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**Coal Liquefaction Process Streams
Characterization and Evaluation,**

**Quarterly Technical Progress Report
April 1 through June 30, 1993**

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

November 1993

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

Under Contract to:

United States Department of Energy
Contract No. DE-AC22-89PC89883

U.S. DOE Patent Clearance was provided by
Chicago Operations Office on October 19, 1993.

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**COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION
QUARTERLY TECHNICAL PROGRESS REPORT, APRIL 1 THROUGH JUNE 30, 1993**

This is the fifteenth Quarterly Technical Progress Report under DOE Contract DE-AC22-89PC89883. Major topics reported are:

- The status of the Participants Program is described. Trips were made to The Pennsylvania State University and the University of Delaware for the purpose of establishing teaming arrangements. The trip reports are appended.
- A description of work in progress is included.
- Two papers are appended. One of these papers describes work performed under subcontract in Phase I of the Participants Program by the University of Kentucky Center for Applied Energy Research. The second paper describes stable carbon isotope analysis of coprocessing materials. Both papers were accepted for publication in *Fuel*.

Section 1

INTRODUCTION

This is the Technical Progress Report for the fifteenth quarter of activities under DOE Contract No. DE-AC22-89PC89883. It covers the period April 1 through June 30, 1993.

OVERVIEW

The Research and Development Department of CONSOL Inc. (CONSOL) is conducting a program to characterize process and product streams from direct coal liquefaction process development projects sponsored by the Department of Energy. In this program, CONSOL obtains samples from current process development activities in coal liquefaction and coal-oil coprocessing, and characterizes them using established analytical techniques. In addition, selected samples are characterized by other analytical techniques to evaluate their potential for aiding process development. These analyses and interpretation of the results in relation to process operations are provided by the subcontractor.

CONTRACT OBJECTIVES

CONSOL is conducting a program to characterize process and product streams from direct coal liquefaction process development projects. The program has two main objectives. The first of these is to support ongoing DOE-sponsored coal liquefaction process development efforts. This is being accomplished by the application of a variety of standard testing techniques to appropriate process samples. The interpretation of the data so obtained aids plant operations and planning. The second objective is to obtain and provide appropriate direct coal liquefaction process-derived samples for the evaluation of novel analytical methods. The criteria used to evaluate the techniques or methods include the usefulness of the method to monitor the liquefaction process and to obtain specific chemical information. Methods which show promise for providing useful information for coal liquefaction process development may be utilized in conjunction with the first objective of this program.

CONTRACT ACTIVITIES - THIS PERIOD

Contract activities for this quarter are listed below.

- Significant progress was made in the Participants Program. A detailed description is provided in this technical report.
- Presentations were made at the HRI Proof of Concept Review Meeting on April 20, 1993. The topics presented were CTSI Run CC-16 process stream characterization results, petroleum inspection tests to be done on CTSI Runs CC-15 and CC-16 products, and routine and non-routine tests planned for CTSI Run CC-15 samples.
- The document "Coal Liquefaction Process Streams Characterization and Evaluation, Topical Report, Analytical Methods for Application to Coal-Derived Resids - A Literature Survey" was printed and issued.
- We hosted visits by Dr. David Wertz of the University of Southern Mississippi (USM) and three students from USM, and Heon Jung and Paul Hajdu of Dr. Irving Wender's group at the University of Pittsburgh. Dr. Masaharu Nishioka of Viking Systems International, Dr. In-Chul Lee of the Korea Institute of Energy Research (KIER) and R. Lett of PETC also visited CONSOL this quarter.
- Ongoing work includes analysis of oils from HRI CTSI Run CC-15 and Wilsonville Run 263, development of a modified version of HRI's method for determining the 975 °F⁺ distillation fraction of coal liquids by thermogravimetric analysis (TGA), and placing the seventh (final) Phase III Participants Program subcontract.
- Two papers were published in the August 1993 issue of *Fuel*. One paper was authored by M. S. Lancet, R. A. Winschel, and F. P. Burke, entitled "Stable Carbon Isotope Analysis of Coprocessing Materials". The other paper, authored by R. F. Rathbone, J. C. Hower, and F. J. Derbyshire, is entitled "The Application of Fluorescence Microscopy to Coal-Derived Resid Characterization". Copies of the two papers are appended to this report.

Section 2

EXECUTIVE SUMMARY

Significant progress was made in the Participants Program this quarter. Two additional Phase III projects were initiated. One project, being conducted by the University of Delaware, involves the evaluation of an empirical method for evaluating the conversion reactivity of coal-derived resids. In the other project, The Pennsylvania State University will evaluate the use of HPLC/MS techniques to analyze resid-containing coal liquids. The first Phase III final report was received, in draft form, from the National Institute for Petroleum and Energy Research (NIPER). That project consists of inspection tests on the net product from HRI CTSL Run CC-15. Preparations are being made to initiate a second project with NIPER under Phase III. This project will consist of inspection tests on the net product from HRI Run CMSL-2. Status reports received from SRI International (FIMS analysis of HRI CTSL Run CC-15 samples) and the University of Delaware indicate good progress in their respective projects. All remaining sample data and processing information packages were issued to subcontractors for their respective sample sets.

Section 3 DISCUSSION

PARTICIPANTS PROGRAM

The following items were accomplished in the fifteenth quarter of this contract.

Phase I

A manuscript was received from SRI International describing work performed under Phase I of the Participants Program for field ionization mass spectrometry (FIMS) analysis of resids. The manuscript was submitted to *Energy and Fuels*.

Phase III

The draft final report was received from National Institute for Petroleum and Energy Research (NIPER) on inspection tests of the net product from HRI CTSL Run CC-15. Copies of the report were sent to Burns and Roe Services Corp. and HRI for review. Comments were received and compiled. A draft statement of work was issued to NIPER to conduct a second set of petroleum inspection tests. The sample which will be tested was produced in HRI Run CMSL-2. This statement of work was formulated in conjunction with Burns and Roe. The NIPER final report will be issued jointly with the final report from the second NIPER project.

Three status reports covering the period March 15 through June 14 were received from SRI International. FIMS analyses were performed on all non-distillate samples in the SRI sample set, which consists of samples from HRI CTSL Runs CC-15 and CC-16. The volatilities of the filtered oils and interstage oils were found to be very high. The pressure-filter cake samples were about 50% volatilized. To ensure representative data, all solid samples are being run in duplicate. A process information package and CONSOL's analytical data were sent to SRI for their sample set.

A project was begun with The Pennsylvania State University to evaluate the use of HPLC/MS to the analysis of resid-containing oils. Samples, analytical data, and process information packages were sent to Penn State. A trip report was issued for the visit to Penn State in which teaming arrangements were made. The trip report is Appendix 1 of this technical report.

A project was begun with The University of Delaware to evaluate a method for obtaining resid conversion kinetics. The work is described in detail in Appendix II. Samples, analytical data, and processing information packages were sent to Delaware. The University of Delaware researchers requested catalyst for their work. One pound of fresh, unsulfided Criterion 324 Ni/Mo/Al catalyst (1/16" extrudate pellets) obtained from PETC was ground to pass a 60 mesh screen. It was classified into 60 x 100 mesh, 100 x 200 mesh, and -200 mesh fractions. The fractions all had the same nickel and molybdenum contents (2.5% and 12.0%, respectively). A second sample (2 lb) of the same catalyst was obtained from PETC; 1 lb of it was ground, classified, and combined with the first sample. The three fractions represented 39.4, 34.7, and 25.9 wt%, respectively, of the original catalyst. The individual size fractions and their analyses were sent to the University of Delaware. A status report was received from the University of Delaware. Modifications were made to the reactor system and work-up procedure. However, because of the high surface area of the preheater and precooler (a combined total of 42 ft of 1/4" tubing) and the viscous nature of the resid samples, hold-up in the reactor system is inevitable. Consequently, recovered products represent only 63 to 76 wt % of the feed resid. Delaware believes that the material recovered is representative of the whole sample, based on determination of the ash content of the recovered material. Therefore, no attempt to improve recoveries will be made in this project. A trip report was issued for the visit to the University of Delaware during which teaming arrangements were discussed. The trip report is Appendix 2 of this technical report.

A processing information package and CONSOL's analytical data were sent to the University of Utah for their sample set. Utah is analyzing oils from HRI CTSL Runs CC-15 and CC-16 by ^{13}C -NMR.

A processing information package was sent to the University of Pittsburgh for their sample set. Pitt is evaluating a method to determine donatable hydrogen in resids.

BASE PROGRAM - ONGOING WORK

Routine characterization work was begun on our entire set of samples from HRI CTSL Run CC-15. Proton distributions and phenolic -OH concentrations were determined on all the liquid samples (SOH, ASOH, PFL, INT). Some analyses were

completed on the solid PFC samples. Interstage samples and the corresponding pressure filter samples will be characterized more extensively than most of the liquid samples, as sample size permits.

A thermogravimetric analysis (TGA) method for the determination of the equivalent 975 °F* (ASTM D1160) distillation bottoms, based on a method developed and routinely used at HRI, is being developed for use in-house. HRI agreed to run four samples (Wilsonville Run 262, V1082, V-130, and V1074; Wilsonville Run 258K, V131B) with their TGA method to assist us in calibration of the method that we are developing. About 200 g each of the latter two samples was sent to HRI so that ASTM D1160 distillations can be performed in addition to the TGA tests.

HRI asked us to explore the possibility of obtaining 200 ton of Burning Star 2 coal containing less than 10% MF ash for PDU operations. This material is not available. We provided HRI with information on alternative Illinois coals and initiated arrangements for them to obtain a low-ash (<10%) shipment of Burning Star 4 coal.

APPENDIX 1

**TRIP REPORT FOR VISIT TO
THE PENNSYLVANIA STATE UNIVERSITY**

Trip Report: The Pennsylvania State University
Date of Visit: March 10, 1993
Address: 209 Academic Projects Building
The Pennsylvania State University
University Park, PA 16802
Principal Contact: Dr. Patrick G. Hatcher
Phone: 814-865-7838

Attendees:

Penn State University
Pat Hatcher

SciTech
Michael Bogdan

CONSOL
R. A. Winschel
S. D. Brandes

DISCUSSION

CONSOL Introduction

The project objectives and approaches were briefly discussed. The proposal made to CONSOL by Dr. Hatcher of The Pennsylvania State University (March 2, 1993) deals with the use of two-dimensional high-performance liquid chromatography (2-D HPLC) and HPLC-mass spectrometry (MS) for the analysis of coal derived process oils.

Penn State University Interest

The proposed project is an evaluation of the state-of-the-art liquid chromatography technique for use in characterizing heavy distillate (650°F⁺) and resid-containing coal liquids in support of liquefaction process development. The unique facets include the use of a newly developed high-performance column and a photodiode array UV detector. Mr. Michael Bogdan of SciTech will act as a consultant to Dr. Hatcher. One graduate student who is experienced in HPLC technology, but has worked with resin samples, will work on the project.

The samples will be first solubilized in 50/50 hexane (or pentane)/methylene chloride and then filtered. We informed Penn State that preliminary results for filtering HRI pressure-filter liquids (PFL) samples in this solvent system show about a 3% loss of insoluble material. After filtering the samples, Penn State will dry the filtrate and filter cake samples in nitrogen and weigh them. Two techniques were considered for HPLC analysis.

The primary method under consideration is a normal-phase separation using a newly available column (Hypersil Green PAH-2 150 x 4.6 mm). This column has outstanding performance for aromatics. The sample would be reconstituted in 50/50 hexane/methylene chloride and a gradient of 50/50 hexane/methylene chloride to 100% methylene chloride would be used for the chromatography. Both Mr. Bogdan and Dr. Hatcher are optimistic about successful separation using this technique.

The fall-back method is EPA Protocol #610, which is a reversed-phase technique in which the sample will be reconstituted in 50/50 acetonitrile (ACN)/water and a gradient of 50/50 ACN/water to 100% water is used for the chromatography. This method was established specifically to identify and quantify 16 polynuclear aromatic hydrocarbons (PAHs). It was agreed that the solubility of coal liquefaction-derived samples in the ACN/water mixture would be poor.

For either method, one to three standard additions of the pure PAH standards (those from EPA method #610) would be made to the starting solution for quantitation of those compounds. Additional compounds will be identified as possible by their UV spectra and retention times. Detection is by a UV spectrometer equipped with a photodiode array detector; spectra will be collected from 200 nm to 400 nm. The UV spectra are plotted vs time. Fractions of the eluate will be collected for further characterization. The number of fractions taken per sample would depend on the ability to obtain separation of the peaks in the UV spectra. If a clear distinction cannot be made, fractions will be taken at predetermined intervals of time. It was expected that between 5 and 10

fractions would be obtained from each sample. Since detection is by UV absorbance, saturated hydrocarbons will not be detected in the HPLC step.

The unfractionated, original samples will be analyzed by gas chromatography/mass spectrometry on a Hewlett Packard 5890 instrument interfaced to a Hewlett Packard 5971A MSD. The column used will be a 50% phenylmethylsilane fused silica capillary column. The fractions from the HPLC separation would be analyzed by heated probe high resolution mass spectrometry using a Kratos MS80 instrument. The probe can be heated from 50°C to 250°C under vacuum at a heating rate of about 15°C/min. Mass spectra are collected at every 2.5°C temperature interval during heating. Mass resolution of this instrument (20,000) is sufficient to obtain exact molecular formulae for compounds of molecular weight up to 800 amu.

We were toured through the laboratory facility where the Waters 600 microflow syringe pump and the Waters Model 990 UV detector, which make up the HPLC equipment, and a Kratos MS-80 high resolution mass spectrometer were located.

General Analytical Needs and Suggestions

Approximately 15 µg of each sample will be required per analysis. We would supply at least 1 g of each sample.

Recommendations

Based on this meeting, we recommend that the normal-phase 20-HPLC and high resolution mass spectrometry techniques be used for the analysis of process oils, either heavy (650°F+) distillates or whole pressure-filter liquid samples which contain no ash and very little, if any, THF-insoluble organic material. Five samples will be examined in the program. These samples will be chosen by CONSOL and specified in a Statement of Work. The method of separation will be the normal phase technique using the PAH-2 column. In the unlikely event that the system fails to elute and detect peaks, then EPA Protocol #610 will be employed.

The data to be collected include sample solubility, GC/MS data on the starting samples, 2D-HPLC chromatograms, quantitation of the 16 PAHs, identification and quantitation (as possible) of other compounds and HRMS characterization of the HPLC fractions. The HRMS data will include tables of peak intensity vs homologous Z numbers and any further molecular characterization possible.

Follow-up

CONSOL will prepare a more detailed program in the form of a Statement of Work for review and comment by Dr. Hatcher and Mr. Bogdan. The proposed work would be completed no later than August 31, 1993. The cost proposal of 3/2/93 for \$8,462 was accepted by CONSOL, pending DOE approval. There was no objection to a purchase order contract, as long as contractual terms and agreements were within the scope of The Pennsylvania State University policy. If contractual arrangements were complete, work could start in April 1993.

APPENDIX 2

**TRIP REPORT FOR VISIT TO
THE UNIVERSITY OF DELAWARE**

Trip Report: University of Delaware
Date of Visit: November 12, 1992
Address: University of Delaware
Department of Chemical Engineering
Newark, DE 19716
Principal Contact: Dr. William H. Calkins
Adjunct Professor
Phone: (302) 451-2213

Attendees:

University of Delaware
Dr. W. H. Calkins
Dr. He Huang, Research Associate

CONSOL
F. P. Burke
R. A. Winschel

DISCUSSION

Consol Introduction

The Participants Program objectives and approach were discussed with Drs. Calkins and Huang.

University of Delaware Interest

Dr. Calkins described his reactor system which is used to obtain very short contact time liquefaction products. The reactor is a one-liter stirred tank. It is fed a constant 7 L/min flow of tetralin and is pressurized to, typically, 900 psi with nitrogen. Most experiments to date have employed Illinois 6 or a subbituminous coal with no catalyst at a reactor temperature of 390°C. The coal charge (50 g) is stored as a tetralin slurry (2/1 solvent to coal) in a charging vessel equipped with a rupture disk at its exit. After reactor line-out with tetralin, the tetralin flow is diverted to the charging vessel, thus destroying the rupture disk and injecting the coal slurry into the reactor almost instantaneously. Isothermal and isobaric conditions are achieved within 20 s after coal injection. Product samples are taken by means of a sampling manifold that consists of a set of parallel tubes and associated valving through which the reactor product is collected, cooled and stored. The slugs of product (samples) thus represent discrete reaction times. Samples are taken about every 20 s after coal injection until about 160 s (in later samples, the coal concentration is too low).

Product work-up usually consists of extraction with methylene chloride. The residue is weighed, analyzed by CP/MAS ^{13}C -NMR and other methods, then low-temperature ashed (LTA) to determine coal conversion by LTA balance. Dr. Calkins found that Fe content is a good surrogate for LTA and so in some cases, rather than determining LTA, the Fe content of the residue is determined by AA. The filtrate is rotary evaporated to remove methylene chloride and then analyzed by GC/MS and other methods. With Illinois 6 coal, conversion to solubles increases to about 20% at 90 s residence time and then stays nearly constant to the end of sampling (about 160 s residence time).

Dr. Calkins' particular area of interest with this system is to determine changes in coal oxygen functionalities during very short residence time liquefaction. To this end, the methylene chloride insolubles are analyzed by fast neutron activation analysis (FNAA) to determine total oxygen, the LTA is analyzed by FNAA to determine mineral oxygen and thus organic oxygen by difference, and the methylene chloride insolubles are analyzed by the methods of Blom et al.¹ and Schafer² to speciate hydroxyl, carboxyl and carbonyl groups. Ethers are determined by difference. Dr. Calkins' flash pyrolysis method is sometimes used as an independent method to determine some of the oxygen functional groups.⁽³⁾ Results on Illinois 6 coal in the above reactor system show that about one third of the hydroxyl oxygen converts to ether oxygen with only minor other changes occurring.

The one-liter reactor system described above requires approximately 7 L of tetralin for each experiment. Dr. Calkins is constructing a smaller, more convenient reactor system that will be up and running this calendar year. In this smaller system, coal slurry will be blown into a preheated batch reactor

and, after the desired residence time, blown into a cooling vessel. Heat-up and cool-down times will be <15 s. The slurry charge can be as large as 30 mL. The reactor can operate at conditions of 550°C and 2500 psi. Authentic liquefaction solvents could be used.

Dr. Huang made a presentation on a review of the literature on the various possible methods for determining and speciating oxygen in coal and its products.

We toured the laboratories, including the 1 L and 30 mL liquefaction systems and the characterization laboratories.

Areas of Potential Collaboration

There seem to be two areas of possible collaboration between Dr. Calkins' group and CONSOL as part of the Participants Program: 1) Dr. Calkins' group could prepare very short contact time liquefaction products from selected coals and oils for characterization at their lab or at the lab of other participants. 2) Dr. Calkins' group could analyze selected resids by the most promising oxygen speciation methods described by Dr. Huang. Several methods designed to obtain the same information could be employed to examine the agreement, consistency and applicability of the various methods.

Wrap-Up

We provided a copy of the Analytical Needs Assessment⁴ and a paper describing the Participants Program⁵ to Dr. Calkins, and we agreed to send him copies of the final reports from those Participants Program subcontracts that concerned oxygen functionality. Dr. Calkins provided us with several papers describing his one-liter reactor system and work conducted with it, and a summary of the oxygen speciation methods described by Dr. Huang.

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5. 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.

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