A CHARACTERIZATION AND EVALUATION OF COAL LIQUEFACTION PROCESS STREAMS

**QUARTERLY TECHNICAL REPORT
OCTOBER 1, 1997 - DECEMBER 31, 1997**

**AUTHORS: G. A. ROBBINS
S. D. BRANDES
R. A. WNSCHEL**

REPORT ISSUE DATE: MARCH 31, 1997

DE-AC22-94PC93054

**CONSOL INC.
RESEARCH & DEVELOPMENT
4000 BROWNSVILLE ROAD
LIBRARY, PA 15129**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This is the Technical Progress Report for the tenth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period October 1 through December 31, 1996. Described in this report are the following activities:

- CONSOL characterized two HTI coal/petroleum coprocessing samples for Ni and V concentrations, as requested by DOE. The results are reported in Appendix 1.
- CONSOL began work to evaluate the potential for producing alkylphenyl ethers, and specifically ethylphenyl ethers, from coal liquefaction phenols. The work includes a literature review and experimentation. The status of this ongoing work is described in this report.
- A set of samples was requested from HTI Run ALC-2 (Appendix 2).
- The University of Delaware is conducting resid reactivity tests and is developing a kinetic mechanistic model of resid reactivity. A summary of Delaware's progress is appended to this report (Appendix 3).
- A paper was submitted for presentation at the 213th National Meeting of the American Chemical Society, April 13-17, 1997, in San Francisco, CA, (Appendix 4).

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY	1
Characterization of Coprocessing Samples for Ni and V Content	1
Synthesis of Alkylphenyl Ethers from Coal Liquid Phenols	1
Resid Reactivity	1
Technology Transfer	1
INTRODUCTION	2
Contract Overview	2
Contract Activities This Period	2
Activities in Progress	3
RESULTS AND DISCUSSION	4
Appended Topics	4
Status of Synthesis of Alkylphenyl Ethers from Coal Liquid Phenols	4
Introduction	4
Literature Search	4
Laboratory Synthesis Work	5
CONCLUSION	6
Characterization of Coprocessing Samples for Ni and V Content	6
Resid Reactivity	6
REFERENCES	7

LIST OF APPENDICES

<u>Appendix</u>	<u>Page</u>
1 Determination of Ni and V Concentrations in HTI Coal/Petroleum Processing Samples	A1-1
2 Request for Samples from HTI Run ALC-2	A2-1
3 University of Delaware Quarterly Report (10/16/96-1/15/97)	A3-1
4 Recent Advances and Future Prospects for Direct Coal Liquefaction Process Development	A4-1

Section 1

EXECUTIVE SUMMARY

CHARACTERIZATION OF COPROCESSING SAMPLES FOR Ni AND V CONTENT

CONSOL characterized two HTI coal/petroleum coprocessing samples for Ni and V concentrations (Appendix 1). The concentration of Ni ranged from 8 mg/kg in the pressure-filter liquid to 611 mg/kg in the tetrahydrofuran-soluble portion of the vacuum still bottoms (428 mg/kg in the whole vacuum still bottoms). The concentration of V ranged from 2 mg/kg in the pressure-filter liquid to 1,600 mg/kg in the tetrahydrofuran-soluble portion of the vacuum still bottoms (1,100 mg/kg in the whole vacuum still bottoms).

SYNTHESIS OF ALKYLPHENYL ETHERS FROM COAL LIQUID PHENOLS

CONSOL began work to evaluate the potential for producing alkylphenyl ethers, and specifically ethylphenyl ethers, from coal liquefaction phenols. The work includes a literature review and experimentation. Reagent phenol and coal liquefaction phenolics were converted to ethers by one synthesis route. A route that is cheaper is being sought for continued development work.

RESID REACTIVITY

The University of Delaware completed hydroconversion tests on the fourteen resids in their sample set. They conclude that convertibility is directly related to the solubility of the resid. The kinetic model was applied to the data set of a single resid sample. Based on the reaction data generated, the model is being refined. A parametric hydroconversion study was begun with two resid samples from the fourteen-resid sample set. The effects of temperature, pressure, residence time, catalyst loading, and resid concentration will be explored. The two samples chosen for the study gave the highest (44.6 wt %) and lowest (33.1 wt %) resid conversions (Wilsonville Run 260 V131B and Wilsonville Run 259 V131B, respectively) under baseline conditions (420 °C, 30 min, 10.3 mpA (1500 psi) H₂, 3 to 1 tetralin-to-resid ratio, 3 wt % molybdenum naphthenate catalyst).

TECHNOLOGY TRANSFER

A paper that was submitted for presentation at the 213th National American Chemical Society Meeting is appended to this report (Appendix 4).

Section 2

INTRODUCTION

This is the Technical Progress Report for the tenth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period October 1 through December 31, 1996.

CONTRACT OVERVIEW

The objectives of this project are to support the DOE direct coal liquefaction process development program and to improve the useful application of analytical chemistry to direct coal liquefaction process development. This project builds on work performed in DOE Contract No. DE-AC22-89PC89883. Independent analyses by well-established methods are obtained on samples produced in direct coal liquefaction processes under evaluation by DOE. Additionally, new analytical instruments and techniques to examine coal-derived samples are being evaluated. The data obtained from this study are used to guide process development and to develop an improved data base on coal and coal liquids properties. A sample bank, established and maintained for use in this project, is available for use by other researchers. The reactivity of the non-distillable resid toward hydrocracking at liquefaction conditions (i.e., resid reactivity) is being examined. From the literature and experimental data, a kinetic model of resid conversion will be constructed. Such a model will provide insights to improve process performance and the economics of direct coal liquefaction.

CONTRACT ACTIVITIES THIS PERIOD

- CONSOL characterized two HTI coal/petroleum coprocessing samples for Ni and V concentrations, as requested by DOE. The results are reported in Appendix 1.
- CONSOL began work to evaluate the potential for producing alkylphenyl ethers, and specifically ethylphenyl ethers, from coal liquefaction phenols. The work includes a literature review and experimentation. The status of this ongoing work is described in this report.
- A set of samples was requested from HTI Run ALC-2 (Appendix 2).

- Product analyses for resid reactivity tests made at CONSOL last quarter were completed and forwarded to the University of Delaware. Analyses included gas chromatography of vented gases and product distributions based on distillation at an atmospheric equivalent temperature of 454 °C (850 °F).
- The University of Delaware is conducting resid reactivity tests and is developing a kinetic mechanistic model of resid reactivity. A summary of Delaware's progress is appended to this report (Appendix 3).
- A paper was submitted for presentation at the 213th National Meeting of the American Chemical Society, April 13-17, 1997, in San Francisco, CA (Appendix 4).

ACTIVITIES IN PROGRESS

- Characterization work is under way on samples from HTI Run PB-04.
- Characterization work was begun on samples from the early part of Run ALC-2.
- Work to evaluate the potential for producing alkylphenyl ethers from coal liquefaction phenols is continuing.
- Individual samples were combined to produce the HTI Run PB-05 product blend for oil assay, the analytical test plan was prepared in conjunction with P. Zhou of BRSC, and arrangements are in progress to have the oil assay performed.
- At PETC's request, the fractional distillation of the net product of HTI Run POC-1 is being repeated to resolve a discrepancy in the distillation results from different aliquots analyzed by NIPER and SwRI.
- The development of a kinetic/mechanistic model of resid reactivity is continuing.

Section 3

RESULTS AND DISCUSSION

APPENDED TOPICS

Results and discussion for two individual topics are presented with their respective data in Appendices 1 and 3. Appendix 1 describes the analysis of HTI coprocessing samples for nickel and vanadium concentration. Appendix 3 describes the University of Delaware's work on resid reactivity.

STATUS OF SYNTHESIS OF ALKYLPHENYL ETHERS FROM COAL LIQUID PHENOLS

Introduction

A scope-of-work for studying etherification (O-alkylation) of phenols from coal-derived liquids was developed in a meeting with E. Klunder and M. Nowak of DOE/FETC, and P. Zhou of BRSC. The planned scope of work, formalized in a letter to M. Nowak dated November 20, 1996, includes a literature search and experimental work on the synthesis of alkylphenyl ethers from coal liquefaction phenols. Conceptually, liquefaction by-product phenols would be reacted with an O-alkylating reagent (possibly ethanol or methanol) to produce alkylphenyl ethers which could be used as a high-octane oxygenate extender for gasoline and possibly as an extender for diesel fuel.

Literature Search

An electronic literature search for laboratory and commercial processes to produce alkylphenyl ethers from phenols was initiated. More than 260 references were identified. The Williamson Synthesis and its modifications are the methods commonly used for the production of ethers from phenols. Since the commercial market is apparently limited to the fine-chemical market, the commercial processes for producing alkylphenyl ethers also use the Williamson Synthesis and its variations. A literature search was conducted at the DOE-FETC library. In the next quarter, CONSOL will complete the literature search of the NIOSH (formerly Bureau of Mines) library in Bruceton, PA. We will attempt to locate and interview former employees of Gulf R&D who were involved with the work conducted under DOE Contract No. DOE/CE/50022, in which methylphenyl ethers were tested as gasoline additives.

Laboratory Synthesis Work

Reagent phenol was reacted with diethylsulfate in basic solution to produce phenetole (ethylphenyl ether) via one version of the Williamson synthesis. This is the route used by Gulf R&D in the contract cited above. Reagent phenol was selected for use to demonstrate the applicability of the chemistry and product analysis techniques. The excess diethylsulfate was hydrolyzed just below the boiling temperature, leaving behind an organic phase consisting of the ether. The product, obtained in high yield, was identified as phenetole via NMR, GC/MS, and FTIR analyses.

Reactions were conducted with coal liquefaction phenolics to verify the reaction sequence and product analysis scheme. The phenolics were obtained by alkali extraction of two distillation fractions of the net products of HTI Run CC-15. The source and characteristics of these phenolics were described elsewhere.¹

The phenolics of the 193-266 °C (380-510 °F) fraction of the products from HTI Run CC-15 were reacted with diethylsulfate. The original phenols, including phenol, cresols, and C₂-phenols, converted to the corresponding ethylphenyl ethers in high yield, as determined by NMR, FTIR, and GC/MS analyses.

The phenolics of the 193-266 °C (380-510 °F) fraction of the products from HTI Run CC-15 were reacted with diethylsulfate. An analysis of the isolated products indicated that substituted ethylphenyl ethers corresponding to the starting phenols were produced in high yield. Ethers with side chains up to four alkyl carbons were identified.

Work next quarter will be directed toward producing the ethers from phenol and either methanol or ethanol, if a suitable procedure can be identified in the literature.

Section 4

CONCLUSION

CHARACTERIZATION OF COPROCESSING SAMPLES FOR NI AND V CONTENT

The concentration of Ni was 8 mg/kg in the pressure-filter liquid and 611 mg/kg in the tetrahydrofuran-soluble portion of the vacuum still bottoms (428 mg/kg in the whole vacuum still bottoms). The concentration of V was 2 mg/kg in the pressure-filter liquid and 1,600 mg/kg in the tetrahydrofuran-soluble portion of the vacuum still bottoms (1,100 mg/kg in the whole vacuum still bottoms).

RESID REACTIVITY

The University of Delaware completed hydroconversion tests on the fourteen resids in their samples set. They conclude that convertibility is directly related to the solubility of the resid. The kinetic model was applied to the data set of a single resid sample. Based on the reaction data generated, the model is being refined. A parametric hydroconversion study was begun with two resid samples from the fourteen-resid sample set. The effect of temperature, pressure, residence time, catalyst loading, and resid concentration will be determined. The two samples chosen for the study gave the highest (44.6 wt %) and lowest (33.1 wt %) resid conversions (Wilsonville Run 260 V131B and Wilsonville Run 259 V131B, respectively) at baseline conditions (420 °C, 30 min, 10.3 MPa (1500 psi) H₂, 3 to 1 tetralin-to-resid ratio, 3 wt % molybdenum naphthenate catalyst).

Section 5

REFERENCES

1. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "Coal Liquefaction Process Streams Characterization and Evaluation, Quarterly Technical Progress Report July Through September, 1993", DOE/PC 89883-86, March 1994.

APPENDIX 1

DETERMINATION OF Ni AND V CONCENTRATIONS IN HTI COAL/PETROLEUM PROCESSING SAMPLES

(Facsimile of letter from R. A. Winschel to M. A. Nowak)

November 25, 1996

412-854-6683

Dr. M. A. Nowak
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

Subject: DOE Contract DE-AC22-94PC93054

Dear Mike:

You requested that CONSOL determine the Ni and V concentrations in two coal/petroleum coprocessing samples. The results are reported here.

Samples. The HTI samples included the pressure filter liquid (PFL) of HTI Run 245-46-43 and the vacuum still bottoms (VSB) of HTI Run 238-21-16B.

Methods. CONSOL separated the VSB sample into tetrahydrofuran (THF)-soluble and insoluble fractions before analysis. The separation was done by pressure filtration with Whatman No. 42 paper and with excess freshly distilled THF. The THF was removed from the solubles by rotary evaporation. The filter cake was dried in an oven at 60 °C overnight. To obtain the nickel and vanadium concentration data, the PFL sample and both fractions of the VSB sample were fused with lithium tetraborate, and the fusion bead was dissolved in nitric acid and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Only Ni and V determinations were requested. However, the extra channels of the ICP-AES were used to determine additional elements.

Results. The THF extraction recovery and yields are presented in Table 1. The recovery of 1.6% excess product indicates that a minor amount of THF remained with the recovered fractions, probably with the solubles. The ICP-AES results are presented in Table 2; the concentrations shown are for the elements, not the oxides. The concentrations of Ni and V (and of most of the elements determined) are lowest in the PFL, somewhat higher in the THF-soluble VSB, and considerably higher in the THF-insoluble VSB.

A second sample of the VSB, extracted with preserved THF rather than freshly-distilled THF , gave yields of 31.6% solubles and 69.0% insolubles and a recovery of 100.6%. This is in good agreement with the first extraction. In this case, the excess recovery may be from THF preservative (butylated hydroxy toluene) or residual THF. When this THF-insoluble fraction was ashed at 800 °C, it gave an ash yield of 54.1% (37.4% on a whole-sample basis).

Sincerely,

R. A. Winschel
Research Group Leader
Exploratory Research Group

/ls

cc: A. G. Comolli - HTI
P.-Z. Zhou - BRSC

TABLE 1

RECOVERIES AND YIELDS OF THF EXTRACTION OF HTI 238-21-16B VSB

	Yield, wt %
THF Solubles	31.8
THF Insolubles	69.8
Total Recovery	101.6

TABLE 2

ELEMENTAL ANALYSES OF HTI COPROCESSING SAMPLES

Sample Fraction	Concentration, mg/kg (ppmw)		
	HTI 245-46-43 PFL As Is	HTI 238-21-16B VSB THF Solubles	HTI 238-21-16B VSB THF Insolubles
<u>Element</u>			
Ni	8.1	27	611
V	2.1	9.3	1,600
Si	18	704	109,000
Al	16	36	57,200
Fe	25	59	32,600
Ca	11	46	22,400
Na	11	63	10,900
Mg	12	19	4,100
Ti	0.8	3.0	4,400
Mn	0.4	1.2	160
Ba	0.2	0.74	629
Cr	1.0	3.2	260
Cu	18	12	213

APPENDIX 2

REQUEST FOR SAMPLES FROM HTI RUN ALC-2

(Facsimile of letter from G. A. Robbins to T. L. K. Lee)

November 7, 1996

412-854-6748

Dr. T. L. K. Lee
Hydrocarbon Technologies, Inc.
1501 New York Avenue
Lawrenceville, NJ 08648

Dear Theo:

Our sample request for Run ALC-2 is described below. We would like to receive from each work-up period:

1. 2 gal of second-stage separator overhead (SOH) oil
2. 250 g of second-stage separator overhead (SOH) water
3. 50 g of first-stage separator overhead (SOH) oil
4. 250 g of first-stage separator overhead (SOH) water
5. 150 g of continuous vacuum still bottoms (CVSB)
6. 100 g of reduced-pressure still overhead (RPSOH)
7. 100 g of reduced-pressure still bottoms (RPSB)
8. 100 g of toluene-extracted oil (TEO)
9. 150 g of toluene-extracted solids (TES)
10. 150 g of O-6 bottoms
11. 200 g of feed slurry
12. 150 g of catalyst-treated feed coal
13. 150 g of interstage slurry sample (first-stage product).
14. Please also include 200 g of the L-814 start-up/make-up oil.

For these samples, we prefer aliquots of the same samples HTI is using for material balance work-ups (i.e., from the last period of a run condition).

Let us know of any problem areas with this request. Thank you for your assistance.

Sincerely,

G. A. Robbins
Sr. Research Chemist
/ls

cc: A. G. Comolli - HTI
M. A. Nowak - DOE/PETC
E. B. Klunder - DOE/PETC
E. N. Givens - UK/CAER
M. Peluso - LDP Associates
F. Stohl - Sandia
R. M. Statnick
R. A. Winschel
S. D. Brandes

APPENDIX 3

UNIVERSITY OF DELAWARE QUARTERLY REPORT 10/16/96 - 1/15/97

**THE KINETICS OF COAL LIQUEFACTION DISTILLATION
RESID CONVERSION**

**QUARTERLY REPORT
10/16/96-1/15/97**

Michael T. Klein
Principal Investigator

William H. Calkins
Co-Principal Investigator

and

Shaojie Wang
Visiting Scientist

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19716

Date Published
January 31, 1996

Subcontract from CONSOL under DOE Contract DE-AC22-94PC93054

EXECUTIVE SUMMARY

Hydroconversion runs have been completed under preselected conditions (3 to 1 tetralin to resid wt ratio, with and without 3% sulfided molybdenum naphthenate catalyst, 1500 ps i hydrogen pressure, and 420 °C for 30 minutes) on 15 resids supplied by CONSOL Inc. Supplementary runs have also been made varying the temperature, hydrogen pressure and catalyst concentration to determine the effect of these variables on two resids selected to represent the extremes of conversion under the preselected conditions. Analysis of these supplementary runs is not yet complete.

A modified molecular structure model for coal derived resid has been assembled and is being tested against the available analytical data for the 15 resids. Most of the analytical properties of these resids are predicted quite accurately. The model will be used to identify the primary reaction pathways in hydroconversion. Rate constants for these pathways will be related to model compounds through quantitative structure reactivity relationships.

QUARTERLY REPORT

HYDROCONVERSION OF COAL DERIVED RESIDS

Hydroconversion of Resids

Hydroconversion runs on the 15 coal derived resids from CONSOL Inc. have been made under the agreed upon preselected conditions (30 minutes at 420 °C at 3 to 1 tetralin to resid ratio and 1500 psi hydrogen). The product workup scheme used is shown in Figure 1 . Conversions to product boiling below 850 °F are shown in Tables 1A and 1B for thermal and catalyzed (3% sulfided molybdenum naphthenate) runs respectively. There is a substantial variation in the conversions for the 15 resids tested. The results also indicate that the resid must be dissolved in the process solvent for conversion to lower boiling material to occur.

A series of additional runs have now been completed on two of the resids. These resids were chosen because they gave the highest (44.6%) and lowest (32.1%) catalyzed conversion to material boiling below 850 °F of the 15 resids tested under the "preselected" conditions. These additional runs were made under a range of conditions of temperature and pressure and catalyst concentrations to learn more about the effect of these changes on the conversion. Product workup and analytical work on the products are in progress. Conditions of these supplementary runs and analytical data obtained thus far on the products are shown in Tables 2A and 2B , respectively.

MODELING OF RESID HYDROCONVERSION

Analysis of SARA samples. To date, molecular weights have been determined for each of the saturate, aromatic, asphaltene, and preasphaltene fractions. The resin fractions which were not dissolved in dichlorobenzene are also completed. However, the six resin samples that were already dissolved in dichlorobenzene yielded results which are too high and these samples are not recoverable. It will be assumed that these samples have molecular weights (MW) of 500. The value of 500 falls within 2 experimental standard deviations of every measured resin, so this assumption should not lead to much error. To allow for this approximation, the constraint in the structural model for these resids which requires the molecular weight of the resin fraction to match the experimentally determined value will be relaxed.

Modeling. A molecular structure model for coal resid has been assembled and several modifications have been made in it. The model has been altered to allow the ratio of paraffins to naphthenics in the saturate fraction to be optimized. Also, the monoaromatics are now considered separately from condensed aromatics. Finally, each fraction now has its own set of unique probability distribution functions (pdf's). However, in order to reduce the number of optimized parameters for these pdf's, most distributions are either exponential or chi-square distributions which are defined by one fewer parameter than a gamma distribution. These changes have allowed much greater control in determining a set of pdf parameters which will closely match a large set of experimental data.

Table 3 lists the values of the pdf parameters and Table 4 lists the experimentally determined and computer predicted analytical properties. Table 3 shows that the different resids

have very different pdf parameters. Table 4 shows that most of the analytical properties for all resids are predicted quite accurately. In fact, most properties for all resids are predicted within one experimental standard deviation. For resids G and H, the remaining properties are all within 1.5 experimental standard deviations. However, the hydrogen content for resid A is quite low, and the predicted value exceeds two experimental standard deviations. This is a problem unique to resid A, as all other resids have a much higher hydrogen content.

With a construction model in hand, an investigation into a complete reaction model is underway. The primary reaction paths are being identified, and all rate constants will be related to model compounds through quantitative structure reactivity relationships. Resids G and H, which gave the highest and lowest conversions experimentally, and perhaps one or two of the intermediate resids will be used to optimize the rate parameters. Once these rate parameters have been identified, they will be used without further optimization for prediction of reactions of the other resids.

SUMMARY AND CONCLUSIONS

1. Hydroconversion runs have been made on all 15 coal derived resids from CONSOL Inc. under conditions agreed upon (using 3 wt% sulfided molybdenum naphthenate catalyst, 30 minutes at 420 °C at 3 to 1 tetralin to resid ratio and 1500 psi hydrogen). There is considerable variation in conversion among the resids tested under these preselected conditions.
2. A series of supplementary runs was made on two resids exhibiting the widest variation in conversion under the preselected conditions, to determine the effect of reaction conditions (temperature, hydrogen pressure and catalyst concentration) on conversion to products boiling below 850 °F. Products from these runs are now being analyzed.
3. A molecular structure model for coal resid has been assembled and modified. Except for one resid which had an especially low hydrogen content, the model predicts the properties of the resids within 1.5 experimental standard deviation.

FUTURE PROGRAM

1. Experiments to determine the effect of hydroprocessing variables on the conversion of two coal derived resids to products boiling below 850 °F will be completed.
2. Tentative primary reaction pathways in hydroconversion of resids will be identified and the rate constants will be related to model compounds through quantitative structure reactivity relationships. Once these rate parameters have been identified, they will be used without further optimization for reaction prediction of the other resids.

PUBLICATIONS

1. A manuscript has been submitted for publication in Industrial and Engineering Chemistry Research titled "An Automated Method for Distillation Using Thermogravimetric Principles" by He Huang, Keyu Wang, Shaojie Wang, Michael T. Klein and William H. Calkins

2. A paper has been submitted for presentation to the ACS Fuel Chemistry Division at the American Chemical Society National meeting in San Francisco in April 1997 titled "Kinetics of Hydroprocessing of Coal-Derived Vacuum Residue" by Shaojie Wang, He Huang, Keyu Wang, M. T. Klein and W.H. Calkins.

Figure 1. Scheme of the Reaction Product Work-up Procedure.

TABLE 1A

CONVERSION OF THERMAL HYDROPROCESSING OF RESID

Resid			Solid Residue		Liquid Residue			Conversion to 850 °F ⁻
Sample Resid	Name	Ash	Ash	TSF	Tetralin	RSF	850 °F ⁺	
A	W258V-131B	17.0	50.1	79.7	88.2	11.8	9.6	15.0
B	W259R-1235	8.7	33.5	81.0	88.0	12.0	9.6	15.9
C	W259V-131B	8.5	35.0	82.7	86.2	13.8	10.8	17.7
D	W261V-131B	9.9	45.8	87.1	87.9	12.1	9.7	17.1
E	W262R-1235	15.6	43.5	76.0	88.4	11.6	8.6	19.6
F	W262V-1067	17.5	47.8	76.9	87.4	12.6	9.7	17.7
G	W262V-131B	15.9	46.5	78.3	88.7	11.3	8.7	18.2
H	W260V-131B	15.2	46.6	79.5	87.7	12.3	9.0	21.3
I	W261V-1067	15.9	50.8	81.8	88.9	11.1	8.5	19.4
J	W259V-1067	10.2	38.7	82.0	86.4	13.6	11.5	12.9
K	W260R-1235	17.2	49.0	78.4	86.9	13.1	9.8	19.7
L	W260V-1067	16.7	51.3	81.0	89.2	10.8	8.3	18.6
M	W261R-1235	13.7	45.6	81.1	90.1	9.9	7.9	16.0
N	HTI POC-01, O-43	0.4	33.0	99.2	80.6	19.4	14.1	27.0
O	HTI POC-02, O-43	4.1	38.0	93.1	70.6	29.4	22.4	22.1

Thermal: 420 °C; 30 min, 1500 psig H₂

Catalytic: 420 °C; 30 min, 1500 psig H₂; 3 wt % Mo

Control: 25 °C; 10 min, 1500 psig H₂

TSF: Tetralin Soluble Fraction of Resid, wt % (daf basis)

RSF: Resid Soluble Fraction in Tetralin, wt %

850 °F⁺: Fraction Boiling Above 850 °F

TABLE 1B

CONVERSION OF CATALYTIC HYDROPROCESSING OF RESID

Resid			Solid Residue		Liquid Residue			Conversion to 850 °F ⁻
Sample Resid	Name	Ash	Ash	TSF	Tetralin	RSF	850 °F ⁺	
A	W258V-131B	17.0	51.5	80.7	82.5	17.5	9.9	35.0
B	W259R-1235	8.7	40.0	85.6	79.8	20.2	11.2	38.1
C	W259V-131B	8.5	41.4	86.8	81.4	18.6	11.5	33.1
D	W261V-131B	9.9	54.9	91.0	77.9	22.1	14.1	32.9
E	W262R-1235	15.6	44.2	76.6	80.6	19.4	11.3	32.1
F	W262V-1067	17.5	49.4	78.3	79.6	20.4	10.7	37.4
G	W262V-131B	15.9	48.3	79.8	79.2	20.8	11.5	35.8
H	W260V-131B	15.2	50.9	82.7	75.6	24.4	11.3	44.6
I	W261V-1067	15.9	56.6	85.5	76.2	23.8	11.9	42.7
J	W259V-1067	10.2	43.8	85.4	76.5	23.5	11.9	42.1
K	W260R-1235	17.2	52.1	80.8	78.1	21.9	12.4	35.2
L	W260V-1067	16.7	53.5	82.6	79.1	20.9	11.7	36.4
M	W261R-1235	13.7	53.7	86.3	80.2	19.8	11.7	35.3
N	HTI POC-01, O-43	0.4	36.4	99.3	67.9	32.1	16.7	47.6
O	HTI POC-02, O-43	4.1	48.3	95.4	70.2	29.8	19.1	34.3

Thermal: 420 °C; 30 min, 1500 psig H₂

Catalytic: 420 °C; 30 min, 1500 psig H₂; 3 wt % Mo

Control: 25 °C; 10 min, 1500 psig H₂

TSF: Tetralin Soluble Fraction of Resid, wt % (daf basis)

RSF: Resid Soluble Fraction in Tetralin, wt %

850 °F⁺: Fraction Boiling Above 850 °F

TABLE 2A
REACTOR RUNS

Run No.	Sample	T, °C	t, min	Note
C140	C	423	5	
C141	C	422	10	
C142	H	420	5	
C143	H	421	10	
C144	C	436	5	
C145	C	435	10	
C146	C	435	30	
C147	H	436	5	
C148	H	438	10	
C149	H	436	30	
C150	C (3)	418	30	
C151	C (4)	421	30	Thermal
C152	C (4)	419	30	
C153	C (4)	421	30	Ni/Mo on alumina
C154	C (5)	20	30	
C155	C	423	30	1 wt % Mo catalyst
C156	C	421	30	1000 psig H ₂
C157	C	422	30	2000 psig H ₂
C158	C	420	30	2 wt % Mo catalyst
C159	C	419	30	5 wt % Mo catalyst

Notes:

1. Run conditions: 1500 H₂ psig; tetralin/resid = 3 wt ratio; 3 wt % Mo (molybdenum naphthenate) based on the amount of the resid charges; ~3 g of methyl disulfide.
2. Sample: C = W259, V-131B; H = W260, V-131B.
3. Insoluble solid residue.
4. Soluble resid in tetralin.
5. Resid C processed in tetralin in ambient conditions.

TABLE 2B
UP-TO-DATE ANALYTICAL DATA

Run No.	Sample	Ash	TSF	850 °F ⁺
C140	C	37.6	84.6	13.3
C141	C	38.7	85.3	10.5
C142	H	44.6	77.7	9.7
C143	H	46.5	79.4	12.3
C144	C	33.2	81.3	12.3
C145	C	38.4	85.1	11.9
C146	C	46.3	89.2	15.1
C147	H	47.3	80.0	10.3
C148	H	50.2	82.2	12.4
C149	H	50.3	82.3	11.9
C150	C (3)	41.6	55.7	
C151	C (4)	N/A	N/A	12.6
C152	C (4)	N/A	N/A	12.6
C153	C (4)	N/A	N/A	
C154	C (5)	24.0	70.6	

Notes:

1. Run conditions: 1500 H₂ psig; tetralin/resid = 3 wt ratio; 3 wt % Mo (molybdenum naphthenate) based on the amount of the resid charges; ~3 g of methyl disulfide.
2. Sample: C = W259, V-131B; H = W260, V-131B.
3. Insoluble solid residue.
4. Soluble resid in tetralin.
5. Resid C processed in tetralin in ambient conditions.

TSF = Tetralin Soluble Fraction of Resid, wt % (daf basis)

TABLE 3
PDF PARAMETERS FOR SELECT COAL RESIDS

		Resid A	Resid G	Resid H
	Dist Type	W258V-131B	W262V-131B	W260V-131B
<u>Saturates</u>				
Paraffin Length	3	19.72	17.31	18.38
No. of Naphthenic Rings	2	3.20 (1.60)	2.20 (1.10)	2.20 (1.10)
No. of Sidechains	1	4.77	3.00	3.00
Length of Sidechains	1	3.53	3.80	4.00
<u>Resins/Aromatics</u>				
Degree of Polymerization	3	1.25	1.71	1.75
No. of Aromatic Rings	3	5.70	5.00	4.37
No. of Naphthenic Rings	1	0.75	1.55	1.30
No. of Sidechains	1	1.55	1.03	1.00
Length of Sidechains	1	2.50	3.10	3.47
<u>Asphaltenes</u>				
Degree of Polymerization	3	5.05	3.01	2.85
No. of Aromatic Rings	3	6.10	6.25	7.01
No. of Naphthenic Rings	1	1.15	1.15	1.00
No. of Sidechains	1	0.11	1.84	0.39
Length of Sidechains	1	2.80	1.77	2.91
<u>Preasphaltenes</u>				
Degree of Polymerization	3	6.14	3.21	2.45
No. of Aromatic Rings	3	2.90	5.75	6.24
No. of Naphthenic Rings	1	0.74	1.75	2.50
No. of Sidechains	1	2.00	3.68	2.25
Length of Sidechains	1	1.90	4.20	3.83
<u>InterSheet Linkages</u>				
Fraction Oxygen		0.269	0.116	0.010
Fraction Sulfur		0.044	0.175	0.200
Fraction Methylene		0.009	0.341	0.010
Fraction Biphenyl		0.678	0.368	0.780
<u>Heteroatom Cores</u>				
Fraction Oxygen		0.141	0.520	0.435
Fraction Sulfur		0.094	0.054	0.013
Fraction Nitrogen		0.185	0.180	0.204
Fraction Internal Naphthenic		0.492	0.194	0.343
Fraction Aromatic Hydrocarbon		0.088	0.010	0.005
Fraction of Cores with Phenolic OH		0.173	0.239	0.179
Fraction of Cores with 1 Aromatic Ring		0.527	0.389	0.377
Fraction of Saturates that are Paraffinic		0.911	0.988	0.984

Distribution types: 1 = exponential; 2 = gamma; 3 = chi-square. Number in parentheses is standard deviation for a gamma distribution.

TABLE 4
EXPERIMENTAL AND PREDICTED ANALYTICAL PROPERTIES
FOR SELECTED COAL RESIDS

	Resid A		Resid G		Resid H	
	Exp	Pred	Exp	Pred	Exp	Pred
Molecular Weight	488	527	543	553	515	541
<u>Elemental wt %</u>						
Hydrogen	5.61	6.23	6.77	7.07	6.35	6.56
Carbon	88.30	87.28	85.84	85.47	87.43	87.00
Sulfur	1.74	1.79	1.73	1.72	1.53	1.55
Nitrogen	1.19	1.19	0.93	0.93	1.10	1.09
Oxygen	3.16	3.50	4.73	4.81	3.59	3.81
<u>SARA wt %</u>						
Saturates	2.2	1.8	9.0	5.8	6.3	4.0
Resins	49.6	52.0	47.8	52.5	51.8	50.6
Asphaltenes	41.0	40.6	34.6	33.0	33.3	35.7
Preasphaltenes	7.3	5.6	8.7	8.7	8.7	9.7
<u>NMR Fractions</u>						
Aromatic	7.6	8.5	3.7	2.5	3.8	4.1
Condensed Aromatic	31.3	35.1	22.2	24.1	29.5	31.9
Alkyl Alpha	9.5	9.6	9.4	10.2	4.5	4.3
Cyclic Alpha	18.8	17.9	18.1	17.2	21.5	19.7
Alkyl Beta	11.9	11.0	21.3	20.5	17.0	16.7
Cyclic Beta	12.9	12.2	15.2	16.4	14.3	16.7
Gamma	8.1	5.7	10.1	8.6	9.3	6.9
Phenolic OH (meq/g)	0.80	0.79	0.85	0.86	0.69	0.69
Objective Function		24.96		7.61		8.28

APPENDIX 4

RECENT ADVANCES AND FUTURE PROSPECTS FOR DIRECT COAL LIQUEFACTION PROCESS DEVELOPMENT

**BY: F. P. Burke, R. A. Winschel (CONSOL Inc.);
and D. Gray (Mitretek Systems)**

For presentation
213th National Meeting of the American Chemical Society
Storch Award Symposium
April 13-17, 1997
San Francisco, CA

RECENT ADVANCES AND FUTURE PROSPECTS FOR DIRECT COAL LIQUEFACTION PROCESS DEVELOPMENT

F. P. Burke and R. A. Winschel
CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

David Gray
Mitretek Systems
7718 Old Springhouse
McLean, VA 22102-3481

Keywords: Direct Liquefaction, Process Development, Economics

ABSTRACT

Over the last fifteen years, the technology for the direct conversion of coal to liquid fuels has undergone significant development. This has been most evident in improvements in product yields (i.e., barrels per ton of coal), product quality, and, ultimately, in projected product costs. These advances have occurred through the optimization of process conditions and, particularly, a better understanding of the selection and use of catalysts. In addition, engineering and economic evaluations of the liquefaction process alternatives, and macroscopic analysis of global fuel production and consumption have been essential in guiding process development and providing a justification for investment in further R&D. This paper will highlight some of the important technical achievements in reaching the current state of direct liquefaction process development, and provide some speculation on the opportunities and obstacles for future research and commercial implementation.

THE WORLD AND UNITED STATES OIL SITUATION

Petroleum use worldwide is about 65 million barrels per day (MMBPD), and the Energy Information Administration (EIA) predicts that by 2015, worldwide demand will increase to between 89 and 99 MMBPD.¹ Over 55% of world petroleum is used in the transportation sector. Liquid hydrocarbon fuels are ideal for transportation since they are convenient, have high energy density, and a vast infrastructure for production, distribution and end use is already in place. The estimated ultimate world resource of oil and natural gas liquids (NGL) is 2.5 trillion barrels; the sum of 1.2 trillion barrels for OPEC and 1.3 trillion barrels for non-OPEC.¹ Estimates of proven reserves of oil vary over time because more of the oil *resource* moves into the *reserve* category as a result of variations in the world oil price (WOP) and available technologies. However, the estimated ultimately recoverable world conventional oil resource (EUR) has been remarkably similar for the last 25 years. James MacKenzie of the World Resources Institute² cites an analysis of 40 estimates of ultimately recoverable oil, for the years 1975 to 1993, conducted by David Woodward of the Abu Dhabi Oil company. In this analysis, Woodward concluded that "there is a fair degree of consistency among the estimates with the average being 2,000 billion barrels (BBO) and 70% falling in the range of 2,000 to 2,400 BBO."

Mitretek has performed analyses of world oil demand and potential supply from the present until 2100.³ The results of these analyses show that when the projected world oil demand is plotted on the ultimate resource curve whose integral is equal to 2.5 trillion barrels, it becomes clear that

conventional world oil production will peak in a timeframe from about 2015 to 2020 and then irreversibly decline because of resource limitations.

Because oil is the primary fuel in the transportation sector, Mitretek also examined the potential impact of the above world oil supply scenario on the U.S. transportation sector.³ This analysis concludes that, even with a rapid penetration schedule for alternatively fueled vehicles, there is likely to be a significant shortfall in petroleum supply in the United States before 2015.

THE DEVELOPMENT OF DIRECT COAL LIQUEFACTION TECHNOLOGY

Direct coal liquefaction is the process by which coal is converted to liquids through the addition of hydrogen or the removal of carbon. Hydrogen can be provided directly from the gas phase, through transfer from a chemical source such as a hydrogen donor, or carbon can be removed by a disproportionation reaction in which the coal is converted to (relatively) hydrogen-rich and carbon-rich products. The reaction generally requires temperatures above the softening point of coal (typically around 600 K) to facilitate mass transport and to achieve adequate rates of reaction. Although liquids of some description can be produced by a number of approaches, the objective usually is to produce transportation grade fuels as substitutes for petroleum-derived gasoline or diesel fuel. The reactions involved include hydrogenation and cracking, and removal of nitrogen, oxygen and sulfur from the coal (primarily as NH_3 , CO , CO_2 , H_2O , and H_2S). The mechanisms of these reactions generally involve both hydrogenation and bond cleavage, although opinions differ as to the reaction sequence.

The cost of producing coal liquids is implicit in these chemical reactions. There is a theoretical minimum amount of hydrogen that is necessary to convert the (empirical) coal structure to liquid products of some specified composition. In practice, the amount of hydrogen consumed (typically 6-7 wt % on a moisture-ash-free coal basis) will be greater than the theoretical minimum because of undesirable side reactions, such as methanation of carbon oxides and C_1 - C_4 gas formation due to cracking. Because hydrogen is expensive, there is a strong incentive to minimize its consumption, but the quality of the product liquid must be known for a comparison of hydrogen consumption values to be meaningful.

The liquefaction reactions require elevated temperatures to proceed at reasonable rates; this requires some pressure containment (~500 psig) to keep the reactants in the liquid phase. If molecular hydrogen is used as the hydrogen source, higher operating pressure (2000-3000 psig) is required for adequate mass transfer. The combination of elevated pressure and temperature is an important factor in determining the capital cost of the liquefaction train, including heat-transfer units, reactors, pumps, pressure let-down systems, etc. Effective catalysts can decrease both the reaction pressure and temperature. Given the heterogeneous nature of coal, the presence of mineral matter, and the variety of functional groups present, it is likely that some form of catalysis occurs, even if an external catalyst is not used. In fact, catalysts are universally employed in practical liquefaction processes, with solid heterogeneous catalysts being the most common. Historically, the first commercial liquefaction plants in Germany used the I. G. Farben process, in which coal was liquefied at 760 K and 10,000 psig in a liquid phase reactor using a relatively inactive iron catalyst. Because of the reaction severity, the German plants produced high hydrocarbon gas yields (30 wt % MAF coal) with a correspondingly high hydrogen consumption (~14 wt % MAF coal).

In the United States, the development of direct liquefaction technology was stimulated by the petroleum shortfalls and price increases of the 1970s. By 1980, three process concepts (SRC-II, EDS and H-Coal) had been sufficiently advanced to merit consideration for commercialization.

An interest in producing a substitute fuel oil for electric utility boilers led the Southern Company and Electric Power Research Institute to explore the Solvent Refined Coal (SRC) process on the 6 tpd Wilsonville, Alabama facility. This was a one-stage thermal process in which coal was solubilized in a recycle solvent, and the product was deashed to remove mineral matter and some sulfur. A variant of this was the SRC-II process, developed by Gulf Oil Company and others. In the SRC-II process, coal was hydrogenated in a one-stage reactor with no catalyst addition, but the distillation bottoms were recycled to take advantage of the catalytic activity of the coal mineral matter. The SRC-II process was piloted on a 50 tpd unit at Ft. Lewis, WA. The Exxon Donor Solvent (EDS) process was developed through the 250 tpd pilot plant scale at Baytown, TX. In the EDS process, the coal was fed to a plug-flow reactor in a recycle solvent (the donor solvent) that was hydrogenated catalytically in an external reactor. The donor solvent provided the hydrogen for the liquefaction reaction. In later development, a bottoms recycle stream was added to the EDS feed to provide additional residence time for conversion, and perhaps to utilize the catalytic activity of the mineral matter. One common feature of these processes, and others such as the CONSOL CSF process and the British Coal LSE process, was that the primary coal liquefaction reactions took place in the absence of any added catalyst, ostensibly to avoid the rapid deactivation of the catalyst that was presumed to occur in the presence of the coal mineral matter.

In the HRI H-Coal process, the issue of catalyst deactivation was addressed by utilizing an ebullated bed reactor which allowed a supported catalyst to be added and withdrawn continuously. The ebullated bed reactor also offered superior performance in terms of heat and mass transfer. The H-Coal process was developed at HRI's bench-scale and PDU facilities in Lawrenceville, NJ, and piloted on a 250 tpd unit in Catlettsburg, KY. Representative operating conditions and yields for the H-Coal pilot plant operations with Illinois basin bituminous coal are shown in Table 1. The process made a relatively light product (proportion of naphtha) but also had a sizeable yield of hydrocarbon gases and unconverted resid, which reduced overall liquid yield.

One problem with the single catalytic stage is that hydrogenation reactions are best done at relatively low temperatures where the equilibrium is more favorable, but conversion (i.e., cracking) reactions are faster at higher temperature. To overcome this, research was conducted on the use of multiple reaction stages, exemplified by work by Lummus and Cities Service in New Brunswick, NJ. In the Lummus/Cities bench unit, the coal was converted to a soluble form in the first stage at relatively high temperature (~720 K) but short contact time (~2 min). The first-stage product was deashed, and converted to distillate liquids at around 670 K in an ebullated bed LC-Finer unit, which simultaneously produced a hydrogenated solvent for recycle to the first stage. A similar configuration was installed at the Wilsonville SRC pilot plant, which employed a Kerr-McGee Critical Solvent Deasher between a thermal first stage and an ebullated bed second stage supplied by HRI.

Lummus first recognized, and Wilsonville later confirmed, that the location of the deashing unit between the two stages had little effect on catalyst life. The most important factor in catalyst deactivation was carbon laydown, not poisoning by metals in the mineral matter. This led to "close coupling" of the two reactor stages, with deashing applied to the second-stage product. It also allowed for "ashy recycle", in which a portion of the second-stage product is recycled directly to the first stage. By concentrating solids in the recycle stream, the amount of material processed by the deasher was significantly reduced, and the unconverted coal was given additional residence time. The Wilsonville unit subsequently was used to explore a variety of staged reactor configurations, including two ebullated bed catalyst stages ("catalytic/catalytic"

mode), the use of a dispersed iron oxide as a first-stage catalyst with subbituminous coal (‘‘thermal/catalytic’’ mode), and alternative temperature staging. As shown in Table 1, this resulted in substantial reductions in hydrocarbon gas and resid production for bituminous coal, with a corresponding increase in distillate liquids, although the product was higher boiling than that of the H-Coal process. Results with subbituminous coal (Table 2) were similar, although a high first-stage temperature was still required to achieve adequate coal conversion. One advantage of the ‘‘thermal’’ first stage is a greater removal of oxygen as carbon oxides. In the single-stage system, carbon oxides are converted catalytically to methane and water, with increased hydrogen consumption.

Although the first stage in the thermal/catalytic mode did not contain a supported catalyst, the Wilsonville unit was fed a powdered iron oxide catalyst to promote coal conversion. This was consistent with research at Mobil R&D showing that solid catalysts promote the conversion of coal to soluble forms. Subsequent work at Wilsonville, HRI, and a number of academic institutions explored the use of dispersed catalysts based on iron, molybdenum, and other metals. In a current collaborative project, CONSOL, the University of Kentucky, LDP Associates, Hydrocarbon Technologies Inc. (HTI), and Sandia National Laboratories have been exploring several advanced concepts for improving direct liquefaction process economics through modifications to the feed coal and recycle solvent and the use of dispersed and impregnated slurry catalysts. This work has progressed through laboratory studies to evaluation of the process concepts in bench-scale continuous unit runs at HTI, the former experimental facilities of HRI. The first run (ALC-1) was made in the all-slurry catalyst mode with molybdenum and iron catalysts. Potential advantages of operation with all-slurry catalysts include: simplified reactor design; simplified operations, constant catalyst activity, more efficient use of reactor volume (no volume needed for catalyst support); and catalyst can be recycled with solids to reduce the fresh catalyst requirements. Raw subbituminous coal was used in condition 1 of Run ALC-1; the same coal cleaned by oil agglomeration was fed in condition 4 (Table 2). In condition 5 (not shown in Table 2), the distillate portion of the recycle solvent was dewaxed and hydrogenated to improve solvent quality. As shown in Table 2, these operations produced exceptional distillate yields of 66% to 69% MAF from subbituminous coal. This was accomplished by near-extinction conversion of residual oils, including unconverted coal. The somewhat higher hydrogen consumptions in these operations resulted, in part, from the higher gas yields due to the higher reaction temperatures, but they also resulted from the use of an in-line gas-phase hydrotreater for the distillate product. These operations produced a low-heteroatom, highly hydrogenated product with low boiling point.

OPPORTUNITIES FOR FUTURE RESEARCH AND DEVELOPMENT

As summarized above, the analysis by Mitretek indicates that the time when worldwide petroleum demand begins to deplete resources may come within the next two decades, even without significant political or economic disruptions. Therefore, it is essential simultaneously to pursue a number of options to mitigate the future shortfall in domestic petroleum. These options are: to continue domestic exploration and production using the best technologies available, to continue to develop and deploy alternatively fueled vehicles, and to continue to improve efficiencies in all sectors of transportation. Yet, even with these steps, this analysis indicates that the domestic demand for liquid fuels will exceed our potential sources of supply. Continuing our reliance on oil imports to alleviate the shortfall is not a long-term solution. Rapidly increasing world oil demand will put ever-increasing pressure on the oil supply and the WOP will rise. The inevitable conclusion is that additional options will be necessary to ensure that the United States will have the necessary liquid fuels supply to be able to continue economic growth into the 21st

century. One of these additional options is to produce liquid fuels from our huge domestic coal resources.

Current direct coal liquefaction technology is technically feasible, but not economically competitive. However, with world oil prices over \$25/bbl at this writing, it is clear that, in the long term, the upward pressure on oil prices persists. Research should be directed toward reducing the cost of liquid products so that these alternative technologies are available as early as possible to have the greatest economic benefit. Several technical issues are pertinent to achieving that objective.

Catalysts. Despite all the research that has been done on catalyst development and testing, improved catalysts still offer the single best opportunity for affecting many of the cost features in a liquefaction process, including yields, selectivity, product quality, hydrogen utilization, and capital cost (through reduced pressure and temperature and increased space velocity). A problem with much catalyst research is that it is done at unrealistic conditions, with results that are not easily translated to a process context. For example, identifying a catalyst that improves coal conversion from 40% to 60% is of little value when the process goal is produce specification products at high yield. On the other hand, identifying a truly improved catalyst could open significant opportunities for redefinition of the basic process concept.

Feedstock Selection. The principal feedstocks are coal and hydrogen. Most coals have been shown to be suitable for most processes. If there is an "opportunity" coal, it will be the result of economic opportunity; for example, the current emphasis on U.S. low-rank coal recognizes its low mine-mouth cost. Reduction in hydrogen cost is problematic. Production of hydrogen from coal involves a large unavoidable capital expenditure for the gasification plant. Production from natural gas is unlikely to be economical in the long term, particularly if petroleum prices have risen. Coprocessing feedstocks, such as waste plastics and heavy resid, may be useful in providing an economic justification for early "pioneer" plants which will demonstrate commercial viability.

New Reaction Mechanisms. Despite its variations, current liquefaction technology remains based in the early German technology, i.e., thermal free radical or radical-initiated hydrogen transfer. There are other possible hydrogen transfer chemistries, including carbonium ion, hydride ion and biochemical mechanisms. Although these have been explored, they have yet to yield a promising candidate. As with the catalyst research, much of the problem may lie in a failure to establish exploratory research goals of such a nature that they can be used to justify further development. A realistic candidate must be able to achieve high yields of liquids that meet some minimum standard of quality or upgradability.

REFERENCES

1. Annual Energy Outlook 1996 With Projections To 2015. Energy Information Administration, January 1996. DOE/EIA-03893 (96).
2. MacKenzie, James J. *Oil as a Finite Resource: When is Global Production Likely to Peak?* Paper from the World Resources Institute, March 1996.
3. Gray, David, and Glen Tomlinson, *Rationale and Proposed Strategy for Commercial Deployment of Coal-Derived Transportation Fuels*, Mitretek Report MP 96W0000209, June 1996.

TABLE 1

**OPERATING CONDITIONS AND YIELDS FOR H-COAL, ITSL, AND CMSL,
ILLINOIS BASIN COAL**

	H-Coal Pilot Plant Run 8	ITSL Wilsonville Run 252B1	ITSL Wilsonville Run 257J	CMSL HTI Run PB-05/2
Year	1981	1987	1989	1996
<u>Conditions</u>				
<u>Stage 1</u>				
T, K	728	705	705	720
H ₂ Partial pressure, psi, inlet	2500	2500	2600	2500*
Catalyst age, lb coal/lb	1690	~1300	645	Dispersed
S.V., lb coal/hr/ft ³ reactor, each stage	29	-	-	42
<u>Stage 2</u>				
T, K	None	672	678	731
Catalyst age, lb coal/lb	None	~470	1309	Dispersed
<u>Yields, wt % MAF</u>				
H ₂ O	7.5	9.6	10.2	4.3
H ₂ S, NH ₃ , COx	3.8	5.1	5.0	6.1
C ₁ x C ₃ Gas	12.8	6.5	5.4	6.7
Naphtha	22.9	17.5	14.5	18.4
Middle Distillate	20.0	7.8	7.1	16.0
Gas Oil	7.6	44.1	44.2	39.0
Total Distillate	50.5	69.4	65.8	73.4
Resid	31.3	16.4	19.7	14.8
H ₂	-6.0	-7.1	-6.0	-5.2
Coal Conversion	96.1	93.0	91.7	96.2

*Unit back-pressure

TABLE 2

**OPERATING CONDITIONS AND YIELDS FOR H-COAL, ITSL, AND CMSL,
POWDER RIVER BASIN COAL**

	H-Coal PDU Run 10	ITSL Wilsonville Run 262D	CMSL HTI Run ALC- 1/1	CMSL HTI Run ALC- 1/4
Year	1980	1991	1996	1996
<u>Conditions</u>				
<u>Stage 1</u>				
T, K	719	713	715	716
H ₂ Partial pressure, psi, inlet	2500	2800	2500*	2500*
Catalyst age, lb coal/lb	742	Dispersed	Dispersed	Dispersed
S.V., lb coal/hr/ft ³ reactor, each stage	25	-	42	26
<u>Stage 2</u>				
T, K	None	694	726	726
Catalyst age, lb coal/lb	None	727	Dispersed	Dispersed
<u>Yields, wt % MAF</u>				
H ₂ O	16.3	13.9	13.8	16.2
H ₂ S, NH ₃ , COx	3.5	6.7	5.9	5.1
C ₁ x C ₃ Gas	11.0	5.3	9.4	12.4
Naphtha	24.3	12.9	18.6	23.0
Middle Distillate	14.5	7.7	11.3	9.7
Gas Oil	11.9	40.1	39.2	33.4
Total Distillate	50.7	60.8	69.0	66.1
Resid	24.1	18.7	9.4	7.1
H ₂	-5.6	-5.5	-7.5	-6.8
Coal Conversion	91.0	90.1	95.0**	97.5**

*Unit back pressure

**SO₃-free ash basis