important information determined by interpretation of the ^{13}C -NMR data obtained in this study is that three types of structural reactions are taking place during the conversion of resid: ring protonation, ring opening, and ring dealkylation. Additionally, differences in the rates of these reactions in the two reactor stages can be inferred from the NMR data. Changes in aromaticity of the process samples (either by ring protonation or loss of sp^3 carbon by dealkylation/cracking mechanisms) can be attributed to the presence of catalyst in the reactors. Extensive ring opening reactions can be surmised to have occurred from data collected on the length of side chains.

The FIMS data indicate that the whole oil and pressure filter cake process samples have a broad smooth molecular weight profile ranging from 200 to 1200 Da; the distillate samples spanned a molecular weight range of 100 to 300 Da. The oils exhibited a bimodal distribution of molecular weights. The two parts of the

distribution could be used to monitor process trends and provide input for a lumped kinetic model. Hydrodenitrogenation activity during liquefaction could be monitored by FIMS because it was found that the sum of the odd mass intensities as a fraction of the sum of all ion intensities correlated with the nitrogen content of the sample (Table 7). Certain prominent peaks in the lower molecular weight range of the mass spectra were identified as being specific analogs of dihydrophenalene (phenalan). These compounds have been previously implicated as coke precursors in petroleum-derived vacuum gas oils.³⁵

The in-house base methods provide analytical data which are responsive to process changes, and provides the chemical/molecular information basis on which the more advanced techniques can build. ¹H-NMR spectroscopy, one of the most useful analytical methods for coal liquefaction process stream characterization, is highly responsive to hydrogenation reactions. In this study, the ¹H-NMR data supported the ¹³C-NMR and FIMS data and provided an insight into the dominating effect of the second-stage supported catalyst on the PFLs, THF-soluble portion of the PFCs, and the product oils. The ¹H-NMR analyses also helped delineate the effect of the addition of impregnated iron catalyst in one run condition on the interstage samples. The phenolic -OH determination by FTIR is simple to conduct, has a short turn-around time, and is quantitative. In this case, the phenolic -OH concentration was responsive to process changes and provided further information relevant to the impact of the iron-based catalyst on resid conversion.

This study demonstrated that the application of both base and advanced analytical techniques to direct coal liquefaction process streams can provide considerable insight into the chemistry of direct coal liquefaction. The integration of the data obtained from the methods used here was shown to be a potentially useful way of understanding the direct liquefaction process. The application of additional methods should further expand the chemical data base attainable with the methods used here and provide data useful to model the mechanisms and kinetics of coal liquefaction. An improved understanding of the chemistry of coal liquefaction by application of advanced techniques, such as those employed in this project, can guide process development. The ultimate goal of economic improvement will be promoted through an improved understanding of the process. Projects such as this one are a major step in that direction.

Part 4

RESID REACTIVITY

The kinetics of direct hydrogenation of coal to produce liquid fuels has not yet been defined clearly. This lack of definition stems in part from a lack of specific chemical information on the feedstock (coal), the products, and reaction intermediates, such as recycled distillate and resid. The needed chemical information falls in two areas: 1) detailed chemical characterization of the materials, and 2) mechanistic information about how the chemistry of hydrocracking proceeds. The resid (operationally defined to be material boiling above a set temperature; e.g., 850 °F or 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. However, the resid chemistry is important because the resid represents the primary intermediate in the conversion of coal to light product distillate. In modern two-stage liquefaction processes, most of the resid is generally recycled, so that it is the major component of the first-stage feed. In addition, it is primarily components of the resid which are involved in retrogressive reactions in the direct liquefaction process. These reactions may be one of the controlling factors in the rate of production and ultimate yield of net liquid products.

A definition of "resid reactivity" might be: the ease of conversion of resid to lower molecular weight products. However, this simple view ignores resid reactivity toward retrograde reactions. A straightforward measure of resid reactivity might be the disappearance of resid under some particular set of reaction conditions. The conditions under which reactivity is measured, however, will have a great influence on the measured reactivity. 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 suitable chemical characteristics and reaction conditions, it can be applicable to a *priori* prediction of feedstock behavior. In this manner, it should be possible to define resid reactivity in a more generalized way based on chemical characteristics and reaction behavior in real liquefaction systems.

No standardized empirical test presently exists for measuring the relative reactivity of resids. Included in the Participants Program was a project designed to begin to address both the chemical and the empirical aspects of resid reactivity.³⁶ A laboratory-scale batch reactor (Short Time Batch Reactor, STBR) (Figure 10) capable of running reactions up to 450 °C and 2500 psi at well-defined reaction times from a few seconds to 30 min or longer was used in this study. By the use of very rapid charging and preheating, this equipment avoids the problems of long heat-up and cool-down times associated with running reactions in the large equipment usually used for such experiments. The small size and batch nature of the reactor also allows the running of many experiments over a range of conditions in a relatively short time.

The project goals in this limited Phase III study were: 1) to investigate the feasibility of using this reactor to determine the reactivity of coal-derived resids to forming lower boiling products, and 2) to develop and verify an experimental protocol for measuring relative resid reactivity toward breakdown into lower boiling (or more soluble) products using tetralin solvent and a standardized catalyst at coal liquefaction conditions.

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 thermogravimetric 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.

A reaction product work-up procedure (Figure 11) was devised which applies these analytical methods, and clearly shows changes in the resid to form lower boiling and more soluble materials. The work-up procedure consists of filtering the product through a sintered glass filter, separating the product into a liquid and a solid (Figure 11), and leaving all the mineral matter in the solid portion for use as a basis to calculate conversion by ash balance. The liquid portion separated from the reaction mixture contains both dissolved material from the original resid and soluble reaction products from the resid conversion process. These are analyzed by a slow ramp (1 °C/min) TGA, which provides a direct measure

of the tetralin content, as well as volatile matter and fixed carbon contents of the liquid. All of the tetralin is removed before the sample reaches about 180 °C.

Changes in the solid (insoluble) portion of the reaction mixture are conveniently determined by use of TGA. A slow ramp TGA (10 °C/min) must be performed in the absence of tetralin; otherwise, further conversion of the resid occurs during the TGA analysis itself. The solid residue is therefore dried, finely ground and further dried in a vacuum oven to eliminate residual tetralin prior to TGA analysis. The volatile matter present and the amount of fixed carbon and ash contents are determined. Any catalyst contributes to the ash content. It was shown that the catalyst content can be determined and corrected for by continuing the TGA run in oxygen to 1000 °C and measuring the further weight loss. The form of the TGA and differential curves gives a measure of the conversion of the 950 °F⁺ resid material during the conversion process. Examples of typical TGA curves for liquid and solid components for catalyzed resid conversion reactions are shown in Figure 12.

Two samples were chosen for the Phase III project. They are the 850 °F⁺ distillation resid of the recycle process stream from two different direct coal liquefaction runs performed at the Wilsonville pilot plant, Runs 259 and 260. Samples were taken from the vessel (V-1067) after the second-stage reactor. They are composites of samples taken over long periods during the individual processing runs. The two resids contain ash and insoluble organic material (IOM). Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration. Run 260 used Wyodak and Anderson seam, Black Thunder Mine coal as feed, and operated for approximately half the run in a thermal/catalytic (and high/low temperature) reactor configuration, and for the remaining half of the run in a catalytic/thermal (and low/high temperature) reactor configuration. Run 259 used Pittsburgh seam, Ireland Mine coal as feed and was operated in a catalytic/catalytic reactor mode.

TGA was used to determine volatile matter (VM), fixed carbon (FC), and ash content of the reaction products, as described above. The tetralin-soluble portion of the products was found to contain no ash. GC and GC/MS analysis of the tetralin-soluble samples showed that much of the material dissolved in the

tetralin was too low in volatility to be detected; the material that was volatile could not be identified.

In uncatalyzed runs, the increase in tetralin-soluble material, as reaction temperature increased, was different for the two resids studied (1 wt % at 412 °C to 6 wt % at 435 °C for Sample 1, 2 wt % at 410 °C to 13 wt % at 434 °C for Sample 2). Greater conversion to tetralin-soluble product was obtained with catalyst present for each of the two resid samples. The percent conversion was found to be both time- and temperature-dependent. Lower temperature runs made at longer reaction times approached the same conversions as higher temperature runs. The ordering of reactivity of the two samples was the same with and without catalyst present. On an ash-free basis, the total conversion to tetralin soluble material was found to be 87% for the Pittsburgh seam coal resid and 91% for the Wyodak and Anderson seam coal resid at one set of conditions.

The TGA volatiles evolution pattern for uncatalyzed soluble reaction products showed a bi-modal distribution. The second (higher temperature) peak is not present in the products of the catalyzed runs. Based on the TGA evolution pattern, it is presumed that the average molecular weight of the products was lower in the catalyzed runs. Replication of experimental TGA results was very good; characteristic values (volatile matter, fixed carbon, and ash) were reproduced to within $\pm 0.5\%$, relative.

Both goals stated above were met in this project. Experimental methods were adapted for the introduction of the resids to the reactor system and work-up procedures were altered to provide the best possible reaction monitoring system. Secondly, an experimental protocol was developed which could determine the relative amount of conversion of the resid unhampered by the catalyst content of the reaction mixture. Reproducible data were obtained over a large matrix of reaction conditions demonstrating the versatility of the technique.

Two important questions yet to be addressed by this method are: 1) Are some components of these resids more easily broken down to useful products than other components or, conversely, do they undergo retrograde reactions, and can we determine these components analytically? 2) How do these resids influence the reactivity of the coal liquefaction system when a substantial amount of them are

recycled to the coal liquefaction process? Studies designed to address the questions could form the basis for future work.

Part 5

ECONOMIC IMPACT OF ANALYTICAL TEST METHODS

Analytical test methods historically have been used to provide information necessary to operate direct coal liquefaction facilities, regardless of scale. The analysis of process stream samples provides information on the process, such as mass and energy balances, conversion and yield values, whether or not the process has reached steady-state operation, the effects of process upsets, the effects of changing process conditions, and the effects of altered process design. Not only can this information be used for monitoring the process, it also can be used to aid in improving process design and eventual development. Consequently, this analytical information can impact the economics of coal liquefaction. Data obtained by monitoring the process for these operational changes, however, are only a portion of the information which can be used to impact the economics of coal liquefaction. Another category of process monitoring information which affects economics is concerned with the chemistry of the material in the process. The chemical properties of the coal and products of coal liquefaction can significantly impact the economics of the process. For example, through a chemical analysis, information can be obtained which will indicate whether there is a build-up of refractory material in the recycle streams, and thus, directly influence day-to-day operations. It is only through chemical analyses that the fate of the heteroatoms in the coal feed can be determined; thus, for example, yielding data useful for catalyst design and use. Many other examples can be offered to show the importance of chemical analysis for providing a full picture of the coal liquefaction process and, therefore, guiding economically sound design and operation of such a process. A compilation of the information needs of the direct coal liquefaction process potentially addressable by analytical techniques, was made by the COLIRN Panel,³⁷ and is given in Table 8. To obtain this required information, chemical characterization data must be obtained.

The Participants Program was designed to survey analytical techniques and methods which have the potential to provide chemical data necessary to characterize the process streams. These techniques and methods can thus provide the kind of information required to improve direct coal liquefaction process design, development, and operational efforts, as outlined in Table 8. The program

focused on characterization of the non-distillable resid portion of liquefaction oils because of the importance of this material to the liquefaction process, as described in Part 1, above. The reaction chemistry of the recycle resid strongly affects the economics of direct-coal liquefaction. It greatly impacts the reactor costs by controlling factors such as space velocity, temperature, necessary reactor volume, catalyst loading, etc. Therefore, it follows that the analyses used to investigate the resids will also have an impact on direct coal liquefaction economics. Further, a better understanding of the reactivity of the resid will provide a better control on the costs of improving product quality.

In the Participants Program, other analytical methods were chosen specifically for the analysis of net product oils. Regardless of the specific technology used to produce transportation fuels from coal, the net product of the liquefaction process will have to undergo additional refining to make finished products. Consequently, there is a need to characterize the material that exits the liquefaction plant as net product, and enters the refinery as feed. The analysis of this material will determine its value, and therefore, have a direct impact on the process economics.

There are numerous cost factors associated with coal liquefaction. Some are beyond the realm of the process (taxes, debt-to-equity ratio, required return on investment). Others are related only marginally to the process (for example, plant location, and thus, constraints on choice of feed coal). Still others are sensitive to process improvements. A few important ones are: 1) coal costs (through the performance of the process based on the coal qualities), 2) coal preparation methods, 3) reactor throughput, 4) hydrogen utilization, 5) catalyst use, 6) product separation, 7) product yield and selectivity, 8) product quality, and 9) process control. Thus, it is clear from this list that opportunities for technology to reduce process costs lay primarily in reducing capital costs, and secondarily in reducing operating costs. Table 9 is a matrix that shows the process cost factors as listed here and the informational needs as outlined in Table 8. The table shows which cost factors those information needs can impact. For example, a practical kinetic model of coal and resid conversion would be valuable for optimizing reactor throughput and product yields, and would prove useful for determining the performance value of coal cleaning. Table 10 is a similar matrix, except that the rows represent various categories of analytical

methods used in the Participants Program. This matrix shows which information needs each analytical method may address. For example, ^{13}C -NMR spectroscopic information is ideally suited to the construction of a kinetic model of coal liquefaction, and it provides structural information on coal and its intermediate products. When applied to hydrogen accounting, it provides information on retrograde reactions and hydrogen utilization.

Table 11, is a selective cross-matrix of Tables 9 and 10. It shows on which liquefaction process cost factors the various analytical techniques surveyed in the program can have an impact. It is apparent that a pivotal information need, and the one which most of the methods surveyed in the participants Program address, is the development of a kinetic model of coal liquefaction. The construction of a kinetic model would aid in optimizing many cost factors related to direct coal liquefaction. The analytical methods which contribute to this model can, thus, be considered key in improving the economics of coal liquefaction.

Part 6

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

The Participants Program successfully achieved its stated objectives. Many novel analytical techniques were applied to direct coal liquefaction process-oriented materials and many analytical researchers were introduced to processing information, some for the first time. This cross-pollination of information between the realms of process development and analytical chemistry is considered the first step in bridging the gap between these two groups. The program proved successful in identification of a number of methods with a high potential for immediate application to coal-derived materials and some methods which, with further development (a task outside the scope of the program), could be applied to process-derived materials to aid in design, development, or operation of a coal liquefaction facility. It is recommended that some of the techniques which were successful for analysis of process-derived samples be explored further. In addition, other unexplored analytical techniques should be examined for application to coal-derived materials.

The investigations performed in this program reaffirmed that a more rigorous knowledge of the reactivity of the distillation resid is required to fully understand the modern two-stage liquefaction process; some preliminary work was done in this program to address that issue. It is recommended that additional effort be made to study resid reactivity and construct a kinetic model.

Part 7

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TABLE 1
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
$f_{a'}$	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 2
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; $\text{SC} = (\sigma + 1) \cdot \text{BL}$
$\sigma + 1$	number of attachments per cluster	MW	total molecular weight; $\text{MW} = (\text{Cx}12.01) / (f_a \cdot \% \text{C} / 100)$
P_O	fraction of intact bridges; $P_O = \{f_a^P + f_a^S - f_{al}^*\} / \{f_a^P + f_a^S\}$	M_s	average molecular weight per attachment

TABLE 3
 PROMINENT IONS IN FIELD IONIZATION MASS SPECTRA
 AND THEIR PROBABLE STRUCTURES

m/z	Probable Structure
242
276
300
316

TABLE 4

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/100mL
- Oxidation Stability (D525), min
- Oxidation Stability (D2274), mg/100mL
- Thermal Stability (JFTOT)(D3341)
- Distillation (ASTM D2892), wt %
- Octane Number Motor Method (D2700)
- Octane Number Research Method (D2699)
- Cetane Index (D976)

TABLE 5
OPERATING CONDITIONS^{39,49}
HRI CTSL RUN CC-15

Feed Coal: Black Thunder Mine (Wyodak and Anderson seams), Wyoming subbituminous

Conditions 1, 2, and 4: Treated with hydrated iron oxide

Condition 3: Untreated

Catalyst: Shell S-317 (NiMo on alumina), second stage only

Unit back-pressure: 2500 psig

Oil/Solids Ratio: 1.4-1.7/1.0^a

Start-up Oil: Filtered process oil from HRI PDU Run 260-03 (L-769)

<u>Condition</u>	<u>Period</u>	<u>Temperatures, °F</u>			<u>Coal Space Velocity^b</u>	<u>Catalyst Age^c</u>
		<u>Pretreater</u>	<u>Stage 1</u>	<u>Stage 2</u>		
1	1A-5C	523	799	775	42	144
2	6A-8C	567	801	776	41	228
3	9A-11C	567	801	774	43	316
4	12A-14C	566	801	774	43	403

- (a) Additional solvent (PFL) equal to about 2.5% of recycle added through buffer pumps in pretreater and about 5.5% in stages 1 and 2
- (b) Coal space velocity units: lb dry coal/hr/ft³ on a settled catalyst volume basis
- (c) Catalyst age units: lb MF Coal/lb Cat., Second Stage, given for last period of Condition

TABLE 6
ANALYTICAL PROCEDURES EMPLOYED FOR ANALYSIS OF
HRI RUN CC-15 PROCESS STREAM SAMPLES

Base Methods	Advanced Methods
Solvent Quality	FIMS Analysis
Phenolic -OH by FTIR	¹³ C Solid-state and ¹ H NMR Analysis
Solubility Fractionation	Inspection Tests on net product oils
Solution ¹ H NMR	
Elemental Analyses	
Distillation	

TABLE 7

**SUMMARY OF FIMS ANALYSIS AND OTHER DATA
FOR HRI RUN CC-15 SAMPLES**

Sample No.	Sample Type	Period No.	FIMS Volatility, %	$\bar{M}_w$ (a)	SUM of (Odd/Even) (b)	N, wt % (c)	Distillate Yield, wt % (d)
1	PFL	8ABC	100 (e)	506	0.365	0.56	64.1
2	PFC	8A	48	450	0.512	0.76	
3	INT	9A	77	529	0.434	0.96	
4	SOH-ASOH	8ABC	(100)	176	0.116	0.40	
5	PFL	11ABC	94	531	0.384	0.54	57.4
6	PFC	11A	50	473	0.549	0.62	
7	INT	12A	100	504	0.46	0.66	
8	SOH-ASOH	11ABC	(100)	179	0.11	0.28	
9	PFL	14ABC	100	526	0.44	0.81	60.2
10	PFC	14A	60	465	0.48	0.81	
11	INT	15A	100	568	0.77	1.05	
12	SOH-ASOH	14ABC	(100)	182	0.20	0.53	

- (a) Weight-average molecular weight.
 (b) The ratio of the sum of all odd-mass intensities to the sum of all even-mass intensities.
 (c) Data provided by CONSOL Inc.
 (d) C₄-975 °F⁺ distillate yields were provided by HRI, and represent steady-state performance for that particular run period.
 (e) The precision of the FIMS total volatility measurement is ± 5 wt %.

TABLE 8
INFORMATIONAL NEEDS POTENTIALLY ADDRESSABLE
BY ANALYTICAL METHODOLOGY (a)

- Develop kinetic models of liquefaction
- Develop coal structure/reactivity relationships
- Identify retrograde reaction structures, mechanisms, kinetics
- Study mechanisms of catalytic hydrogenation and cracking reactions
- Investigate homogeneous and dispersed catalysts
- Improve hydrogen utilization
- Investigate role of mineral matter
- Elucidate the nature of the higher molecular weight non-distillable (soluble and insoluble) residual materials which constitute the process streams in the direct liquefaction process
- Characterize the functional groups associated with the components of the coal liquefaction process streams
- Use new computational techniques, such as chemometrics, to analyze and interpret coal liquefaction data
- Determine product quality

(a) List drawn from Ref. 37

TABLE 9
COST FACTORS AND INFORMATION NEEDS

Cost Factors	Information Needs					
	Kinetic Model	Coal Structure/Reactivity	Retrograde Reactions	Catalysts	H ₂ Utilization	Minerals
Coal Costs		++				
Coal Prep	+	++				+
Reactor Throughput	++	++	++	++	++	+
H ₂ Use	+					
Catalyst Use	+		+	++		
Product Separation			+			++
Product Yield/Selectivity	++	+	+		+	
Product Quality				++	++	
Process Control	+				+	

+ Potential Impact

++ Large Potential Impact

TABLE 10
ANALYTICAL METHODS (BY CATEGORY) AND COST FACTORS

Analytical Method Category	Cost Factors								
	Coal Costs	Coal Prep.	Reactor Throughput	Hydrogen Use	Catalyst Use	Product Separation	Product Yield/Selectivity	Product Quality	Process Control
Product Inspection Tests				+	+		+	+	
NMR			+	+			+	+	
Mass Spectrometry			+	+	+	+	+		
Heteroatom Speciation			+	+			+		
Separations	+		+	+	+	+	+		
Microscopy			+		+		+		+
ESR			+	+	+				
Catalytic Dehydrogenation			+	+	+		+		
Resid Reactivity	+	+	+	+	+		+	+	+

+ Successfully demonstrated in Participants Program for Application to Affect Cost Factor

TABLE 11
ANALYTICAL METHODS (BY CATEGORY) AND INFORMATION NEEDS

Analytical Method Category	Information Needs					
	Kinetic Model	Coal Structure/Reactivity	Retrograde Reactions	Catalysts	H ₂ Utilization	Minerals
Product Inspection Tests				+	+	
NMR	+	+	+		+	
Mass Spectrometry	+	+	+			
Heteroatom Speciation	+	+	+		+	
Separations	+	+				
Microscopy	+					+
ESR	+			+		+
Catalytic Dehydrogenation	+		+	+	+	
Resid Reactivity	+	+	+	+	+	

+ Potential Impact

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

CA-2177-2

Figure 2. Deconvolution of FIMS of Wilsonville Run 257 Interstage Oil (Catalytic/Catalytic, Illinois 6 Coal) into Components A and B.

Figure 3. Proton Aromaticity.

Figure 4. Phenolic -OH Concentration

Figure 5. Hydroaromatic and Paraffinic Proton Content.

Figure 6. Carbon Aromaticity of Samples from HRI Run CC-15.

Figure 7. Fractions of Aromatic Carbon that are Protonated.

Figure 8. Carbons per Side Chain per 100 Carbons for Samples from HRI Run CC-15.

Figure 9. Weight Average Molecular Weight Determined by FIMS of Samples from HRI Run CC-15.

Figure 10. Apparatus for Short Contact Time Coal-Derived Resid Conversion.³⁴

Figure 11. Schematic Diagram of the Experimental Procedure³⁴ for Work-Up of Resid Conversion Products.

Figure 12. Typical TGA Curves for Filtered Solid Resid (A) and Liquid Filtrate (B) of a Catalyzed Resid Conversion Experiment.

APPENDIX A

CONSOL EVALUATION AND SUMMARIES FOR PARTICIPANTS PROGRAM PHASE III PROJECTS

Program Description

This Appendix describes the work performed at The Pennsylvania State University, the University of Pittsburgh, the University of Delaware, SRI International, the University of Utah, and the National Institute for Petroleum and Energy Research under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The second objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction process development facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials. Methods which demonstrate high potential for process stream analysis, and concurrently provide information potentially useful for process design or operation, and thus, those which have the potential for immediate impact on process economics, are further tested by application to a comprehensive set of process-derived materials.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM THE PENNSYLVANIA STATE UNIVERSITY ^a

PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), The Pennsylvania State University studied the use of two-dimensional, high performance liquid chromatography (HPLC), using normal-phase separation with ultraviolet (UV) diode array detection to analyze coal-derived process stream materials. High resolution heated probe mass spectrometry was used to provide additional information on the HPLC fractions. Gas chromatography/mass spectrometry (GC/MS) also was used to characterize the samples. A report summary authored by The Pennsylvania State University researchers is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the method for application to coal derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal derived materials at the conclusion of this contract.

Summary

This study demonstrated the considerable potential of using two-dimensional, high performance liquid chromatography (HPLC) with normal-phase separation and ultraviolet (UV) diode array detection for the examination of filtered process liquids and the 850 °F distillate materials derived from direct coal liquefaction process streams. A commercially available HPLC column (Hypersil Green PAH-2) provided excellent separation of the complex mixture of polynuclear aromatic hydrocarbons (PAHs) found in coal-derived process streams. Some characteristics of the samples delineated by the separation could be attributed to processing parameters. Mass recovery of the process-derived samples was low (5-50 wt %). Penn State believes, however, that improved recovery can be achieved. High resolution mass spectrometry and gas chromatography/mass spectrometry (GC/MS) also were used in this study to characterize the samples and the HPLC fractions. The GC/MS technique was used to preliminarily examine the

^aClifford, D. J.; McKinney, D. E.; Hou, L.; Hatcher, P. G. "Coal Liquefaction Process Streams Characterization and Evaluation, High Performance Liquid Chromatography of Coal Liquefaction Process Streams Using Normal-Phase Separation with UV Diode Array Detection, Topical Report", DOE/PC 89883-85, January 1994.

GC-elutable portion of the samples. The GC/MS data were compared with the data from the HPLC technique. The use of an ultraviolet detector in the HPLC work precludes detecting the aliphatic portion of the sample. The GC/MS allowed for identification and quantification of that portion of the samples. Further development of the 2-D HPLC analytical method as a process development tool appears justified based on the results of this project.

Methodology

The Penn State researchers employed two-dimensional, high performance liquid chromatography (HPLC) using normal-phase separation with ultraviolet (UV) diode array detection to analyze pressure filtered liquids and the 850 °F distillates from coal liquefaction process streams. High resolution mass spectrometry was used to further characterize the HPLC fractions. To provide additional information, gas chromatography/mass spectrometry was also used in this study. The samples were produced at the HRI Inc. bench unit No. 227 and the Wilsonville pilot plant. The HRI samples differ in two ways: feed coal and catalyst age. Wyodak and Anderson seam coal was used in Run CC-15 (Sample 1) and Illinois No.6 coal was used in Run CC-16 (Samples 2 and 3). Sample 2 was obtained early in the run (period 4) and Sample 3 was obtained later when the supported catalyst used in the process had aged (period 13). Samples from the HRI unit are pressure filtered liquids (PFLs) and contain little or no ash or insoluble organic material (IOM). Different feed coals were used in the two Wilsonville runs: Illinois No. 6 in Run 257 (Sample 4) and Wyodak and Anderson seam coal in Run 262 (Sample 5). Wilsonville samples are composites of samples taken over long periods of single runs. The parent samples were taken from the location after the second-stage reactor. The Wilsonville samples were distilled at 850 °F by CONSOL; Penn State examined the 850 °F distillate portion of the sample.

Major Findings

The following principal observations were reported by Penn State University for the application of 2-D HPLC with normal-phase separation to coal liquefaction materials. Additional information derived from GC/MS analysis of the samples is also discussed.

The use of the Hypersil Green PAH-2, normal-phase column resulted in excellent separation of the samples. The samples could be distinguished by processing

facility or sample type (Samples 1, 2, and 3, PFLs from HRI, were found to be similar and differed from Samples 4 and 5, 850 °F distillates of Wilsonville oils) and, to some extent, by changes in processing conditions, such as feed coal and catalyst aging. The HPLC traces, for all samples, are comprised of both sharp peaks and broad unresolved areas. High resolution mass spectrometry aided in identification of the eluted fractions. Multi-ring polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs, with three to nine condensed rings, were identified.

Gas chromatography/mass spectrometry was used to determine the major components in that portion of the samples that was GC-elutable. The use of an internal standard (eicosane) allowed for quantification of the n-alkane component of each sample. This information was used in the overall mass balance data for the HPLC separations because these compounds were invisible to the UV diode array detection system used for the HPLC analysis. The total ion chromatograms (TICs), which indicated differences between the samples produced at the two facilities, were used to support the HPLC data.

CONSOL Evaluation

High performance liquid chromatography (HPLC) using normal-phase separation with ultraviolet (UV) diode array detection was shown to have considerable potential for the analysis of direct coal liquefaction distillate and solids-free samples and for providing direction for process development. The researchers of Penn State believe separation of the coal-derived samples in this project are the best ever achieved with any coal liquids by a simple normal-phase liquid chromatographic method.

The method has a major drawback at this stage of development: less than 50% of each HRI PFL sample was recovered, and only about 5% of each Wilsonville 850 °F distillate sample was recovered. This low mass recovery may be partially attributed to the fact that the UV detection is insensitive to compounds which do not contain chromophores. Another reason for the poor mass recovery may be that compounds (particularly polar oxygenates) are retained on the PAH-2 column. Additional work would be required to improve the recovery from the column and to augment the detection system with methods that will detect the non-chromophoric materials. This problem appears to be surmountable.

Despite this drawback, the method is recommended for further investigation for application to direct coal-derived liquefaction samples. Qualitative examination of the 2-D and 3-D HPLC plots provides an excellent way of highlighting differences among the samples and readily indicates the appropriate wavelengths to use to produce 1-D plots with a minimum of interfering peaks. Expanded identification work and quantitative analysis of the HPLC data would increase the potential of the method for monitoring the progress of forward (or retrogressive) reactions in the process streams.

The Waters 600E HPLC and Waters 991 photodiode array detector and associated software cost \$42,325. A personal computer and laser printer add about \$3,500 to that cost. The Hewlett Packard 5890 II gas chromatograph coupled with a Hewlett Packard 5971A mass selective detector used in this work costs approximately \$70,000. The Hypersil Green PAH-2 column costs \$650 and has a lifetime of approximately 300-500 analyses. Including sample preparation, separation, and data conversion approximately 2 hr per sample is required to perform the HPLC experiments as described here. Expendable supplies (solvents) for the analysis of the five samples described in the appended report cost approximately \$800. The high resolution mass spectrometer (Kratos MS-80 RFA) costs approximately \$350,000. High resolution mass spectrometric (HRMS) analysis requires approximately 1 hr per sample. HRMS data interpretation is not trivial and requires a professional trained in mass spectrometric methods.

Further Development

There are a number of avenues for further development of the 2-D HPLC technique for coal-liquefaction-derived samples. Improvements in the mass recovery must be made before this technique can be used to full advantage for characterizing process-derived samples. A combined HPLC/UV/GC/MS system may be useful in this regard. Additional investigation of the potential of the PAH-2 column for separation of polar oxygenates (presently believed to be retained on the column) would best be carried out with a solvent gradient as well as a solvent concentration gradient.

Statement of Work

Analyses will proceed as follows: the samples first will be solubilized in 50/50 hexane/methylene chloride. The soluble sample will be analyzed by gas

chromatography/mass spectrometry on a Hewlett Packard 5890 instrument interfaced to a Hewlett Packard 5971A MSD. The column used will be a 50% phenylmethylsilane fused silica capillary column. To the remainder of the solubilized sample standard additions (up to three) will be made with 16 pure PAH standards. The sample, with standards added, will then be filtered. After filtering, Penn State will dry the samples in nitrogen and weigh the filtrate to obtain the percent of sample soluble in this solvent system.

The primary method of HPLC separation will be normal phase HPLC using a 150 x 4.6 mm Hypersil Green PAH-2 column. The sample will be reconstituted in 50/50 hexane/methylene chloride, and a gradient of 50/50 hexane/methylene chloride to 100% methylene chloride will be used for chromatography. An ultraviolet (UV) spectrometer with diode array detection system will be used to obtain three-dimensional plots of wavelength vs. intensity vs. time. Wavelengths scanned will be from 200-400 nm. Five to ten fractions will be collected from the HPLC. These fractions will be taken based on distinguishable peak separation. If this is not possible, fractions will be taken on regular time intervals. The fractions collected will be placed in a probe which is introduced into the MS source of a Kratos MS80 high resolution mass spectrometer. The probe will be heated from 50 °C to 250 °C under vacuum at a heating rate of about 15 °C/min. Mass spectra will be collected at every 2.5 °C temperature interval during heating.

If no sample separation can be accomplished with the Hypersil Green PAH-2 column and the method described above, Penn State will employ a fall-back method, EPA Protocol #610, which is a reverse-phase technique in which the sample will be reconstituted in 50/50 acetonitrile (ACN)/water and a gradient of 50/50 ACN/water to 100% water will be used for the chromatography. Fractions will be collected and analyzed by mass spectrometry as detailed above for the primary method.

The five samples will be supplied to Penn State with the following information, as available: elemental analyses, phenolic -OH concentration, hydrogen classes by ¹H-NMR. Sample size will be at least 1 g. The samples will be filtered process streams or heavy distillates.

The Pennsylvania State University, Executive Summary

We have analyzed a group of coal liquefaction process stream samples using normal-phase separation, two dimensional, high performance liquid chromatography (HPLC) with diode array detection. The general objectives of this work were to evaluate this analytical technique's applicability for the characterization of PAHs in these process streams and to note any differences that could be delineated among the widely varying sample types.

The 2-D HPLC analysis of five samples from coal liquefaction process streams (three from HRI's facility and two from the Wilsonville facility) was carried out and excellent separation of polycyclic aromatic hydrocarbons (PAHs) was obtained for all samples, allowing for identification of components, using off-line heated probe/mass spectrometry, and quantification. This separation of PAHs was attainable due to the inherent properties of a newly available normal-phase HPLC column which is selective to PAHs. Also, using the recently available diode array detection method, we were able to detect components that would have gone undetected using conventional monochromatic HPLC detection techniques.

With separation and identification of components of each sample possible, major differences between samples of differing facilities was noticed, and also significant differences between samples from the same facility could be observed. The differences between facilities is expected since each facility uses different coal liquefaction conditions to obtain liquid hydrocarbon products, and it was not surprising to notice differences between samples from the same facility since different feed coals were used, too. The major differences between facilities in product distributions was that the Wilsonville facility samples, which are 850 °F distillate portions of the whole process stream, tended to contain compounds with generally fewer than five rings and virtually no compounds with more than five rings other than coronene, in contrast to HRI's samples which spanned a larger range of PAHs, including up to nine fused aromatic rings. Generally, samples from the same facility were similar, but important subtle differences could be determined which reflected on process conditions and feed coal. For example, quantitative and qualitative analysis showed that samples liquefied from the Illinois 6 coal appeared to have more of the 5-condensed ring PAHs than samples from the Wyodak coal, consistent with the fact that higher

ranks of coal are more likely to yield more of the higher condensed ring compounds.

Gas chromatography/mass spectrometry also was used to characterize each sample for several reasons: 1) GC/MS was used as a probe to determine what types of components would be expected in the gc amenable range for the HPLC analysis. 2) The two analytical techniques could be compared in order to note any differences. 3) Since the aliphatic portion of the coal liquefaction process stream samples is invisible to uv detection and, therefore, invisible to the HPLC technique, GC/MS allowed for identification and quantification of the aliphatic portion of the samples.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM THE UNIVERSITY OF PITTSBURGH^b

PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), The University of Pittsburgh studied the use of a catalytic dehydrogenation method for determination of the donatable hydrogen content in process-derived samples. A report summary authored by the University of Pittsburgh is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the method for application to coal-derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of this contract.

Summary

This study demonstrated the feasibility of using catalytic dehydrogenation for the examination of direct coal liquefaction process-derived materials. The technique, which was developed for the examination of coals, was applied to the 850 °F^a distillation resids of process stream samples and the tetrahydrofuran (THF)-soluble portion of those resids. Additionally, selected resid samples were silylated to block phenolic -OH groups, then subjected to the catalytic removal of hydroaromatic hydrogen to determine the effect of phenolics on hydrogen evolution and hydrogen transfer ability of the resids. The results of this study indicate that the dehydrogenation method may, with additional development, become a useful tool for the analysis of the process-derived materials.

Methodology

The University of Pittsburgh used a catalytic dehydrogenation technique for the examination of four 850 °F^a distillation resids of process stream samples and the corresponding tetrahydrofuran (THF)-soluble portion of those four resids. In addition, one ash-containing resid and the corresponding deashed resid were silylated to block the phenolic -OH groups, then catalytically dehydrogenated.

^bTierney, J. W.; Wender, I. "Coal Liquefaction Process Streams Characterization and Evaluation, Assessment of Coal Liquefaction Intermediates by Means of Catalytic Dehydrogenation, Topical Report", DOE/PC 89883-87, February 1994.

The samples were obtained originally from the recycle streams of the Wilsonville pilot plant and the HRI Inc. bench unit. Pairs of samples with and without ash and insoluble organic material (IOM) were provided for study of the effects of ash and IOM on the catalytic dehydrogenation results.

Major Findings

The following principal observations for the application of catalytic dehydrogenation to coal liquefaction resid were reported by the University of Pittsburgh.

Two quantities were defined and then measured by the researchers at Pitt. The first quantity, total donatable hydrogen content is defined as the cumulative amount of hydrogen evolved from the resid samples at 150 min in a phenanthridine vehicle at 350 °C with Pd/CaCO₃ as catalyst. It represents all hydrogen that can be evolved, under these conditions, from the hydroaromatic compounds and, as was demonstrated in this study, phenolic -OH groups in the samples. The rate of H₂ evolution also was monitored. The second quantity, hydrogen donor ability, is defined as the cumulative amount of hydrogen transferred to a hydrogen acceptor (stilbene) at 300 min at a lower temperature (248 °C) in quinaldine with Pd/C catalyst. The amount of hydrogen transferred to the stilbene was determined by monitoring the accumulation of bibenzyl in the reaction system by GC/MS. This quantity is expected to represent that amount of hydrogen that is reactive under these conditions with a "coal-like" acceptor. A series of experiments were performed to establish these reaction conditions as optimum for work with direct coal liquefaction resids.

The rate of H₂ evolution varies for all samples studied in the reaction system with Pd/CaCO₃ as catalyst, and phenanthridine as a vehicle. The evolution rate for all samples was greatest at the beginning of the reaction and tapered off at approximately 120 min. At 150 minutes, the total amount of hydrogen evolved from the eight samples varied substantially (from 175 cc/g to 286 cc/g). The evolved hydrogen is between one-third and one-fifth of the initial hydrogen content of the samples.

Pitt compared the hydrogen donor abilities of the resid derived from an Illinois No. 6 coal (Sample 2) and of an Illinois No. 6 coal sample previously determined.

The total donatable hydrogen content of the resid was about 30% higher than that of the starting coal. Pitt interprets this finding to indicate that some of the polycyclic aromatic rings of the coal were hydrogenated to produce the resid in the direct coal liquefaction process. The aromaticities of the samples were determined before (by CONSOL) and after dehydrogenation (by Pitt) using $^1\text{H-NMR}$. The aromatic proton content of the resids increased in each case indicating that hydroaromatic hydrogen was removed in the catalytic dehydrogenation procedure.

The hydrogen donor ability of the eight samples was determined, as defined above. On an absolute basis, the resids were found to donate 5 to 10% of their total hydrogen content to the acceptor. The samples have the following order of donor ability: Ref. 2 > Ref. 4 > Ref. 8 > Ref. 3 > Ref. 1 > Ref. 6 > Ref. 5 > Ref. 7. Samples 2, 4, and 6 are THF-soluble portions of Samples 1, 3, and 5. It was found that on an absolute basis the hydrogen donor ability of the ash- and IOM-containing samples is lower than that of the ash-free samples. Two explanations offered by Pitt are: 1) that the mineral matter ties up the donatable hydrogen, or 2) the mineral matter interferes with the effectiveness of the Pd catalyst. Recalculation of the data on an MAF basis (CONSOL Table A) shows that the absolute differences noted by Pitt are small (e.g., for samples 3 and 4, the difference is less than 5%). This indicates that the ash is a diluent and does not affect the hydrogen evolution.

Blocking the phenolic hydrogen by silylation reduced the amount of total donatable hydrogen, relative to the initial sample (on an absolute basis). The difference in hydrogen evolution between the initial sample and the silylated sample was apparent only after 60 min of reaction. Pitt interprets this to mean that the hydrogen in the phenolic groups is released after the hydroaromatic hydrogen is removed, and thus that the phenolics are poorer hydrogen donors than the hydroaromatics.

CONSOL Evaluation

In this study, the catalytic dehydrogenation technique was explored for use with direct coal liquefaction-derived materials. The researchers at the University of Pittsburgh were able to draw some conclusions on the relative ease of hydrogen donation and hydrogen donor ability of the resids studied. All evaluation was

done by Pitt on values presented on an absolute basis (i.e., cc H₂ per gram of sample).

Recasting those values on a gram hydrogen evolved or reacted with stilbene per gram hydrogen in the sample basis was done using CONSOL elemental analytical data and Pitt's catalytic dehydrogenation data (CONSOL Table A). Many of Pitt's conclusions are supported in this presentation of the data. It is apparent that the presence of ash and IOM in the resid reduces the total donatable hydrogen for all three sets of samples (1 and 2, 3 and 4, and 5 and 6). However, on this basis, the hydrogen donor ability is barely affected by the ash and IOM content. Also, the two HRI samples can be seen to be very different from each other. The sample produced from HRI Run CC-15, in a period of the run when the feed coal was impregnated with an iron catalyst, has a much higher donatable hydrogen content and hydrogen donor ability than a sample produced in a different run at HRI from the same feed coal (Sample 7). Finally, as was pointed out by Pitt, the HRI CC-15 PFL (Sample 8) is seen to have a much higher hydrogen donor ability and donatable hydrogen content than the resid produced from the same feed coal at the Wilsonville facility (Samples 5 and 6).

The data presented on a percent of hydrogen in the resid basis indicate that the resids produced from the Pittsburgh seam coal have a higher hydrogen donor ability and donatable hydrogen content (as a percent of total hydrogen) than the Illinois No. 6 coal-derived resids. This is reverse of the order obtained by evaluating the data on an absolute basis.

The catalytic dehydrogenation data produced in this project suggest that this method can be used to determine the amount of donatable hydrogen in the resids. Differences among samples were distinguishable and they appear to relate to factors such as coal rank, processing facility, and ash content.

The brief investigation of the effect of phenolic -OH on the total donatable hydrogen content indicates that silylation of the phenolic -OH prior to catalytic dehydrogenation reduces by a small amount the total donatable hydrogen (about 10%). When the data are examined on the basis of grams of hydrogen evolved per gram of hydrogen in the sample as phenolic -OH, the reduced amount of evolved

CONSOL TABLE A

Sample Number	Sample Description: Run, Coal, ash or THF-soluble, wt % H ₂ as det. base (a)	Total Donatable H ₂ (Absolute Base), cc H ₂ /g sample (b)	Total Donatable H ₂ (Absolute Base), cc H ₂ /g MAF sample	Total Donatable H ₂ as percent of Resid H ₂ Content, %	Hydrogen Donor Ability (Absolute Base), cc H ₂ /g sample ^c	Hydrogen Donor Ability as percent of Resid H ₂ Content, %
1	Wilsonville 257, Illinois No. 6, ash, 7.33	235	260	28.6	67.7	8.3
2	Wilsonville 257, Illinois No. 8, THF-soluble, 8.15	266	288	31.3	74.3	8.2
3	Wilsonville 259, Pittsburgh seam, ash, 5.95	215	238	32.3	68.9	10.3
4	Wilsonville 259, Pittsburgh seam, THF-soluble, 8.74	248	248	32.5	70.0	9.3
5	Wilsonville 262 B, Wyodak and Anderson, ash, 8.58	175	202	23.7	49.3	6.7
6	Wilsonville 262 B, Wyodak and Anderson, THF-soluble, 8.19	243	248	27.0	81.7	8.7
7	HRI CC-2, P2, Wyodak and Anderson, THF-soluble, 8.16	194		21.2	48.7	5.4
8	HRI CC-15, P3, Wyodak and Anderson, THF-soluble, 7.46	280		31.1	71.3	8.5

a) analysis provided by CONSOL

b) taken from Table 10 (see attached report)

c) taken from Table 12 (see attached report)

hydrogen is more than twice the amount of the phenolic -OH present in the sample. This indicates that the silylation technique may not be optimum for reaction with the resids. However, if it can be assumed that all of the phenolic -OH are silylated, this technique may be useful for investigating the effect of phenolic -OH on catalytic dehydrogenation.

The equipment used in these studies was designed and built at the University of Pittsburgh. It is not commercially available equipment. The time required to perform a single experiment is approximately one day.

Further Development

A catalytic dehydrogenation method for the analysis of direct coal liquefaction resid samples was explored in this project. A number of avenues for further research are suggested by the findings presented here. They are the following: 1) Improved phenolic -OH derivatization techniques, and studies with samples of different phenolic -OH content are recommended to determine the effect of phenolic -OH on the dehydrogenation of the resids which in turn impacts on the mechanism and kinetics of coal liquefaction. 2) A better understanding of the influence of the ash and insoluble organics on the determined hydrogen donor ability and donatable hydrogen content is desirable. 3) Batch microreactor studies using a suite of partially dehydrogenated resids and standard coal could provide information for kinetic and mechanistic modeling. 4) The researchers at Pitt suggest that batch microreactor studies using resids and dehydrogenation catalysts could evaluate catalyst reactivity. 5) Pitt also recommends the use of solid-state NMR spectrometry for analysis of the dehydrogenated resids.

Statement of Work

Optimum catalytic dehydrogenation conditions will be determined with two tetrahydrofuran (THF)-soluble 850 °F distillation resid samples (Sample Nos. 5 and 7). This will be accomplished by varying the solvent, by addition of hydrogen acceptor, and by examining the dehydrogenated resid at different times by NMR. Based on this optimization study, resid samples with Sample Nos. 3, 4, 6, and 8 will be catalytically dehydrogenated. These samples will be monitored for hydrogen evolution and the partially or completely dehydrogenated resid samples will be removed from the reaction flask at various times and examined by NMR. All six samples will be evaluated for the amount of hydroaromatic hydrogen.

The hydrogen donor ability of the resids will be determined and compared. The effect of mineral matter on the efficacy of hydrogen donatability will be determined. If time permits, samples with Sample Nos. 1 and 2 will be studied in the same way. The phenolic -OH groups in two samples will be derivatized to trimethylsilyl ethers. These samples then will be catalytically dehydrogenated to determine the effect of phenolics on hydrogen evolution and the hydrogen transfer ability of the resids.

The samples will be supplied to the University of Pittsburgh with the following information, as available: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by ^1H -NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). The samples are the 850 °F distillation resids of whole process oils obtained from the recycle streams in direct coal liquefaction facilities, and the THF-soluble portion of the 850 °F distillation resids. The resids contain THF-insoluble organic material and ash. Sample size will be 1-10 g, based on availability.

University of Pittsburgh, Executive Summary

Eight well-documented samples obtained from process development units were provided by CONSOL Inc. The plan of this research is to determine donatable hydrogen content and hydrogen donor ability by means of catalytic dehydrogenation and to explore the possibility that catalytic dehydrogenation can be used as an analytical method for determination of the reactivity of DCL resids and to achieve insights into the chemistry of DCL. Optimum catalytic dehydrogenation conditions were determined with two distillation resids. This has been accomplished by varying the dehydrogenation vehicles, by addition of a hydrogen acceptor, and by examining the dehydrogenated resids at different reaction times by ^1H -NMR. Phenanthridine (b.p. 350 °C) was found to be a good high boiling solvent, but quinaldine (248 °C), a low boiling solvent, also was found to be effective, but only in the presence of a hydrogen acceptor. Stilbene, in the presence of quinaldine, is an effective hydrogen acceptor in the catalytic dehydrogenation of the resids at low temperatures. The maximum amount of hydrogen transferred to stilbene was comparable to the amount of hydrogen evolved within 150 min when phenanthridine was used as a vehicle. It appeared that within 150 min the hydrogen that was evolved was hydroaromatic in nature, whereas

beyond 150 min adduction between vehicle and resid became a chief source of hydrogen. Evidence for this was obtained by ^1H -NMR and elemental nitrogen analysis. The amount of hydrogen evolved within 150 min was chosen to represent total donatable hydrogen content.

Based on the optimization studies, resid samples 1, 2, 3, 4, 6, and 8 were catalytically dehydrogenated using both the high boiling vehicle and the low boiling vehicle. The reaction was interrupted at different time intervals to obtain partially dehydrogenated samples which were then characterized by ^1H -NMR. It was found that in time their aromaticity increased considerably. The hydrogen donor ability of these resid samples was determined based on hydrogen transfer ability to a hydrogen acceptor at low temperature. It appeared that samples 2, 4, and 8, THF-soluble resids, should behave as good donor solvents in coal liquefaction.

The effect of phenolic groups on the evolution of hydroaromatic hydrogen was studied. The phenolic -OH groups in two samples were converted to their trimethylsilyl ethers. The phenolic -OH groups did give off hydrogen at 350 °C in phenanthridine. It was ascertained by GC-MS that reaction between -OH and aromatics took place and molecular hydrogen was released from the reaction. It was found that the rate of hydrogen released from -OH groups was slower than from hydroaromatic hydrogen, implying that hydroaromatic hydrogen is more readily donated than phenolic hydrogen.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM THE UNIVERSITY OF DELAWARE^c

PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), The University of Delaware explored the use of a short contact-time batch reactor system to measure the kinetics of direct coal liquefaction resid reactivity. Products of the resid reaction were separated based on solubility and evaluated by thermogravimetric analysis (TGA), gas chromatography (GC), and gas chromatography/mass spectrometry (GC/MS). The following assessment briefly highlights the major findings of the project and evaluates the potential of the method for application to coal-derived resid materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of this contract.

Summary

This study evaluated the use of a novel laboratory-scale batch reactor, designed by the University of Delaware, to study the kinetics of coal liquefaction resid reactivity. The short time batch reactor (STBR) is capable of conducting reactions at temperatures up to 450 °C and pressures up to 2500 psi at well-defined reaction times from a few seconds to 30 min or longer. By the use of very rapid charging and preheating, this equipment avoids the problems of long heat-up and cool-down times associated with equipment traditionally used for such experiments. The small size, and batch nature of the reactor, also allows the running of many experiments over a range of conditions, in a relatively short time. Sixty experiments were conducted with the STBR in this project.

The products of the resid/tetralin/hydrogen reaction were separated by solubility, and several analytical procedures were used to evaluate the reaction products, including thermogravimetric analysis (TGA), gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Changes were monitored in the

^cKlein, M. T.; Calkins, W. H.; Huang, H. "Coal Liquefaction Process Streams Characterization and Evaluation, The Preliminary Evaluation of the Kinetics of Coal Liquefaction Distillation Resid Conversion, Topical Report", DOE/PC 89883-89, February 1994.

boiling ranges of the products, as a function of process conditions (time, temperature, and tetralin donor solvent-to-resid ratio), with and without catalysts. Two distillation resid samples were studied; Sample 1 is the resid of the second stage product stream from Wilsonville Run 259 which used Pittsburgh seam coal (Ireland mine) bituminous coal, and Sample 2 is the resid of the same stream from Wilsonville Run 260 which used Wyodak and Anderson (Black Thunder Mine) subbituminous coal. It was determined that the resid reactivity was different for the two samples studied. The results of this study demonstrate that further development of this experimental method is warranted to empirically assess resid reactivity and to provide data for use in the construction of an empirical model of coal conversion in the direct liquefaction process.

Methodology

The University of Delaware employed two 850 °F distillation resids which contained ash and insoluble organic material (IOM) for this resid reactivity study. Both samples were distillation resids of material produced at the Wilsonville pilot plant and obtained from the atmospheric flash bottoms vessel (V-1067) after the second-stage reactor. The samples are composites of samples taken over long periods of individual processing runs. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration. Run 259 used Pittsburgh seam, Ireland Mine, bituminous coal as feed, and was operated in the catalytic/catalytic reactor mode. Run 260 used Wyodak and Anderson seam coal, Black Thunder mine, subbituminous coal as feed and operated for approximately half the run in a thermal/catalytic reactor configuration (and high/low reactor temperature sequence), and for the remaining half of the run in a catalytic/thermal reactor configuration (and low/high reactor temperature sequence). The resids were reacted with tetralin and hydrogen and the products were analyzed. Reaction variables included time, temperature, solvent/resid ratio, and presence of catalyst. In total, sixty reactions were conducted. Reaction products were separated by solubility in tetralin. Both soluble and insoluble fractions were analyzed by TGA to determine volatile matter (VM), fixed carbon (FC), and ash content. Because ash contents of the products were used to determine the extent of conversion of the resid, it was necessary to correct the ash analyses for samples which contained catalyst.

Major Findings

The following principal observations were reported by the University of Delaware for the exploratory study of a method to determine direct coal liquefaction resid conversion kinetics.

The tetralin-soluble portion of the products was found to contain no ash. This was key to the data analysis because conversion measurements are based on the relative ash contents of the unconverted resid and the conversion products. It was found that in the TGA analysis of the reaction products, slow heating rates resulted in conversion of unreacted resid. In order to avoid resid conversion during the TGA analysis, a relatively high heating rate (10 °C/min) was used.

The percent conversion for the two resid samples was found to be both time and temperature dependent. Lower temperature runs, performed for longer reaction time, approached the same conversions as higher temperature runs performed for shorter reaction times. In catalyzed and un-catalyzed runs, the increase in tetralin-soluble material, as reaction time increased from 0 to 30 min., was different for the two resids studied. For the un-catalyzed system, the difference found for the Run 259 resid (Sample 1) was 1 wt% at 412 °C to 6 wt% at 435 °C, and for the Run 260 resid (Sample 2) 2 wt% at 410 °C to 13 wt% at 434 °C. For the catalyzed case, the differences were found to be 10 wt% at 418 °C and 17 wt% at 435 °C for Sample 1, and 30 wt% at 421 °C and 32 wt% at 442 °C for Sample 2. The ordering of reactivity of the two samples was the same with and without catalyst present. Resid sample 2 was found to be more reactive than resid sample 1.

The TGA evolution pattern for un-catalyzed soluble reaction products showed a bi-modal distribution. The second (higher temperature) peak was not present in the products of the catalyzed runs. Based on the TGA evolution pattern, it was presumed that the average molecular weight of the products was lower in the catalyzed runs. Delaware estimated that as much as 20 wt % of the resid was cracked to compounds volatile enough for detection by GC. However, most of the material that dissolved in tetralin was too low in volatility to be detected by GC and GC/MS analysis; the material that was volatile enough could not be identified. Replication of experimental results by TGA was very good;

characteristic values (volatile matter (VM), fixed carbon (FC), and Ash) were reproduced to within $\pm 0.5\%$, relative.

CONSOL Evaluation

The project goals in this limited study were: 1) to investigate the feasibility of using the STBR to determine the reactivity of coal-derived resids to forming lower boiling products; and 2) To develop and verify an experimental protocol for measuring relative resid reactivity for conversion to lower boiling products using tetralin solvent and a standardized catalyst and coal liquefaction conditions. Both goals were met. Experimental methods were adapted for the introduction of the resids to the reactor system and work-up procedures were altered to provide the best possible reaction monitoring system. An experimental protocol was developed to determine the relative amount of conversion of the resid, unhampered by the catalyst content of the reaction mixture. Reproducible data were obtained over a large matrix of reaction conditions, demonstrating the versatility of the technique.

The STBR was designed and built at the University of Delaware. It could be reproduced for about \$6000. The TGA used in this study costs about \$20,000. The GC and GC/MS systems cost \$25,000 and \$45,000, respectively.

Further Development

Some avenues for further development of this technique lie in improvement of the work-up procedures. In this study, solubility was used to measure the degree of resid conversion. As "resid" is defined by boiling point in plant operations, it is recommended that the resid conversion be monitored by analyzing the boiling point distribution of reaction products instead of solubility properties. This could be achieved by employing micro-distillation procedures or methods which can provide equivalent values such as TGA techniques.^d

Additionally, adding to the TGA, GC, and GC/MS analyses would enhance the potential for this method to provide chemical information that could be incorporated in an empirical model of resid conversion and reactivity. The

^dRobbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "Coal Liquefaction Process Stream Characterization and Evaluation, Technical Progress Report, October 1 Through December 31, 1993", DOE/PC 89883-86, February 1994.

following analytical procedures are suggested by the researchers at the University of Delaware for this purpose: 1) Thermogravimetric analysis followed by analysis of the effluent of the TGA by mass spectrometry and Fourier transform infrared spectrometry (TGA/MS/FTIR); 2) Vacuum TGA to analyze the volatile products of the reaction; 3) Vapor phase osmometry (VPO), gel permeation chromatography (GPC), or field ionization mass spectrometry (FIMS) for determination of the molecular weight distribution of the resid reaction products; or alternatively, 4) pyrolysis-mass spectrometry (PyMS) for the same purpose.

Statement of Work

Two different resid samples containing known ash contents will be selected by CONSOL. Reactions will be carried out in tetralin with hydrogen atmosphere at two selected concentrations (2:1 and 3:1 of tetralin-to-resid ratios) and run at 775 and 825 °F at least two reaction times (5 and 30 min). Hydrogen pressures of 1500 psi or, if possible, up to 2000 psi will be used. The same reactions will be run under the same conditions in the presence of catalyst supplied by CONSOL at a catalyst to resid ratio to be selected. In addition, a few selected runs will be made at other temperatures and concentrations to allow reasonable estimation of reaction order and the kinetic parameters (activation energy and frequency factor).

After each reaction is completed, a sample of the collected products will be analyzed by TGA with fast temperature ramp rates to determine the 975 °F resid and high temperature ash contents. Resid conversion will be calculated on the basis of the 975 °F resid content of the feedstock (as determined by TGA) and that of the reacted products. This conversion also will be compared with the resid-to-ash ratio of the feedstock and the reacted products.

The liquid reaction products will then be stripped of tetralin and other low boiling compounds in a Rotavapor. The low boilers removed in the Rotavapor will be analyzed by GC/MS for naphthalene, methylindan, benzene and other lower boiling products. The stripped product will be taken up in methylene chloride and again analyzed by TGA at a slow (5 °C/min) temperature ramp rate to determine the amount of resid which has been converted both to lower boiling products and to higher boiling retrograde products. The use of methylene chloride is an aid

to transfer the liquid from the Rotavapor, since we have found that a slow temperature ramp rate in the presence of tetralin results in further reaction during the TGA analysis, whereas there is no such effect of methylene chloride on the TGA analysis.

A kinetic analysis of the reactions may not be straightforward, since resid is a very complex mixture, both low and high boiling materials are likely to be formed and some gases and very low boiling products may also result. An effort will be made to develop a simple treatment of the data based on the reduction of the high boiling (over 524 °C or 975 °F) fraction based on TGA, with calculation of the kinetic parameters (activation energies and exponential factors).

University of Delaware, Executive Summary

By the use of a novel short-contact-time-batch reactor (STBR), a special product work-up procedure, and thermogravimetric analysis (TGA), a method has been developed to measure the reactivity (kinetics) of coal-derived vacuum resids toward conversion to low molecular weight more processible fuel materials. Gas chromatography and GC/MS also were used to examine the lower boiling products. This technique is designed to provide information concerning the behavior of these resids on recycling in a coal liquefaction process.

Only two resids from the Wilsonville plant derived from a bituminous and a subbituminous coal have been studied thus far, showing somewhat different conversion reactivities. Little conversion of these resids was observed under coal liquefaction conditions without a catalyst. With the use of a Ni/Mo on alumina catalyst, significant conversion is observed, although only about 20 wt % of the resid was converted to gasoline and diesel boiling ranges under the times and conditions studied. The rest of the resid showed a breakdown into soluble and somewhat lower molecular weight materials, but ones requiring further processing to be useful liquid fuel materials.

The tetralin-soluble portion of the unreacted resids studied showed a bimodal distribution of evolution rates (TGA). When reacted in the presence of the Ni/Mo on alumina catalyst, however, the high temperature peak disappears, and the low temperature peak shifts to still lower temperatures, indicating a breakdown of the resid structure.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM SRI INTERNATIONAL^e PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), SRI International analyzed selected direct coal liquefaction-derived materials by field ionization mass spectrometry (FIMS). A summary of the final report authored by the SRI researchers is presented here. The following assessment briefly highlights the major findings of the project, and describes how FIMS can provide information about the complex chemistry inherent in the conversion of coal to liquid products. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal derived materials, and the potential impact of the use of these methods on process economics, at the conclusion of this contract.

Summary

This study was designed to apply the method of field ionization mass spectrometry (FIMS) for the analysis of direct coal liquefaction process-stream samples. The FIMS method was shown to have a high potential for application to direct coal liquefaction-derived samples in a Phase I project in this program.^f In this Phase III project, the FIMS method was applied to a set of samples produced in HRI bench-scale liquefaction Runs CC-15 and CC-16. FIMS was used to obtain the molecular weight profile of the samples and to identify specific prominent peaks in the low end (160-420 Da) region of the molecular weight profile. In the samples examined in this study, species were identified which previously were recognized as precursors to the formation of high molecular weight structures associated with the formation of coke in petroleum vacuum gas oils.

^eMalhotra, R.; McMillen, D. F. "Coal Liquefaction Process Streams Characterization and Evaluation, FIMS Analysis of Direct Coal Liquefaction Process Streams, Topical Report", DOE/PC 89883-91, March 1994.

^fMalhotra, R.; McMillen, D. F. "Coal Liquefaction Process Streams Characterization and Evaluation, Characterization of Coal Liquids by Field Ionization Mass Spectrometry and Iodotrimethylsilane Derivatization, Topical Report", DOE/PC 89883-39, January 1992.

Methodology

SRI used field ionization mass spectrometry (FIMS) to analyze a set of eighteen process stream samples from HRI CTSI bench unit Runs CC-15 and CC-16. Five of the samples analyzed were filtered process liquids (PFLs). Three samples were viscous process streams obtained from the first-stage internal recycle loop. These samples, designated as "Interstage", contain ash and insoluble organic material (IOM). Five samples were pressure filter cakes (PFCs) which contain approximately 50% soluble organic material and 50% ash and IOM. Five samples were light distillates produced by blending the atmospheric still overhead (ASOH) and separator overhead (SOH) materials. The eighteen samples were supplied to SRI with the following analytical information, as available: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, and hydrogen classes by $^1\text{H-NMR}$. FIMS spectra were recorded from 48 to 1400 Da. Final ion source conditions were 500 °C and 10^{-6} torr. At such conditions, materials with atmospheric equivalent boiling points (AEPB) up to 1400 °C are expected to vaporize completely and materials with AEBPs up to 1600 °C are expected to vaporize at least partially.

Major Findings

The following principal observations for the application of FIMS to coal liquefaction materials were reported by SRI.

All samples examined gave broad, smooth molecular weight profiles. The distillate sample spectra were confined to the 100 to 300 Da molecular weight range; the other process samples exhibited a molecular weight range of 200 to 1200 Da. The intensity vs molecular weight profiles, excluding those of the distillates, were bimodal in form. No attempt was made to deconvolute the profiles. Chemical structures were assigned to prominent peaks in the 165 to 420 Da range of the FIMS profile. These structural assignments correspond closely to those obtained by other workers with petroleum vacuum gas oils.⁹ They include the compounds identified in Wilsonville two-stage liquefaction resids, which were examined by SRI in a Phase I project in this program.^f

⁹Sullivan, R. F.; Boduszynski, M. M.; Fetzer, J. C. *Energy and Fuels* 1989, 3, 603.

Evidence presented indicates that simple volatilization, not thermal decomposition, is the mechanism for transference of samples from the mass spectrometer inlet to the ionization chamber in the FIMS analysis. SRI reports that the solids-free distillates and PFL samples were 100% ($\pm 5\%$) volatilized and detected, whereas only 44 to 100% ($\pm 5\%$) of the solids-containing PFC and INT samples were volatilized. Thus, the FIMS spectra of the INT and PFC samples may reflect a disproportionate amount of lower molecular weight species than the fully volatilized PFL and ASOH/SOH sample spectra. In addition to the lack of full volatilization, the PFC samples were difficult to sample accurately because of the presence of a lighter oil, possibly filter wash oil.

SRI established that the sum of the odd mass intensities, as a fraction of the sum of the even mass intensities, correlated with the nitrogen content in the sample. This correlation corroborates other evidence presented by SRI that very little fragmentation occurs in the FIMS analysis.

The influence of process conditions on the molecular weight profiles was examined. The weight average molecular weights (M_w) for each sample were compared by run period. The effect of increasing reactor temperature in Run CC-16 between periods 5 and 13 resulted in a decreased M_w of both the PFL and PFC samples, and an increased concentration of suspected coke precursors. Although the process distillate yield increased with the elevated reactor temperature, the resid was more refractory (based on CONSOL solvent quality data and proton NMR analyses) with a higher percentage of coke precursors (as determined by FIMS). In both HRI runs, the liquefaction process distillate yield was found to correlate inversely with the weight average molecular weight of the PFL samples. The effects of additional process conditions on the properties of the samples from Run CC-15 also were examined. SRI concludes that because there is no clear evidence of nitrogen incorporation in the FIMS spectra of Run CC-15 samples from Periods 8 and 14 (when a dispersed iron catalyst was impregnated in the feed coal using an ammonium nitrate as a participation agent), the elevated N content (determined by CONSOL) in the samples is due to incorporation of ammonia or an amine of MW <48 Da.

CONSOL Evaluation

FIMS was shown to be useful for the analysis of direct coal liquefaction samples in Phase I of the Participants Program. In this Phase III project, FIMS was applied to eighteen samples from two direct coal liquefaction tests. SRI interpreted the FIMS results in the context of the coal liquefaction run conditions.

The speciation of the lowest molecular weight peaks in the FIMS profile provides some important clues to the fundamental chemistry involved in coal processing. It is likely not coincidental that the same compounds are found in other fossil fuel derived materials (such as petroleum vacuum gas oils), and it is probable that these compounds, as coke precursors, are indicators of resid reactivity. FIMS appears to be an excellent tool to detect and monitor these materials in process stream samples.

In this project, SRI demonstrated that very little thermal decomposition occurred in the probe and very little ion fragmentation occurred in the FIMS analysis; thus, the distribution of molecular weights is representative of the volatilized sample. SRI's results indicate that the molecular weight profiles obtained in this work are not significantly distorted because of the lack of complete sample volatility. This issue was unresolved at the conclusion of the Phase I project; this work resolved this issue and shows that FIMS can be successfully applied to coal-liquefaction samples in support of process development. The capital investment for FIMS equipment is approximately \$250,000. Operating cost are about \$40 per sample. It requires 1.5 to 3 hours for sample preparation and analysis.

Further Application

There are a number of avenues for further application of FIMS for coal liquefaction materials. The correlation drawn between the nitrogen contents of the samples and the FIMS odd-mass profile may be useful for examining hydrodenitrogenation (HDN) in process-derived samples. Examination by FIMS spectra of samples with a wide range of nitrogen contents may be useful. The use of a curve fitting routine may provide further insight into the subtlety of shifts in the molecular weight distributions attributable to processing conditions. Additional investigation of process derived samples for compounds

(those which are considered coke precursors) in the lower molecular weight range of the FIMS profile will provide information useful for kinetic and mechanistic modeling of the coal liquefaction process.

SRI suggests several lines of research derived from this work. All are related to further examining the role of the suspected coke precursors identified here in coke formation.

Statement of Work

The FIMS technique will be used to analyze eighteen samples obtained by CONSOL from the HRI Inc. bench-scale liquefaction unit. The eighteen samples will be supplied to SRI with the following information, as available: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by ¹H-NMR. Sample size will be at least one gram. Five samples will be filtered process streams, three samples will be viscous process streams which contain ash and insoluble organic material (IOM), five samples will be filter cakes which contain approximately 50% soluble organic material and 50% ash and IOM, and five samples will be light distillates.

SRI International, Executive Summary

Under a subcontract with CONSOL Inc., SRI International performed field ionization mass spectrometric (FIMS) analysis of 18 coal liquefaction process stream samples. These samples came from liquefaction of a Black Thunder and an Illinois 6 coal at HRI in HRI's two-stage ebullated-bed bench unit 227. The samples covered a wide range of distillability and solubility; they included whole interstage liquids, pressure filtered liquids, filter cakes, and atmospheric still distillates. The primary objective of the FIMS analysis was to provide additional composition data about these samples, including changes that result from differing conditions in different run periods. Of particular interest was compositional information related to factors affecting resid reactivity. Analysis of these samples follows on SRI's earlier FIMS analyses, under this same program, of process stream samples from the Wilsonville liquefaction pilot plant. In this report we will repeatedly make reference to these earlier samples.

FIMS analysis was found to give reliable and reproducible data for distillates and for filtered liquid samples. We experienced difficulty in getting reproducible spectra with pressure filter cake samples. The problem was attributed to the fact that these samples retain varying amounts of soluble wash oils in the insoluble matrix. An examination of the thermal evolution of various peaks in the FI mass spectra revealed that during FIMS analysis volatiles were released purely by evaporation with very little thermal decomposition in the probe. We also observed that the liquids in these samples were essentially 100% vaporized (i.e., 95% or higher with a 5% error limit); the materials insoluble in the process stream or in the wash oil were vaporized from ~50% to 80%.

The HRI process whole oil or filter cake samples showed broad, smooth, molecular weight profiles ranging from 200 to 1200 Da. The distillate samples spanned a MW range of 100 to 300 Da. As in the case of Wilsonville liquefaction resid, the HRI whole oils tended to show a bimodal distribution of molecular weights. However, in the present study, we did not perform mathematical deconvolution to quantify the relative amounts of the two components. Such an exercise could provide useful input for lumped kinetic modeling of coal liquefaction. An inverse correlation was observed between the distillate yield of the process in the various periods and weight-average molecular weight (M_w) of the PFL samples produced in those periods. Also, we found that the sum of odd mass intensities as fraction of the sum of all ion intensities correlated with the nitrogen content of the sample. This correlation reiterates the absence of fragmentation during FIMS analysis, and provides a means of assessing HDN activity with FIMS.

As with the Wilsonville samples analyzed earlier, these HRI samples exhibited certain prominent peaks in the lower molecular weight edge of the mass spectra. These peaks correspond to specific analogs of dihydrophenalene (phenelan) that have been previously implicated as coke precursors in petroleum-derived vacuum gas oils. Interestingly, these components tended to be more abundant in oil samples with high insolubles content. These findings suggest that FIMS can be a useful tool in a systematic effort to monitor and elucidate the chemistry in the build up of coke precursors.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM THE UNIVERSITY OF UTAH^h

PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), The University of Utah applied the technique of ^{13}C -nuclear magnetic resonance (NMR) spectrometry to the analysis of selected, direct coal liquefaction-derived materials. A summary of the final report authored by the University of Utah researchers is presented here. The following assessment briefly highlights the major findings of the project, and describes the application of ^{13}C -NMR to provide information on the complex chemistry inherent in the conversion of coal to liquid products. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials and the potential impact of the use of these methods on process economics at the conclusion of this contract.

Summary

This study was designed to apply ^{13}C -nuclear magnetic resonance (NMR) spectrometry to the analysis of direct coal liquefaction process-stream materials. ^{13}C -NMR was shown to have a high potential for application to direct coal liquefaction-derived samples in Phase II of this program.ⁱ In this Phase III project, ^{13}C -NMR was applied to a set of samples derived from the HRI Inc. bench-scale liquefaction Run CC-15. The samples include the feed coal, net products and intermediate streams from three operating periods of the run. High-resolution ^{13}C -NMR data were obtained for the liquid samples and solid-state CP/MAS ^{13}C -NMR data were obtained for the coal and filter-cake samples. The ^{13}C -NMR technique is used to derive a set of twelve carbon structural parameters for each sample (CONSOL Table A). Average molecular structural descriptors can then be derived from these parameters (CONSOL Table B).

^hPugmire, R. J.; Solum, M. S. "Coal Liquefaction Process Streams Characterization and Evaluation, Analysis of Black Thunder Coal and Liquefaction Products from HRI Bench Unit Run CC-15, Topical Report", DOE/PC 89883-90, February 1994.

ⁱSolum, M. S.; Pugmire, R. J. "Coal Liquefaction Process Streams Characterization and Evaluation, ^{13}C -NMR Analysis of CONSOL THF-Soluble Residual Materials from the Wilsonville Coal Liquefaction Process, Topical Report", DOE/PC 89883-65, November 1992.

CONSOL EVALUATION TABLE A
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^r	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		

CONSOL EVALUATION TABLE B
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; $\text{MW} = (\text{Cx}12.01)/(f_a \times \%C/100)$
P_O	fraction of intact bridges; $P_O = \{f_a^P + f_a^S - f_{al}^*\} / \{f_a^P + f_a^S\}$	M_s	average molecular weight per attachment

Methodology

The University of Utah used ^{13}C -NMR spectrometry to analyze one coal sample and a set of 12 process-stream samples from the HRI Inc. bench unit Run CC-15 (also known as HRI Run 227-75). The samples included the feed coal and the major products and intermediate process streams from three run conditions (2, 3, and 4) which include run periods 8, 11, and 14, respectively. Three samples are filtered process liquids (PFLs); three samples are viscous process streams, designated "Interstage", obtained from the first-stage internal recycle loop that contain ash and insoluble organic material (IOM); three samples are pressure filter cakes (PFCs) which contain approximately 50% ash and IOM; three samples are light distillates, produced by blending the atmospheric still overhead (ASOH) and separator overhead (SOH) materials; and one sample is the feed coal for Run CC-15, Wyodak and Anderson seam, Black Thunder mine, subbituminous coal. The thirteen samples were supplied to Utah with the following analytical information, as available: elemental analyses, ash content, ash elemental analysis, phenolic - OH concentration, calorific value, and hydrogen classes by ^1H -NMR.

High-resolution ^{13}C -NMR spectra were obtained for the liquid samples (using inversion-recovery and quantitative techniques) and solid-state cross-polarization/magic angle spinning (CP/MAS) ^{13}C -NMR spectra were obtained for the coal and filter-cake sample. Bloch decay experiments were attempted on one filter-cake sample. Distortionless-enhanced proton transfer (DEPT) ^{13}C -NMR and quantitative ^1H -NMR spectra also were obtained for one liquid sample.

Major Findings

The following principal observations from the application of ^{13}C -NMR spectrometry to coal liquefaction materials were reported by Utah.

The molecular structural information, obtained from high resolution ^{13}C -NMR studies on the nine liquid samples, was used to identify three major structural reactions; ring protonation, ring opening and ring dealkylation. The aromaticity of the samples, degree of substitution, and the length of side chains for samples obtained from different locations in the liquefaction plant was obtained from the ^{13}C -NMR spectra and the derived parameters.

Analyses of the PFC samples proved to be problematic. These solid samples, under the conditions of the cross polarization (CP) analysis, released an oily component which could not be contained in the rotor spinning at 4100 Hz. This non-solid component could not be quantitatively detected in the CP experiment because of the occurrence of motional averaging of the dipolar interaction required for polarization. In a Bloch decay experiment on a single sample, it was determined that this oily component of the PFC sample was more aliphatic in character than the remaining solid material. However, in the Bloch decay experiment there was a broad probe background which could not be suppressed. Because of the problems associated with the presence of the oily component in the PFC samples, ^{13}C -NMR data obtained on the PFC samples should be used only for qualitative purposes.

A low signal in the NMR spectral region associated with bridgehead carbon for the ASOH/SOH samples, led to the assumption that these materials contain structures with, on average, only one 6-membered aromatic ring. However, the average cluster size of the PFL and interstage samples (8-12 aromatic carbons per 100 carbons) is only slightly smaller than that of the starting coal (13 aromatic carbons per 100 carbons).

The carbon aromaticity (f_a') of the PFL samples increased as the run proceeded, presumably due to second-stage catalyst aging. The carbon aromaticity of the interstage samples increased slightly in the later run periods. Although the samples are slightly more aromatic, the ring carbons in the interstage samples are more protonated in the later run periods, indicating an increasing degree of hydrogenation. The PFL samples, while more aromatic in run period 11 than in run period 8, show a lower degree of aromatic carbon hydrogenation (f_a^H/f_a') in run period 11. This may indicate that in the absence of the dispersed iron oxide catalyst (run period 11) condensation reactions were more prominent in the second stage at the expense of hydrogenation reactions. The interstage samples show the reverse behavior in the percent of protonated aromatic C. In run period 11, they have a higher f_a^H/f_a' than in run period 8, indicating that in the absence of the iron oxide catalyst side chains are cleaved, the size of the clusters decreases, the number of aromatic carbons per cluster decreases, and hydrogenation of the ring occurs.

The number of carbons per side chain for the interstage samples is similar to the starting coal (on the order of two). The PFL samples early in the run (period 8) show a large increase from the feed coal in the number of carbons per side chain, which may be indicative of ring opening reactions. In later run periods this value was lower, possibly as a result of decreasing second-stage catalyst activity. The long side chains on the ASOH/SOH samples (5.0 ± 0.5 , 4.5 ± 0.4 , and 6.0 ± 0.7 per side chain for the three samples examined are believed to arise from ring opening reactions.

CONSOL Evaluation

Utah presented the information obtained from the nine liquid process-stream samples by categorizing the samples by time and by sampling location. The combination of information available about the process conditions, process yield data, analytical data obtained from other analytical methods, and the data derived in this project allows for a cursory description of the chemical mechanisms of coal conversion in the liquefaction process.

Experimental problems associated with the PFC samples can be resolved in further work by washing the sample of the oily component and analyzing the soluble and insoluble fractions separately.

The precision of the two ^{13}C -NMR solution techniques (inversion-recovery and quantitative ^{13}C -NMR) used to analyze the nine liquid samples is high; measurements are highly reproducible. The inversion-recovery technique requires 48 hr acquisition time per sample and the quantitative ^{13}C -NMR method required 15-20 hr total acquisition time per sample. The four solid samples (three PFC's and the coal) were examined by solid-state ^{13}C -NMR techniques. The experimental time required for the solid sample is on the order of two days per sample to complete both the variable contact time and dipolar dephasing experiments. The 100 MHz instrument used for solid state experiments in this study costs approximately \$200,000, the 500 MHz instrument used for the liquid samples costs about \$500,000.

Further Application

Continued application of ^{13}C -NMR spectrometry to provide a set of carbon structural parameters and average molecular structural descriptors for process

samples is recommended. Not only will additional data increase our chemical understanding of the nature of coal-derived materials, these data can be used to surmise the general mechanism of direct coal-liquefaction reactions. It is recommended that an expanded suite of coal liquefaction samples be examined by this method, including process stream samples and the corresponding feed coals. The structural parameters developed for the process samples can contribute to the development of a comprehensive model of coal liquefaction.

Statement of Work

The CP/MAS ^{13}C -NMR technique will be used to analyze one coal sample and three process-derived solid samples obtained from the HRI Inc. bench unit. From this analysis, the Utah researchers will derive a set of twelve carbon structural parameters for each sample. These twelve parameters will include: fraction of aromatic carbon, fraction of carbonyl carbon, fraction of protonated aromatic carbon, fraction of non-protonated aromatic carbon, etc. (see Solum et al.¹ for a full list of the twelve parameters). Average molecular structural descriptors will then be derived from these parameters. These descriptors will include: mole fraction of bridgehead carbons, aromatic carbons per cluster, number of attachments per cluster, molecular weight per cluster, etc. (see Solum et al.¹ for a full list of these eight descriptors). Nine liquid samples will be analyzed by four consecutive methods: quantitative ^1H -NMR, quantitative ^{13}C -NMR, a proton-carbon correlation experiment (HETCOR), and relaxation experiment. These four experiments will provide structural information (similar to the solid samples) for the liquid samples. The thirteen samples will be supplied to the University of Utah with the following information as available: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by ^1H -NMR. Sample size will be at least 5 g. Three samples will be filtered process streams, three samples will be viscous process streams which contain ash and insoluble organic material (IOM), three samples will be filter cakes which contain approximately 50% soluble organic material and 50% ash and IOM, three samples will be light distillates, one sample will be coal.

University of Utah, Executive Summary

In an effort to gain insight into changes that occur at the molecular level in coal liquefaction, detailed ^{13}C -NMR studies were carried out on a selected set

of samples provided by CONSOL Inc. personnel. In an initial study conducted in 1992, a detailed solid state ^{13}C -NMR study was conducted on a set of 11 THF-soluble resid samples obtained from direct liquefaction processing streams at the Wilsonville facility. Structural parameters were derived that were used to characterize the carbon skeletal structure and functional group distribution of the selected resid samples. In the context of our initial study and recommendations, CONSOL Inc. carefully selected a set of process products obtained from a single coal. The sample set consisted of the starting coal (Wyodak and Anderson seam, Black Thunder Mine, subbituminous), 3 filter cakes and 9 coal-derived liquid products. The liquids were collected at different stages of the process (HRI bench unit Run CC-15). High resolution ^{13}C -NMR data were obtained on the liquid samples and solid state NMR data were obtained for the parent coal and filter cake samples. A complex analysis of the liquid samples was made in order to extract as much information as possible from the rich set of data made available for this study.

The data obtained on the liquid samples studied provides a complex set of parameters. Three major types of structural reactions can be identified from the NMR data, ring protonation, ring opening, and ring dealkylation. It also appears that differences can be found in the rates of these reactions that occur in the two stages of the reactor. In the first processing stage, the interstage liquid samples exhibit a small increase in aromaticity (relative to the parent coal), but it is not evident that the catalyst used has any effect on the aromaticity. The pressure filter liquids, on the other hand, exhibit marked differences in aromaticity that may be related to catalyst and aging effects. Changes in aromaticity can occur in two different ways; ring protonation or loss of sp^3 carbons by a wide variety of dealkylation or cracking mechanisms. The significant increase in the presence of protonated aromatic carbon observed in the PFL and INT samples can occur only if ring protonation reactions occur in both stages of the process. Data are obtained which suggest that both hydrogenation and dealkylation reactions have occurred in both stages of the process. From a consideration of data on the side chain length (with respect to the parent coal), it appears that extensive ring opening reactions have occurred in both stages of the process, particularly in the PFL liquids obtained downstream from the second stage of the reactor.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM THE NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH¹

PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), IIT Research Institute, National Institute for Petroleum and Energy Research (NIPER) applied a suite of petroleum inspection tests to two direct coal liquefaction, net product oils produced in two direct coal liquefaction processing runs. Two technical reports, authored by NIPER, are summarized here. The following assessment briefly describes the two coal liquefaction runs and highlights the major findings of the project. It generally is concluded that the methods used in these studies can help define the value of liquefaction products and the requirements for further processing. The application of these methods adds substantially to our understanding of the coal liquefaction process and the chemistry of coal-derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of this contract.

Background

Regardless of the specific technology used to produce transportation fuels from coal, at least some portion of the net product of the liquefaction process will have to undergo additional refining to make finished products. The presence of an on-line hydrotreater will minimize further refining requirements of the total products. However, there is a need to characterize that portion of the material leaving the liquefaction plant as net product and going to the refinery as feed. In addition, correlations drawn between operating variables of the liquefaction and finishing processes and net product characteristics will be extremely useful in directing future production efforts. It also is necessary to obtain accurate estimations of upgrading costs to produce specification fuels. Although it is acknowledged that the standard petroleum inspection tests are not tailored for the analysis of coal liquids, it is believed that they are the best starting point for this analysis currently available.

¹Sturm, G. P., Jr.; Kim, J.; Shay, J. "Coal Liquefaction Process Streams Characterization and Evaluation, Analysis of Coal-Derived Synthetic Crude from HRI CTSL Run CC-15 and HRI Run CMSL-2, Topical Report", DOE/PC 89883-92, January 1994.

It was recommended in CONSOL's Analytical Needs Assessment^k that standard petroleum tests be performed on coal liquefaction syncrudes to assess the applicability of those tests. Therefore, in a directed attempt to meet this particular analytical need, standard petroleum inspection tests were performed on products of the Wilsonville pilot plant^{l,m} and, as described herein, on products of the HRI Inc. bench unit.

Processing Runs and Samples

Two separate studies were conducted by NIPER, both are summarized here. The first study was performed on the net product oil of HRI bench unit Run CC-15. The second study was performed with HRI bench unit CMSL-2 net product oil. The net product oil from HRI Run CMSL-2 was chosen for study because this run is considered to be representative of state-of-the-art direct coal liquefaction technology. It should be noted that, in both bench unit runs, some low-boiling material was lost during product collection and sampling. Thus, the lowest boiling components are artificially depleted somewhat in the samples analyzed here.

Run CC-15

The objective of HRI's CTSL Run CC-15, also called Run 227-75, was to test a predispersed (impregnated) hydrated iron oxide catalyst. The feed coal was Wyodak and Anderson seam, Black Thunder Mine, subbituminous coal. Start-up and make-up oil for Run CC-15 was filtered process-derived liquid, produced in HRI Run 260-03, which also used Black Thunder Mine coal. Throughout Run CC-15 the first stage reactor was operated thermally; Shell S-317 Ni/Mo on alumina catalyst was present in the second-stage reactor. No on-line hydrotreater was used in the

^kBrandes, S. D.; Robbins, G. A.; Winschel, R. A.; Burke, F. P. "Coal Liquefaction Process Streams Characterization and Evaluation, Analytical Needs Assessment, Topical Report", DOE/PC 89883-18, March 1991.

^lKramer, R. L. "Modified Light Oil, Southern Clean Fuels Inc.-Coal Liquefaction Material, Sample Number C9034, Research Report" in "Coal Liquefaction Process Streams Characterization and Evaluation, Technical Progress Report, October 1 through December 31, 1990", DOE/PC 89883-24, June 1991.

^mKramer, R. L. "Modified Light Oil, Southern Clean Fuels Inc.-Coal Liquefaction Material, Sample Number C90116, Research Report" in "Coal Liquefaction Process Streams Characterization and Evaluation, Technical Progress Report, July 1 through September 30, 1991", DOE/PC 89883-24, November 1991.

run. The net product sample analyzed in this subcontract was produced by compositing a total of 26 sample aliquots obtained during the run from the separator overhead (SOH) process stream and the atmospheric still overhead (ASOH) process stream.

Run CMSL-2

The main objective of HRI's Run CMSL-2, also called Run 227-78, was to investigate the effect of a high coal concentration on process performance. The higher coal concentration in the coal-solvent slurries was accomplished by lowering the solvent-to-coal ratio from 1.2 (to as high as 1.6) used in previous bench-scale runs, to a value of 0.9 in Run CMSL-2. The feed coal was Illinois No. 6, Burning Star 2, bituminous coal. Throughout Run CMSL-2, the first- and second-stage reactors were operated catalytically; Shell S-317 Ni/Mo on alumina catalyst was present in both reactors. No on-line hydrotreater was used in the run. The net product sample analyzed in this subcontract was produced by compositing a total of 10, one-half gallon sample aliquots obtained during periods 8 through 12 of the run from the separator overhead (SOH) process stream and the atmospheric still overhead (ASOH) process stream.

Overview of Results

Run CC-15

The methodology employed was to analyze the whole net product sample, which in Run CC-15 was a blend of the SOH and ASOH from Conditions 2, 3, and 4. The whole sample was fractionated into four distillation cuts; naphtha (IBP-380 °F), kerosene (380-510 °F), diesel (510-650 °F), and resid (650 °F+). Each of the straight-run fractions was inspected using an appropriate suite of methods. The naphtha and kerosene fractions then were caustic washed for the removal of phenolic compounds. The washed fractions were then re-tested.

The coal liquid product quality was assessed by comparison of the physical and chemical property test data for the distillation fractions (IBP-380 °F, 380-510 °F, and 510-638 °F) to the corresponding specifications for gasolines, aviation turbine fuels, diesel fuels or fuel oils, respectively. The properties of the net product oil and its distillate fractions show that the coal-derived material has many desirable qualities. The whole crude has low sulfur, metals, ash and resid contents and boils below the maximum temperature allowed for the

production of transportation fuels. The naphtha fraction (IBP-380 °F), which represents 40% of the net product, is highly naphthenic and has a low benzene content. The naphtha fraction appears to be amenable to mild hydrotreating to produce a good gasoline blendstock or reformer feedstock. The kerosene (380-510 °F) fraction, which represents 33% of the net product, is too cyclic for use as aviation fuel and it is recommended that this fraction be distributed into the two cuts on either end of it (diesel and gasoline feedstocks). The 510-680 °F fraction, which represents 22% of the net product, met most specifications as a diesel fuel and heating fuel, although its cetane index would need to be boosted for premium diesel fuel use. Caustic washing removed 2% and 4% phenolics from the naphtha and jet fuel fraction, respectively, and provided minor improvements in the qualities of the washed fractions.

Run CMSL-2

The methodology used was to analyze the whole sample from Run CMSL-2 and then to fractionate it into four distillation cuts; naphtha (IBP-350 °F), kerosene (350-400 °F), diesel (400-550 °F), and resid (>550 °F). Each of the straight-run fractions was inspected using an appropriate suite of methods. A portion of the kerosene fraction was caustic washed for the removal of phenolic compounds and the washed fraction was then re-tested.

As in the previous case, the coal liquid product quality was assessed by comparison of the physical and chemical property test data for the distillation fractions to the corresponding specifications for gasolines, aviation turbine fuels, diesel fuels or fuel oils. This syncrude has many desirable properties. It is a low-sulfur crude that is nearly free of metals, ash and resid. The naphtha fraction (IBP-350 °F), which represents 25% of the crude, met a number of the specifications for gasoline. This material would be an acceptable feedstock for a catalytic reformer if the olefin content were reduced by mild hydrotreating. The biggest deficiency with the kerosene fraction (350-400 °F), which represents 6% of the crude, for use as an aviation turbine fuel is its high aromatic content; aromaticity affects combustion performance. Hydrogenation should improve its properties. However, the severity of hydrotreating necessary to make acceptable aviation jet fuel may not be economically favorable. It is recommended that this low-sulfur kerosene fraction, instead, be distributed into the cuts on either end of it (diesel and gasoline feedstocks). The 400-550 °F

fraction, which represents 35% of the crude, meets most of the specifications for diesel fuel and heating fuel. The cetane number would need to be boosted for use as a premium diesel fuel. The >550 °F fraction, which represents 34% of the crude, met most specifications for No. 4 heating oils, and many specifications for lighter grade heating fuels.

CONSOL Evaluation and Recommendations

Although it is acknowledged that the petroleum inspection tests were not designed for analysis of coal liquids, these tests provide the best available method for evaluation of the quality and value of the direct coal liquefaction product oils. The properties of the net product oils and the distillation fractions were shown in this work to have many desirable qualities. Verification of the suitability of these tests for coal liquids would be advantageous. It is our recommendation that test programs such as these be applied more frequently to the products of ongoing process development programs. This would provide guidance for process improvement efforts.

National Institute for Petroleum and Energy Research, Executive Summary

CONSOL Inc. is conducting a program to aid in the advancement of direct coal liquefaction process development under contract from the U.S. Department of Energy (Contract DE-AC22-89PC89883). In this program, a number of research laboratories, including the IIT Research Institute, National Institute for Petroleum and Energy Research (NIPER), are analyzing direct coal liquefaction-derived materials under subcontract from CONSOL. NIPER recently investigated the properties of a synthetic crude oils produced by HRI Inc., in Catalytic Two-Stage Liquefaction (CTSL) Run CC-15 and Catalytic Multi-Stage Liquefaction (CMSL) Run 2.

HRI Run CC-15

The objective of HRI's CTSL Run CC-15, also called Run 227-75, was to test a predispersed (impregnated) hydrated iron oxide catalyst. The feed coal was Wyodak and Anderson seam, Black Thunder Mine, subbituminous coal. Start-up and make-up oil for Run CC-15 was filtered process-derived liquid, produced in HRI Run 260-03, which also used Black Thunder Mine coal. Throughout Run CC-15, the first stage reactor was operated without a catalyst bed at ca. 427 °C. Criterion 317 Ni/Mo on alumina catalyst was present in the second-stage reactor, which was

operated at about 413 °C. The impregnated catalyst was activated with H₂S at 275-300 °C in a pretreater vessel. The on-line hydrotreater was not used in the run. The net product sample analyzed in this subcontract was produced by compositing a total of 26 sample aliquots obtained during the run from the Separator Overhead process stream and the Atmospheric Still Overhead process stream.

The composite coal-derived synthetic crude was distilled by ASTM Method D 2892 to produce an IBP-380 °F distillate (40.2 wt %), a 380-510 °F distillate (33.4 wt %), a 510-638 °F distillate (22.5 wt %), and a >638 °F (2.7 wt %). Portions of the IBP-380 °F and 380-510 °F distillate cuts were subjected to a caustic wash procedure to remove phenolic compounds (2.4 and 4.0 wt %, respectively) and produce two additional fractions. The total sample, the three distillate fractions, the resid, and the two caustic-washed fractions were characterized by a total of approximately 175 chemical and physical property tests using ASTM, UOP, and other standard and published methods developed for petroleum and petroleum products.

The coal liquid product quality was briefly assessed by comparison of the physical and chemical property test data for the appropriate fraction against the specifications for gasolines, aviation turbine fuels, diesel fuels or fuel oils. However, it should be noted that these specifications apply to finished fuels that are normally comprised of blends of various refinery streams along with additives and thus do not even apply strictly to straight-run petroleum distillates, let alone coal liquid distillates.

The IBP-380 °F distillate fraction failed the corrosion, gum, oxidation stability, octane and distillation specification tests. However, the 190-380 °F portion of a petroleum crude is normally processed by catalytic reforming before blending into gasoline. This coal liquid distillate may need further processing to remove olefins before becoming suitable for reforming. Caustic washing of this fraction gave an improved product, although most of the specification tests still were not met. The greatest improvements were in oxidation stability and acidity.

The 380-510 °F distillate fraction passed many of the specification tests for aviation turbine fuels although some important specification tests including aromatic content, smoke point, freezing point, and thermal stability were not met. The caustic-washed 380-510 °F distillate fraction showed a significant improvement in mercaptan content and some other minor improvements. However, both of these fractions should benefit from hydrogenation or hydrocracking for blending into finished fuel.

The 510-638 °F distillate fraction met most of the specifications for diesel fuel and heating fuel oils although the cetane index calculated met the specification only for Grade No. 4-D diesel fuel oil.

Overall, the coal liquid should benefit from further hydroprocessing. In particular, conversion of aromatics to naphthenes would be necessary to produce an acceptable blending product for aviation turbine fuels.

HRI Run CMSL-2

The main objective of HRI's Run CMSL-2, also called Run 227-78, was to investigate the effect of a high coal concentration on process performance. In this continuous two-stage liquefaction run the higher coal concentration in the coal-solvent slurries was accomplished by lowering the solvent-to-coal ratio from 1.2 (to as high as 1.6) used in previous bench-scale runs, to a value of 0.9 in CMSL-2. The feed coal was Illinois No. 6, Burning Star 2, bituminous coal. Throughout Run CMSL-2 the first- and second-stage reactors were operated catalytically; Shell S-317 Ni/Mo on alumina catalyst was present in both reactors. No on-line hydrotreater was used in the run. The net product sample analyzed in this subcontract was produced by compositing a total of 10, one-half gallon sample aliquots obtained during periods 8 through 12 of the run from the Separator Overhead process stream and the Atmospheric Still Overhead process stream.

The composite coal-derived synthetic crude was distilled by ASTM Method D 2892 in a preliminary run to produce an IBP-180° F distillate (2.8 weight percent), a 180-350 °F distillate (19.6 weight percent), and a 350-400 °F distillate (7.9 wt %). A subsequent large scale distillation by a slightly modified ASTM D 2892 procedure was made in an attempt to produce a sufficient quantity of the

350-400 °F distillate for testing. This distillation produced an IBP-350 °F distillate (25.1 wt %), a 350-400 °F distillate (5.6 wt %), a 400-550 °F distillate (35.2 wt %), and a >550 °F residue (34.1 wt %). Losses amounted to only 0.62 wt %. A portion of the 350-400 °F distillate cut was subjected to a caustic wash procedure to remove phenolic compounds (1.1 wt %) and produce an additional fraction. The total sample, the three distillate fractions, the resid, and the caustic washed fraction were characterized by a total of approximately 130 chemical and physical property tests using ASTM, UOP, and other standard and published methods developed for petroleum and petroleum products.

The coal liquid product quality was briefly assessed by comparison of the physical and chemical property test data for the appropriate fraction against the specifications for gasolines, aviation turbine fuels, diesel fuels or fuel oils. However, it should be noted that these specifications apply to finished fuels which are normally comprised of blends of various refinery streams along with additives and thus do not even apply strictly to straight run petroleum distillates, let alone coal liquid distillates.

The IBP-180 °F and 180-350 °F fractions from the preliminary distillation were tested for specific gravity (API gravity was calculated). Unless otherwise noted, all subsequent tests were run on the distillate fractions from the large scale modified D 2892 distillation.

The IBP-350 °F distillate fraction failed the corrosion and octane tests, and exceeded the maximum temperature for the 50% point in the distillation specification test. However, the 190-380 °F portion of a petroleum crude is normally processed by catalytic reforming before blending into gasoline. This coal liquid distillate may need further processing to remove olefins before becoming suitable for reforming.

The 350-400 °F distillate fraction passed many of the specification tests for aviation turbine fuels although some important specification tests including aromatic content, smoke point, density, and luminometer number were not met. The caustic washed 350-400 °F distillate fraction showed a significant improvement in mercaptan content and some other minor improvements.

The 400-550 °F distillate fraction met most of the specifications for diesel fuel and heating fuel oils although the cetane index calculated met the specification only for Grade No. 4-D diesel fuel oil and the 90% off distillation temperature was slightly below the minimum specified for grade 2-D diesel fuel. The >550 °F resid met the specifications for a number 4 fuel oil.

Overall, the coal liquid might benefit from further hydroprocessing. In particular, conversion of aromatics to naphthenes or blending with a suitable low-aromatic blending stock would be necessary to produce an acceptable product for aviation turbine fuel.

APPENDIX B

CONSOL ANALYTICAL DATA FOR ALL PARTICIPANT PROGRAM SAMPLES

WILSONVILLE 850 °F RESIDS

Run Number	250	250	250	251-II	251-II	251-II
Balance Period	Composite	Composite	Composite	Composite	Composite	Composite
Sampling Point	V131B	R1236	V1067	R1258	V131B	V1067
Feed Coal Seam	Illinois No.6	Illinois No.6	Illinois No.6	Wyodak	Wyodak	Wyodak
Feed Coal Mine	Burning Star #2	Burning Star #2	Burning Star #2	Clovis Point	Clovis Point	Clovis Point
Ultimate:						
Ash wt % as det.	0.2	6.13	10.2			26.98
C, wt % MAF	89.73	89.65	89.9	88.27	87.81	88.03
H, wt % MAF	7.43	6.33	7.16	6.07	6.85	6.68
N, wt % MAF	1	1.27	1.1	1.23	0.97	1.05
S, wt % MAF	0.28	1.02	1.11	1.85	2.32	2
O (diff), wt % MAF	1.56	1.73	0.73	2.58	2.06	2.23
Ash Elementals (%):						
Na ₂ O	0.48	0.26	0.29			1.37
K ₂ O	1.98	1.84	1.52			0.46
CaO	8.96	5.45	10.17			19.43
MgO	1.56	0.91	0.8			3.7
Fe ₂ O ₃	17.7	17.78	18.56			11.71
TiO ₂	1.85	0.9	0.72			0.78
P ₂ O ₅	0.87	0.35	0.3			0.61
SiO ₂	46.51	47.45	42.76			30.57
Al ₂ O ₃	18.81	18.79	16.14			15.57
SO ₃		4.57	7.57			13.32
Unaccounted	1.29	1.7	1.18			2.48
Proton Distribution of THF Sols, %						
Condensed Aromatics	20.2	29.3	21.1	26.8	22.2	25.6
Uncondensed Aromatics	5.9	5.2	5.2	6.4	4.6	5.4
Cyclic Alpha	19.1	20.8	19.9	20.2	19.7	21.2
Alkyl Alpha	9.6	9.5	9.7	8.9	8.7	9.5
Cyclic Beta	16.6	13.9	17.8	13.1	15.4	14.2
Alkyl Beta	18.2	13.6	16.4	16.5	20	16.2
Gamma	10.4	7.8	10	8	9.4	8
Phenolic -OH Concentration of THF Sols, meq/g	0.74	1.07	0.71	1.1		
Phenolic Peak Location, cm ⁻¹	3299	3292	3298	3294	3298	3297
Insoluble Org. Matter, wt %, as det.	0.2	4.6	5.2	16	13.4	16.5

WILSONVILLE 850 °F RESIDS

Run Number	251-III	251-III	251-III	255	255
Balance Period	Composite	Composite	Composite	Composite	Composite
Sampling Point	V131B	V1258	V1067	V131B	R1235
Feed Coal Seam	Wyodak	Wyodak	Wyodak	Texas Lignite/ Ohio 6	Texas Lignite/ Ohio 6
Feed Coal Mine	Clovis Point	Clovis Point	Clovis Point		
Ultimate:					
Ash wt % as det.	28.64	27.9	30.33	26.77	27.69
C, wt % MAF	87.42	87.96	87.4	90.76	89.05
H, wt % MAF	6.78	6.66	6.89	6.96	6.33
N, wt % MAF	0.91	1	0.82	1.22	1.38
S, wt % MAF	2.56	2.58	2.78	2.43	2.95
O (diff), wt % MAF	2.33	1.8	2.11	-1.37	0.29
Ash Elementals (%):					
Na ₂ O			1.37		
K ₂ O			0.31		
CaO			22.38		
MgO			4.1		
Fe ₂ O ₃			14.94		
TiO ₂			0.65		
P ₂ O ₅			0.57		
SiO ₂			26.77		
Al ₂ O ₃			12.31		
SO ₃			14.55		
Unaccounted			2.05		
Proton Distribution of THF Sols, %					
Condensed Aromatics	23.2	30	17.1	23.9	29.2
Uncondensed Aromatics	3.5	3.5	3.8	3.8	3.1
Cyclic Alpha	21.6	21	20.1	22	22.8
Alkyl Alpha	9	8.8	8.7	8.9	9.2
Cyclic Beta	16.4	13.8	18.3	16.4	15.4
Alkyl Beta	17	16.4	22.3	17.3	14.4
Gamma	9.4	6.5	9.7	7.8	5.8
Phenolic -OH Concentration of THF Sols, meq/g	0.52	0.85	0.57	0.65	0.55
Phenolic Peak Location, cm ⁻¹	3303	3294	3303	3299	3294
Insoluble Org. Matter, wt %, as det.	16.1	20.4	19.3	16.7	18.4

WILSONVILLE 850 °F RESIDS

Run Number	255	256	256	256	256
Balance Period	Composite	B	B	E	E
Sampling Point	V1067	V131B	R1236	V131B	R1236
Feed Coal Seam	Texas Lignite/ Ohio 6	Ohio 6	Ohio 6	Ohio 6	Ohio 6
Feed Coal Mine		Holmes	Holmes	Crooksville	Crooksville
Ultimate:					
Ash wt % as det.	29.37	7.19	7.67	9.85	10.36
C, wt % MAF	90.32	81.81	80.65	79.86	78.97
H, wt % MAF	6.63	5.88	5.74	6.48	6.33
N, wt % MAF	1.27	1.5	1.49	0.82	0.94
S, wt % MAF	3.02	1.61	1.79	1.04	1.14
O (diff), wt % MAF	-1.24	1.96	2.61	1.9	2.22
Ash Elementals (%):					
Na ₂ O	1.16				
K ₂ O	0.45				
CaO	14.42				
MgO	3.45				
Fe ₂ O ₃	16.93				
TiO ₂	1.06				
P ₂ O ₅	0.16				
SiO ₂	32.92				
Al ₂ O ₃	12.85				
SO ₃	14.64				
Unaccounted	1.96				
Proton Distribution of THF Sols, %					
Condensed Aromatics	22.8	21.3	28.2	22.8	24.3
Uncondensed Aromatics	4.1	11.2	5.8	5.1	3.7
Cyclic Alpha	21.5	17.9	21.7	19.7	21.7
Alkyl Alpha	9	10.5	10.4	9.3	9.8
Cyclic Beta	16.9	12.2	12.7	16.2	16.1
Alkyl Beta	17.4	17.2	14.2	17	15.6
Gamma	8.3	9.7	7	9.9	8.7
Phenolic -OH Concentration of THF Sols, meq/g	0.68	1.2	1.25	0.66	0.83
Phenolic Peak Location, cm ⁻¹	3300	3295	3294	3298	3298
Insoluble Org. Matter, wt %, as det.	18.2		7.8	4	4.7

WILSONVILLE 850 °F+ RESIDS

Run Number	257	257	257	257	257
Balance Period	Composite	Composite	Composite	F	G
Sampling Point	R1235	V131B	V1067	R1236	R1235
Feed Coal Seam	Illinois No.6	Illinois No.6	Illinois No.6	Illinois No.6	Illinois No.6
Feed Coal Mine	Burning Star #2	Burning Star #2	Burning Star #2	Burning Star #2	Burning Star #2
Ultimate:					
Ash wt % as det.	12.52	9.28	13.49	13.31	12.33
C, wt % MAF	88.05	88.64	87.99	76.5	76.26
H, wt % MAF	7.7	8.08	7.87	6.73	6.48
N, wt % MAF	0.86	0.78	0.77	0.69	0.83
S, wt % MAF	1.34	0.79	1.2	1.24	1.36
O (diff), wt % MAF	2.05	1.71	2.16	1.53	2.74
Ash Elementals (%):					
Na ₂ O			0.41		
K ₂ O			1.88		
CaO			6.55		
MgO			0.91		
Fe ₂ O ₃			17.12		
TiO ₂			0.76		
P ₂ O ₅			0.15		
SiO ₂			46.77		
Al ₂ O ₃			17.74		
SO ₃			6.15		
Unaccounted			1.56		
Proton Distribution of THF Sols, %					
Condensed Aromatics	18.1	16.8	16.9	15.9	15.7
Uncondensed Aromatics	3.7	3.1	3.4	2.8	3.8
Cyclic Alpha	19.6	19.1	19.4	19.7	19
Alkyl Alpha	9.2	8.9	9.2	9.1	8.8
Cyclic Beta	19.2	20.7	19.8	20.3	19.2
Alkyl Beta	19.9	20.7	20.7	21	20.5
Gamma	10.4	10.6	10.7	11.3	12.9
Phenolic -OH Concentration of THF Sols, meq/g	0.68	0.5	0.57	0.62	0.83
Phenolic Peak Location, cm ⁻¹	3300	3302	3302	3299	3298
Insoluble Org. Matter, wt %, as det.	21.3	14.8	21.3	7.6	11.2

WILSONVILLE 850 °F RESIDS

Run Number	258	258	259	259	259	262
Balance Period	Composite	Composite	Composite	Composite	Composite	B
Sampling Point	V131B	R-1235	R1235	V131B	V-1067	V131B
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Pittsburgh	Pittsburgh	Pittsburgh	Wyodak & Anderson
Feed Coal Mine	Black Thunder	Black Thunder	Ireland	Ireland	Ireland	Black Thunder
Ultimate:						
Ash wt % as det.	16.62	17.21	8.74	8.51	10.21	13.4
C, wt % MAF	91.24	90.9	90.12	91.01	90.24	89.78
H, wt % MAF	6.04	5.86	6.19	6.5	6.39	7.68
N, wt % MAF	1.18	1.21	1.15	1.04	1.05	0.96
S, wt % MAF	1.95	2.1	1.5	1.25	1.49	1.48
O (diff), wt % MAF	-0.41	-0.06	1.04	0.2	0.83	0.18
Ash Elementals (%):						
Na ₂ O			0.52	0.52	0.51	
K ₂ O			1.63	1.65	1.6	
CaO			2.62	2.97	2.72	
MgO			0.84	0.87	0.84	
Fe ₂ O ₃			20.67	20.76	21.83	
TiO ₂			0.91	0.93	0.91	
P ₂ O ₅			0.15	0.15	0.15	
SiO ₂			44.3	44.01	43.8	
Al ₂ O ₃			24.77	25.29	24.3	
SO ₃			1.46	1.09	1.37	
Unaccounted			2.13	1.76	1.88	
Proton Distribution of THF Sols, %						
Condensed Aromatics	34	39.5	30.7	26.1	27.8	19.7
Uncondensed Aromatics	5.8	6.9	2.6	5.4	3.8	3.3
Cyclic Alpha	20.2	20.1	20.9	18.9	21.2	18.3
Alkyl Alpha	9	9.4	10.2	9.4	9.6	8.5
Cyclic Beta	12.6	10.6	13.8	14.8	15.5	16.7
Alkyl Beta	12	11.2	13.4	14.6	13.4	23.2
Gamma	6.3	5.8	8.4	10.8	8.7	10.7
Phenolic -OH Concentration of THF Sols, meq/g	0.85	1.09	0.92	0.69	0.7	0.73
Phenolic Peak Location, cm ⁻¹		3294	3295	3296	3296	3299
Insoluble Org. Matter, wt %, as det.	12.8	15.3				13.7

WILSONVILLE 850 °F DISTILLATES

Run Number	257	262
Balance Period	Composite	Composite
Sampling Point	V-1067	V-1067
Feed Coal Seam	Illinois No. 6	Wyodak and Anderson
Feed Coal Mine	Burning Star No. 2	Black Thunder
Ultimate:		
Ash wt % as det.		
C, wt % MAF	89.11	89.22
H, wt % MAF	10.47	10.37
N, wt % MAF	0.29	0.31
S, wt % MAF	0.03	0.03
O (diff), wt % MAF	0.10	0.07
Proton Distribution of THF Sols, %		
Condensed Aromatics	7.6	7.9
Uncondensed Aromatics	5.2	3.7
Cyclic Alpha	15.8	13.0
Alkyl Alpha	9.4	7.7
Cyclic Beta	23.0	17.4
Alkyl Beta	25.2	34.9
Gamma	13.9	15.3
Phenolic -OH Concentration of THF Sols, meq/g	0.20	0.42
Phenolic Peak Location, cm ⁻¹	3315	3310
Insoluble Org. Matter, wt %, as det.		

WILSONVILLE THF-SOLUBLE 850 °F+ RESIDS

Run Number	250	250	250	251-II	251-II	251-II
Balance Period	Composite	Composite	Composite	Composite	Composite	Composite
Sampling Point	R1236	V131B	V-1067	V-1067	V-131B	R-1258
Feed Coal Seam	Illinois No.6	Illinois No.6	Illinois No.6	Wyodak	Wyodak	Wyodak
Feed Coal Mine	Burning Star No.2	Burning Star No. 2	Burning Star No.2	Clovis Point	Clovis Point	Clovis Point
Ultimate:						
C, wt % MAF	89.38	89.18	89.91	89.88	89.72	89.38
H, wt % MAF	6.51	7.39	7.14	6.75	7.08	6.13
N, wt % MAF	1.16	0.89	1.02	1.22	1.04	1.33
S, wt % MAF	0.5	0.25	0.27	0.05	0.06	0.15
O (diff), wt % MAF	2.45	2.29	1.66	2.1	2.1	3.01
Proton Distribution of THF Solis, %						
Condensed Aromatics	30.8	20.9	20.4	26.5	23.4	31.9
Uncondensed Aromatics	5.2	4.4	5.6	3.5	3.6	5.1
Cyclic Alpha	19	18.6	18.7	21.3	19.9	18.1
Alkyl Alpha	10.3	9.8	9.8	9.6	8.7	9.4
Cyclic Beta	13	16.8	17.2	15.1	15.9	12.6
Alkyl Beta	12.9	17.6	17.2	16.3	19	14.3
Gamma	8.8	11.8	11.2	7.7	9.5	8.6
Phenolic -OH Concentration, meq/g	1.07	0.74	0.55	0.81	0.75	1.17
Phenolic Peak Location, cm ⁻¹	3292	3299	3297	3298	3297	3292

WILSONVILLE THF-SOLUBLE 850 °F+ RESIDS

Run Number	251-III	251-III	251-III	255	255	255	255
Balance Period					B	B	B
Sampling Point	V131B	R1258	V1067	R-1236	V-1067	V-131B	R-1235
Feed Coal Seam	Wyodak	Wyodak	Wyodak	Texas Lignite	Texas Lignite	Texas Lignite	Texas Lignite
Feed Coal Mine	Clovis Point	Clovis Point	Clovis Point	Martin Lake	Martin Lake	Martin Lake	Martin Lake
Ultimate:							
C, wt % MAF	89.43	89.38	88.75	89.27	89.4	89.39	89.06
H, wt % MAF	7.92	7.26	8.02	6.64	7	7.12	6.7
N, wt % MAF	0.74	0.88	0.7	1.3	1.28	1.23	1.37
S, wt % MAF	0.03	0.06	0.32	0.18	0.13	0.09	0.19
O (diff), wt % MAF	1.88	2.42	2.21	2.61	2.19	2.17	2.68
Proton Distribution of THF Sols, %							
Condensed Aromatics	19.1	24.4	18.6	29.2	23.1	22.4	26.7
Uncondensed Aromatics	3.3	4.1	3.2	3.1	3.7	4.3	5.4
Cyclic Alpha	18.6	17.6	19.3	22.8	20.8	19.2	19.1
Alkyl Alpha	9.2	8.9	9.2	9.2	9.5	9.5	9.7
Cyclic Beta	17.1	14.2	16.2	15.4	16.2	15.9	13.8
Alkyl Beta	22	20.5	22.7	14.4	17.9	18.5	16.4
Gamma	10.6	10.3	10.7	5.8	8.7	10.3	8.8
Phenolic -OH Concentration, meq/g	0.52	0.85	0.42	1.04	0.77	0.71	1.03
Phenolic Peak Location, cm⁻¹	3303	3294	3308	3294	3298	3298	3295

WILSONVILLE THF-SOLUBLE 850 °F+ RESIDS

Run Number	256	256	256	256	257	257
Balance Period	B	B	E	E	Composite	Composite
Sampling Point	V131B	R1236	V131B	R1236	V131B	R1235
Feed Coal Seam	Ohio No.6	Ohio No.6	Ohio No. 6	Ohio No. 6	Illinois No. 6	Illinois No. 6
Feed Coal Mine	Holmes	Holmes	Crooksville	Crooksville	Burning Star No.2	Burning Star No.2
Ultimate:						
C, wt % MAF	88.54	88.19	90.07	89.88	88.75	88.41
H, wt % MAF	6.37	6.42	7.25	7.21	8.15	8.04
N, wt % MAF	1.61	1.61	0.95	1.03	0.66	0.86
S, wt % MAF	0.65	0.74	0.05	0.12	0.14	0.26
O (diff), wt % MAF	2.83	3.78	1.68	1.76	2.3	2.43
Proton Distribution of THF Sols, %						
Condensed Aromatics	21.3	27.5	23	24.3	16.7	17.8
Uncondensed Aromatics	11.2	6	5.6	4.1	4.4	4.9
Cyclic Alpha	17.9	20.5	18.3	21.5	17.9	18.6
Alkyl Alpha	10.5	10.4	9.5	9.7	9.4	9.2
Cyclic Beta	12.2	12.5	15.7	15.7	18.6	18.1
Alkyl Beta	17.2	14.4	16.8	15.6	20.4	19.7
Gamma	9.7	8.6	11.2	9.1	12.5	11.7
Phenolic -OH Concentration, meq/g	1.2	1.25	0.66	0.83	0.5	0.68
Phenolic Peak Location, cm⁻¹	3295	3294	3298	3298	3302	3300

WILSONVILLE THF-SOLUBLE 850 °F+ RESIDS

Run Number	257	257	257	258	258	259
Balance Period	Composite	F	G	Composite	Composite	Composite
Sampling Point	V1067	R1235	R-1235	V-131B	R-1235	V131B
Feed Coal Seam	Illinois No. 6	Illinois No. 6	Illinois No. 6	Wyodak and Anderson	Wyodak and Anderson	Pittsburgh
Feed Coal Mine	Burning Star No. 2	Burning Star No. 2	Burning Star No. 2	Spring Creek/ Black Thunder	Spring Creek/ Black Thunder	Ireland
Ultimate:						
C, wt % MAF	88.32	89.45	88.11	90.6	90.11	90.54
H, wt % MAF	8.16	7.96	7.76	6.2	6.1	6.74
N, wt % MAF	0.65	0.77	0.87	1.12	1.21	0.91
S, wt % MAF	0.15	0.23	0.45	0.04	0.1	0.39
O (diff), wt % MAF	2.72	1.59	2.81	2.04	2.48	1.42
Proton Distribution of THF Sols, %						
Condensed Aromatics	17.7	16.4	15.4	32	33.7	26.1
Uncondensed Aromatics	3	3.2	4.5	6.7	6.7	5.4
Cyclic Alpha	18.9	18.4	17.7	18.7	18.3	18.9
Alkyl Alpha	9.3	8.9	9.8	9.8	9.9	9.4
Cyclic Beta	19.5	20.5	18.9	12.3	11.3	14.8
Alkyl Beta	19.6	20.8	21.9	12.3	12	14.6
Gamma	11.9	11.7	11.8	8.2	8	10.8
Phenolic -OH Concentration, meq/g	0.57	0.59	0.81	0.85	1.09	0.69
Phenolic Peak Location, cm ⁻¹	3301	3296	3295	3295	3292	3296

WILSONVILLE THF-SOLUBLE 850 °F+ RESIDS

Run Number	259	259	260	260	260	260
Balance Period	Composite	Composite	ABC	ABC	ABC	C
Sampling Point	R1235	V1067	V131B	V-1067	R-1235	V-1067
Feed Coal Seam	Pittsburgh	Pittsburgh	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson
Feed Coal Mine	Ireland	Ireland	Black Thunder	Black Thunder	Black Thunder	Black Thunder
Ultimate:						
C, wt % MAF	89.79	89.8	89.56	91.22	90.72	89.74
H, wt % MAF	6.49	6.8	6.51	6.44	6.31	6.46
N, wt % MAF	1.06	1	1.09	1.14	1.17	1.12
S, wt % MAF	0.63	0.41	0.04	0.03	0.05	0.04
O (diff), wt % MAF	2.03	1.99	1.8	1.17	1.75	2.64
Proton Distribution of THF Sols, %						
Condensed Aromatics	30.7	28.6	33.8	32.4	33.4	30.5
Uncondensed Aromatics	2.6	3.6	2.4	5.1	3.7	4.7
Cyclic Alpha	20.9	21.7	18.4	20.3	19.9	20.8
Alkyl Alpha	10.2	9.1	9.1	8.6	9.3	9.4
Cyclic Beta	13.8	14.8	13.2	12.9	12.6	13.8
Alkyl Beta	13.4	13.5	14.7	13.3	14.3	13
Gamma	8.4	8.7	8.4	7.4	6.8	7.8
Phenolic -OH Concentration, meq/g	0.92	0.7	0.71	0.7	0.97	0.61
Phenolic Peak Location, cm ⁻¹	3295	3296	3296	3296	3295	3294

WILSONVILLE THF-SOLUBLE 850 °F+ RESIDS

Run Number	260	260	260	260	260	260
Balance Period	C	C	D	D	DEF	E
Sampling Point	V-131B	R-1235	V-1067	R1235	R-1235	V-1067
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson
Feed Coal Mine	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder
Ultimate:						
C, wt % MAF	90.9	90.41	89.1	89.2	88.72	89.24
H, wt % MAF	6.32	6.25	6.95	7.13	7.11	6.92
N, wt % MAF	1.11	1.14	1.33	1.08	0.98	1.19
S, wt % MAF	0.03	0.04	0.03	0.03	0.09	0.07
O (diff), wt % MAF	1.64	2.16	2.59	2.56	3.1	2.58
Proton Distribution of THF Sols, %						
Condensed Aromatics	32.2	32.8	24.7	23.2	20.3	24.8
Uncondensed Aromatics	5.1	4.6	3.8	4.4	4.3	4.8
Cyclic Alpha	18.1	20	19.3	18.6	17.2	18
Alkyl Alpha	9.2	9.4	9.3	8.7	9.4	9.1
Cyclic Beta	13.6	12.7	15.8	15.7	15.3	14.4
Alkyl Beta	13.9	14.5	18.8	19.9	21.2	19.5
Gamma	7.8	6	8.2	9.5	12.3	9.5
Phenolic -OH Concentration, meq/g	0.67	0.97	0.88	0.82	0.95	0.93
Phenolic Peak Location, cm ⁻¹	3296	3295	3298	3299	3294	3296

WILSONVILLE THF-SOLUBLE 850 °F⁺ RESIDS

Run Number	260	260	261	261	261	262	262
Balance Period	E	E	ABCD	D	E	Composite	B
Sampling Point	V-131B	R-1235	R-1235	V-131B	V-131B	R-1235	V-131B
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Illinois No. 6	Illinois No. 6	Illinois No. 6	Wyodak and Anderson	Wyodak and Anderson
Feed Coal Mine	Black Thunder	Black Thunder	Burning Star No. 2	Burning Star No. 2	Burning Star No. 2	Black Thunder	Black Thunder
Ultimate:							
C, wt % MAF	89.46	89.54	89.41	90.19	90.52	88.59	88.63
H, wt % MAF	6.69	6.96	6.95	5.93	5.22	7.37	8.19
N, wt % MAF	1.13	1.13	1.25	1.61	1.25	0.89	1.29
S, wt % MAF	0.05	0.05	0.47	0.23	0.28	0.11	0.04
O (diff), wt % MAF	2.67	2.32	1.92	2.04	2.73	3.04	1.85
Proton Distribution of THF Sols, %							
Condensed Aromatics	22.5	23.3	24.4	25.3	33.1	30.9	15.9
Uncondensed Aromatics	5.1	4	5.5	4.1	4.6	1.4	5.6
Cyclic Alpha	16.8	18.2	21.4	18.3	19.4	18.8	16.8
Alkyl Alpha	9.3	9.1	9.2	9.2	9.5	9.7	8.9
Cyclic Beta	14.4	15.2	15.7	16.1	13.3	13.6	16.9
Alkyl Beta	21.2	20.4	14.6	17.1	12.5	15.9	24.9
Gamma	10.8	9.8	9.2	9.9	7.7	9.7	11.0
Phenolic -OH Concentration, meq/g	0.89	0.96	1.01	0.77	0.83	1.14	0.73
Phenolic Peak Location, cm⁻¹	3297	3296	3296	3297	3296	3297	3299

WILSONVILLE PYRIDINE-SOLUBLE 850 °F+ RESIDS

Run Number	250	257	257	258	259	259
Balance Period	Composite	Composite	Composite	Composite	Composite	Composite
Sampling Point	R1235	V-131B	R-1235	R-1235	V-131B	R-1235
Feed Coal Seam	Illinois No. 6	Illinois No. 6	Illinois No. 6	Wyodak and Anderson	Pittsburgh	Pittsburgh
Feed Coal Mine	Burning Star #2	Burning Star #2	Burning Star #2	Black Thunder	Ireland	Ireland
Ultimate:						
C, wt % MAF	88.18	87.52	87.72	89.19	89.83	89.27
H, wt % MAF	6.04	7.38	7.32	5.59	6.38	6.07
N, wt % MAF	1.60	0.9	0.97	1.57	1.19	1.31
S, wt % MAF	0.49	0.15	0.28	0.06	0.38	0.62
O (diff), wt % MAF	3.69	4.05	3.71	3.59	2.22	2.73
Proton Distribution of THF Soils, %						
Condensed Aromatics	27.8	16.1	17.3	29.2	23.5	26.2
Uncondensed Aromatics	6.0	4.8	6.3	7.3	6	8.3
Cyclic Alpha	17.7	15.6	15.8	17.4	17.8	17.1
Alkyl Alpha	9.4	9.2	8.7	9	9.2	8.9
Cyclic Beta	14.6	19.3	18.6	12.1	14.6	14
Alkyl Beta	13.8	21.6	19.8	14.2	16.8	15
Gamma	10.7	13.3	13.3	10.8	12.1	10.5
Phenolic -OH Concentration of THF Soils, meq/g	1.07	0.5	0.68	1.09	0.69	0.92
Phenolic Peak Location, cm ⁻¹	3292	3302	3300	3294	3296	3295
Pyridine Soluble, % of Parent Resid	91.09	86.49	80.21	71.45	84.51	83.63

WILSONVILLE THF-INSOLUBLE 850 °F+ RESIDS

Run Number	262	262	262	263	263	263
Balance Period	B	B	B	E	E	E
Sampling Point	V1067	R1235	V131B	V131B	R1235	V1067
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson
Feed Coal Mine	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder
Ultimate:						
Ash wt % dry	52.01	49.05	47.79	65.37	62.37	65.79
C, wt % dry	42.5	44.54	45.56	34.36	35.93	33.73
H, wt % dry	2.55	2.67	2.77	1.84	1.97	1.8
N, wt % dry	0.77	0.76	0.82	0.51	0.52	0.52
S, wt % dry	4.94	4.61	4.52	6.31	5.99	6.2
O (diff), wt % dry	-2.77	-1.63	-1.46	-8.39	-6.78	-8.04
Ash Elementals (%):						
Na ₂ O	0.39	0.41	0.4	0.22	0.22	0.22
K ₂ O	0.26	0.25	0.24	0.35	0.35	0.35
CaO	16.3	16.2	16.28	16.35	16.76	16.31
MgO	3.53	3.48	3.5	3.26	3.29	3.26
Fe ₂ O ₃	22.2	22.17	22.49	22.76	22.75	22.49
TiO ₂	0.86	0.86	0.87	0.84	0.85	0.85
P ₂ O ₅	1.96	1.92	1.74	1.3	1.31	1.29
SiO ₂	21.7	22.16	21.5	21.67	21.35	22.38
Al ₂ O ₃	11.55	11.43	11.49	13.1	13.07	13.18
SO ₃						
Unaccounted						
Mo, ppm of dry sample	3133	2852	2411	1312.5	1265.5	1315.5

WILSONVILLE WHOLE PROCESS OILS

Run Number	251-II	255	257	259
Balance Period	A	B	E	G
Sampling Point	V131B	V131B	V131B	R1235
Feed Coal Seam	Wyodak	Texas Lignite/ Ohio No. 6	Illinois No. 6	Pittsburgh
Feed Coal Mine	Clovis Point		Burning Star #2	Ireland
Ultimate:				
Ash wt % as det	14.40	9.34	6.81	6.62
C, wt % MAF	88.24	89.81	88.31	89.32
H, wt % MAF	8.15	8.75	8.42	7.42
N, wt % MAF	0.89	0.94	0.75	0.31
S, wt % MAF	0.71	0.78	0.65	1.07
O (diff), wt % MAF	2.00	-0.28	1.86	1.87
Proton Distribution of THF Sols, %				
Condensed Aromatics	16.5	13.6	12.7	21.6
Uncondensed Aromatics	5.0	3.7	4.8	4.0
Cyclic Alpha	15.8	15.7	15.1	19.7
Alkyl Alpha	9.7	9.1	8.8	9.0
Cyclic Beta	15.4	18.0	19.9	15.4
Alkyl Beta	25.4	25.1	23.1	18.4
Gamma	12.5	14.8	15.6	11.9
Phenolic -OH Concentration				
of THF Sols, meq/g	0.41	0.33	0.26	0.60
Phenolic Peak Location, cm ⁻¹	3309	3307	3307	3297
Insoluble Organic Matter,				
wt %, as det.	9.4	6.4	4.4	
THF Soluble 850°F⁺ Resid,				
wt %, as det.	34.5	31.7	71.4	
850°F Distillate, wt % as det.	40.1	48.7	16.6	

WILSONVILLE WHOLE PROCESS OILS

Run Number	259	259	259	259
Balance Period	G	G	G	G
Sampling Point	V1067	V131B	V161+V182	V164
Feed Coal Seam	Pittsburgh	Pittsburgh	Pittsburgh	Pittsburgh
Feed Coal Mine	Ireland	Ireland	Ireland	Ireland
Ultimate:				
Ash wt % as det	7.42	6.36	0.44	0.005
C, wt % MAF	90.83	90.63	86.41	86.66
H, wt % MAF	7.97	7.73	13.01	11.91
N, wt % MAF	0.22	0.18	0.09	0.17
S, wt % MAF	0.97	0.81	0.05	0.14
O (diff), wt % MAF	0.0	0.64	0.44	1.11
Proton Distribution of THF Sols, %				
Condensed Aromatics	19.6	21.7	2.2	5.2
Uncondensed Aromatics	4.2	4.1	6.3	4.9
Cyclic Alpha	16.7	17.8	4.8	8.7
Alkyl Alpha	9.0	8.4	7.6	7.6
Cyclic Beta	16.4	16.6	18.8	23.9
Alkyl Beta	19.9	20.3	30.1	29.3
Gamma	14.3	11.1	30.3	20.4
Phenolic -OH Concentration				
of THF Sols, meq/g	0.42	0.34	0.18	0.27
Phenolic Peak Location, cm	3299	3300	3323	3317
Insoluble Organic Matter,				
wt %, as det.		5.8		
THF Soluble 850°F Resid,				
wt %, as det.		53.2		
850°F Distillate, wt % as det.		33.8		

WILSONVILLE - FEED COALS

Coal Seam	Illinois No. 6	Wyodak and Anderson	Wyodak	Pittsburgh
Feed Coal Mine	Burning Star #2	Black Thunder	Clovis Point	Ireland
Proximate, wt % Dry:				
Ash	10.92	6.35	8.34	4.68
Volatile Matter	38.74	45.01	48.25	43.82
Fixed Carbon	50.34	48.64	43.41	51.50
Sulfur Total	3.39	0.48	1.09	3.13
Moisture, wt % as det.	7.61	0.07	19.89	0.85
Ultimate, wt % Dry:				
Ash	10.92	6.35	8.34	4.68
C	71.49	70.30	65.62	77.44
H	4.78	5.03	4.65	5.69
N	1.36	0.96	0.87	1.31
Cl	0.048	0.073	0.053	0.062
S (total)	3.39	0.48	1.09	3.13
O (dif)	8.01	16.81	19.38	7.69
Sulfur Forms, wt % Dry				
Pyritic	1.71	0.08	0.11	0.68
Sulfate	0.06	0.03	0.25	<0.01
Organic	1.62	0.37	0.73	2.45
Ash Elementals, %:				
Na ₂ O	0.28	1.00		0.35
K ₂ O	1.85	0.33		1.48
CaO	5.85	20.52		2.69
MgO	0.92	4.43		0.79
Fe ₂ O ₃	18.26	4.53		26.08
TiO ₂	0.88	1.19		0.95
P ₂ O ₅	0.03	0.91		0.12
SiO ₂	47.81	32.39		40.24
Al ₂ O ₃	18.42	15.56		22.70
SO ₃	4.37	18.50		3.10
Unaccounted	1.33	0.64		1.50
Calorific Value, Btu/lb, dry	12720	12085	11004	14114
Basis	MAF 14279	12904	12005	14807

HRI 850 °F+ RESIDS AND WHOLE PROCESS OILS

Run Number	CC-1	CC-1	CC-1	CC-2*	CC-2
Balance Period	14A	13	13	14A/B/C	14
Sampling Point	1st Stage FL	SO/PD	PFL	PFL	PFL
Feed Coal Seam	Illinois No. 6	Illinois No. 6	Illinois No. 6	Wyodak and Anderson	Wyodak and Anderson
Feed Coal Mine	Burning Star #2	Burning Star #2	Burning Star #2	Black Thunder	Black Thunder
Ultimate:					
C, wt % MAF	89.03	85.82	88.65	90.12	90.15
H, wt % MAF	9.75	12.63	9.18	8.14	9.64
N, wt % MAF	0.19	0.05	0.26	0.41	0.3
S, wt % MAF	0.02	0	0.01	0.03	0.03
O (diff), wt % MAF	1.01	1.5	1.9	1.30	-0.12
Proton Distribution of THF Sols, %					
Condensed Aromatics	10.7	2.9	11.6	20.3	11.8
Uncondensed Aromatics	3.9	3.9	4.3	3.1	3.2
Cyclic Alpha	13.4	7.1	13.6	16.6	13.1
Alkyl Alpha	8.2	6.4	8.5	8.3	7.9
Cyclic Beta	19.6	24.8	18.5	17.1	19.1
Alkyl Beta	28.6	31.9	28.1	23.1	29.2
Gamma	15.6	23.1	15.3	11.5	15.7
Phenolic -OH Concentration of THF Sols, meq/g	0.46	0.04	0.22	0.24	0.13
Phenolic Peak Location, cm ⁻¹	3299	3353	3299	3299	3309

*Resid

HRI 850 °F+ RESIDS AND WHOLE PROCESS OILS

Run Number	CC-2	CC-2	CC-2	CC-5	CC-5	CC-5
Balance Period	15A	14 A/B/C	15A	15A/B/C	16A	15
Sampling Point	1st Stage FL	PFL	1st Stage FL	PFL	FL	PFL
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson
Feed Coal Mine	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder
Ultimate:						
C, wt % as det.	88.68	89.94	89.47	90.67	89.39	88.46
H, wt % MAF	8.83	8.16	8.88	7.56	8.45	8.95
N, wt % MAF	0.34	0.43	0.41	0.56	0.51	0.39
S, wt % MAF	0.03	<0.03	<0.03	0.03	0.03	0.03
O (diff), wt % MAF	2.12	1.47	1.22	1.18	1.62	2.19
Proton Distribution of THF Sol, %						
Condensed Aromatics	14.5	20.3	14.5	24.7	17.1	15.9
Uncondensed Aromatics	3.2	3.1	3.2	2.9	2.5	3.7
Cyclic Alpha	16.1	16.6	16.1	17.5	18.6	15
Alkyl Alpha	8	8.3	8	8.7	9	8.4
Cyclic Beta	18.5	17.1	18.5	16.3	18.5	17.8
Alkyl Beta	25.7	23.1	25.7	20	23	25.8
Gamma	14.1	11.5	14.1	10	11.3	13.4
Phenolic -OH Concentration of THF Sol, meq/g	0.25	0.24	0.25	0.38	0.49	0.18
Phenolic Peak Location, cm ¹	3306	3301	3306	3296	3303	3306

HRI 850 °F* RESIDS AND WHOLE PROCESS OILS

Run Number	CC-5*	CC-5*	I-27	I-27	I-27	I-27
Balance Period	16A	15A/B/C	18	2	25	8
Sampling Point	1st Stage FL	PFL	PFL	PFL	PFL	PFL
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6
Feed Coal Mine	Black Thunder	Black Thunder	Burning Star #2	Burning Star #2	Burning Star #2	Burning Star #2
Ultimate:						
C, wt % as det.	80.65	90.47	89.58	88.06	90.31	88.25
H, wt % MAF	6.88	7.59	7.12	9.14	6.5	8.18
N, wt % MAF	0.76	0.56	0.9	0.48	1.09	0.59
S, wt % MAF	0.22	<0.03	0.15	0.03	0.16	0.06
O (diff), wt % MAF	5.16	1.38	2.25	2.29	1.94	2.92
Proton Distribution of THF Sol, %						
Condensed Aromatics	17.1	24.7	25.3	12	33.5	17.8
Uncondensed Aromatics	2.5	2.9	3.9	2.5	4.8	2.9
Cyclic Alpha	18.6	17.5	20.8	18.9	19.7	19.6
Alkyl Alpha	9	8.7	9.4	9.2	9.1	8.7
Cyclic Beta	18.5	16.3	16.5	23.9	13.9	20
Alkyl Beta	23	20	15.2	22.5	11.8	19.8
Gamma	11.3	10	8.8	10.9	7.1	11.2
Phenolic -OH Concentration of THF Sol, meq/g	0.49	0.38	0.66	0.25	0.71	0.41
Phenolic Peak Location, cm ⁻¹	3303	3296	3297	3305	3296	3301

*Resid

HRI 850 °F RESIDS AND WHOLE PROCESS OILS

Run Number	CC-15	CC-15	CC-15	CC-15	CC-15
Balance Period	8ABC	8A	9A	8A	11ABC
Sampling Point	PFL	PFC	Interstage	SOH-ASOH (BLEND)	PFL
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson
Feed Coal Mine	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder
Ultimate:					
Ash wt % as det.		29.14	4.84		
C, wt % as det.	88.88	60.36	84.19	86.39	89.35
H, wt % as det.	9.98	5.39	8.28	13.04	9.07
N, wt % as det.	0.56	0.76	0.96	0.40	0.54
S, wt % as det.	0.03	2.41	0.42	0.03	0.03
O (diff), wt % MAF	0.53		1.30	0.14	1.00
Ash Elementals (%):					
Na ₂ O		0.51	0.57		
K ₂ O		0.22	0.23		
CaO		22.20	17.44		
MgO		4.57	3.61		
Fe ₂ O ₃		17.79	15.14		
TiO ₂		1.06	0.94		
P ₂ O ₅		0.86	0.66		
SiO ₂		21.73	33.82		
Al ₂ O ₃		11.77	10.69		
SO ₃		19.79	16.01		
Unaccounted		-0.50	0.89		
Proton Distribution of THF Sols, %					
Condensed Aromatics	9.7	12.3	13.2	2.5	13.8
Uncondensed Aromatics	5.1	3.7	6.4	4.2	4.7
Cyclic Alpha	12.0	13.8	12.8	7.4	15.8
Alkyl Alpha	7.5	7.8	8.6	6.6	8.6
Cyclic Beta	17.2	17.8	15.3	25.1	16.2
Alkyl Beta	31.9	29.0	28.5	31.3	27.2
Gamma	16.9	25.6	15.0	22.9	12.9
Phenolic -OH Concentration of THF Sols, meq/g	0.21	0.28	0.61	0.17	0.23
Phenolic Peak Location, cm ⁻¹	3308	3302	3301	3357	3305
Insoluble Org. Matter, wt %, as det.		23.6	4.93		

HRI 850 °F RESIDS AND WHOLE PROCESS OILS

Run Number	CC-15	CC-15	CC-15	CC-15	CC-15
Balance Period	11A	12A	11A	14ABC	14A
Sampling Point	PFC	Interstage	SOH-ASOH (BLEND)	PFL	PFC
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson
Feed Coal Mine	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Black Thunder
Ultimate:					
Ash wt % as det.	20.33	3.72			29.28
C, wt % as det.	69.06	88.28	86.09	86.14	63.36
H, wt % as det.	5.80	8.16	12.83	9.04	5.36
N, wt % as det.	0.62	0.66	0.28	0.81	0.81
S, wt % as det.	0.82	0.28	0.06	0.03	2.20
O (diff), wt % MAF	3.37	-1.12	0.74	3.96	-1.01
Ash Elementals (%):					
Na ₂ O	1.08	0.90			0.65
K ₂ O	0.36	0.34			0.19
CaO	24.59	21.42			21.68
MgO	5.14	4.05			4.26
Fe ₂ O ₃	7.09	7.43			17.97
TiO ₂	1.35	1.12			1.10
P ₂ O ₅	1.21	0.89			0.82
SiO ₂	30.44	37.63			23.09
Al ₂ O ₃	17.27	14.44			11.50
SO ₃	9.73	11.11			17.81
Unaccounted	1.74	0.67			0.93
Proton Distribution of THF Sols, %					
Condensed Aromatics	15.3	20.5	3.3	13.3	15.4
Uncondensed Aromatics	4.6	5.8	4.6	6.2	5.0
Cyclic Alpha	14.8	11.2	8.4	13.9	14.5
Alkyl Alpha	8.6	7.7	7.4	8.4	8.6
Cyclic Beta	16.6	13.2	25.8	16.7	16.4
Alkyl Beta	26.8	26.8	31.4	27.6	25.4
Gamma	13.4	14.8	19.0	13.9	14.8
Phenolic -OH Concentration of THF Sols, meq/g	0.31	0.49	0.20	0.30	0.43
Phenolic Peak Location, cm ⁻¹	3303	3298	3322	3306	3304
Insoluble Org. Matter, wt %, as det.	29.4	6.29			22.3

HRI 850 *F* RESIDS AND WHOLE PROCESS OILS

Run Number	CC-15	CC-15	CC-16	CC-16	CC-16
Balance Period	15A	14A	5C	5C	5C
Sampling Point	Interstage	SOH-ASOH (BLEND)	PFL	PFC	SOH-ASOH (BLEND)
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Illinois No.6	Illinois No.6	Illinois No.6
Feed Coal Mine	Black Thunder	Black Thunder	Burning Star #2	Burning Star #2	Burning Star #2
Ultimate:					
Ash wt % as det.	4.71			29.09	
C, wt % as det.	85.20	86.27	90.01	59.65	86.59
H, wt % as det.	7.83	12.47	9.87	5.64	12.58
N, wt % as det.	1.05	0.53	0.30	0.39	0.12
S, wt % as det.	0.28	<0.03	<0.03	2.62	<0.03
O (diff), wt % MAF	0.91	0.69		2.50	0.67
Ash Elementals (%):					
Na ₂ O	0.56			0.48	
K ₂ O	0.23			1.77	
CaO	17.12			5.96	
MgO	3.54			0.90	
Fe ₂ O ₃	14.93			19.49	
TiO ₂	0.90			0.76	
P ₂ O ₅	0.67			0.06	
SiO ₂	33.51			44.15	
Al ₂ O ₃	11.24			18.17	
SO ₃	15.62			7.67	
Unaccounted	1.68			0.59	
Proton Distribution of THF Sols, %					
Condensed Aromatics	15.0	2.8	9.5	11.6	2.0
Uncondensed Aromatics	8.0	4.4	3.8	2.8	3.9
Cyclic Alpha	13.9	7.5	13.8	14.4	6.4
Alkyl Alpha	8.9	7.0	7.9	7.7	6.2
Cyclic Beta	14.5	24.8	20.7	22.1	27.0
Alkyl Beta	25.6	30.8	27.5	27.0	30.0
Gamma	14.1	22.8	16.8	14.5	24.5
Phenolic -OH Concentration of THF Sols, meq/g	0.62	0.25	0.14	0.17	0.06
Phenolic Peak Location, cm ⁻¹	3301	3357	3306	3305	3339
Insoluble Org. Matter, wt %, as det.	5.54			19.1	

HRI 850 °F RESIDS AND WHOLE PROCESS OILS

Run Number	CC-16	CC-16	CC-16
Balance Period	13C	13C	13C
Sampling Point	PFL	PFC	SOH-ASOH (BLEND)
Feed Coal Seam	Wyodak and Anderson	Wyodak and Anderson	Wyodak and Anderson
Feed Coal Mine	Black Thunder	Black Thunder	Black Thunder
Ultimate:			
Ash wt % as det.		37.55	
C, wt % as det.	89.14	53.32	86.88
H, wt % as det.	8.85	4.62	12.25
N, wt % as det.	0.35	0.54	0.09
S, wt % as det.	0.06	3.23	0.03
O (diff), wt % MAF	1.60	0.60	0.75
Ash Elementals (%):			
Na ₂ O		0.50	
K ₂ O		1.79	
CaO		5.38	
MgO		0.88	
Fe ₂ O ₃		20.30	
TiO ₂		0.70	
P ₂ O ₅		0.04	
SiO ₂		45.37	
Al ₂ O ₃		18.28	
SO ₃		6.54	
Unaccounted		0.22	
Proton Distribution of THF Sols, %			
Condensed Aromatics	12.9	16.6	3.1
Uncondensed Aromatics	5.6	3.4	4.8
Cyclic Alpha	14.5	16.1	7.2
Alkyl Alpha	8.4	8.1	7.0
Cyclic Beta	18.6	20.2	25.9
Alkyl Beta	24.0	23.2	30.4
Gamma	16.1	12.4	21.6
Phenolic -OH Concentration of THF Sols, meq/g	0.30	0.41	0.12
Phenolic Peak Location, cm ⁻¹	3301	3299	3326
Insoluble Org. Matter, wt %, as det.		17.9	

HRI THF-SOLUBLE 850 °F+ RESID

Run Number	CC-2
Balance Period	14
Sampling Point	PFL
Feed Coal Seam	Wyodak and Anderson
Feed Coal Mine	Black Thunder
Ultimate:	
C, wt % as det.	89.94
H, wt % as det.	8.16
N, wt % as det.	0.43
S, wt % as det.	<0.03
O (diff), wt % MAF	1.47
Proton Distribution, %	
Condensed Aromatics	20.3
Uncondensed Aromatics	3.1
Cyclic Alpha	16.6
Alkyl Alpha	8.3
Cyclic Beta	17.1
Alkyl Beta	23.1
Gamma	11.5
Phenolic -OH Concentration, meq/g	0.24
Phenolic Peak Location, cm ⁻¹	3301

LUMMUS 850°F+ RESIDS AND WHOLE PROCESS OILS

Run Number	3LCF10	3LCF10
Balance Period	0111	0128
Sampling Point	Feed	Feed
Feed Coal Seam	Wyodak/ Illinois No. 6	Wyodak/ Illinois No. 6
Feed Coal Mine		
Ultimate:		
Ash, wt % as det.	0.79	9.97
C, wt % MAF	87.75	78.53
H, wt % MAF	6.09	4.80
N, wt % MAF	0.79	0.99
S, wt % MAF	0.29	0.56
O (diff), wt % MAF	4.27	5.11
Proton Distribution of THF Sols, %		
Condensed Aromatics	31.6	35.1
Uncondensed Aromatics	10.8	7.6
Cyclic Alpha	13.8	16.5
Alkyl Alpha	8.4	8.5
Cyclic Beta	11.0	12.9
Alkyl Beta	14.0	12.2
Gamma	9.5	7.2
Phenolic -OH Concentration of THF Sols, meq/g	0.96	1.19
Phenolic Peak Location, cm⁻¹	3290	3289

APPENDIX C

**PARTICIPANTS AND ASSOCIATED ORGANIZATIONS, PROJECT TITLES,
AND ANALYTICAL TECHNIQUES FOR ALL
PARTICIPANTS PROGRAM PROJECTS**

APPENDIX C

TABLE 1

PARTICIPANTS PROGRAM - PHASE I

<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 ^1H / ^{13}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

APPENDIX C

TABLE 2

PARTICIPANTS PROGRAM - PHASE II

<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

APPENDIX C

TABLE 3

<u>PARTICIPANTS PROGRAM - PHASE III</u>			
<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