Coal Liquefaction Process Streams Characterization and Evaluation,

VOLUME I

Base Program Activities

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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.

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 °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

supporting data for process developers and for DOE's overall liquefaction program. In addition, a study of the conversion reactivity of coal liquefaction 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	3/94	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 <u>89883-</u>	<u>Date Issued</u>	<u>Topic</u>
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)

<u>Report No. DOE/PC 89883-</u>	<u>Date Issued</u>	<u>Topic</u>
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.

Appears in Technical Report No.		
<u>No.</u>	<u>DOE/PC 89883-</u>	<u>Citation</u>
3	77	Mohan, T.; Verkade, J. G. "Determination of Total Phenol Concentrations in Coal Liquefaction Resids by ^{31}P NMR Spectroscopy" <i>Energy and Fuels</i> 1993, 7, 222-226.
4	78	Lancet, M. S.; Winschel, R. A.; Burke, F. P. "Stable Carbon Isotope Analysis of Coprocessing Materials", <i>Fuel</i> 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", <i>Fuel</i> , 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" <i>Energy & Fuels</i> , 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" <i>Energy & Fuels</i> , 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", <i>Catalysis Today</i> , 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 <i>Energy & Fuels</i> .
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>I&EC Research</i> .

PAPERS AND SEMINARS

Appears in Technical Report No.		
<u>No.</u>	<u>DOE/PC 89883-</u>	<u>Citation</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.

No.	Appears in Technical Report No. DOE/PC 89883-	Citation
2	10	Burke, F. P. "Application of Coal Liquefaction Solvent Quality Measurements", Frontiers in Coal Science and Technology, Fukuoka, Japan, October 29-31, 1989.
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.

Appears in Technical Report No.		Citation
No.	DOE/PC 89883-	
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.
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.

No.	Appears in Technical Report No. DOE/PC 89883-	Citation
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.
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	-	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.

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY	i
Overall Contract	i
Bibliographic Summary of Contract	iv
ABSTRACT	xvi
Section 1	1
SUMMARY OF ACTIVITIES COMPLETED IN FINAL REPORTING PERIOD	1
Wilsonville Run 263	1
HRI Proof-of-Concept Run	3
Phenol Method Improvements	3
Publications and Presentations	3
Section 2	6
RESULTS AND DISCUSSION	6
Wilsonville Run 263	6
Wilsonville Run 263 Overview	6
Plant Description	9
Abbreviated History of Run 263	10
Sample Descriptions	15
Analyses	15
Process Oil Properties	16
Hybrid Catalyst Operations (Periods I through M)	16
Ash Recycle Stream Modification (Period F)	17
Oil Properties in Miscellaneous Periods	18
Comparison of Oils from Run 263 with Oils from Run 262	19
HRI CTSL Run POC-1	20
Analytical Plan	20
Characterization Data	21
Phenol Method Improvements	22
Wet Samples	22
Solids-Containing Samples	24
Correction of Microautoclave Test Results	24
Section 3	26
EXPERIMENTAL	26
Section 4	27
ACKNOWLEDGMENTS	27
Section 5	28
REFERENCES	28

TABLE OF CONTENTS (Continued)

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Operating Conditions and Yields for Material Balance Periods, Wilsonville Run 263	30
2	Elemental Analyses of Selected Samples, Wilsonville Run 263	33
3	Elemental Analyses of Solids-Containing Samples, Wilsonville Run 263	34
4	Elemental Analyses of Solids-Free Liquid Samples, Wilsonville Run 263	35
5	Component Distribution of Whole Samples, Wilsonville Run 263	35
6	Proton Distribution of Whole Samples, Wilsonville Run 263	36
7	Proton Distribution of Distillate and Resid Samples, Wilsonville Run 263	37
8	Phenolic -OH Concentrations and Donor Solvent Qualities, Wilsonville Run 263	38
9	HRI Run POC-1 Sampling Plan for CONSOL R&D	39
10	Component Concentration and Solvent Quality of Whole POC-1 Samples	40
11	Proton Distributions and Phenolic -OH Concentrations, HRI Run POC-1, Period 9 Samples	41
12	Oxidation Index of HRI Coal Samples	42
13	Elemental Analyses of Contaminated Illinois 6 Feed Coal, HRI Run POC-1	43
14	Phenolic -OH Concentrations of Wet and Dry Coal-Derived Liquid Samples	44
15	Correction of Microautoclave Test Results, Wilsonville Run 262, HRI Run CC-16, Standard Coal Reactivity Calibration	45

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Simplified CC-ITSL Process Diagram for Wilsonville Run 263	46
2	Partial CC-ITSL Process Diagram for Wilsonville Run 263 Showing Major Distillate Streams	47
3	Adapted FTIR Method Performance for Phenolic -OH Determination	48
4	Adapted FTIR Method Performance for Determination of THF Solubles	49

APPENDICES

<u>Appendix</u>		<u>Page</u>
A	HRI Run Plan for POC-1	51
B	Evaluation of Advanced Analytical Methods for Direct Liquefaction Process Development	57
C	Characterization of Coal Liquefaction Resids by Field Ionization Mass Spectrometry: Correlating Spectral Features with Processing Parameters	73

APPENDICES (Continued)

<u>Appendix</u>		<u>Page</u>
D	Characterization of Coal Liquefaction Heavy Products Using ^{252}Cf Plasma Desorption Mass Spectrometry	83
E	Thermal Conversion of Coal Liquefaction Resids: Temperature-Programmed Electron Spin Resonance and Thermogravimetric Investigations	93
F	High Performance Liquid Chromatography (HPLC) of Coal Liquefaction Process Streams Using Normal-Phase Separation with Diode Array Detection	111
G	The Use of a Novel Short Contact Time Batch Reactor and Thermogravimetric Analysis to Follow the Conversion of Coal-Derived Resids During Hydroprocessing	133
H	The Use of Thermogravimetric Analysis to Follow the Conversion of Coal-Derived Resids in the Resid Recycling Process	169
I	Premium Distillate Products from Direct Liquefaction of Coal	181

ABSTRACT

This is Volume I of the Final Technical Report under DOE Contract DE-AC22-89PC89883. It provides a summary of the entire contract, and covers in detail activities completed in the final reporting period (October 1, 1993, through March 6, 1994). Major topics reported are:

- Available characterization data are reported for process oils from Wilsonville Run 263. The set of 47 process samples from Wilsonville Run 263 was analyzed to provide information on process performance. Run 263 was operated from October 31, 1991, through February 23, 1992, in the slurry-catalyst-only and hybrid catalyst modes (i.e., slurry/slurry and slurry/supported catalysts, respectively). The feed coal was Black Thunder Mine (Wyodak and Anderson seams) coal and the supported catalyst (when used) was Criterion 324 Ni/Mo supported extrudate catalyst. The run was made to test slurry catalyst and hybrid catalyst operations. Characterization results were only partially completed, due to other contract priorities.
- The sampling and analytical plan for CONSOL support of HRI Proof-of-Concept (POC) Run 1 is described. Eleven samples from early in Run POC-1 were analyzed to provide information on process performance. These characterization data are reported. It is planned to characterize additional samples from this run later.
- Two improvements to the method for determination of phenolic -OH concentration in coal liquids by FTIR are reported.
- Appended to this report are seven papers and publications. Two papers published in a peer-reviewed journal, one paper accepted for publication in a peer-reviewed journal, two papers submitted to peer-reviewed journals, and one preprint for a presentation at a national meeting were authored by researchers at subcontractor organizations, and describe work performed under the Participants Program. One paper authored by CONSOL researchers was presented at the DOE United Kingdom/United States Technical Exchange Meeting and Liquefaction Workshop, Pittsburgh, PA, 9/24/93. One paper

submitted for presentation in a national meeting was co-authored by a CONSOL R&D researcher, and describes coal liquefaction product quality.

Preprints and reprints removed. Conference paper removed and cycled separately.

Section 1

SUMMARY OF ACTIVITIES COMPLETED IN FINAL REPORTING PERIOD

Summarized here are activities completed under DOE Contract DE-AC22-89PC89883 during the final reporting period (October 1, 1993, through March 6, 1994). These activities are described in detail in Section 2. The Executive Summary of this report describes the activities performed throughout the entire contract.

WILSONVILLE RUN 263

The background of Wilsonville Run 263 and available characterization data are reported. Forty-seven process samples from Wilsonville Run 263 were analyzed to provide information on process performance. Run 263 was operated from October 31, 1991, through February 23, 1992, in the slurry catalyst and hybrid catalyst modes (i.e., slurry/slurry catalyst and slurry/supported catalyst, respectively). The feed coal was Black Thunder Mine (Wyodak and Anderson seams) coal, the slurry catalyst was a dispersed molybdenum catalyst, and the supported catalyst was Criterion 324 Ni/Mo supported extrudate catalyst. The run was made to test slurry catalyst and hybrid catalyst operations and to determine the effect of dispersed catalysts on solids buildup. All the planned characterization was not completed, because of other contract priorities.

The samples analyzed generally were less paraffinic and more aromatic than corresponding samples from Wilsonville Run 262, which was made with the same coal. Perhaps this is a consequence of operation at higher space velocity and higher temperature in Run 263. The donor solvent quality of V-131B distillates was generally higher in Run 263, probably reflecting the higher aromaticity and lower paraffinicity. The V-131B process oils from Run 263 generally contained less distillate, more resid, less IOM, and more ash than their Run 262 counterparts. Relative to the corresponding Run 262 samples, the Run 263 V-131B 850 °F⁻ distillates were lower in phenolic -OH concentration, but the 850 °F⁺ resids were higher in phenolic -OH concentration (only hybrid catalyst periods were compared).

The characterization of the Run 263 V-131B process solvent samples was more complete than that of any other sample type. V-131B distillate donor solvent

quality was poor (64 to 69%) in Periods A and C, good (82%) in Period F, and fair (72 to 79%) in all the other periods.

Several oil properties changes were noted for Periods I through M, when hybrid catalyst operation was used, relative to the prior run periods, when only slurry catalyst was used. Other differences in conditions which were also in effect in Periods I through M were an increased coal concentration and an increased coal feed rate. The proton distribution changes generally indicated better hydrogenation of certain streams, especially the V-131B distillate and the product distillates, when hybrid catalyst was used. There was not any significant change in donor solvent quality with the switch to hybrid catalyst operation in Periods I through M. In Periods I through M, the V-131B process solvent was much lower in phenolic -OH concentration than in the slurry catalyst portion of the run (Periods A through H). The supported catalyst evidently plays an important role in deoxygenation of the process oils.

During Period F (considered transitional), the source of the ash recycle was the V-1067 stream, instead of the V-1082 bottoms stream used in the remainder of the run. Distillation conditions were also changed to accommodate the heavier product distillate. The V-131B sample from Period F appears to have an unusually high ash content and an unusually low resid content. The highest V-131B distillate donor solvent quality (82%) occurred in Period F, (64 to 79% in the other periods). Perhaps the improved distillate solvent quality in Period F results from decreased paraffinicity and slightly increased aromaticity. During Period F, the V-131B distillate sample became more phenolic, and a shift in the phenol peak indicated that the phenolic species were more-alkylated and less-aromatic.

The Period A process oils shared several features with the corresponding process oils from Run 262 (the start-up solvent was produced in Run 262). The Period 263A V-131B distillate exhibited poor donor quality, was quite high in paraffins (alkyl beta + gamma protons) and low in condensed aromatic protons, and was lower in phenolic -OH concentration than in the following periods of slurry catalyst operation (Periods B through H). It appears that Period A was transitional with regard to many of the V-131B distillate oil properties, although Wilsonville staff considered the plant performance to be stable.

HRI PROOF-OF-CONCEPT RUN POC-1

A sampling and analytical plan for CONSOL support of HRI Run POC-1 was formulated in conjunction with HRI and DOE. A description of the plan is provided.

Some analyses were completed on a set of process samples from early in HRI's Proof-of-Concept Run 1. Oil samples were generally low in donor solvent quality, low in phenolic -OH concentration and fairly high in paraffinic hydrogen concentrations, perhaps reflecting high initial catalyst activity. The feed coal appears to be unoxidized, but one sample was found to be contaminated with foreign (non-coal) materials. Perhaps this resulted from contact with contaminated coal-handling equipment prior to receipt by CONSOL.

PHENOL METHOD IMPROVEMENTS

Two adaptations were made to our FTIR method for phenolic -OH concentration in coal liquids. The changes extend the method's versatility by accommodating moisture-containing and solids-containing samples. In one modification, a method was devised to eliminate water interference from the determination of phenolic -OH in coal liquids. The drying method worked well in samples ranging from slightly wet to severely wet, and thus appears to have general applicability to coal liquid samples which are wet. In the other modification, a shortcut method was devised to allow fast determination of phenolic -OH in solids-containing samples; the main modification is the use of a rapid tetrahydrofuran (THF) extraction to produce the soluble samples. The method was tested on a small number of samples. It performed fairly well over the -OH concentration range of 0.17 to 1.22 meq/g, with samples containing from about 20 to 50 wt % THF-insolubles. It will not, however, replace the more precise and accurate method of -OH determination on fully-extracted THF solubles.

PUBLICATIONS AND PRESENTATIONS

- A paper presented at the DOE United Kingdom/United States Technical Exchange Meeting and Liquefaction Workshop, Pittsburgh, PA, 9/24/93, is included as Appendix B. "Evaluation of Advanced Analytical Methods for Direct Liquefaction Process Development" was authored and presented by F. P. Burke.
- A peer-reviewed paper published under the Participants Program is included as Appendix C. "Characterization of Coal Liquefaction Resids by Field

Ionization Mass Spectrometry: Correlating Spectral Features with Processing Parameters" was authored by R. Malhotra, D. F. McMillen, E. L. Watson, and D. L. Huestis of SRI International and published in *Energy and Fuels*, 1993, 7, 1079-1087.

- A peer-reviewed paper published under the Participants Program is included as Appendix D. "Characterization of Coal Liquefaction Heavy Products Using ²⁵²Cf Plasma Desorption Mass Spectrometry" was authored by J. W. Larsen, A. R. Lapucha, P. Wernett, and W. R. Anderson of Lehigh University and published in *Energy and Fuels*, 1994, 8, 258-265.
- A peer-reviewed paper to be published under the Participants Program is included as Appendix E. "Thermal Conversion of Coal Liquefaction Resids: Temperature-Programmed Electron Spin Resonance and Thermogravimetric Investigations" was authored by M. Seehra and M. M. Ibrahim of West Virginia University and accepted for publication in a special issue of *Catalysis Today*.
- A paper submitted for journal publication under the Participants Program is included as Appendix F. "High Performance Liquid Chromatography (HPLC) of Coal Liquefaction Products Using Normal-Phase Separation with Diode Array Detection" was authored by D. E. McKinney, D. J. Clifford, L. Hou, and P. G. Hatcher of The Pennsylvania State University and M. G. Bogdan of Sci Tech, Inc. and submitted for publication in *Energy and Fuels*.
- A paper submitted for journal publication under the Participants Program is included as Appendix G. "The Use of a Novel Short Contact Time Batch Reactor and Thermogravimetric Analysis to Follow the Conversion of Coal-Derived Resids During Hydroprocessing" was authored by H. Huang, W. H. Calkins, and M. T. Klein of the University of Delaware and submitted for publication in *Industrial and Engineering Chemistry Research*.
- A preprint submitted for presentation at the 207th National Meeting of the American Chemical Society, San Diego, CA, 3/13-18/94 under the Participants Program is included as Appendix H. "The Use of Thermogravimetric Analysis to Follow the Conversion of Coal Derived Resids in the Resid Recycling

Process" was authored by H. Huang, W. H. Calkins, and M. T. Klein of the University of Delaware.

- A preprint submitted for presentation at the 208th National Meeting of the American Chemical Society, Washington, DC, 8/21-25/94 under the Participants Program is included as Appendix I. "High-Quality Distillate Products from Direct Liquefaction of Coal" was authored by P.-Z. Zhou of Burns and Roe Services Corp., R. A. Winschel of CONSOL R&D, and E. B. Klunder of DOE/PETC.
- A presentation to be made at the 42nd Meeting of the American Society of Mass Spectrometry, Chicago, IL, June 3, 1994, describes work conducted under the Participants Program. "Characterization of Coal-Derived Materials Using Field Desorption Mass Spectrometry" is being authored by J. A. Campbell, R. B. Lucke, and C. D. Cody of Battelle Pacific Northwest Laboratory. No written materials were available for inclusion in this report.

Section 2

RESULTS AND DISCUSSION

WILSONVILLE RUN 263

WILSONVILLE RUN 263 OVERVIEW

CONSOL analyzed a portion of the 47 process oil samples received from Wilsonville Run 263, which was operated with subbituminous coal from the Black Thunder Mine and with slurry-only and hybrid (slurry first stage/supported second stage) catalysts.¹⁻⁵ Slurry-catalyst-only operation had been tested briefly in Run 262, after hybrid catalyst operation for most of the run.⁶ Run 263 was operated from October 31, 1991, through February 23, 1992, in the Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) configuration with ash recycle. The high/low temperature sequence was used throughout the run. Molyvan L or Molyvan 822 slurry catalyst precursor was fed to the first stage, along with iron oxide and dimethyl disulfide (DMDS) as a sulfiding agent. In theory, the iron oxide promotes coal conversion, and the Mo catalyst provides hydrogenation. The latter is intended to help prevent the coking which contributed to interstage deposition in runs prior to Run 262 with this coal. In Run 262, Molyvan L use largely succeeded in avoiding severe interstage deposition.^{4,6} However, deposition was not entirely prevented; some deposition occurred in the interstage separator and in the first-stage reactor. No deposition occurred in the transfer lines or the second-stage reactor, as had taken place prior to Run 262. Molyvan L and Molyvan 822 are oil-soluble lubricant additives (friction reducer, antioxidant, antiwear, and extreme pressure agent properties) produced by R. T. Vanderbilt Company. Molyvan L consists of the organometallic compound molybdenum di(2-ethylhexyl)phosphorodithioate in a petroleum oil. It contains 8.1% Mo, 12.3% S, 6.4% P, and no N by weight. Molyvan 822 is described by the manufacturer as a sulfurized oxymolybdenum dithiocarbamate in a petroleum oil. It contains 4.9% Mo, 6.0% S, no P, and an unreported amount of N by weight (presumed to be about 1% N or lower). Presumably, under liquefaction conditions, the soluble Molyvan precursor is converted to finely divided, well-dispersed particles of MoS_2 . The supported catalyst used in the second stage during part of the run was Criterion 324 (Ni/Mo on 1/16" extrudate unimodal alumina support). Criterion 324, equivalent to Shell 324, is produced in Europe. The iron oxide used was obtained from Bailey Engineers, Fairfield, AL. The iron oxide used in previous runs (obtained from Kerr-McGee Chemical Company, Mobile, AL) was much higher in contaminant

concentrations, and was thought to provide chlorine for the halite found in deposits from Runs 258 and 260.^{1,4}

Run 263 was made using 50% of the available volume of each reactor. The interstage separator was in use throughout the run. The major operating variables were catalyst variables (presence or absence of supported catalyst, supported catalyst addition rate, use of Molyvan L vs. Molyvan 822, dispersed Mo and Fe concentrations), second-stage reactor temperature, coal feed rate (and consequently, space velocity), inlet hydrogen partial pressure, recycle resid concentration, and ashy recycle source. The ashy recycle stream was V-1082 bottoms, except in Period F, when the V-1067 atmospheric flash bottoms were used for ashy recycle.

The objectives for Run 263 were: 1) to evaluate the performance of a dispersed molybdenum catalyst for processing a low-rank coal, 2) to investigate and eliminate solids buildup during low-rank coal operation, and 3) to evaluate the performance of a hybrid catalyst system with dispersed molybdenum and Criterion 324 supported catalysts. Some of the Wilsonville 263 run results are highlighted below.

An "all-distillate" product slate (resid yield of -1 to 4 wt % MAF) was achieved using only slurry catalyst in periods 263E-H. During these periods, distillate yields were 57 to 62 wt % MAF and organic rejection was 14-15 wt % MAF. Molyvan 822 was found in tests at Auburn University to perform better than Molyvan L, however, little difference in resid + UC conversion was observed when the catalyst precursor was switched from Molyvan L to Molyvan 822. Reducing the iron oxide concentration from 2 to 1 wt % appeared to have no impact on resid + UC and coal conversions.

The presence of supported catalyst in the second stage reactor gave a significant (26-33%) improvement in the projected distillate production rate (in lb/hr), relative to slurry-catalyst-only operation. The improvement resulted from the higher space velocities used with supported catalyst present. Performance in periods 263I and 263J was similar to that given above for slurry catalyst operation.

Process performance with atmospheric flash bottoms (V-1067) recycle was similar to that with vacuum flash bottoms (V-1082) recycle, except for an increase in product boiling point. It appeared that there was predominately a physical displacement of the lighter V-1067 when it was recycled. That is, the product distillate contained an amount of heavier distillate about equal to the amount of lighter material recycled.

As in Run 262, the transfer lines between the reactors and after the second-stage reactor remained free of deposits, apparently as a result of Molyvan L or Molyvan 822 use. In Run 263, deposition did occur in the interstage separator, as well as in the first-stage reactor. However, the deposits did not seem to cause operating difficulties. Nearly halfway through Run 263, 100 lb of solids were removed from the interstage separator during an outage. About 20 lb was a hard wall deposit; the rest was gummy material. At the end of the run, 150 lb of deposit material was removed from the interstage separator, and 45 lb of deposit material was removed from the first-stage reactor. This is significantly more than the 54 lb of total material removed in Run 262. Contributing factors to the increased deposition in Run 263 appear to be: Run 263 was nearly twice as long as Run 262; Run 263 was operated longer without supported catalyst; and reactor temperatures were generally higher in Run 263 (especially in the first-stage reactor). Wilsonville personnel believe^{1,4} that a different interstage separator design could eliminate the deposition problems.

Only 69% of the supported catalyst was recovered at the end of the run. The low recovery was attributed to catalyst attrition resulting from bypass of gas and slurry through holes which had worn into the reactor plenum and the gas/slurry distribution device.

Hybrid catalyst operation with Black Thunder coal gave a higher projected distillate production rate (lb/hr) per reactor volume than operation with Illinois 6 coal.¹⁻⁵ Wilsonville personnel found that hybrid catalyst operation resulted in a 30-60% increase in projected distillate production rate over operation with slurry catalyst or supported catalyst alone, when processing Black Thunder coal. The higher production rates resulted primarily from operation at higher coal feed rates.

Relative to supported catalyst only, the addition of 100 ppm Mo significantly improved coal and resid conversion, allowed operation at lower first-stage thermal severity and higher second-stage thermal severity; it also resulted in higher distillate yield and higher distillate selectivity from resid + UC conversion (i.e., percent of converted resid + UC that is distillate).

Hybrid catalyst operation gave better quality products than slurry-catalyst-only operation. Slurry catalyst seemed to improve first stage coal and resid hydrogenation, resulting in higher first stage conversion; it apparently played less of a role in hydrogenation of process solvent and products than did the supported catalyst. A decrease in Mo addition concentration from 200 to 100 ppm appeared to have no effect on coal or resid conversion.

Operating conditions and yields¹ for material balance periods appear in Table 1. A simplified flow scheme⁷ of the Wilsonville plant, as configured for Run 263, appears in Figure 1. More detail on the part of the plant involving the major distillate streams is shown in Figure 2.

PLANT DESCRIPTION

During Run 263, the Wilsonville plant (Figures 1 and 2) was operated with ash recycle in the slurry-catalyst-only mode and hybrid catalyst mode (slurry/supported catalyst). The standard plant configuration, as used during most of the run, is described below. Following that, the exception to the standard configuration (i.e., a change in the ashy recycle stream) is described.

For standard operation, coal was slurried with a mixture of second-stage vacuum-flash bottoms (ashy resid, V-1082 bottoms), second-stage heavy distillate (V-1074), and deashed second-stage product resid (V-130). The pasting solvent stream is called V-131B. The coal/pasting solvent slurry was mixed with hydrogen and passed through the preheater and first-stage backmixed reactor (R-1235). Run 263 was made with the interstage separator (V-1258) in place. The interstage separator removed the gas and light products from the first-stage products prior to processing in the second stage. The liquid portion of the separator overheads was sent to the product distillation system. The separator bottoms were sent to the second stage, along with make-up hydrogen. The second-stage ebullated-bed reactor (R-1236) was operated as a backmixed thermal reactor when no supported

catalyst was used in the first part of Run 263. Gases and light oils were separated from the second-stage product in an atmospheric flash (V-1250). The atmospheric flash bottoms (V-1067) were separated in a vacuum flash into distillate (V-1082 overheads) and resid (V-1082 bottoms). The V-1067 stream contains ash, IOM, resid and distillate, and represents the bulk of the recycled material prior to partial deashing. A portion of the V-1082 bottoms stream was recycled to the first stage as a component of the pasting solvent. The remainder of the V-1082 bottoms stream was deashed in the Kerr-McGee ROSE-SR (formerly called Critical Solvent Deashing) unit, which rejected an ash concentrate and produced a deashed resid product (V-130). The deashed resid was recycled to V-131B as the second component of the pasting solvent. The atmospheric flash overhead liquids and the V-1082 overheads were sent to the distillation system (consisting of the T-105 atmospheric tower, followed by the T-102 vacuum tower), which produced naphtha (V-161, the T-105 overheads), middle-distillate (V-182, the T-102 overheads), and heavy distillate (V-1074, the T-102 bottoms). The heavy distillate was recycled as the third component of the pasting solvent. The withdrawal tube flush stream during Run 263 consisted of T-102 vacuum column bottoms (V-1074), the heavy gas oil used for recycle. Prior to Run 262, the lighter V-182 material had been used.

The only exception to the standard plant configuration occurred during Period 263F, when the operation was changed so that V-1067 became the ashy recycle component, instead of V-1082 (Figures 1 and 2). To accommodate the change, the T-102 vacuum tower was set to operate at higher pressure, thus producing a higher boiling distillate product.

ABBREVIATED HISTORY OF RUN 263

This section is paraphrased from Wilsonville technical review meeting handouts and the final run report.^{1,2} Run 263 began on October 31, 1991, in the slurry-catalyst-only CC-ITSL mode with ash recycle. The feed coal was Black Thunder Mine, Wyodak and Anderson seams subbituminous coal. Slurry catalysts and sulfiding agent were fed to the first-stage reactor as follows: iron oxide (2 wt % of the MF coal) was mixed with the coal slurry and Molyvan L (Mo was 200 ppm of the MF coal) was mixed with dimethyl disulfide (DMDS) sulfiding agent and injected into the feed line before the first-stage preheater. The first-stage reactor was R-1235 and the second-stage reactor was R-1236. Both reactors

were configured to use 50% of the available reactor volume. The interstage separator (V-1258) was in use throughout the run. The start-up solvent was produced in Run 262 from the same subbituminous coal. The run was to start up with reactor temperatures of 810/825 °F, but there was too little reaction heat and the second-stage temperature reached only 800 °F. The conditions were then changed to 825/810 °F. Other target start-up conditions were: 300 MF lb/hr coal feed rate, 25 wt % coal in the slurry (3.00 solvent/coal ratio), 45 wt % resid and 20 wt % cresol insolubles (CI) in the recycle solvent. Resid injection (tried in Run 262) was not used, because plugging of the system was encountered in Run 262, causing substantial variation in flow rate and adversely affecting material balances.

After operation with slurry catalyst only (after Period H), the second-stage reactor was charged with 170 lb (dry) of Criterion 324 1/16-inch (Ni/Mo) catalyst withdrawn from Run 262. The initial catalyst age, equivalent to a 3 lb/ton addition rate at equilibrium, was 668 lb MF coal/lb cat, or 1386 lb resid + CI/lb cat.

A chronological account of the run follows:

- 10/31/91: Run 263 started.
- 11/1: An outage occurred because of a valve blockage in the V-1082 vacuum flash vessel recirculation loop.
- 11/2: Plugging occurred in the oil/water separator which handles the V-1258 (interstage separator) overheads; steam tracing was added to the oil/water separator; waxy products were noted.
- 11/3: Level control on V-1250 overhead separator was not working; additional steam tracing was added; waxy products noted.
- 11/4: To improve second-stage temperatures, DMDS was added to the second-stage reactor, and the withdrawal tube flush rate was lowered.
- 11/5: Reactor temperatures were adjusted to 825 °F in the first stage and 790 °F in the second stage.
- 11/6: Target resid concentration in the pasting solvent was changed from 42 wt % to 45 wt %. Slurry became too viscous to pump; V-101B recirculation was lost. T-102 overhead material was added to thin out the slurry.

11/7: Second-stage reactor temperature was adjusted to 810 °F.

11/10-14: **Material balance period 263A**

11/11: 10-20 gallons of lubricating oil entered the slurry feed when the slurry tank recirculation pump leaked.

11/12: An increase in the material level and density in the V-1258 interstage separator provided a possible indication of solids accumulation.

11/15: The dispersed catalyst (Molyvan L precursor) addition rate was decreased from Mo concentration of 200 to 100 ppm of MF coal.

11/17,18,20-22: **Material balance period 263B**

11/22-27: An outage was caused by failure of the first-stage ebullating pump; the uninterruptable power system also failed. The V-1258 level and density decreased, perhaps indicating a washout of the V-1258 solids. On attempted startup, a line from T-102 to V-1074 failed, requiring replacement.

11/27: First-stage temperature was increased from 825 °F to 840 °F

12/1-2: An outage was caused when the reactors were accidentally depressurized while the C1206 second-stage recycle compressor was being repaired. The V-1258 and V-1247 overhead lines were cleared.

12/3,6-9: **Material balance period 263C**

12/8: V-1079 was bypassed because the flow was too low; new flow rates were estimated.

12/10: The target coal feed rate was decreased from 300 to 265 lb MF/hr and the target resid concentration in the pasting solvent was decreased from 45 to 42 wt %.

12/13-17: **Material balance period 263D**

12/15: An increase in the material level and density in the V-1258 interstage separator provided a possible indication of solids accumulation.

12/17: When the V-1074 oil became too viscous, the withdrawal tube flush was changed to use T-102 overheads.

12/18: The target resid concentration in the pasting solvent was increased from 42 to 45 wt %.

12/19-22: An outage was caused by failure of the P1236 second-stage ebullating pump.

12/19: The V-1258 interstage separator was inspected: a 3" deposit was found on one wall, and there was gummy material in the bottom 3 feet of the vessel. About 100 lb of solids were removed.

12/22: On startup after the outage, a low-reading thermocouple at the bottom of the first-stage reactor indicated the possible presence of solids in the bottom of the reactor.

12/24: Shutdown of the P1222 first-stage ebullating pump, possibly caused by plugging.

12/26-28,31,1/1: **Material balance period 263E**

12/27,29: Shutdown of the P1222 first-stage ebullating pump may have been caused by plugging.

12/29: A low-reading thermocouple at the bottom of the first-stage reactor indicated the possible presence of solids.

1/1 on: Daily shutdown of the P1222 first-stage ebullating pump caused the recycle flow to stop for a few minutes each day.

1/2: The catalyst precursor was changed from Molyvan L to Molyvan 822; Mo concentration remained at 100 ppm of MF coal. The ashy recycle was changed from V-1082 to V-1067; T-102 pressure was set to 2.5 psia.

1/4-6: **Material balance period 263F was considered transitional, because it was relatively short.**

1/4-6: The ROSE-SR feed had a high solvent content, due to plugging of the V-1082 overheads condenser.

1/7: The T-102 settings were returned to normal, in order to control V-1074 inventory.

1/8: The ashy recycle was changed back to V-1082.

1/9-13: **Material balance period 263G**

1/10: The second-stage temperature fell below the target value, as a result of cold weather.

1/12: The slurry feed was interrupted, due to loss of slurry recirculation in feed tank.

1/14: The second-stage temperature fell below the target value, as a result of cold weather. The iron oxide concentration was decreased from 2 to 1 wt % of MF coal.

1/16-20: **Material balance period 263H**

1/17: A low temperature excursion in both reactors was caused by an instrument air outage.

1/21: 170 lb (dry weight) of Run 262 catalyst was added to the second-stage reactor. Catalyst replacement rate was set at 3 lb/ton MF coal.

1/22: The target coal concentration in the slurry was increased from 25 to 30 wt % and the target coal feed rate was increased from 265 to 350 lb MF coal/hr.

1/23,25-27: **Material balance period 263I** was considered transitional, because of the recent addition of supported catalyst to the second stage.

1/23: Coal was fed from a new coal pile.

1/24: Plant was taken off coal feed for 12.5 hour and put on solvent circulation only, in an unsuccessful attempt to remove solids from V-1258 interstage separator.

1/26: The slurry feed was interrupted, due to failure of stirring motor on slurry feed tank.

1/27: Began feeding Molyvan L catalyst precursor, when the supply of Molyvan 822 ran out.

1/28: The coal feed rate was decreased to 300 lb MF coal/hr for 1/2 day due to unavailability of tote bins.

1/29: The target resid concentration in the pasting solvent was decreased from 45 to 40 wt %.

1/29-31,2/1,3: **Material balance period 263J**

1/30: A plugged impulse line in the V-1258 interstage separator caused erroneous pressure readings.

1/31-on: The ROSE-SR feed pumps were not working well, because of an increase in the feed solids content.

2/1-3: Erroneous flow rates resulted from oil accumulation in the second-stage recycle gas flowmeter.

2/4: The hydrogen partial pressure in the first-stage reactor was decreased by 400 psia (from about 2800 to about 2400 psia).

2/5: Erroneous flow rates resulted from oil accumulation in the second-stage recycle gas flowmeter.

2/6-9: **Material balance period 263K**

- 2/8: Catalyst replacement was stopped, so that the catalyst could be aged batchwise to represent an equilibrium age of 2 lb/ton MF coal replacement rate.
- 2/10: Replacement of vacuum jets enabled T-102 to reach pressures lower than 2 psia. The hydrogen partial pressure in the first-stage reactor was increased back to its original value (from about 2400 to about 2800 psia).
- 2/11,14-16: **Material balance period 263L**
- 2/12-13: An outage was caused by failure of the C102 first stage recycle compressor.
- 2/13: The P-1222 first-stage ebullation pump was taken off-line after it failed. Operation of the first stage without forced backmixing continued through the end of the run.
- 2/17: Catalyst replacement was started at 2 lb/ton MF coal.
- 2/18-22: **Material balance period 263M**
- 2/19: A decrease in the temperature reading in the middle of the V-1258 interstage separator indicated solids accumulation.
- 2/23: End of Run 263

SAMPLE DESCRIPTIONS

CONSOL received 47 process oil samples from Run 263. The process oils consisted of a recycle oil (V-131B) sample, an interstage oil (R-1235) sample, and a second-stage product oil (V-1067) sample composited from each of the thirteen material balance periods A through M. V-1067 is the second-stage flashed bottoms product. Net product distillates (V-161, V-164, V-182) and ROSE-SR bottoms product (V-107, the ash concentrate) from periods G and J were also obtained. At CONSOL's request, Wilsonville personnel composited samples over the complete material balance period for each sample. This was done to reduce uncertainty in interpretation of analytical results from one period to another.

ANALYSES

Elemental and other routine analyses were performed on selected samples from Periods E, G, and J. Elemental analyses are reported in Tables 2, 3, and 4. Proton distributions were obtained by ¹H-NMR for V-131B, R-1235, and V-1067 whole samples (Table 6). The whole samples were distilled (Table 5) to 320 °C pot/270 °C column/5 torr (850 °F/atm). Each 850 °F⁺ resid was analyzed by ¹H-NMR

(Table 7) and FTIR for phenolic -OH content (Table 8). Each 850 °F distillate was analyzed by ¹H-NMR (Tables 7) and FTIR (Table 8). Microautoclave tests were made at the modified equilibrium conditions with each 850 °F distillate (Table 8). All samples for proton distribution by NMR were dissolved in 99.96% deuterated pyridine (whole or resid samples) or in CDCl₃ (distillate samples) and integrated electronically. Other details of the sample work-up and analytical procedures have been presented elsewhere.^{8,9}

The suite of analyses is incomplete, as of the end of this contract.

PROCESS OIL PROPERTIES

Characterization results were only partially completed, due to other contract priorities. The characterization of the V-131B process solvent samples was more complete than that of any other sample type. The component distributions of the V-131B samples are shown in Table 5. The sample from Period F appears to have an unusually high ash content and an unusually low resid content. These may have resulted from the ashy recycle stream changes in Period F, which also was considered a transitional period. In Period J, the V-131B was high in distillate and low in resid, as a result of the change to lower target resid concentration in the process solvent. Since Period I was transitional, perhaps the effects of other operating changes associated with the start of hybrid catalyst operation in Period I did not begin to show up much until Period J.

V-131B distillate donor solvent quality (Table 8) was poor (64 to 69%) in Periods A and C, good (82%) in Period F, and fair (72 to 79%) in all the other periods. Distillate donor quality and other properties of the solvents in these periods are discussed below.

Hybrid Catalyst Operation (Periods I Through M)

Several oil properties changes were noted for Periods I through M when hybrid catalyst operation was used, relative to the prior run periods when only slurry catalyst was used. Undoubtedly, the use of supported catalyst in the second stage in Period J was a major factor in the observed differences, although there also were differences in other conditions (an increased coal concentration and an increased coal feed rate). The proton distribution changes generally indicated better hydrogenation of certain streams, especially the V-131B

distillate, when hybrid catalyst was used. The proton distributions of whole V-131B oils (Table 6) showed a distinct increase in cyclic beta protons in Periods I through M. The proton distributions of the V-131B distillate samples (Table 7) show that the concentration of condensed aromatic protons decreased and that of the cyclic beta protons increased in Periods I through M. This indicates better hydrogenation of distillate when hybrid catalyst was used.

Of three R-1235 samples from Periods E, G, and J, the sample from Period J had the highest concentrations of cyclic beta, alkyl beta and gamma protons, and the lowest concentration of condensed aromatic protons (Table 6). In the proton distributions of the V-182 and V-161 product distillate samples (Table 6), the samples from Period J were lower in aromatic protons, especially uncondensed protons; they were also lower in alkyl alpha protons, and higher in cyclic beta, alkyl beta, and gamma protons. No differences in the proton distributions of V-164 samples from Period G and Period J were evident (Table 6), apparently because the V-164 samples represent light oils only from the first reactor stage (see Figure 2). Supported catalyst hydrogenation effects were evident in the R-1235 oil, but not in the light (separator overhead) oil.

There was not any significant change in donor solvent quality with the switch to hybrid catalyst operation in Periods I through M.

In Periods I through M of Run 263, the V-131B process solvent was much lower in phenolic -OH concentration (Table 8) than in Periods A through H. The supported catalyst evidently plays an important role in deoxygenation of the process oils. The phenolic -OH concentrations in the V-131B distillates and resids increased slightly in Periods L and M, relative to Period K, apparently because of decreasing catalyst activity with increasing catalyst age.

Ash Recycle Stream Modification (Period F)

During Period F (considered transitional), the source of the ash recycle was the V-1067 stream, instead of the V-1082 bottoms stream used in the remainder of the run. Distillation conditions were also changed to accommodate the heavier product distillate. Also beginning in Period F (and continuing through Period I) was the use of Molyvan 822 catalyst precursor, in place of the Molyvan L

catalyst precursor used in the remainder of the run. However, Wilsonville personnel ascribed no process performance difference to the use of Molyvan 822.

The whole V-131B oils from periods F and G exhibited relatively high concentrations of cyclic alpha protons and low concentrations of alkyl beta protons. The cause is not readily apparent, except that it may be related to the ash recycle stream/distillation change which took place in Period F. Perhaps the system did not recover from the change until after Period G. The proton distribution of the V-131B distillate sample (Table 7) in Period F was high in uncondensed aromatic protons, and in cyclic and alkyl alpha protons and was very low in alkyl beta protons, relative to the other V-131B distillates. The whole V-1067 oil from Period F (Table 6) was relatively high in uncondensed aromatic protons, and alkyl alpha protons, and low in alkyl beta protons. It appears that these changes in oil properties are caused by the recycle stream changes.

During Period F, there was a significant increase in the phenolic -OH concentration in the V-131B distillate sample (Table 8). In addition, the phenol peak maximum, ν , shifted to a higher frequency, indicating that the phenolic species were more-alkylated and less-aromatic. This is not inconsistent with the proton distribution of this sample (Table 7), which in Period F was high in uncondensed aromatic protons, and in cyclic and alkyl alpha protons and was very low in alkyl beta protons.

V-131B distillate donor solvent quality (Table 8) was good (82%) in Period F, better than in all the other periods, which ranged from poor (64%) to fair (79%). Other than decreased paraffinicity and slightly increased aromaticity in the Period F distillate, it is not clear why the solvent quality should be significantly better in Period F.

Oil Properties in Miscellaneous Periods

V-131B distillate donor solvent quality (Table 8) was poor in Periods A and C, (64 and 69%, respectively), and fair to good (72 to 82%) in the other periods. Perhaps the Period A solvent properties still reflected the poor donor quality of the start-up solvent, which was produced in Run 262.⁶ Just prior to Period C, the use of higher first-stage reactor temperatures was begun.

The V-131B distillate sample (Table 7) from Period A was quite high in paraffins (alkyl beta + gamma protons), and low in condensed aromatic protons. The high paraffinicity is probably a factor in the low donor solvent quality, and also reflects properties of the start-up oil from Run 262. In Period A, the distillate phenolic -OH concentration was relatively low, but the corresponding resid was relatively high in phenolic -OH concentration (Table 8). In Run 262, hybrid catalyst operation was used through nearly the entire run, and the distillate phenolic -OH concentration was lower than in the first part (Periods A through H) of Run 263, which used slurry catalyst. As in the other Period A properties, the distillate phenolic -OH concentration reflects start-up oil properties. It appears that Period A was transitional with regard to many of the oil properties, although Wilsonville staff considered the plant performance to be stable.

Reduction of the coal feed rate and resid concentration in Period D appears to have decreased the distillate phenolic -OH concentration by about 0.1 meq/g (Table 8).

COMPARISON OF OILS FROM RUN 263 WITH OILS FROM RUN 262

In general, the Run 263 samples analyzed were less paraffinic and more aromatic (Tables 6 and 7) than corresponding samples from Run 262,⁶ which was made with the same coal. Perhaps this is a consequence of operation at high space velocity and high temperature in Run 263. The donor solvent quality (Table 8) of V-131B distillates was generally higher in Run 263, probably reflecting the influence of the higher aromaticity and lower paraffinicity.

The V-131B whole oils from Run 263 generally contained less distillate, more resid, less IOM, and more ash than their Run 262 counterparts. Relative to the corresponding Run 262 samples, the Run 263 V-131B 850 °F distillates were lower in phenolic -OH concentration, but the 850 °F resids were higher in phenolic -OH concentration (only hybrid catalyst periods were compared). The magnitude of the concentration differences were such that the whole V-131B oil phenolic -OH concentrations (calculated from those of the components) were equivalent for the hybrid catalyst portions of Runs 262 and 263. Thus, the higher space velocity, higher temperature, and higher resid concentration in Run 263, had offsetting effects on the V-131 whole oil phenolic -OH concentration.

HRI CTSL Run POC-1

Analytical Plan

A plan was established with HRI for samples from Run POC-1 to be collected and sent to CONSOL for analytical characterization. The plan was based on CONSOL's anticipated sample needs, the characterization information desired, and the sample availability. A description of the plan finalized with HRI prior to the start of the run is presented here. Because the run plan subsequently was changed, the samples eventually received by CONSOL may differ from those specified in the sampling plan.

Discussions were held at the POC technical review meeting on August 24, 1993, with HRI personnel about samples from POC Run 1 for characterization work. HRI's current run plan and analytical plan was used as the basis for identifying sampling locations and frequency. The HRI run plan, on which CONSOL's sample plan was based, is presented in Appendix 1. A formal sampling plan was submitted to HRI. It was revised subsequent to discussions with HRI and DOE personnel. The sampling plan, as finalized with HRI before the start of the run, is presented in Table 9. The sampling plan was specified to allow HRI flexibility if the run plan is altered. The following discussion provides the rationale for the sampling plan.

As was done with several past HRI PDU runs, CONSOL plans to analyze the daily (once-per-period) sample that will provide the best indication of the chemical/molecular composition of the reactor products. This sample was identified as the reactor liquid flash drum bottoms (RLFDB). These samples will be subjected to a routine suite of characterization tests (^1H -NMR, phenolic -OH by FTIR, liquid column fractionation, THF-solubility, and solvent quality tests). In addition, other, more sophisticated, separation and spectroscopic analyses will occasionally be employed.

Samples of coal, recycle oil, reactor inventory, net product, and solids rejection samples were requested once-per-condition (including line-out), preferably taken during work-up periods to provide the best correspondence with HRI's analyses. The plan is to use these samples for more complete chemical/molecular analyses (e.g., solid state NMR, field ionization mass spectrometry, heteroatom speciation, and hydrogen accounting) similar to that which was done in the

Participants Program with the bench-scale Run CC-15 samples.¹⁰ Two additional reactor inventory samples (K1) from steady-state periods during each condition were requested, because of their importance to the evaluation of chemical reaction mechanisms and kinetics. Coal samples will be analyzed for oxidation, or other evidence of change during the run.

The 6-gallon net product sample to be taken once-per-run will be used for product inspection tests similar to that which was done under the Participants Program for Runs CC-15 and CMSL-2.¹¹ This sample will be selected to be representative of the overall run performance. A large (100 gal) sample of the recycle oil components (from the end of the run), and a 5-lb catalyst sample from each condition were requested for inclusion in our sample bank. CONSOL requested that samples be shipped on a weekly schedule during the run.

Characterization Data

Eleven samples were obtained from periods 8 and 9 of HRI Run POC-1. The samples include the feed coal, withdrawn catalyst from each reactor, naphtha stabilizer bottoms, atmospheric still bottoms, vacuum still overheads and bottoms, reactor liquid flashed bottoms, recycle oil, clean oil and make-up oil. This is the first set of samples obtained since start-up on October 29, 1993. The vacuum still served as the solids-removal device in use during period 9. Period 9 was considered a line-out period preceding the major test periods of the run. Similar sets of samples have been received from subsequent run periods 19, 26, 43, and 57, and additional daily RLFDDB samples were received from periods 17, 49, and 58), but none of these samples have been analyzed. Presented here are analysis results obtained on the set of samples from Period 9 of POC Run 1.

The solvent qualities (Table 10) of the oils, as measured by microautoclave assay tests, are generally low, especially that of the 0-43 recycle oil. Perhaps this results from low donor quality of the start-up oil, coupled with high catalyst activity early in the run. This explanation is supported by data from Run CC-16. In Run CC-16 (with Illinois 6 coal), solvent quality was low (58% coal conversion) early in the run, but increased rather quickly to a good quality solvent (83% coal conversion) as the run progressed.¹²

Proton NMR and phenolic -OH data are shown in Table 11. The Period 9 samples have very low phenolic -OH concentrations (<0.1 meq/g) and fairly high paraffinic proton concentrations (about 30% alkyl beta protons). It would appear that these properties reflect the high activity of the young catalyst.

The oxidation index was obtained, in duplicate, by diffuse reflectance FTIR analysis for three test grind coal samples, and a sample of the Illinois 6 coal fed during Period 9 (Table 12). The range of oxidation indexes from Illinois 6 coals previously analyzed by CONSOL are included in Table 12 for comparison. The oxidation indexes of the HRI samples do not appear to be high for Illinois coal, and differences among the four samples are small. There is no indication that these samples are oxidized. The observed differences could represent sample variation.

A sample of HRI's feed coal, which was submitted for ultimate analysis, was found to be contaminated with bits of white plastic, and black flakes, and "prills" of other carbonaceous material. Perhaps this occurred prior to receipt by CONSOL from contact with coal-handling equipment contaminated from use with non-coal materials. The analyses of this contaminated coal sample is given in Table 13.

Phenol Method Improvements

Two adaptations were made to the FTIR method^{9,13,14} for determination of phenolic -OH concentration in coal liquids. The changes extend the method's versatility by accommodating moisture-containing and solids-containing samples. One modification was devised to eliminate water interference from the determination of phenolic -OH in coal liquids. The other modification, a shortcut method, was devised to allow determination of phenolic -OH in solids-containing samples without long tetrahydrofuran (THF) extraction periods to produce the soluble samples. These are described below.

Wet Samples

Occasionally, samples for phenolic -OH determination contain water. Although a small amount of water presents no problem, water in sufficient quantity interferes with the phenolic -OH determination by FTIR. When the method was first developed, a subjective criterion was adopted for identification of significant water interference.¹³ The interference is considered significant

when the highest water peak in the infrared spectrum of a sample is greater than one-half the height of the phenol peak. The following modification of the standard method was developed for wet samples. Each oil sample is weighed and diluted with dry HPLC grade tetrahydrofuran in a 2 mL volumetric flask, per the usual procedure. The solution is mixed well, about 50 mg of molecular sieve (Davison grade 516, 14-30 mesh granules, 4 Å effective pore size) is added, and the solution is left in contact with the molecular sieve for several hours (or overnight). A liquid sample is then withdrawn and run in the normal manner. It can be determined from the spectrum if the drying time is sufficient. The recommended drying time is about two hours or more, but the minimum time required has not been determined.

As a test of this experimental drying treatment, phenolic -OH determinations were made both with and without drying on a set of samples which ranged from completely dry to quite wet (as indicated by the relative heights of the interfering water peaks and phenol peaks). The wettest samples most recently encountered were from DOE Contract DE-AC22-91PC91040, and consisted of extracts from coker tars produced at the University of Kentucky Center for Applied Energy Research, and dewaxed distillate solvents which were hydrogenated by Sandia National Laboratories (most using CO/steam instead of hydrogen). These samples were used as the test cases for the method. Drying the hydrogenated samples from Sandia (Table 14) increased the phenolic -OH concentration determined by 0.01 to 0.05 meq/g (essentially equal to the measurement reproducibility). The phenolic -OH concentration determined in one sample which was initially dry did not change when the sample was subjected to the drying treatment. These results indicate that the spectral baseline originally chosen for the analytical method provides a good elimination of water interference. However, the baseline correction is insufficient for the few extremely wet samples encountered in which the interference was severe. The phenolic -OH concentrations of several samples (feed oils and hydrotreatment products) dried by this method are shown in Table 14.

Using this method, phenolic -OH determinations also were completed on three coker tars received from UK/CAER as methylene chloride extracts. The samples were found to be quite wet, and the method adaptation was necessary to thoroughly dry them (Table 14). In fact, it was possible to use the phenol peak heights in the spectra of the wet and dry samples to obtain an indirect estimate of the water

content of the samples. These compared favorably with conventional laboratory determinations of moisture content: 22.1 wt % (lab) vs. 31.8 wt % (FTIR) for sample SR-3; 6.0 wt % (lab) vs. 5.9 wt % (FTIR) for sample SR-4; and 4.1 wt % (lab) vs. 3.2 wt % (FTIR) for sample SR-5. These results suggest that some variation of the FTIR phenolic -OH method might provide a way to measure the moisture content of coal-derived liquids.

Because the drying method worked well in samples ranging from slightly wet to severely wet, it appears to have general applicability to coal liquid samples which are wet.

Solids-Containing Samples

A few experiments were conducted to develop a fast method for obtaining phenolic -OH concentration in solids-containing samples (to be reported on a solids-free basis). Results were fairly good, but prior THF filtration (i.e., the conventional sample treatment^{9,13,14}) is still recommended for the highest accuracy and precision. The new method consists of preparing a THF "solution" of the whole sample, filtering it through a syringe filter, evaporating the solvent on the filter, weighing the retained solids, and then analyzing the solids-free solution to determine phenolic -OH concentration. The extra effort is primarily needed to determine the percent solubles in the whole sample. Addition of molecular sieve to reduce solution moisture content (as described above) is needed because the THF is exposed to the atmosphere as a result of additional handling. Absolute errors ranged from -0.05 to +0.06 meq/g in six trials with four samples (two samples were run in duplicate). The range of phenolic -OH concentrations represented was 0.17 to 1.22 meq/g. The samples consisted of two pressure filter cakes (about 50 wt % insolubles) from HRI Run CC-16, and two recycle solvents (V-131B) from Wilsonville Run 263 (about 20 wt % insolubles). The results for phenolic -OH concentration and the determined concentration of THF solubles used for correcting the determination are shown in Figures 3 and 4, respectively. The THF-solubles content from this approach are not highly accurate, but they appear to result in fairly accurate phenolic -OH concentrations.

Correction of Microautoclave Test Results

It was discovered that incorrect ash values were used for work-up calculations of some of our microautoclave tests which used the standard Old Ben Mine No. 1

coal. Results were recalculated for the affected runs, which were originally made during part of 1992 and 1993. A few revised results were from Wilsonville Run 262⁶ and HRI CC-16¹², which were already reported. The correction lowered most MAF coal conversions by 0.3 to 0.8% absolute (typically by about 0.5% absolute), but had no effect on reported conclusions. Correction of one set of coal calibration tests performed in 1992¹⁵ resulted in lower coal conversions by about 0.9% MAF, again with no effect on reported conclusions. The originally reported and corrected values for these runs are reported in Table 15.

Section 3

EXPERIMENTAL

Experimental details are described, where appropriate, in the Discussion section of this report. Details of the other analytical techniques used in this work were reported previously.^{8,9}

Section 4

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Section 5

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TABLE 1
OPERATING CONDITIONS AND YIELDS FOR MATERIAL BALANCE PERIODS
Wilsonville Run 263

Operating Period Date, 1991 Operation Days	263A, 11/10-14 10-14	263B 11/17,18,20-22 17,18,20-22	263C 12/3,6-9 26,29-32	263D 12/13-17 36-40
<u>Coal</u>				
Feed rate, MF lb/hr	299.0	298.8	293.6	259.7
Ash, wt % MF	7.7	7.0	7.6	7.2
Conc. in slurry, wt % MF	24.8	25.0	24.4	24.6
<u>Process Solvent, wt %</u>				
Resid	45.2	44.1	43.3	41.1
Cl	20.0	20.0	20.2	19.6
<u>First Stage</u>				
Reaction temp., °F (avg)	826	825	840	840
Inlet H ₂ partial pressure, psia	2756	2797	2707	2759
Total gas flow, scfh	4886	5014	4684	5044
Recycle gas, scfh	1534	1449	1196	1528
Space vel., lb MF coal/hr/ft ³ (C=constant)	79.0C	78.6C	77.6C	68.6C
Iron Oxide, wt % MF coal	2	2	2	2
Moly Conc., ppm MF coal	200	100	100	100
<u>Second Stage</u>				
Reactor temp., °F	810	809	810	810
Inlet H ₂ partial pressure, psia	2436	2420	2415	2477
Total gas flow, scfh	4765	4872	4757	5094
Recycle gas, scfh	2570	2775	2628	3115
Space vel., lb MF coal/hr/ft ³ reactor	79.0C	78.6C	77.6C	68.6C
Catalyst type	-	-	-	-
Catalyst age, lb (res+Cl)/lb cat	-	-	-	-
lb MF coal/lb cat	-	-	-	-
Cat replacement rate, lb/ton MF coal	-	-	-	-
ROSE-SR SM DAS type	2334	2304	2394	2404
<u>Yield, wt % MAF coal</u>				
H ₂	-4.3±0.3	-4.9±0.5	-4.6±0.6	-5.2±0.2
Water	11.6±1.8	13.4±1.8	13.7±0.7	13.0±0.7
H ₂ S	0.3±0.2	0.4±0.4	0.2±0.0	0.4±0.2
CO, CO ₂	6.2±1.3	6.0±0.7	5.8±0.3	6.3±0.3
NH ₃	0.4±0.1	0.3±0.0	0.3±0.2	0.5±0.1
C ₁ -C ₃ gas	6.7±0.5	6.3±0.2	7.8±1.1	9.1±1.2
C ₄ + distillate	47.9±4.8	51.8±1.8	52.1±0.6	54.6±4.3
C ₄ -C ₆	2.4±0.3	2.7±0.6	3.0±0.3	3.0±0.3
IBP-350°F	7.9±2.0	8.0±1.2	8.9±0.9	9.1±1.2
350-450°F	8.4±1.5	9.3±1.0	11.3±0.9	10.3±1.3
450°F-EP	29.1±6.7	31.9±1.4	28.8±1.2	32.1±6.5
Resid	9.4±5.3	8.6±2.8	6.6±2.4	5.5±3.3
Int. Acc. UC	0.7±1.2	1.0±0.9	0.4±0.3	0.3±1.0
ROSE-SR SM Bottoms Product (ash-free)	21.3±1.5	17.0±0.9	17.5±0.6	15.8±0.7
H ₂ efficiency, %	11.1±0.9	10.8±1.2	11.6±1.4	10.4±0.9
C ₁ -C ₃ selectivity, %	14.1±2.3	12.3±0.7	14.9±2.1	16.7±2.5
<u>Coal conversion, wt % MAF</u>				
First stage	80.4±5.9	82.2±3.2	86.1±3.9	87.0±1.4
Second stage	92.7±0.9	93.4±0.3	93.7±0.1	94.5±0.2
Overall TSL	92.8±1.4	92.5±1.4	92.9±0.5	93.1±0.5
<u>Resid + UC conversion, wt % feed</u>				
1st stage	17.9±3.0	16.6±1.3	19.9±1.0	20.1±1.2
2nd stage	8.4±4.2	13.7±3.4	9.6±1.5	12.7±1.5
<u>Resid + UC conversion, wt % MAF coal</u>				
1st stage	48.7±9.7	41.8±5.2	53.4±2.7	51.9±3.3
2nd stage	19.9±8.5	31.6±5.1	22.0±3.2	26.6±2.7
Overall	68.7±4.0	73.5±2.2	75.4±1.7	78.5±3.9

TABLE 1 (Continued)

**OPERATING CONDITIONS AND YIELDS FOR MATERIAL BALANCE PERIODS
Wilsonville Run 263**

Operating Period Date, 1991 Operation Days	263E, 12/26-28,31,1/1 46-48,51,52	263F (Transitional) 1/4-6 55-57	263G 1/9-13 60-64	263H 1/16-20 67-71
<u>Coal</u>				
Feed rate, MF lb/hr	260.9	254.3	263.5	263.9
Ash, wt % MF	7.1	6.9	7.1	6.8
Conc. in slurry, wt % MF	24.5	23.9	24.8	24.7
<u>Process Solvent, wt %</u>				
Resid	44.0	43.7	44.6	44.8
Cl	20.1	20.2	19.7	20.2
Recycle Cls from:	Vac. Fl.	Atm. Fl.	Vac. Fl.	Vac. Fl.
<u>First Stage</u>				
Reaction temp., °F (avg)	840	840	841	840
Inlet H ₂ partial pressure, psia	2724	2771	2771	2756
Total gas flow, scfh	4614	4769	4858	4575
Recycle gas, scfh	1234	1324	1616	1322
Space vel., lb MF coal/hr/ft ³ (C=constant)	68.9C	67.2C	69.6C	69.7C
Iron Oxide, wt % MF coal	2	2	2	1
Moly Conc., ppm MF coal	100	100	100	100
Moly Precursor	MV L	MV 822	MV 822	MV 822
<u>Second Stage</u>				
Reactor temp., °F	809	808	809	806
Inlet H ₂ partial pressure, psia	2546	2533	2546	2554
Total gas flow, scfh	4850	4829	5010	4785
Recycle gas, scfh	3021	3074	3094	2917
Space vel., lb MF coal/hr/ft ³ reactor	68.9C	67.2C	69.6C	69.7C
Catalyst type	—	—	—	—
ROSE-SR SM DAS type	2414	2364	2424	2424
<u>Yield, wt % MAF coal</u>				
H ₂	-5.5±0.2	-5.2±0.2	-5.1±0.2	-5.6±0.3
Water	13.2±1.3	13.6±0.6	14.2±1.0	14.4±0.9
CO, CO ₂	5.7±0.2	6.0±0.6	5.9±0.2	4.2±1.1
NH ₃	0.3±0.2	0.6±0.2	0.5±0.1	0.4±0.1
H ₂ S	0.4±0.1	0.5±0.2	0.3±0.1	0.1±0.1
C ₁ -C ₃ gas	9.0±0.3	9.1±0.4	8.9±0.7	9.4±1.0
C ₄ + distillate	60.7±2.0	61.5±3.3	57.0±1.1	60.9±2.7
C ₄ -C ₆	3.3±0.5	2.4±0.2	3.0±0.6	3.3±0.3
IBP-350°F	8.0±0.6	9.1±0.5	9.3±1.3	8.4±0.6
350-450°F	10.5±0.7	10.0±0.3	9.7±0.8	10.3±0.8
450°F-EP	39.0±2.4	40.0±2.6	35.0±1.8	38.9±3.1
Resid	2.4±0.9	0.2±3.1	4.1±0.6	2.4±1.8
Int. Acc. UC	-0.3±0.1	-0.8±0.7	0.2±0.2	0.0±0.7
ROSE-SR SM Bottoms Product (ash-free)	14.1±0.4	14.5±0.9	14.0±0.7	13.8±0.6
H ₂ efficiency, %	11.0±0.4	11.8±0.2	11.2±0.6	10.9±0.3
C ₁ -C ₃ selectivity, %	14.9±0.7	14.8±1.0	15.6±1.2	15.4±2.2
<u>Coal conversion, wt % MAF</u>				
First stage	90.2±1.3	88.7±1.4	89.3±2.8	88.4±2.5
Second stage	94.7±0.4	95.2±0.4	94.9±0.3	94.9±0.4
Overall TSL	94.1±0.8	94.9±0.4	94.1±0.6	94.3±0.4
<u>Resid + UC conversion, wt % feed</u>				
1st stage	22.7±0.6	22.8±0.7	22.7±0.8	22.0±0.7
2nd stage	9.7±1.0	9.8±2.3	9.9±0.8	10.0±1.5
<u>Resid + UC conversion, wt % MAF coal</u>				
1st stage	62.1±2.4	64.2±3.4	60.9±2.0	61.7±1.7
2nd stage	21.7±1.8	21.8±3.9	20.8±2.0	22.2±3.2
Overall	83.8±0.7	86.0±2.9	81.7±1.3	83.8±1.6

TABLE 1 (Continued)

OPERATING CONDITIONS AND YIELDS FOR MATERIAL BALANCE PERIODS
Wilsonville Run 263

Operating Period Date, 1991 Operation Days	263I (Transitional) 1/23,25-27 74,76-78	263J 1/29-31,2/1,3 80-83,85	263K 2/6-9 87-91	263L 2/11,14-16 93,96-98	263M 2/18-22 100-104
Coal					
Feed rate, MF lb/hr	342.6	344.9	344.1	345.1	348.0
Ash, wt % MF	6.7	6.7	6.5	6.6	6.5
Conc. in slurry, wt % MF	29.4	29.8	29.7	29.6	29.9
Process Solvent, wt %					
Resid	44.8	40.5	38.9	39.8	39.6
Cl	20.4	20.4	19.9	19.8	19.9
First Stage					
Reaction temp., °F (avg)	840	840	842	842	840
Inlet H ₂ partial pressure, psia	2773	2744	2386	2782	2785
Total gas flow, scfh	4460	4465	4042	4613	4505
Recycle gas, scfh	1162	1212	1773	755	655
Space vel., lb MF coal/hr/ft ³ (C=constant)	90.5C	91.1C	90.9C	91.2C	91.9C
Iron Oxide, wt % MF coal	1	1	1	1	1
Moly Conc., ppm MF coal	100	199	100	100	100
Moly Precursor	MV 822	MV L	MV L	MV L	MV L
Second Stage					
Reactor temp., °F	810	810	809	810	810
Inlet H ₂ partial pressure, psia	2482	2542	2515	2537	2549
Total gas flow, scfh	4943	5721	5423	4672	4829
Recycle gas, scfh	2061	2816	2493	2141	2291
Space vel., lb MF coal/hr/ft ³ reac	90.5C	91.1C	90.9C	91.2C	91.9C
Space vel., lb MF coal/hr-ft ³ cat	108.8	109.5	109.4	109.7	110.5
Catalyst type	Crit. 324	Crit. 324	Crit. 324	Crit. 324	Crit. 324
Catalyst age, lb (res+Cl)/lb cat	1386	1355	1292	1758	1891
lb MF coal/lb cat	668	662	640	889	963
Cat replacement rate, lb/ton MF coal	3.0	3.0	3.0	-	2.0
ROSE-SR SM DAS type	2404	2394	2354	2374	2364
Yield, wt % MAF coal					
H ₂	-5.6±0.1	-5.8±0.2	-5.7±0.2	-5.5±0.1	-5.2±0.1
Water	15.0±0.9	14.9±0.8	16.5±1.2	14.0±0.6	15.3±0.9
CO, CO ₂	6.5±1.0	6.0±1.1	4.8±1.5	7.2±0.6	7.1±0.5
NH ₃	0.7±0.1	0.8±0.2	0.7±0.0	0.6±0.0	0.6±0.1
H ₂ S	0.2±0.0	0.2±0.1	0.3±0.1	0.03±0.0	0.3±0.0
C ₁ -C ₃ gas	7.5±0.2	7.9±0.8	7.4±0.5	7.9±0.3	7.4±0.3
C ₄ + distillate	60.9±0.7	58.4±1.3	57.8±1.4	56.1±2.3	54.6±0.4
C ₄ -C ₆	2.7±0.3	3.3±0.5	3.2±0.5	3.6±0.3	2.8±0.2
IBP-350°F	12.4±2.0	11.9±0.8	11.7±1.5	11.5±1.7	10.4±1.3
350-450°F	8.7±0.4	8.3±0.5	8.2±0.2	8.5±1.0	7.8±0.8
450°F-EP	37.2±3.2	35.0±1.5	34.7±2.2	32.6±1.5	33.7±2.1
Resid	1.2±1.1	3.7±1.5	4.3±1.3	3.6±1.5	5.1±0.4
Int. Acc. UC	0.0±0.3	0.5±0.4	0.5±0.4	0.0±0.5	0.0±0.2
ROSE-SR SM Bottoms Product (ash-free)	13.7±0.6	13.4±0.3	13.5±0.1	15.9±0.7	14.8±0.6
H₂ efficiency, %	10.9±0.2	10.1±0.5	10.1±0.3	10.1±0.5	10.5±0.1
C₁-C₃ selectivity, %	12.4±0.4	13.6±1.3	12.8±0.9	14.1±0.9	13.5±0.6
Coal conversion, wt % MAF					
First stage	91.4±0.9	89.6±1.1	88.2±1.8	89.7±1.2	90.5±0.9
Second stage	93.7±0.2	94.1±0.3	93.8±0.1	93.5±0.2	93.5±0.1
Overall TSL	93.3±0.7	93.6±0.5	93.7±0.3	92.7±0.5	92.7±0.4
Resid + UC conversion, wt % feed					
1st stage	23.0±2.0	23.2±0.3	21.9±1.4	25.1±1.0	25.4±0.6
2nd stage	15.3±1.8	17.6±1.1	19.2±2.6	13.8±1.3	14.3±1.2
Resid + UC conversion, wt % MAF coal					
1st stage	55.6±5.2	51.8±0.9	47.9±2.8	56.4±2.4	56.0±1.4
2nd stage	29.6±4.1	30.6±2.3	33.9±4.5	24.2±3.1	24.1±2.2
Overall	85.2±1.7	82.4±1.7	81.7±1.8	80.6±1.9	80.1±0.9

NOTES: MV L = Molyvan L (263A-E, I-M); MV 822 = Molyvan 822 (263 F-H); Vac. FI = Vacuum Flash Bottoms; Atm. FI = Atmospheric Flash Bottoms

TABLE 2
ELEMENTAL ANALYSES OF SELECTED SAMPLES
Wilsonville Run 263

Sample	V-131B	V-131B	R-1235	V-1067
Fraction	Whole-Sample THF-Insolubles	850 °F* THF- Insolubles	850 °F* THF- Insolubles	850 °F* THF- Insolubles
Period	263E	263E	263E	263E
Wilsonville Sample No.	30180	30180	30191	30192
Moisture, wt % As-Determined	0.72	0.70	0.54	0.61
Ultimate Analysis, wt % Dry				
Carbon	33.35	34.36	35.93	33.73
Hydrogen	1.80	1.84	1.97	1.80
Nitrogen	0.54	0.51	0.52	0.52
Sulfur	6.46	6.31	5.99	6.20
Ash, Including SO ₃	65.98	65.37	62.37	65.79
Oxygen (by Diff.), Incl. Ash-SO ₃	-8.13	-8.39	-6.78	-8.04
Ash, SO ₃ -Free	53.18	52.45	50.08	52.43
Oxygen (by Diff.), SO ₃ -Free	4.67	4.53	5.51	5.32
Mo, mg/kg of Ash	1347	1312	1265	1315
Elemental, wt % of Ash				
Na ₂ O	0.16	0.22	0.22	0.22
K ₂ O	0.36	0.35	0.35	0.35
CaO	15.95	16.35	16.76	16.31
MgO	3.30	3.26	3.29	3.26
Fe ₂ O ₃	23.46	22.76	22.75	22.49
TiO ₂	0.85	0.84	0.85	0.85
P ₂ O ₅	1.31	1.30	1.31	1.29
SiO ₂	21.52	21.67	21.35	22.38
Al ₂ O ₃	13.16	13.10	13.07	13.18
SO ₃	19.40	19.76	19.70	20.30
Unaccounted	0.53	0.39	0.35	-0.63

Analyses performed by CONSOL R&D.

TABLE 3
ELEMENTAL ANALYSES OF SOLIDS-CONTAINING SAMPLES
Wilsonville Run 263

Sample	V-131B	R-1235	V-107	V-131B	R-1235	V-107
Period	263G	263G	263G	263J	263J	263J
Wilsonville Sample No.	30271	30272	30278	30281	30282	30288
Ultimate Analysis, wt % As-Determined						
Carbon	77.44	76.94	52.35(a)	78.87	77.58	54.18(b)
Hydrogen	6.44	6.34	3.08(a)	6.84	6.81	3.15(b)
Nitrogen	1.19	1.19	0.89(a)	0.77	0.83	0.86(b)
Sulfur	1.27	1.35	4.15(a)	0.87	0.91	2.79(b)
Ash, Including SO ₃	13.26	13.54	43.32(a)	12.46	11.94	37.99(b)
Oxygen (by Diff.), Incl. Ash-SO ₃	0.40	0.64	-3.79(a)	0.19	1.93	1.03(b)
Ash, SO ₃ -Free	-	-	34.89(a)	-	-	32.03(b)
Oxygen (by Diff.), SO ₃ -Free	-	-	4.64(a)	-	-	6.99(b)
Elemental, wt % of Ash						
Na ₂ O	-	-	0.28	-	-	0.57
K ₂ O	-	-	0.30	-	-	0.32
CaO	-	-	14.93	-	-	18.51
MgO	-	-	3.07	-	-	3.84
Fe ₂ O ₃	-	-	23.41	-	-	17.62
TiO ₂	-	-	0.79	-	-	1.05
P ₂ O ₅	-	-	1.06	-	-	1.16
SiO ₂	-	-	22.28	-	-	26.04
Al ₂ O ₃	-	-	12.49	-	-	14.05
SO ₃	-	-	19.45	-	-	15.70
Unaccounted	-	-	98.06	-	-	98.86

Analyses performed by CONSOL R&D; samples were assumed to be free of moisture.

- (a) Dry basis; as-received moisture was 0.32 wt %.
(b) Dry basis; as-received moisture was 0.40 wt %.

TABLE 4
ELEMENTAL ANALYSES OF SOLIDS-FREE LIQUID SAMPLES
Wilsonville Run 263

Sample Type	V-164	V-182	V-161	V-164	V-182	V-161
Period	263G	263G	263G	263J	263J	263J
Sample No.	30274	30276	30275	30284	30286	30285
Ultimate Analysis, wt % As-Determined						
Carbon	83.60	85.82	79.68	81.82	87.77	81.78
Hydrogen	10.52	9.89	11.41	10.40	10.20	12.13
Nitrogen	0.77	0.89	0.56	0.72	0.61	0.47
Sulfur	0.07	0.04	0.09	0.09	<0.03	0.09
Oxygen (by difference)	5.03	3.36	8.26	6.95	1.39	5.53

Notes: Analyses performed by CONSOL R&D, samples were assumed to be free of moisture and ash. ND = Not Determined

TABLE 5
COMPONENT DISTRIBUTION OF WHOLE SAMPLES
Wilsonville Run 263

Period	wt % of Sample			
	850 °F Dist	THF-Soluble Resid	IOM	Ash
<u>V-131B</u>				
A	21.2	56.1	10.1	11.7
B	25.1	56.7	8.0	9.7
C	22.9	55.9	8.1	12.4
D	24.6	54.6	7.7	12.5
E	25.2	54.6	7.4	12.5
F*	24.8	48.7	9.2	16.6
G	20.7	58.5	7.4	12.6
H	20.0	59.8	7.4	12.1
I*	20.6	54.8	9.1	11.6
J	27.7	50.3	9.4	12.0
K	23.8	53.9	9.5	11.1
L	25.7	52.9	9.8	10.9
M	26.9	53.1	9.1	10.4
<u>V-1067</u>				
E	29.1			
<u>R-1235</u>				
E	19.7			
G	20.5			
J	21.7			

*Transitional Period

TABLE 6
PROTON DISTRIBUTION OF WHOLE SAMPLES
Wilsonville Run 263

Period	Sample No.	Proton Distribution, %						
		Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
<u>V-131B</u>								
A	30163	22.1	5.4	16.7	8.3	12.3	23.7	11.5
B	30166	22.0	4.9	16.8	8.5	12.7	23.9	11.1
C	30169	23.6	4.4	17.2	8.5	13.0	22.8	10.4
D	30185							
E	30180	24.8	7.1	16.8	8.5	11.9	20.6	10.4
F*	30243	24.5	6.6	19.2	8.9	12.2	18.9	9.7
G	30246	25.4	4.7	19.0	8.3	13.3	18.9	10.4
H	30249	24.7	5.3	18.1	8.8	12.0	21.0	10.2
I*	30252	23.5	4.8	17.7	8.8	14.3	20.6	10.2
J	30211	23.5	3.6	18.4	8.5	14.8	22.2	9.0
K	30219	23.2	3.8	17.6	8.8	14.7	21.6	10.3
L	30222	22.9	4.9	17.0	8.8	14.3	21.5	10.4
M	30225	22.2	5.3	16.1	9.0	14.1	21.5	11.8
<u>V-1067</u>								
A	30165	22.7	4.3	19.8	9.8	14.6	19.6	9.0
B	30168	21.7	4.6	19.2	9.7	14.7	19.0	11.2
C	30170	24.7	4.1	19.9	9.7	13.9	19.1	8.6
D	30187	23.1	5.0	19.6	10.1	14.1	18.2	9.9
E	30192	24.0	6.9	16.6	9.7	12.5	19.6	10.6
F*	30242	22.4	8.2	17.8	10.8	13.1	17.4	10.3
G	30245	23.5	6.5	18.0	10.0	13.1	18.2	10.7
H	30248	23.5	6.1	18.3	9.9	13.3	18.9	10.1
I*	30251							
J	30210							
K	30218							
L	30221	20.5	6.3	17.1	10.0	14.5	19.2	12.4
M	30224	21.3	4.9	18.3	9.7	14.9	19.9	11.1
<u>Miscellaneous</u>								
G V-182	30276	9.1	10.8	14.2	12.2	14.2	26.9	12.7
G V-161	30275	3.0	12.2	5.3	13.7	19.3	26.6	19.8
G V-164	30274	6.8	10.6	9.3	11.5	15.5	30.0	16.3
J V-182	30286	7.9	6.6	14.3	10.6	18.7	28.3	13.6
J V-161	30285	2.6	8.5	5.8	10.3	22.8	28.7	21.3
J V-164	30284	6.5	11.8	11.0	12.1	14.4	29.0	15.2
J V-107 (THF-Sol)	30288	31.1	4.4	23.7	9.0	12.5	12.6	6.7
<u>R-1235</u>								
E	30191	24.4	5.6	17.4	9.6	12.4	20.2	10.4
G	30247	24.8	5.5	17.9	10.0	12.1	20.7	9.1
J	30212	21.8	5.6	16.5	9.2	13.0	22.7	11.1

*Transitional Period

TABLE 7
PROTON DISTRIBUTION OF DISTILLATE AND RESID SAMPLES
Wilsonville Run 263

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
<u>V-131B Distillates</u>							
A	12.2	5.9	12.6	8.1	12.6	35.6	13.1
B	14.0	5.6	14.7	8.6	13.5	33.7	9.9
C	13.9	4.9	14.8	8.8	13.2	33.8	10.6
D	14.6	6.3	14.6	8.5	12.6	32.0	11.3
E	15.3	6.3	15.0	7.9	12.8	31.1	11.6
F*	14.3	8.9	16.0	10.5	12.9	26.7	10.7
G	15.6	6.7	14.7	8.5	12.1	31.2	11.2
H	15.9	4.8	15.2	8.6	12.5	32.6	10.4
I*	13.5	4.9	14.2	8.0	14.5	33.1	11.8
J	13.9	4.4	14.3	8.1	14.5	32.9	11.8
K	13.9	3.1	14.5	8.2	14.7	33.1	12.6
L	14.0	3.9	14.8	7.8	14.1	33.2	12.1
M	14.3	4.6	15.0	8.1	14.0	31.6	12.3
<u>V-1067 Distillates</u>							
G	11.6	10.4	14.7	8.5	15.3	27.8	11.7
<u>R-1235 Distillates</u>							
J	11.2	7.1	13.0	10.0	13.2	32.0	13.4
<u>R-1235 Resids</u>							
J	30.7	4.7	20.7	8.9	12.9	14.9	7.3

*Transitional Period

Note: Proton distributed NMR analysis solvents: chloroform 99.8% D with 1% TMS used with distillates, pyridine 99.96% D used with whole samples and resids. Whole sample and resid samples were filtered over a Gelman PTFE 0.45 m syringe filter prior to analysis to remove insolubles.

TABLE 8
PHENOLIC -OH CONCENTRATIONS AND DONOR SOLVENT QUALITIES
Wilsonville Run 263

V-131B	Phenolic -OH Concentration by FTIR				Donor Solvent Quality of V-131B 850 °F Distillates (a)
	850 °F Distillates		850 °F ⁺ Resids (THF Solubles)		
	meq/g	v, cm ⁻¹	meq/g	v, cm ⁻¹	
A	0.96	3305	1.22	3298	64.0
B	1.11	3304	1.17	3299	72.7
C	1.13	3304	1.18	3298	69.0
D	1.04	3304	1.19	3298	74.3
E	1.03	3303	1.11	3298	75.8
F*	1.33	3308	1.19	3298	82.0
G	1.06	3304	1.14	3298	76.5
H	1.13	3303	1.11	3298	76.9
I*	0.53	3308	0.75	3298	76.0
J	0.43	3307	0.72	3298	76.3
K	0.42	3307	0.74	3298	73.9
L	0.47	3307	0.79	3298	75.8
M	0.46	3307	0.80	3298	77.0

*Transitional Period

(a) wt % MAF coal conversion at Modified-Equilibrium microautoclave test conditions: 9 g distillation, 6 g Old Ben Mine No. 1 (Indiana V seam) coal, 750 °F, 30 min.

TABLE 9

**HRI RUN POC-1 SAMPLING PLAN FOR CONSOL R&D
(October 8, 1993)**

Description	Frequency			Notes
	Run	Condition	Period	
Composite Net Distillates N-5 Bottoms N-2 Bottoms N-3 Overheads	6 gallons	100 g 100 g 100 g		A. 100 g samples per condition. (Periods 4, 12, 20, 28, 36, 44, and 52) B. 6 gallon sample taken during period recommended by HRI (tentatively selected Period 36)
Residues N-3 Bottoms Filter Cake ROSE Bottoms ROSE-SR Feed (N-3 Btms)		100 g 100 g 100 g 100 g		Taken from work-up periods Period 4 Period 52 Periods 12, 20, 28, 36, and 44 Periods 12, 20, 28, 36, and 44
Recycle Oils O-41 P-3	2 drums 2 drums	1 gallon 1 gallon		A. 1 gallon O-41 and P-3 samples taken during work-up periods (Periods 4, 12, 20, 28, 36, 44, and 52) B. 2 drums of P-3 sample taken at the end of the run from inventory. C. 2 drums of O-41 composite sample.
O-13 Bottoms			750 g	Taken each period from O-46.
K-1 Reactor Samples		500 g		Taken from Periods 4, 11, 19, 27, 35, 43, and 51 before THF washing. (500 g or 1/2 of whole sample after the in-house requirement has been satisfied.)
Composite Recovered Catalyst	5 lb.	400 g		A. 400 g samples per reactor taken from work-up periods (Periods L/O, 12, 20, 28, 36, 44, and 52). B. K-1: 2.5 lb. composite sample from Periods 1 to 8. C. K-2: 2.5 lb. composite sample from Periods 1 to 8.
Coal		8 oz.		Samples taken during work-up periods (Periods 4, 12, 20, 28, 36, 44, and 52).
Start-up Oil O-48 Filtrate O-65 Deashed Oil	1 quart	500 g 500 g		Filtrate: Period 52 DAO: 12, 20, 28, 36, and 44.

TABLE 10
COMPONENT CONCENTRATION AND SOLVENT QUALITY OF WHOLE POC-1 SAMPLES

Sample Description	Period	HRI Sample No., LO-	Component, wt % of Whole Sample			Solvent Quality in Microautoclave Test (a), % MAF Coal
			THF Solubles	IOM	Ash	
Rx Liq. Flashed Bottoms (O-46)	9	6276	73.2	7.1	19.7	67.0
Recycle Oil (O-43)	9	6274	84.4	4.5	11.1	61.1/60.6
Clean Oil Tank (P-3)	9	6275	Assumed 100 %	-	-	70.2
Make-Up Oil Tank (Tank 4)	9	6280	Assumed 100 %	-	-	69.9

(a) Standard Modified-Equilibrium test conditions: 9 g whole solvent, 6 g Old Ben Mine No. 1 (Indiana V seam) coal, 750 °F, 30 min.

Analyses performed by CONSOL R&D.

TABLE 11

PROTON DISTRIBUTIONS AND PHENOLIC -OH CONCENTRATIONS
HRI Run POC-1, Period 9 Samples

	HRI Sample No., LO-	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	Phenolic -OH Conc., meq/g
Naphtha Stabil. (N-5) Bottoms	6270	2.0	3.8	7.1	7.1	24.9	31.0	24.1	<0.05
Atmos. Still (N-2) Bottoms	6271	4.1	2.9	8.0	6.6	19.8	36.4	22.2	<0.05
Vac. Still (N-3) Overheads	6272	6.7	4.3	10.6	7.9	19.3	31.2	20.1	0.04
Vac. Still (N-3) Bottoms	6273	8.8	3.7	12.0	7.6	18.9	30.5	18.5	-
Rx Liq. Flashed Bottoms (O-46)	6276	11.8	4.0	12.2	8.3	17.7	28.2	17.8	0.09
Recycle Oil (O-43)	6274	6.9	3.4	10.6	7.5	19.0	32.5	20.1	0.06
Clean Oil Tank (P-3)	6275	5.5	4.3	10.9	9.3	17.3	32.2	20.5	0.05
Make-Up Oil (Tank 4)	6280	5.7	4.2	11.9	9.8	17.3	32.2	18.9	0.05

Analyses performed by CONSOL R&D.

TABLE 12
OXIDATION INDEX OF HRI COAL SAMPLES

Sample Source	Description	Sample Number		Oxidation Index (a), Avg. $\pm$ Std. Dev. of Duplicates
		HRI-	LO-	
Test Grind	Ground	6156	6257	0.74 $\pm$ 0.02
Test Grind	Raw (b)	6157	6258	0.84 $\pm$ 0.02
Test Grind	P-2	6158-P-2	6259	0.87 $\pm$ 0.02
POC-1	Period 9 (c)	-	6279	0.82 $\pm$ 0.01
Illinois 6 Coals Previously Analyzed by CONSOL		-	-	0.9 - 1.2

- (a) Oxidation index obtained by diffuse reflectance FTIR is described in the following references: 1) Huffman, G. P.; Huggins, F. E.; Dunmyre, G. P.; Pignoco, A. J.; Lin, M.-C., *Fuel* 1985, 64, 847-856; and 2) Wu, M. M.; Robbins, G. A.; Winschel, R. A.; Burke, F. P., *Energy & Fuels* 1988, 2, 150-157.
- (b) This sample was received as chunks; all others were received finely ground. This sample was prepared by oven-drying for 30 min at 105 °C, then grinding it in a Holmes laboratory mill to approximately -200 mesh.
- (c) Contaminated sample, c.f. text.

TABLE 13

**ELEMENTAL ANALYSES OF CONTAMINATED ILLINOIS 6 FEED COAL
HRI Run POC-1**

Sample	Illinois 6 Feed Coal Run POC-1 P-2 Sample
HRI Sample No.	L0-6279
Moisture, wt % As-Determined	4.95
Ultimate Analysis, wt % Dry	
Carbon	70.02
Hydrogen	4.97
Nitrogen	1.16
Chlorine	0.103
Sulfur	4.17
Ash, Including SO ₃	12.28
Oxygen (by Diff.), Incl. Ash-SO ₃	7.30

Note: A reproducible heating value determination could not be made. The sample was found to be contaminated with particles of white plastic, and flakes and "prills" of carbonaceous material of unknown origin.

Analyses performed by CONSOL R&D.

TABLE 14

PHENOLIC -OH CONCENTRATIONS OF WET AND DRY COAL-DERIVED LIQUID SAMPLES

Sample No.	Original Sample Condition		Phenolic -OH (a)			
			Undried Samples		Dried Samples	
	Description	Approx Ratio, Water Peak/Phenol Peak	Concentration, meq/g	ν , cm^{-1}	Concentration, meq/g	ν , cm^{-1}
Sandia Hydrotreated Samples						
5-92804	Quite Wet	0.8	0.15	3316	0.16	3316
5-92906	Moderately Wet	0.6	0.20	3314	0.22	3314
5A-110404	Quite Wet	1.2	0.32	3311	0.36	3309
5A-110505	Quite Wet	1.3	0.32	3310	0.37	3309
5A-110507	Moderately Wet	0.5	0.35	3309	0.38	3308
5A-110602	Quite Wet	0.8	0.32	3311	0.35	3311
5A-110607	Slightly Wet	0.2	0.45	3306	0.47	3307
5C-102205	Quite Wet	1.0	0.26	3313	0.29	3312
5C-102305	Moderately Wet	0.5	0.32 (0.29)	3310 (3311)	0.32	3310
CAER Coker Tars						
SR-3	Severely Wet	>>1.0	Indeterminate-phenol peak overwhelmed		0.77	3296
SR-4	Severely Wet	>>1.0	0.57	3290	0.78	3295
SR-5	Severely Wet	>>1.0	0.53	3304	0.81	3295

Note: The H_2O was removed by the method described in the discussion.

- (a) Uncertainties in phenolic -OH concentration are typically 0.02 to 0.05 meq/g, depending on sample type and characteristics; uncertainties in peak position (ν) are typically 1 to 2 cm^{-1} .

TABLE 15

CORRECTION OF MICROAUTOCLAVE TEST RESULTS
Wilsonville Run 262, HRI Run CC-16, Standard Coal Reactivity Calibration

Description	Microautoclave Test Results, % MAF Coal Conversion		
	Originally Reported Value	Corrected Value	Change
Wilsonville Run 262, Whole Oils^a, MOD-EQ Test Conditions			
V-131B Period B	37.0	36.6	-0.4
V-131B Period F	48.1	47.6	-0.5
R-1235 Period C2	53.1	52.6	-0.5
R-1235 Period D	39.7	39.4	-0.3
R-1235 Period E	58.8	58.2	-0.6
HRI Run CC-16¹², MOD-EQ Test Conditions			
LO-6154, Make-up Oil	80.5	79.9	-0.6
LO-6161, PFL Period 13C	85.3	84.6	-0.7
LO-6157, Distillate Period 5C	70.2	69.7	-0.5
LO-6159, Distillate Period 9C	74.8	74.2	-0.6
LO-6161, Distillate Period 13C	75.8	75.2	-0.6
Standard Old Ben No. 1 Mine Coal Reactivity Calibration, 3/24/92¹⁵			
KIN Test, 5 wt % Tetralin (a)	64.3	63.6	-0.7
KIN Test, 25 wt % Tetralin (a)	73.6	72.8	-0.8
KIN Test, 50 wt % Tetralin (a)	78.3	77.4	-0.9
KIN Test, 100 wt % Tetralin	71.8	71.0	-0.8
EQ Test, 5 wt % Tetralin (a)	60.0	59.2	-0.8
EQ Test, 25 wt % Tetralin (a)	74.1	73.2	-0.9
EQ Test, 50 wt % Tetralin (a)	81.6	80.7	-0.9
EQ Test, 100 wt % Tetralin	87.1	86.1	-1.0
MOD-EQ Test, 5 wt % Tetralin (a)	57.9	57.1	-0.8
MOD-EQ Test, 25 wt % Tetralin (a)	71.9	71.0	-0.9
MOD-EQ Test, 50 wt % Tetralin (a)	80.5	79.6	-0.9
MOD-EQ Test, 100 wt % Tetralin	87.2	86.3	-0.9

(a) Balance of Solvent was 1-Methylnaphthalene.

KIN = Kinetic Test: 12 g solvent, 1.5 g coal, 10 min, 750 $\pm$ F.
EQ = Equilibrium Test: 10 g solvent, 5 g coal, 30 min, 750 $\pm$ F.
MOD-EQ = Modified Equilibrium Test: 9 g solvent, 6 g coal, 30 min, 750 $\pm$ F.

Figure 1. Simplified CC-ITSL Process Diagram for Wilsonville Run 263.

Figure 2. Partial CC-ITSL Process Diagram for Wilsonville Run 263 Showing Major Distillate Streams.

Figure 3. Adapted FTIR Method Performance for Phenolic -OH Determination.

Figure 4. Adapted FTIR Method Performance for Determination of THF Solubles.

APPENDIX A

HRI Run Plan for POC-1

Run Plan (Rev. #7) for POC-01

Coal: Illinois No.6 Crown II Mine
Catalyst: Akzo AO-60 1/16" Extrudate

13-Sep-93

Condition	Period	No. of Days	Solid Separation	On-line Hydrotreater	Space Velocity	Temperature [F]		Solv/Coal Ratio	Catalyst Rep. Rate	Remarks
						K-1	K-2			
L/O	1-2	2	Vac. Still	Yes	20	715-735	750-775	2.0	0.5/1 lb/T	with Ashy Recycle
L/O	3-4	2	Vac. Still	Yes	20	735-750	775-800	1.5	0.5/1 lb/T	with Ashy Recycle
1	5-12	8	ROSE-SR	Yes	20	770	815	1.2	0.5/1 lb/T	with Ashy Recycle
2	13-20	8	ROSE-SR	Yes	20	770	815	1.2	0.5/1 lb/T	without ashy recycle
— decision point on the mode of deasher: continue with ROSE-SR or switch to filter operations —										
3	21-28	8	ROSE-SR	Yes	20	770	815	1.2	1.5/3.0 lb/T	Sample for End Use
4	29-36	8	ROSE-SR	Yes	30	775	825	1.2	1.5/3.0 lb/T	Studies
5	37-44	8	ROSE-SR	Yes	30	775	825	0.9	1.5/3.0 lb/T	
6	45-60	16	FILTER	Yes	30	775	825	0.9	1/2 lb/T	

Condition	Period	Remarks:
L/O	1-4	Temperature line out at basecase coal space velocity with half the catalyst replacement rate and at alternate days.
1,2	5-20	Catalyst equilibration with same space velocity and catalyst replacement rate as the L/O Conditions Solid Rejection: switching from Vacuum Still to ROSE-SR Ashy recycle operations will be used in Condition 1, while solid-free recycle mode in Condition 2 solid-free recycle mode will be used for next 3 conditions.
3	21-28	Triple the catalyst replacement rates to 1.5 and 3.0 lb/Ton coal for K-1 and K-2, respectively.
4	29-36	Increase coal space velocity (1.5xBase); Continue on ROSE-SR operations. Increase K-1 and K-2 temperatures to 775 and 825 F.
5	37-44	Effect of solvent to coal ratio (reduce from 1.2 to 0.9) at higher reaction severity
6	45-60	Lower catalyst replacement rate to 1 and 2 lb/ton mf coal; switch to filter operation 16 days testing of filter operations at lower catalyst replacement rates.

Note:

- Feed to the On-line Hydrotreater will be sampled by bypassing the hydrotreater for long enough time to purge out the distillate receiver.
- Space Velocity: lb mf coal/h/ft³ reactor/stage Catalyst Replacement Rate: lb cat/Ton of mf coal

PROOF-OF-CONCEPT RUN # 1 (POC-01)

PDU 260-04 (Rev. #7)

Analytical Schedule

Condition	Mode of Solid Separation	Transition Period	Steady State Period	Workup Period
L/O	Vacuum Tower	1, 2, 3		4
1	ROSE-SR	5, 6	7, 8, 10, 11	9, 12
2	ROSE-SR	13, 14	15, 16, 18, 19	17, 20
3	ROSE-SR	21, 22	23, 24, 26, 27	25, 28
4	ROSE-SR	29, 30	31, 32, 34, 35	33, 36
5	ROSE-SR	37, 38	39, 40, 42, 43	41, 44
6A	Filter	45, 46	47, 48, 50, 51	49, 52
6B	Filter	53, 54	55, 56, 58, 59	57, 60

PDU Run 260-04 Daily Samples

Solids Separation: Vacuum Tower
Periods 1 to 4

Period No: _____

Sample Type	Quantity	Sub-period A	Sub-period B
Gases			
Vent Gas	Flow Bottle	_____	_____
Bottoms Gas	Flow Bottle	_____	_____
Liquids			
Naphtha Stabilizer (N-5) Bottoms	1/2 Gallon		
Atmospheric Still (N-2) Bottom	1/2 Gallon		
Vacuum Still (N-3) Overheads	1/2 Gallon		_____
Sour Water (O-45)	Pint		_____
Slurry Tank Condensate	Pint		_____
Slurries			
Feed Slurry (P-4)	Pint		
Reac. Liquid Flash Drum (O-13) Btms.	Quart		_____
Vac. Still (N-3) Bottoms	1/2 Gallon		_____
Recycle Holding Tank (O-41)	Pint		_____
Reactor #1 Slurry (*)	All		_____
Reactor #2 Slurry (*)	All		_____
Solids			
Feed Coal	100 Grams		_____
1st Stage Catalyst			
Drained	All		
Draining	Storage	_____	_____
2nd Stage Catalyst			
Drained	All		_____
Draining	Storage	_____	_____

(*) Period 4 only

PDU Run 260-04 Daily Samples

Solids Separation: ROSE-SR

Periods 21 to 44

Period No: _____

Sample Type	Quantity	Sub-period A	Sub-period B
Gases			
Vent Gas	Flow Bottle	_____	_____
Bottoms Gas	Flow Bottle	_____	_____
Liquids			
Naphtha Stabilizer (N-5) Bottoms	1/2 Gallon	_____	_____
Atmospheric Still (N-2) Bottoms	1/2 Gallon	_____	_____
Cold Separator (O-5) Bottoms (+)	1/2 Gallon	_____	_____
Vacuum Still (N-2) Overheads	Quart	_____	_____
ROSE Recycle Oil Receiver (O-65)	Quart	_____	_____
ROSE Recycle Solvent Drum (O-67)	Pint	_____	_____
Sour Water (O-45)	Pint	_____	_____
Slurry Tank Condensate (P-4)	Pint	_____	_____
Slurries			
Feed Slurry (P-4)	Pint	_____	_____
Reac. Liquid Flash Drum (O-13) Btms.	Quart	_____	_____
Recycle Holding Tank (O-41)	Quart	_____	_____
Vacuum Still (N-3) Bottoms	Quart	_____	_____
Reactor #1 Slurry (*)	All	_____	_____
Reactor #2 Slurry (*)	All	_____	_____
Solids			
Feed Coal	100 Grams	_____	_____
Solid Receiver (O-63 A/B)	Quart (Lab)	_____	_____
	Gallon (Storage)	_____	_____
1st Stage Catalyst			
Drained	All	_____	_____
Draining	Storage	_____	_____
2nd Stage Catalyst			
Drained	All	_____	_____
Draining	Storage	_____	_____

(*) Periods 11, 19, 27, 35, and 43

(+) Special O-5 liquid Sample to be taken in Period 31 ONLY while the Hydrotreater is Off-li

PDU Run 260-04 Daily Samples

Solids Separation: Pressure Filter

Periods 45 to 60

Period No: _____

Sample Type	Quantity	Sub-period A	Sub-period B	Every Filtr. Cycle
Gases				
Vent Gas	Flow Bottle	_____		
Bottoms Gas	Flow Bottle	_____		
Liquids				
Naphtha Stabilizer (N-5) Bottoms	1/2 Gallon			
Atmospheric Still (N-2) Bottoms	1/2 Gallon		_____	
Vacuum Still (N-3) Overheads	1/2 Gallon		_____	
Cold Separator (O-5) Bottoms (+)	1/2 Gallon		_____	
Filtrate Holding Tank (O-48)	Pint			_____
Wash Oil Tank (O-51)	Pint			_____
Recycle Holding Tank (O-41)	Quart		_____	
Sour Water (O-45)	Pint		_____	
Slurry Tank Condensate (P-4)	Pint		_____	
Slurries				
Feed Slurry (P-4)	Pint		_____	
Reac. Liquid Flash Drum (O-13) Btms.	Quart		_____	
Filter Feed Tank (O-47)	Pint		_____	
Reactor #1 Slurry (*)	All		_____	_____
Reactor #2 Slurry (*)	All		_____	
Solids				
Feed Coal	100 Grams		_____	
Filter Cake	Quart (Lab)			_____
	Gallon (Storage)		_____	
1st Stage Catalyst				
Drained	All	_____		
Draining	Storage	_____		
2nd Stage Catalyst				
Drained	All	_____		
Draining	Storage	_____		

(*) Period 51.

(+) Special O-5 liquid Sample to be taken in Period 55 while the Hydrotreater is off-line.