A Characterization and Evaluation of Coal Liquefaction Process Streams

Quarterly Technical Progress Report
January 1 through March 31, 1995

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Section 1
EXECUTIVE SUMMARY

CHARACTERIZATION OF SAMPLES FROM HTI RUN CMSL-8

We received 27 samples from HTI's coal/plastics bench unit Run CMSL-8, prepared an overall analytical plan for the samples, and completed many analyses on the available samples. Three interstage samples have not yet been received. Sample requests were received from DOE/PETC and West Virginia University (WVU), and the requested samples were distributed.

Two product oil samples (separator overhead (SOH) and atmospheric still overhead (ASOH)) from periods in which the on-line hydrotreater was by-passed are much poorer in quality than the SOHs produced with the hydrotreater in place. ¹H-NMR and GC-MS indicate the presence of ethylbenzene and cumene (isopropyl benzene) in the SOH net distillate products from the coal/mixed-plastic periods; these are believed to be polystyrene liquefaction products.

The pressure filter liquids (PFLs, the recycle oils) from coal/plastics periods contain 15 to 30 wt % tetrahydrofuran (THF) insolubles; virtually no insolubles were found in the coal-period samples. The Fourier transform infrared (FTIR) spectra of the insolubles from the coal/plastics-period samples identified them as polyethylene (PE)-like material. PFL distillation bottoms from two of three coal/mixed-plastics periods separated into two solid phases upon cooling; none of the other PFL resids behaved in this way. The two phases differed in physical characteristics. Diffuse reflectance FTIR was used to examine both phases of one of the resids; the upper phase appears to be predominantly plastic derived (much of it PE), and the lower phase is predominantly coal derived. Samples of both phases were provided to PETC.

We provided J. Larsen of Lehigh University with three samples from the coal/polyethylene period of Run CMSL-8 for analysis by plasma desorption mass spectrometry (PDMS) to help define the fate of the polyethylene. The samples included the feed high density polyethylene (HDPE), the 850 °F⁺ PFL, and the pressure filter cake (PFC) from a coal/HDPE period. The HDPE could not be dissolved for analysis. For the PFL 850 °F⁺ resid, Lehigh reported a number

average molecular weight (M_n) = 705 amu, and a weight average molecular weight (M_w) = 1117 amu; for the PFC, M_n = 748 amu and M_w = 1224 amu.

We participated in two meetings at DOE/PETC to present and review Run CMSL-8 results, discuss distribution of CMSL-8 samples, and discuss future bench-scale and PDU-scale runs. We also provided DOE with our recommendations for Run CMSL-9.

INSPECTION OF HTI POC-1 AND POC-2 NET PRODUCTS

A subcontract was initiated with Conoco Inc. to conduct inspection tests on the net products of HTI Runs POC-1 and POC-2. The analytical plan appears in Appendix 3.

UNIVERSITY OF DELAWARE

A subcontract modification authorizing work on Subtask 1.4.2 was initiated with the University of Delaware. CONSOL visited the University of Delaware on January 17 to plan work under Subtask 1.4.2. A trip report for that visit was issued (see Appendix 2). Samples of coal liquefaction resids from a number of Wilsonville and HTI runs and the associated analytical data for these samples were sent to Delaware for reactivity studies. Analytical data on numerous coal liquefaction resids acquired under DOE Contract DE-AC22-89PC89883 were compiled and issued to Delaware. These data will be used in building the kinetic model. The Delaware quarterly technical report is appended to this document (Appendix 1).

TECHNOLOGY TRANSFER

An abstract was submitted for the 210th National ACS meeting entitled "Caustic Washing for Refining of Direct Coal Liquefaction Products". The abstract appears as Appendix 4.

Section 2

INTRODUCTION

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 will build on work performed in DOE Contract No. DE-AC22-89PC89883. Independent analyses by well-established methods will be obtained of samples produced in direct coal liquefaction processes under evaluation by DOE. Additionally, analytical instruments and techniques which are currently underutilized for the purpose of examining coal-derived samples will be evaluated. The data obtained from this study will be used to help guide current process development and to develop an improved data base on coal and coal liquids properties. A sample bank will be established and maintained for use in this project and will be available for use by other researchers. The reactivity of the non-distillable resids toward hydrocracking at liquefaction conditions (i.e., resid reactivity) will be examined. From the literature and data experimentally obtained, a mathematical kinetic model of resid conversion will be constructed. It is anticipated that such a model will provide insights useful for improving process performance and thus the economics of direct coal liquefaction.

CONTRACT ACTIVITIES THIS QUARTER

- We completed many of the analyses on the 27 samples received from HTI bench-scale Run CMSL-8, in which coal, coal/mixed plastics, and coal/HDPE were fed. Distribution of requested samples from this run to other sites was completed. Three additional samples are expected from HTI, and additional analytical work will continue next quarter. We provided DOE with our recommendations for planning HTI Run CMSL-9.
- An analytical plan was formulated in conjunction with Burns and Roe Services Corp for the inspection tests of the net products from HTI Runs POC-1 and POC-2. A 20 mL sample of HTI Run POC-2 net product was sent to Conoco Inc. Conoco performed a simulated distillation with the small sample so that an estimate could be made of the number of large distillations required to produce sufficient quantity of each fraction for

completion of the planned petroleum inspection tests. Conoco and Pittsburgh Applied Research Center provided cost estimates for the proposed inspection tests. A subcontract subsequently was placed with Conoco Inc. to perform petroleum inspection tests on the net product oils of HTI Runs POC-1 and POC-2. Six-gallon samples of each of the two oils were shipped to Conoco. The samples were originally supplied to us by Southwest Research Institute as being representative of the materials they are using in the End-Use Study. The analytical plan which will be used by Conoco appears in Appendix 3.

- Delaware made substantial progress in their experimental program under Task 1.4.1. Delaware's quarterly technical progress report is appended to this document. A subcontract modification authorizing work on Subtask 1.4.2 was initiated with the University of Delaware. CONSOL visited the University of Delaware on January 17 to plan work under Subtask 1.4.2. A trip report for that visit was issued (see Appendix 2).

The 850 °F⁺ resid and the 850 °F⁻ distillate of Wilsonville Run 261, Period A V131B were recombined in two ratios (50:50 and 75:25, distillate:resid, w/w). These samples and the whole V131B oil (which has a resid + ash + IOM content of 65%) and a sample of HTI Run POC-2, Period 36 0-43 whole oil (resid + ash + IOM = 42%) were sent to the University of Delaware to be used as standards for the Delaware thermogravimetric analysis (TGA) method. Fourteen samples of coal liquefaction resids from a number of Wilsonville and HTI runs were analyzed and then sent to Delaware for reactivity studies using the short time batch reactor (STBR). Also, analytical data for the resid composite from Wilsonville Run 258 V131B was sent to Delaware. This is the sample that Delaware is using to establish operating conditions in the STBR. In addition, analytical data on numerous coal liquefaction resids acquired under DOE Contract DE-AC22-89PC89883 were compiled and issued to Delaware. These data will be used in building the kinetic model.

Hydrogen treat rates were calculated for Wilsonville Run 262D and compared to those used by Delaware. This information, plus a package of information describing Wilsonville 259G (including mass balances, temperatures, flow

diagram, etc.) was sent to Delaware as an example of a representative two-stage liquefaction run.

- A draft of the status assessment (Task 1.1) was completed. It will be issued to DOE for review next quarter.
- Eighteen oil/coal coprocessing samples were received from I. Wender of the University of Pittsburgh and were analyzed for phenolic -OH content by FTIR. Eleven samples from Pitt also were received for elemental analyses. All samples were generated under Pitt's DOE Contract No. DE-AC22-91PC91054.

ACTIVITIES IN PROGRESS

- Analyses are being conducted on samples received from HTI bench-scale Run CMSL-8. Additional samples are expected from HTI, analytical work will continue into the next quarter.
- We obtained a draft CMSL-9 run plan from HTI; the run is expected to start early next quarter. A full set of samples was requested from HTI (Appendix 6). DOE requested that we again serve as the clearinghouse for sample distribution.
- The Conoco inspection tests are scheduled to be complete late next quarter.
- Plans are being made to initiate in-house resid reactivity work. We requested a description of the pressure regulation system HTI employs for their microautoclaves so that it can be adapted for use. The analysis scheme for the reaction products is being considered.
- A paper is being prepared for the 210th National ACS meeting entitled "Caustic Washing for Refining of Direct Coal Liquefaction Products".

Section 3

RESULTS AND DISCUSSION

PROGRESS OF CONSOL CHARACTERIZATION OF SAMPLES FROM HTI RUN CMSL-8

Sample Acquisition and Distribution

We received 27 samples from HTI's coal/plastics bench unit Run CMSL-8. HTI informed us that two of the interstage samples we requested could not be obtained. The other interstage samples are being re-composited prior to shipment to us.

We are acting as the clearinghouse for samples from Run CMSL-8. In this regard, we received sample requests from K. Rothenberger of DOE/PETC, from U. Rao of DOE/PETC for some of our two-phase PFL distillation bottoms (see discussion below) to give to R. Pugmire (Univ. of Utah) for solid-state NMR characterization, and from M. Seehra and E. Kugler of West Virginia University (WVU). We supplied the requested samples to DOE and WVU. The samples for M. Seehra include some of our distillation fractions.

Analytical Characterization

We prepared an overall analytical plan for the HTI Run CMSL-8 samples (Appendix 5) and completed many of the analyses on the available samples. Two product oil (SOH and ASOH) samples from a period in which the on-line hydrotreater was by-passed are much poorer in quality than the SOHs produced with the hydrotreater in place. Differences included: medium brown in color vs. colorless, presence of a "coal liquid" odor, higher aromaticity, and considerably higher phenolic -OH concentration. The effects of hydrotreating observed in this run are greater than those that were observed in Run POC-2. This may be because the distillate hydrotreated in Run CMSL-8 is a thermal distillate, and the distillate of Run POC-2 came from a catalytic reactor.

We found ethylbenzene features in the ^1H -NMR spectra of the SOH net-distillate products from the coal/mixed-plastic periods. There was none evident in the coal-period sample, and only a small amount was evident in the coal/HDPE-period sample. In the GC/MS chromatograms of these same samples, intense ethylbenzene and cumene (isopropyl benzene) peaks were observed in the coal/mixed-plastics

period samples. These components also are detectable at trace levels in the coal-period SOH sample. As in Run POC-2,¹ we believe that these components represent polystyrene liquefaction products.

The pressure filter liquids from coal/plastics periods contain light brown or tan THF insolubles. 15 to 30 wt % insolubles was found in the coal/plastics-period PFL samples, and almost none in the coal-period sample. The insolubles from samples obtained late in the run were darker in color. The FTIR spectra of insolubles from coal/plastics-periods 11 and 22 were similar and indicated that they are polyethylene-like material.

PFL distillation bottoms from coal/plastics periods 11 and 20 separated into two solid phases upon cooling at the end of the distillation. The upper phase was lighter in color (brown, instead of black) and much less brittle than the lower phase. The upper phase constituted 66.7 wt % of the period 11 bottoms and 34.6 wt % of the period 20 bottoms. The feedstocks to both periods 11 and 20 were coal/mixed plastics. Resids from the PFLs of period 6 (coal), period 16 (coal/mixed plastics), and period 22 (coal/polyethylene) did not exhibit obvious phase separation. Diffuse reflectance FTIR was used to examine the two solid phases of the Period 11 PFL distillation resid. The spectrum of the upper brown phase indicated primarily aliphatic hydrocarbons with PE-like features (sharp double peaks around 1470 and 720 cm^{-1}). Aromatic hydrocarbon peaks also were significant features of the spectra, but there were essentially no features representing heteroatomic functional groups. The spectrum of the lower black phase showed more intense aromatic hydro-carbon signals than did the upper phase. There is a significant amount of aliphatic hydrocarbon in the lower phase, but its spectrum does not show the distinctive PE-like features. The spectrum of the lower phase also contains prominent peaks from heteroatomic functionality, perhaps N-H and O-H. Thus, the upper phase seems to represent a predominantly plastic-derived component (much of it PE), and the lower phase a predominantly coal-derived component. Neither phase completely dissolved in the pyridine- d_5 used for the ^1H -NMR analysis. We believe that it was primarily polyethylene products in the upper phase that were insoluble in the pyridine.

Polyethylenes are considered chemically inert.² At room temperature, they can withstand exposure to nearly all chemicals for up to 24 hours. However, aromatic

and aliphatic hydrocarbons (including benzene) and halogenated hydrocarbons (such as butyl chloride) can cause softening of the polymer; strong oxidizing agents can cause oxidation and eventual embrittlement of the polymer. Interaction of hydrocarbons with the polymer structure is enhanced at elevated temperatures. For example, at 50 °C benzyl alcohol and chloroform, which have little effect at 20 °C, will attack HDPE and cause swelling; however, no solubilization is reported. It is, therefore, difficult or impossible to completely dissolve the HDPE and HDPE-containing recycle and other samples for certain analytical procedures. A possible approach may be to use elevated temperatures and selected solvents.

We provided J. Larsen of Lehigh University with three samples from CMSL-8 Period 22 (the coal/polyethylene period) for analysis by plasma desorption mass spectrometry (PDMS) to help define the fate of the polyethylene. The samples included the feed high density polyethylene (HDPE), the pressure filter cake (PFC) and the 850 °F⁺ resid of the pressure filter liquid (PFL) from a coal/HDPE period. PDMS sample preparation for analysis requires solubilization of the sample. Lehigh was able to dissolve the resid samples in pyridine at about 50 to 60 °C. However, attempts to dissolve HDPE at the same temperature for six days in tetralin, dichlorobenzene, and tetrachloroethane, failed. Consequently, they were able to provide an analysis of the PFC and PFL resid, but not of the feed HDPE. For a mass (m/z) integration range of 78-3000, they reported for the PFL resid, $M_n = 705$ amu and $M_w = 1117$ amu, and for the PFC, $M_n = 748$ amu and $M_w = 1224$ amu. These molecular weights seemed low, since higher MW components might be expected. In their earlier work with coal liquefaction samples,³ it was reported that non-polar materials, such as polystyrene, give a low response by PDMS. Larson confirmed that the method became insensitive for polystyrene of MW greater than a few hundred amu, and expected even lower sensitivity for polyethylene.⁴ Additional data analysis of the recorded spectra was requested.

Technology Transfer

We participated in a meeting at PETC with HTI on January 13 to review Run CMSL-8 results, discuss distribution of CMSL-8 samples, and discuss future bench-scale and PDU-scale runs. We participated in a meeting at PETC with DOE, HTI, and Consortium for Fossil Fuels Liquefaction Science (CFFLS) representatives on

January 26 to discuss Run CMSL-8 and related coal/waste coprocessing results.
We presented our results from Run CMSL-8, and related Run POC-2 results.

Section 4

EXPERIMENTAL

Experimental details are described, where appropriate, in the Discussion section of this report.

Section 5

REFERENCES

1. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "A Characterization and Evaluation of Coal Liquefaction Process Streams, Quarterly Technical Progress Report October 1 through December 31, 1994", DOE/PC 93054-10, March 1995.
2. 1995 Nalgene® Labware Catalog, Reference Section, Nalge Company, Rochester, NY.
3. Larsen, J. W.; Lapucha, A. R. "Coal Liquefaction Process Streams Characterization and Evaluation, The Application of ^{252}Cf -Plasma Desorption Mass Spectrometry to Analysis of Direct Coal Liquefaction Heavy Products", DOE/PC 89883-58, October 1992.
4. J. W. Larsen, personal communication.

APPENDIX 1

UNIVERSITY OF DELAWARE QUARTERLY TECHNICAL REPORT FOR PERIOD 1/15/95 - 4/15/95

THE KINETICS OF COAL LIQUEFACTION DISTILLATION
RESID CONVERSION

QUARTERLY REPORT
1/15/95-4/15/95

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QUARTERLY REPORT

DEVELOPMENT OF A TGA BOILING RANGE TEST METHOD

Since our Short Contact Time Batch Reactor (SCTBR) which we use for measuring the conversion kinetics of coal derived vacuum resids is small, it was necessary to develop a test method for boiling range of the converted samples which could be run on relatively small samples. This motivated us to develop a test based on Thermogravimetric Analysis (TGA) which uses sample sizes of the order of 20 to 80 mg. Two methods for running the TGA boiling range test were investigated: a controlled ramp method, and an isothermal or isotrack method in which the temperature is very rapidly increased to a steady predetermined value and held there while the sample is volatilized. Both methods involve the use of small quartz cylindrical pans with small holes at the top to limit the diffusion of the volatile material out of the pan. With the hole size small and holding the gas sweep rate and temperature ramp constant, the objective is to make the rate of weight loss proportional to the partial pressure of the sample in the sample pan and therefore to the boiling range.

We have found that using constant conditions and ramping until the sample is dissipated (the ramp method), a broad range of weight loss is obtained reflecting the total composition of the sample. However, with large amounts of high boiling material present in resids the weight loss is due to pyrolysis as well as the volatility of the sample.

Since we are primarily interested in the fraction boiling below 850°F, we have selected the isothermal method as the principal measurement technique for determining the boiling range of the converted material in the resid. In this method, the TGA chamber is very rapidly heated to a predetermined temperature within 5 minutes, usually one providing an evolution rate equivalent to 850 °F under the conditions of the test. The temperature of the TGA chamber is then held constant and the rate of weight loss determined as a function of time. A representative temperature-time plot for a synthetic mixture of hydrocarbons (Table 1) is shown in Figure 1. The DTG curve for this calibration mixture is shown in Figure 2. The plot which describes a linear relationship of $\log (\text{rate of weight loss})$ vs $1/T_b$ (Figure 3) in accordance with the Clausius-Claperon equation demonstrates that we are indeed measuring a function of vapor pressure.

For a mixture containing some components boiling under 850°F (453°C), the rate of weight loss (DTG curve) describes a curve such as that shown in Figure 4 for a light paraffinic vacuum distillate. This curve can be translated into a boiling range distribution which is shown in Figure 5. A computer program in MATLAB language was written to make this translation.

A conversion run has been made on a sample of Wilsonville # 258 resid using sulfided molybdenum naphthenate at 403 °C for 60 min under 1500 psig H_2 . The DTG curve for this material is shown in Figure 6. The boiling range of this material is shown in Figure 7.

For samples containing large amounts of volatile material, the test must be run at lower temperatures than 850 °F equivalent because of the rapid loss of volatiles and subsequent loss of precision. In such cases, the test can be run at more than one temperature; a lower temperature to detect the volatile fraction and a higher temperature to detect the higher boiling fraction. When a large amount of very high boiling resid is present, sample pans with fairly large holes are necessary for mechanical reasons. In some cases the TGA can be run under vacuum if the high boiler content is very high. In this case, a calibration curve run under the vacuum conditions must be used.

The TGA test involves the taking of a great many points along the weight loss curve. It has been necessary to smooth the data for maximum accuracy in the determination. For that purpose, a smoothing routine has been developed which has been very effective in preparing the weight loss curve for translation into the boiling range.

A more detailed description of the TG boiling range method is shown in Appendix I.

RESID CONVERSION STUDIES

A series of resid conversion runs have been made mostly in the presence of catalyst and hydrogen for a range of tetralin to resid ratios. This work has shown that when Mo-Ni/Alumina catalyst is used, to get satisfactory product recovery from the reactor, it is necessary to have a tetralin to resid ratio of at least 4:1. This is because the solid catalyst is used in such high concentration (equal to the resid) that the viscosity of the reaction mixture is very high.

The procedure for workup of resid reaction products has been to filter the product into a solid and a liquid. The solid is washed with tetralin. Previously, we have used both tetralin and methylene chloride washes in the work up of coal liquefaction runs in order to remove residual tetralin. However, we have been able to show that the methylene chloride wash is unnecessary with resid conversion products probably because there are no pores in the resid.

Samples of reactor solids from about 20 such runs have been made and are being submitted to CONSOL for elemental analysis. This should allow us to more accurately calculate the conversions in these runs. We will need this information to decide whether to do future resid conversion runs with the Mo-Ni/Alumina catalyst or the sulfided Molybdenum naphthenate catalyst or both.

Table 2 shows a list of reactor runs on Wilsonville run # 258 over a range of conditions.

RETROGRADE REACTIONS OF COAL DERIVED VACUUM RESIDS

Conversion runs of Wilsonville resid #258 in the absence of catalyst at elevated temperatures have shown that the resid is profoundly changed either in the presence of nitrogen or hydrogen. TG scans of that resid after exposure in nitrogen (Figure 8) and hydrogen (Figure 9) at 410°C are significantly changed compared to the original resid (Figure 10). This process

will be investigated further. Whether this is a retrograde process which could occur during hydroprocessing of the resid is not yet clear.

Table 1 Concentrations and properties of the C₁₀-C₃₂ components in the synthetic mixture

No. of Carbon	Name	MW	b.p., °C	m.p., °C	W, g	C, wt%
10	Decane	142.28	174.1	-29.7	1.2298	18.26 %
15	Pentadecane	212.41	270.6	10.0	1.2068	17.92 %
20	Eicosane	282.54	343.0	36.8	1.1238	16.69 %
25	Pentacosane	352.67	401.9	55.0	1.0716	15.91 %
30	Triacontane	422.80	449.7	65.8	1.0402	15.45 %
32	Dotriacontane	450.85	467.0	69.7	1.0618	15.77 %

Table 2 List of reactor runs (P=1500 psig)

Run	T, C	t, min	Catalyst	SA	T:R	Gas	Rec., wt%
C001	19	15			3	H2	79.8%
C002	414	15			3	N2	25.5%
C003	408	15			3	H2	73.6%
C004	410	7			3	N2	74.3%
C005	409	15			3	N2	84.4%
C006	411	15		Yes	3	H2	91.2%
C007	408	15		Yes	3	N2	76.5%
C008	406	15	Mo-naph	Yes	3	N2	98.1%
C009	408	15	Mo-naph	Yes	3	H2	76.3%
C012	400	15	Mo-naph		3	N2	42.6%
C013	400	15	Mo-naph		3	N2	38.0%
C014	392	15	Mo-naph		5	N2	55.2%
C015	403	15	Mo-naph		3	H2	92.6%
C016	406	15	Mo-naph		3	N2	38.7%
C017	409	0.06	Mo-naph	Yes	3	H2	80.2%
C018	408	1	Mo-naph	Yes	3	H2	76.3%
C019	412	3	Mo-naph	Yes	3	H2	62.1%
C020	410	5	Mo-naph	Yes	3	H2	91.3%
C021	411	10	Mo-naph	Yes	3	H2	95.1%
C022	408	30	Mo-naph	Yes	3	H2	80.9%
C023	422	40	Mo-naph	Yes	3	H2	68.5%
C024	408	60	Mo-naph	Yes	3	H2	95.4%
C025	419	0.06	Mo-Ni/Alumina		2	H2	47.5%
C026	420	1	Mo-Ni/Alumina		2	H2	54.4%
C027	410	3	Mo-Ni/Alumina		2	H2	66.2%
C028	409	5	Mo-Ni/Alumina		2	H2	65.2%
C029	410	10	Mo-Ni/Alumina		4	H2	69.4%
C030	400	15	Mo-Ni/Alumina		2	H2	36.2%
C031	405	15	Mo-Ni/Alumina		3	H2	49.1%
C032	405	15	Mo-Ni/Alumina		4	H2	80.5%
C033	412	60	Mo-Ni/Alumina		4	H2	70.6%
C034	405	30	Mo-Ni/Alumina		4	H2	72.8%

Temperature-time plot for the calibration sample of a synthetic mixture of hydrocarbons of C₁₀ to C₃₂

Figure 1

DTG decay curve for the calibration run

Figure 2

log (rate of weight loss) vs. $1/T_b$ (T_b , the boiling point of C_{20} - C_{32})

Figure 3

DTG decay curve for the light paraffinic vacuum distillate

Figure 4

Simulated distillation curve for the light paraffinic vacuum distillate

Figure 5

DTG decay curve for the resid conversion liquid

Figure 6

Simulated distillation curve for the liquid sample of Wilsonville # 258 resid conversion run C024
(catalyst: sulfided molybdenum naphthenate; 403°C; 60 minutes; 1500 psig H₂)

Figure 7

Figure 8

Sample: C005S (solid sample)

Size: 35.4820 mg

Method: Resid Conversion I

Comment: 10 °C/min to 950 °C, 9.3, N2

TGA

File: C: C005S.001

Operator: Keyu Wang

Run Date: 7-Mar-95 08:48

Figure 9

Sample: C003 S

Size: 37.4730 mg

Method: DOE Coal Liquefaction

Comment: 10 °C/min to 950 °C, N₂, 100 ml/min.

TGA

File: C: C003S.001

Operator: Keyu Wang

Run Date: 13-Apr-95 09:53

Figure 10

Sample: Resid A (solid)

Size: 33.2350 mg

Method: DOE Coal Liquefaction

Comment: 10 °C/min to 950 °C, N2, 100 ml/min

TGA

File: C: CRA01.003

Operator: Keyu Wang

Run Date: 28-Mar-95 11:27

Appendix I

SIMULATED DISTILLATION BY THERMOGRAVIMETRIC ANALYSIS

(SimDis TGA)

1. Development of Computer Programs for TGA Data Processing

DTG obtained from numerically differentiating TG data (t, w) of a calibration sample (a synthetic mixture of hydrocarbons of C_{10} to C_{32} (Table 1)) and a petroleum sample (light paraffinic vacuum distillate from Amoco) are shown in Figures 1a and 2a, respectively. In order to obtain the calibration data (rate of weight loss, T_b) from a calibration sample and the simulated distillation data (T_b , rate of weight loss) for a test sample, it is crucial to acquire the smoothed (noise-free) and a representative DTG decay curve from either original TG data (t, w) or numerical DTG data ($t, dw/dt$). We have tried several common methods for this purpose, but none of them gives satisfactory results. Using the characteristics of TG data, we have developed a novel smoothing technique, called 'n points linear smoothing routine', which gives the most satisfactory results. DTG from numerically differentiating TG data (t, w) and DTG decay curves from the linear smoothing routine with $n = 11$ for both calibration and test samples are shown in Figures 1b and 2b, respectively. The DTG decay curves are also plotted in Figures 1c and 2c for clear presentation. The results indicated that smoothed, noise-free, and representative DTG decay curves were acquired by this smoothing technique from original TG data (t, w).

The principle used in this method is the use of the characteristics of TGA data (t, w). Figure 3 is the plot of the 31 TG data points (t, w), randomly taken from the sample run. It is obvious that, in any short period, the relationship between t (time) and w (weight) is linear. Therefore, we can use odd points of n ($n = 3, 5, 7, 9, 11, \dots$) from points i to $i+n-1$ to calculate the slope (i.e. dw/dt) for the middle point of points i to $i+n-1$, i.e., the DTG data of point $(2i+n-1)/2$. Figure 4 is the plot for one of the results using the data of the test sample by this smoothing routine. The n is set at 11 for this case. We have used two levels of mean-error

filter in this linear smoothing routine program to filter experimental noise. The program flowsheet and the source code of the program in MATLAB are presented in Appendix A.

2. TGA Method for Simulated Distillation.

Thermogravimetric analyzer used in this study is TA51 of TA Instruments. Two methods (a ramp method and an isothermal method) have been investigated for running the TGA boiling range test. In the isothermal method, the temperature in the TGA chamber is held constant controlled by the sample thermocouple, which is located very close to the sample pan. Both methods involve the use of cylindrical TGA pans with small holes at the top to control the diffusion of the volatile material out of the pan. If the gas sweep rate and temperature or ramp are held constant, the rate of the weight loss is proportional to the partial pressure of the sample, which is equal to the vapor pressure of the sample and therefore the boiling range.

For a mixture sample, its distillation curve, i.e., boiling temperature vs. wt% distilled, can be determined by the initial temperature-isotrack method. In this method, the TGA sample is very rapidly heated to a predetermined temperature without overshooting and the temperature is then held constant. To do so, first we set the initial temperature to the predetermined temperature and keep the sample pan still under the ambient temperature. In this initial temperature mode, the temperature of the TGA chamber is isothermally controlled at the predetermined temperature by the furnace thermocouple. When the Ready signal is on (this means the TGA chamber has reached the predetermined temperature), the sample pan system is inserted into the TGA chamber and then the temperature is set for isothermal operation. In this isotrack mode, the temperature of the TGA chamber is isothermally controlled by the sample thermocouple. Using these steps, the temperature of the sample is very rapidly heated to the

predetermined temperature within 2 minutes and precisely controlled at this preset temperature within 0.3 °C after 5 minutes. The weight change and the DTG decay (i.e., the rate of weight loss) are determined as a function of time.

The temperature-time plot for a calibration run using a synthetic mixture of hydrocarbons of C₁₀ to C₃₂ (Table 1) is shown in Figure 5. The predetermined temperature was 280 °C. The DTG decay curve for this calibration is shown in Figure 6. Although the temperature of the sample reached the predetermined temperature of 280 °C within 2 minutes, the loss of the light fractions in the synthetic mixture, such as C₁₀ and C₁₅, occurred before the temperature became stable. In other words, the light fractions in the synthetic mixture of C₁₀ and C₁₅ were evolved from the pan within this initial 2-5 minutes. This is clearly illustrated in Figures 7 and 8, the plot of wt% of sample in the pan vs. temperature and wt% of sample in the pan vs. DTG decay, respectively. From the concentrations of the C₁₀-C₃₂ components in the synthetic mixture given in Table 1, we can find the rates of weight loss at which the components were evolved from the pan. The plot which describes a linear relationship of log (rate of weight loss) vs 1/T_b (T_b, the boiling point of C₂₀-C₃₂) is shown in Figure 9, in accordance with the Clausius-Clapeyron equation. This shows that the DTG decay determined by TGA technique is indeed measuring the vapor pressure and therefore boiling range.

For a mixture containing a wide range of boiling materials, such as the light paraffinic vacuum distillate from Amoco, the DTG decay determined under the same conditions of running the calibration mixture can be translated into a boiling range distribution using the equation of

$$T_b = \frac{B}{\ln(r) - A} \quad (1)$$

where *r* is the decay rate of the test sample and *A* and *B* are parameters determined by

calibration (for this case, $A = -21.06$ and $B = 12778$).

The temperature-time plot for the test sample of the light paraffinic vacuum distillate is shown in Figure 10. The DTG decay curve is shown in Figure 11. Although the temperature of the sample reached the predetermined temperature of 280 °C within 2 minutes, the 10 wt% of light fractions in the vacuum distillate were lost before the temperature became stable, i.e., the 10 wt% of light fractions in the vacuum distillate were evolved from the pan within this initial 2-5 minutes. It is clearly illustrated in Figures 12 and 13, the plot of wt% of sample in the pan vs. temperature and wt% of sample in the pan vs. DTG decay, respectively. The simulated distillation curve for this vacuum distillate is shown in Figure 14.

A simulated distillation run by the isotrack method has been made on a sample of Wilsonville # 258 resid converted using sulfided molybdenum naphthenate at 403°C for 60 minutes. The DTG curve for this material is shown in Figure 15. The fraction of material in which the product boiled below 850 °F was 93.8 wt% (including tetralin fraction).

3. Strategies for Choosing the Optimum Conditions to Run Simulated Distillation.

The variables to run the simulated distillation using the TGA technique include:

- 1). time-temperature course: ramp and isothermal;
- 2). pressure: 1 atm. and vacuum (up to 0.05 atm.);
- 3). Size of the hole on the pan;
- 4). gas flow rate.

For a pure compound, SimDis TGA can be run using either the ramp or isothermal method. However, for a mixture, the isothermal method is the only technique to obtain the information on the distillation curve. This method is to translate the decay of the rate of weight

loss into the boiling point distribution. Therefore, the optimum conditions to run the simulated distillation by TGA are those conditions which gives the highest sensitivity and stable decay curve. To accomplish this, the optimum conditions for SimDis TGA run is dependent on the boiling distribution of the test sample. For examples, for light samples, it is better to run the SimDis TGA at lower isothermal temperature, smaller hole size of pan, and 1 atm. For very heavy samples, TGA should be run at higher isothermal temperature, larger hole size of pan, and highest vacuum. For the mixture containing a very broad boiling range, the test can be run at either more than one temperature or more than one pressure (vacuum) to detect the very volatile fraction as well as the higher boiling fraction. The desired conditions for the different samples with different boiling fraction characteristics are given in Table 2.

The general steps to run an unknown sample for simulated distillation using TGA technique are:

- 1). ramp at 5 °C/min to 950 °C under 1 atm and/or vacuum (ca. 40 mmHg) at 100 cm³/min N₂, then O₂ introduced to burn off the combustible materials (fixed carbon). In this run, IBP (Initial Boiling Point), FBP (Final Boiling Point) and/or PT (Pyrolysis Temperature), the boiling range and volatile fraction, fixed carbon content, and ash fraction (if any), are determined.
- 2). based on the results obtained from Step 1, determine the optimum conditions of hole size of pan, isothermal temperature, pressure, etc. (referring to Table 2) for the simulated distillation.

4. Calibration of TGA for the Simulated Distillation.

TGA can be calibrated for the simulated distillation by either synthetic mixture which

contains compounds of known boiling or 'standard' mixture similar to the mixtures to be measured, of which distillation curve is available. For a synthetic mixture, the paraffins provide a wide range of boiling components for calibration. The properties of the paraffins from C_5 to C_{32} , which are commercially available, are given in Table 3. The boiling point vs. carbon number for these paraffins is plotted in Figure 16. For a 'standard' mixture, any petroleum sample with suitable known boiling range distribution could be selected for the 'Standard'. If the distillation curve is not available, we can run modified ASTM D86 method to obtain it.

5. Advantages of the TGA Simulated Distillation Method

There are a lot of advantages using the TGA technique for simulated distillation. The most significant ones are:

- 1). TGA simulated distillation test is run at much lower temperature than other techniques. Especially, combined with vacuum, it can further decrease the running temperature. For example, we can measure the boiling range up to 700 °C with a running temperature at below 280 °C under ca. 40 mmHg vacuum. At these lower temperatures, thermal reactions and pyrolysis are avoided or minimized. Therefore, the simulated distillation results are not interfered by these reactions;
- 2). There is no limitation on the sample type. The sample can be very light or very heavy, even a sample with very wide range of boiling materials. For solid samples, if a solvent can be found to dissolve it, it can be run without difficulty;
- 3). Very reproducible results were obtained on the samples tested. The experimental cycle for one run can be 1 to 12 hrs, and the long run can be scheduled during the night and short ones in the day;

- 4). Sample size is very small. It only requires 20 to 80 mg sample for each run.
- 5). The SimDis TGA method measures the true boiling characteristics of the sample and is not based on retention times determined by SimDis GC or other features not directly related to vaporization.

Appendix A

Program flowsheet and the source code in MATLAB

Scheme of the program for TGA data processing

```

function [r, rs, ws] = smooth(n,t,w)
%SMOOTH This is a function to process TGA data by Linear
% Regression. Smoothed and noise-free DTG data are
% obtained by (2m+1) convolution method. A filter for the
% removal of the experimental random errors is based on the
% error analysis.
% [r, rs, ws] = smooth(n,re0,t,w): r, rs, and ws
% are the numerical differentiation (r), smoothed and noise-free DTG
% data (rs), and smoothed and noise-free weight data (ws)
% respectively; and n, re0, t, and w are the number of points
% (2m+1) used for smoothing (n), preset re value (re0), time (t),
% and weight (w), respectively.

% Keyu Wang & He Huang, 03-12-95; MATLAB

re0=10^(-5);

a=size(t);
n1=a(1,1); % size of t or w
m=(n1-1)/2; % (2m+1) = n1, an odd number

r=-diff(w)./diff(t); r(n1)=r(n1-1); % numerical differetiation

for i=m:n1-m-1,

    for j=1:n,
        x(j,1)=t(i-m+j);
        y(j,1)=w(i-m+j);
    end

    a = filter1(n,re0,x,y);

    rs(i+1,1)=-a(1,1);
    ws(i+1,1)=a(1,1)*t(i+1,1)+a(1,2);
end

for i=1:m, % determine the end points
    rs(i,1)=r(i,1);
    ws(i,1)=w(i);
end

for i=n1-m+1:n1
    rs(i,1)=r(i,1);
    ws(i,1)=w(i);
end

```

```

function a = filter1(n,re0,x,y)
%FILTER1 Linear regression filter for TGA data processing.
%      a = filter1(n,re0,x,y)

%      Keyu Wang & He Huang, 03-12-95; MATLAB

re=100;

while re > re0,
    a=polyfit(x,y,1);
    ys=a(1,1)*x+a(1,2);
    e0=y-ys;
    std0=std(e0);
    re=std0*abs(a(1,1));
    for j=1:n,
        if abs(e0(j)) > std0,
            y(j)=ys(j);
        end
    end
end
end

```

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Table 1 Concentrations and properties of the C₁₀-C₃₂ components in the synthetic mixture

No. of Carbon	Name	MW	b.p., °C	m.p., °C	W, g	C, wt%
10	Decane	142.28	174.1	-29.7	1.2298	18.26 %
15	Pentadecane	212.41	270.6	10.0	1.2068	17.92 %
20	Eicosane	282.54	343.0	36.8	1.1238	16.69 %
25	Pentacosane	352.67	401.9	55.0	1.0716	15.91 %
30	triacontane	422.80	449.7	65.8	1.0402	15.45 %
32	Dotriacontane	450.85	467.0	69.7	1.0618	15.77 %

Table 2 The desired conditions for the different samples with different boiling fraction characteristics

Boiling characteristics of the sample	Size of the hole on the TGA pan	Pressure	Temperature
very light	small	1 atm.	very low
light	small or middle	1 atm.	low
heavy	middle or large	1 atm. or vacuum	middle
very heavy	large	high vacuum	high
broad range	small to large	1 atm. to high vacuum	multi-runs

Table 3 Properties of the paraffins from C₅ to C₃₂

No. of Carbon	Name	MW	b.p., °C	m.p., °C
5	Pentane	72.15	36.1	-130.0
6	Hexane	86.17	69.0	-95.0
7	Heptane	100.20	98.4	-90.6
8	Octane	114.22	125.7	-56.8
9	Nonane	128.25	150.8	-51.0
10	Decane	142.28	174.1	-29.7
11	Undecane	156.30	196.0	-26.0
12	Dodecane	170.33	216.3	-9.6
13	Tridecane	184.35	235.4	-5.5
14	Tetradecane	198.38	253.7	5.9
15	Pentadecane	212.41	270.6	10.0
16	Hexadecane	226.43	287.0	18.2
17	Heptadecane	240.46	301.8	22.0
18	Octadecane	254.48	316.1	28.2
19	Nonadecane	268.51	329.7	32.1
20	Eicosane	282.54	343.0	36.8
21	Heneicosane	296.56	356.5	40.5
22	Docosane	310.59	368.6	44.4
23	Tricosane	324.61	380.0	47.6
24	Tetracosane	338.64	391.3	54.0
25	Pentacosane	352.67	401.9	55.0
26	Hexacosane	366.69	412.2	56.4
27	Heptacosane	380.72	419.2	59.5
28	Octacosane	394.74	431.6	64.5
29	Nonacosane	408.77	440.8	63.7
30	Triacontane	422.80	449.7	65.8
31	Untriacontane	436.82	458.0	67.9
32	Dotriacontane	450.85	467.0	69.7

DTG data obtained from numerically differentiating TG data (t,w) of a calibration sample (a synthetic mixture of hydrocarbons of C_{10} to C_{32} (Table 1))

Figure 1a

DTG data (dots) from numerically differentiating TG data (t, w) and DTG decay curves from the linear smoothing routine with $n = 11$ for the calibration sample

Figure 1b

The DTG decay curve from the linear smoothing routine with $n = 11$ for the calibration sample

Figure 1c

DTG data obtained from numerically differentiating TG data (t,w) of a petroleum sample (light paraffinic vacuum distillate from Amoco)

Figure 2a

DTG data (dots) from numerically differentiating TG data (t,w) and DTG decay curves from the linear smoothing routine with $n = 11$ for the test sample

Figure 2b

The DTG decay curve from the linear smoothing routine with $n = 11$ for the test sample

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Plot of the 31 TG data points (t,w), randomly taken form the sample run

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Plot of 11 data points of time vs. weight for the test sample using this smoothing routine

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Figure 6

Plot of wt% of sample in the pan vs. temperature for the calibration run

Figure 7

Plot of wt% of sample in the pan vs. DTG decay for the calibration run

Figure 8

log (rate of weight loss) vs. $1/T_b$ (T_b , the boiling point of C_{20} - C_{32})

Figure 9

Temperature-time plot for the test sample of the light paraffinic vacuum distillate

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DTG decay curve for the light paraffinic vacuum distillate

Figure 11

Plot of wt% of sample in the pan vs. temperature for the light paraffinic vacuum distillate

Figure 12

Plot of wt% of sample in the pan vs. DTG decay for the light paraffinic vacuum distillate

Figure 13

Simulated distillation curve for the light paraffinic vacuum distillate

Figure 14

DTG decay curve for the resid conversion liquid

Figure 15

Boiling point vs. carbon number for the paraffins from C_5 to C_{32}

Figure 16

APPENDIX 2

REPORT OF TRIP TO THE UNIVERSITY OF DELAWARE January 17, 1995

Trip Report: University of Delaware
Date of Visit: January 17, 1995
Address: Department of Chemical Engineering
Colburn Laboratory
University of Delaware
Newark, DE 19716-3110
Principal Contact: Dr. W. H. Calkins
Phone: 302-831-2213

Attendees:

University of Delaware

Mike Klein
Bill Calkins
He Huang
Shaojie Wang
Keyu Huang

CONSOL

Frank Burke
Dick Winschel
Susan Brandes

DISCUSSION

Subject: University of Delaware subcontract from CONSOL under DOE Contract DE-AC22-94PC93054

Bill Calkins hosted our visit to the University of Delaware on January 17, 1995. The purpose of our visit was to discuss the expansion of the program that Delaware is conducting to study direct coal liquefaction resid reactivity. The expanded program will include Task 1.4.2 of the subject contract. This task includes the construction of a mathematical kinetic model.

Frank Burke informed Delaware that the expanded program provides an additional \$67,000 (approximate) for completion of Task 1.4.2. by Delaware. It also provides funds for subcontracting with other organizations to provide special analyses. Suggestions for what analyses would be useful were solicited from Delaware. They believe that ^1H -NMR and ^{13}C -NMR (especially the type of analyses provided by Ron Pugmire of the University of Utah) will be very useful. Molecular weight determinations are considered useful, but their reliability is viewed with some concern, regardless of whether the method is vapor phase osmometry (VPO) or field ionization mass spectrometry (FIMS). Bill Calkins believes that size exclusion chromatography (SEC) (or gel permeation chromatography (GPC)) is a preferable method for determination of molecular weight ranges.

He Huang made a presentation of the work completed to date on using the TGA apparatus to obtain a simulated distillation. During our previous discussion (November 14, 1994), he indicated that one reason TGA is a poor method to simulate distillation is because, depending on the geometry of the TGA pan, mass transport rates can change as the sample volatilizes. He proposed to design and construct TGA pans made from quartz that have a cavity and a small circular opening in the top. The appropriate size of the opening will depend on gas flow rate, pressure, volatility, and heating rate. This design, he believes, will eliminate the variable mass-transfer rate of the liquid going into the gas phase. At this meeting we were shown three 'closed' vessels which were made by drawing quartz tubing. The closed vessels are generally cylindrical in shape, approximately 1 cm high, with concave tops and bottoms internally. In the top of the closed vessel a circular hole was made. Each of the three 'pans' has a different diameter opening of 0.615 mm, 0.974 mm, or 1.538 mm. These openings can be reproduced within a tolerance of ± 0.005 mm.

Using these pans, experiments were made initially with water (because of the large quantity of available data on the behavior of water). The experimental data gave a reproducible straight line relation of $\ln$ rate loss vs $1/T$ which shows a parallel relationship to literature data of $\ln p_{\text{vap}}$ vs. $1/T$. The relationship between vapor pressure and rate of weight loss was found to be good. Data plotted as $\ln$ (rate of weight loss) vs. $1/T$ also produced a reproducible straight line (with an $r^2 = 0.99$). The heat of vaporization could be calculated from the Clausius-Clapeyron relationship ($\Delta H^{\text{vap}} = -R[d(\ln p^{\text{sat}})/d(1/t)]$); however, this was not yet done. A simple model was proposed: $\text{rate} = k p_{\text{vap}}(T)$ (or $k p_{\text{vap}}(T)^n$); where $\text{rate} = f(p_{\text{vap}}(T), T, \text{molecular properties})$. Data from the TGA of a set of model compounds (water, tetralin, pyrene, and others) with known boiling points were fitted to these curves. Data fitted straight lines up to

temperatures of about 380 °C. No pyrolysis was evident up to about 400 °C. Initial work was done at constant heating rates (1 °/min, 2 °/min, and 5 °/min). At higher heating rates (5 °/min), a temperature lag (constant for that heating rate) was apparent. This was corrected for each data point in the temperature range used. Each model compound studied under the same conditions gave highly reproducible results. It was concluded that under these conditions the rate of weight loss was a function of only p_{vap} .

From this work, an equation to calculate resid conversion from STBR runs and TGA analysis was proposed:

$$\text{Conversion} = S \times \frac{W_{T_o} - W_{tet}}{W_o - W_{tet}}$$

where: W_{T_o} = the amount of material which boils below T_o (the temperature of interest, e.g., 850 °F)
 W_o = the weight of material charged to the TGA pan
 W_{tet} = the weight of the tetralin used as a solvent (obtained from GC analyses)
 S = solubility

In order to determine W_{T_o} , three methods were considered. To obtain a boiling point from a simple ramping run would be very difficult (if not impossible). Rate-constant runs could be used where the rate of weight loss would be held constant at that rate which corresponds to the boiling point, but this, in practice, would be difficult to control. The third method is something Delaware is calling the "Jump and Iso-track" (JIT) method. In this method W_{T_o} is determined by a rate-decay curve. The experiment is run at some fixed temperature. To obtain better control of the experiment, the thermocouple positioned to measure the sample temperature (not the one near the TGA pan) was used to control temperature. A decay rate curve is obtained and examined. An equivalent temperature to W_{T_o} is determined by calibration with model compounds of known boiling points. The method is constrained by keeping the unknown samples below pyrolysis temperatures. This can be achieved by lowering the temperature of the TGA experiment and taking advantage of the finding that the rate of weight loss under these conditions is a function of the vapor pressure (which is a function only of temperature). Pressure also can be reduced which also allows operation at lower temperature.

The sweep-gas flow rate was examined and found to be a factor. Higher gas flow rates (100 mL/min) are considered preferable so that vaporized material is rapidly carried away from the TGA balance.

Bill proposed to use the TGA experiment for further analyses. He believes that the rate of weight loss can be held constant (corresponding to a certain boiling point, for example 850 °F) and directly transfer the effluent from the TGA into a gas chromatograph to examine the volatile materials.

Mike Klein reviewed the University's lumped kinetic modeling/network construction (Delplot) work that was done on petroleum asphaltene (as an example of what information the computerized system provides; mainly kinetic rate constants,

activation energies, etc.). Mike cautioned that this method provides kinetic information, but no structural information. He referred to these methods as 'data analysis' and assured us that given enough rate data, his group could produce kinetic information with these techniques with the computer programs in place in the chemical engineering department.

In order to get a molecular model and the same kinetic information, a structural model can be "built" using a Monte Carlo technique. In this technique, structures are built based on the probability distribution that they can exist. These structures then are "reacted" based on the probability that they can undergo certain molecular scission and combination reactions. The system at the completion of reaction is neutral; all reactions end in termination steps. The properties of the 'reacted' system then are checked against measured properties of the materials being modeled. An iterative procedure is used to cause the computer simulated model to conform to the experimental data. Some experimental data is not useful at this time, because no (good) correlations exist to relate the measured value with molecular structure. Where good correlations are available, the experimental data can be used. Examples of experimental methods previously used to provide data in this modeling work are solubility class separations such as saturates, aromatics, naphthenes, aliphatics (SARA), high resolution mass spectrometry, ^1H - and ^{13}C -NMR spectroscopy, elemental analyses, high performance liquid chromatography, and vapor phase osmometry (for molecular weight determination).

Conversion and characterization data on samples of interest can be incorporated into the model as it is being constructed. Experiments performed in systems other than Delaware's STBR, such as in microautoclaves, can provide data useful in the refinement of the model. Characterization data on products of reaction of coal liquefaction resid which would be useful for the modeling work include elemental analysis, ^1H - and ^{13}C -NMR analyses, molecular weight analyses, and SARA(-like) separations, and the same analyses on the solubility fractions as would be performed on the whole product.

Analytical data compiled by CONSOL on many coal liquefaction resid samples (not necessarily just those that Delaware will be analyzing) will be helpful in constructing the model. CONSOL will compile as much of this information as possible and send it to Delaware. Most of the data will come from the previous contract and the Participants Program from that contract. Data on some samples will include analyses by field ionization mass spectrometry (FIMS), ^{13}C -NMR, ^1H -NMR, solubility separation, electron spin resonance (ESR) spectroscopy, and Fourier transform infrared spectroscopy (FTIR).

Follow-up

The following items will be acted on by CONSOL.

- CONSOL will modify the subcontract with the University of Delaware to authorize work on Phase 2.
- A set of analytical data for coal liquefaction resid samples will be compiled by CONSOL and sent to Delaware for use in constructing the kinetic model.

- The computer software format that is appropriate for delivery of the final kinetic model will be determined by CONSOL on consultation with the DOE. This information will be transmitted to Delaware.
- CONSOL agreed to perform elemental analyses of STBR products for Delaware. It is expected that 3 to 7 samples per week may be sent by Delaware.
- Further discussion with Delaware will be scheduled to specify the final form of the kinetic model.

APPENDIX 3

ANALYTICAL PLAN FOR INSPECTION OF NET PRODUCTS FROM HTI RUNS POC-1 AND POC-2

COAL LIQUID ASSAY - ANALYTICAL PLAN

Samples: HRI POC-1 and HRI POC-2

TBP Boiling Ranges (°F)	Total Liq.	IBP-180	180-350	350-400	400-500	500-550	550-650	650 ⁺
Yield (TBP), wt%		x	x	x	x	x	x	x
Specific Gravity @60 °F	x	x	x	x	x	x	x	x
Elemental Analysis: C	x		x	x	x	x	x	x
H	x		x	x	x	x	x	x
S	x	x	x	x	x	x	x	x
N	x	x	x	x	x	x	x	x
O	x		x	x	x	x	x	x
Basic N					x	x	x	x
Mercaptan S				x	x			
Trace Metals: V	x							
Ni	x							
Fe	x							
Cu	x							
Ash	x							
Viscosity: @104 °F					x	x	x	
@210 °F				x	x	x	x	x
@-20 °C				x	x			
Reid Vapor Pressure		x	x	x	x			
Smoke Point				x	x			
Luminometer No.				x	x			
Flash Point				x	x	x		
Pour Point				x	x	x	x	x
Freezing Point	x			x	x			
Conradson Carbon								x
Aniline Point					x	x	x	x
Hydrocarbon Group:								
Paraffins			x	x	x	x	x	
Naphthenes			x	x	x	x	x	
Aromatics		x	x	x	x	x	x	
Olefins			x	x	x			
Benzene		x						
Naphthalene				x	x			
GC Analysis (specific compounds/isomers)		x						
Thermal Stability				x	x			
Research Octane No.		x	x	x				
Motor Octane No.		x	x	x				
Cetane Index				x	x	x	x	
Distillation D86	x	x	x	x	x	x	x	
Net Heat of Combustion			x	x	x			
Acidity	x		x	x	x			
Copper Corrosion			x	x	x	x		
Existent Gum			x	x	x	x		
Oxidation Stability			x	x	x	x		

APPENDIX 4

ABSTRACT FOR 210th NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY

P. 76
Conference abstract
Removed
on 8/23/25

APPENDIX 5

**ANALYTICAL PLAN FOR SAMPLES FROM
HTI RUN CMSL-8**

SAMPLE ANALYSIS PLAN FOR HRI RUN CMSL-8 (227-85)
COAL: CROWN II, ILL. 6 BITUMINOUS

PRINTED:
04:04 PM 03/30/95

LIST UPDATED:
1/18/95

SAMPLES			ANALYSES																
			X = ANALYSIS PLANNED, SHADED = COMPLETED																
LO-#	TYPE	PER.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
6517	SP1 FEED SLURRY	6																	
6518	SP1 FEED SLURRY	11																	
6519	SP1 FEED SLURRY	16																	
6520	SP1 FEED SLURRY	20																	
6521	SP1 FEED SLURRY	23																	
0	SP2 IS SAMPLE	6		X		X					X	X	X	X	X	X	X	X	X
0	SP2 IS SAMPLE	11		X		X					X	X	X	X	X	X	X	X	X
0	SP2 IS SAMPLE	16		X		X					X	X	X	X	X	X	X	X	X
6533	SP3 ASOH-HTU BYPAS	9		X	X														
6528	SP4 SOH-HTU BYPASS	9	1	X	X														
6527	SP4 SOH	6	1	X	X														
6529	SP4 SOH	11	1	X	X														
6530	SP4 SOH	16	1	X	X														
6531	SP4 SOH	20	1	X	X														
6532	SP4 SOH	23	1	X	X														
6522	SP5 CAS BTMS	6		X			X	X	X	X									
6523	SP5 CAS BTMS	11		X			X	X	X	X									
6524	SP5 CAS BTMS	16		X			X	X	X	X									
6525	SP5 CAS BTMS	20		X			X	X	X	X									
6526	SP5 CAS BTMS	23		X			X	X	X	X									
6534	SP6 PFL	6	2	X		X	X		X	X	X	X	X	X	X	X	X	X	X
6535	SP6 PFL	11	2	X		X	X		X	X	X	X	X	X	X	X	X	X	X
6536	SP6 PFL	16	2	X		X	X		X	X	X	X	X	X	X	X	X	X	X
6537	SP6 PFL	20	2	X		X	X		X	X	X	X	X	X	X	X	X	X	X
6538	SP6 PFL	22	2	X		X	X		X	X	X	X	X	X	X	X	X	X	X
6539	SP7 PFC	6		X			X	X	X	X									
6540	SP7 PFC	11		X			X	X	X	X									
6541	SP7 PFC	16		X			X	X	X	X									
6542	SP7 PFC	20		X			X	X	X	X									
6543	SP7 PFC	22		X			X	X	X	X									
0	COAL		3																
6458	POLYSTYRENE		4																
6459	HDPE		4																
6460	PET		4																

COUNT

30

LEGEND

A = SPECIAL ANALYSES, SEE KEY	J = 850°F- DISTILLATE: ¹ H-NMR
B = WHOLE SAMPLE: ¹ H-NMR	K = 850°F- DISTILLATE: PHENOLIC -OH
C = WHOLE SAMPLE: PHENOLIC -OH	L = 850°F- DISTILLATE: MICROAUTOCLAVE TEST
D = WHOLE SAMPLE: MICROAUTOCLAVE TEST	M = 850°F+ RESID: THF EXTRACTION
E = WHOLE SAMPLE: THF EXTRACTION	N = THF-INSOLS OF 850°F+ RESID: ASH
F = THF-INSOLS OF WHOLE SAMPLE: ASH	O = 850°F+ RESID: ¹ H-NMR
G = THF-SOLS OF WHOLE SAMPLE: PHENOLIC -OH	P = THF-SOLS OF 850°F+ RESID: PHENOLIC -OH
H = THF-SOLS OF WHOLE SAMPLE: SOLVENT FRACTION. (O,A,P)	Q = THF-SOLS OF 850°F+ RESID: SOLVENT FRACTION. (O,A,P)
I = WHOLE SAMPLE: 850°F DISTILLATION	
KEY TO SPECIAL ANALYSES	1 = GC/MS
	2 = INSPECT FOR HDPE
	3 = ULT., PROX., CI, BTU, ASH ELEMENTS, S FORMS (OXIDATION INDEX)
	4 = ULT., ASH FROM POC-2

APPENDIX 6

REQUEST FOR SAMPLES FROM HTI RUN CMSL-9

CONSOL Inc.

Research & Development
4000 Brownsville Road
Library, PA 15129-9566
412-854-6600
FAX: 412-854-6613
412-854-6748

March 24, 1995

Dr. V. Pradhan
Hydrocarbon Technologies, Inc.
P. O. Box 6047
New York and Puritan Avenues
Lawrenceville, NJ 08648

Dear Vivek:

Our sample request for Run CMSL-9 is described below. As in the case of Run CMSL-8, DOE has asked us to serve as the clearinghouse for distribution of the samples to PETC and the Consortium groups. Therefore, we are requesting material in sufficient quantities to allow for sample distribution. We understand that you cannot always provide the requested amounts, and we can work with smaller quantities.

We would like to receive from each CMSL-9 run condition: (1) 250 g of separator overhead (SOH) and 250 g of atmospheric still overhead (ASOH) or 250 g of SOH/ASOH blended in the correct product ratio; (2) 350 g of start-up/make-up oil; (3) 350 g of pressure-filter liquid (PFL); (4) 350 g of pressure-filter cake (PFC); (5) 350 g of continuous atmospheric still (CAS) bottoms; (6) 350 g of interstage sample (first-stage product); and (7) 250 g of feed slurry. Please also include 250 g samples of SOH and ASOH liquids from any bypass periods of the in-line hydrotreater. We would also like to receive a fresh 300 g sample of the feed coal, and 250 g of any plastic feed that is different from the ones we already have (i.e., the Run POC-2 feeds).

We have not yet received the three interstage samples we were expecting from Run CMSL-8. Also, we still are interested in similar sample sets you may have from Runs CMSL-6 and CMSL-7, even though the sample quantities may be limited. We would appreciate any of these samples that you can provide.

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

Sincerely,

G. A. Robbins
Sr. Research Chemist

GAR:ls

cc: A. G. Comolli - HTI	F. P. Burke
M. A. Nowak - PETC	R. A. Winschel
E. B. Klunder - PETC	S. D. Brandes