A Characterization and Evaluation of Coal Liquefaction Process Streams

Quarterly Technical Progress Report
January 1 through March 31, 1996
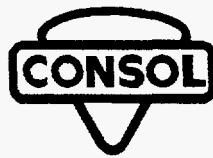
RECEIVED

NOV 19 1996

OSTI

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

July 1996

CONSOL

MASTER

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

Under Contract to:

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

Section 1

EXECUTIVE SUMMARY

UNCONVERTED HDPE EXTRACTION METHOD AND APPLICATION

In order to recover and characterize incompletely converted high-density polyethylene (HDPE), and to determine its concentration in ashy liquefaction stream samples, an analytical procedure was developed to extract HDPE from ashy stream samples. The method is an extraction of HDPE from the sample using hot (150 °C) decalin (decahydronaphthalene), in which the HDPE is soluble. The method, verification tests, and application to HTI Run CMSL-8 and Run CMSL-9 sample characterization are described in this report. Highlights from this work are itemized below.

- An HDPE extraction method was developed that can be routinely applied to ashy coal/plastics co-liquefaction stream samples. The method requires about four hours for extraction and several hours for solvent removal from recovered fractions. The method details are appended.

- The HDPE extraction method shows little interference from coal-derived material. In samples of resid from continuous atmospheric still bottoms (CASB) and of pressure-filter cake (PFC) from the coal-only period of Run CMSL-8, only 0.06 to 0.30 wt % of each resid sample reported as "HDPE". Similarly, corresponding samples from coal-only operation in Run CMSL-9 previously showed only 0.17 to 0.32 wt % of each sample reporting as "HDPE".

- Results from the HDPE extraction method show that during coal/plastics operations with pressure filtration, little HDPE exits the process in the PFC stream; instead, most of the unconverted HDPE is recycled in the pressure-filter liquid (PFL) stream. During coal/plastics periods of Run CMSL-8, there was a concentration of about 5 wt % HDPE in the PFC stream, and 16 to 37 wt % HDPE in the PFL stream. During coal/plastics periods of Run CMSL-9 the concentration was about 2 wt % HDPE in the PFC stream, and about 23 wt % HDPE in the PFL stream.

- HDPE extraction results were combined with material balance data to calculate HDPE balances and conversions during Run CMSL-8, as previously was done for Run CMSL-9). HDPE extraction results obtained from PFC and VSB samples appear to be consistent and reliable; however, this work indicated that some of the CASB samples provided by HTI were non-representative samples, or that sampling of the CASB material in CONSOL's laboratory was not representative.

1

- Overall HDPE conversions during Run CMSL-8 were about 70% in Periods 11, 20, and 22/23 (Conditions 2, 4, and 5), and only about 40% in Period 16, Condition 3. Single-pass HDPE conversions during Run CMSL-8 were about 24% in Periods 11, 20, and 22/23 (Conditions 2, 4, and 5), and only about 8% in Period 16, Condition 3.

- Future issues to address using the HDPE extraction method include: consideration of HDPE conversion kinetics, measurement of HDPE concentration in municipal solid waste plastics fed in subsequent liquefaction runs at HTI, and the degree of interference with HDPE determination by other polyolefins and petroleum resid fed in subsequent runs at HTI.

CHARACTERIZATION OF UNIVERSITY OF NORTH DAKOTA LIQUEFACTION OIL

At DOE's request, CONSOL characterized a sample of process oil from the University of North Dakota liquefaction program identified as "N-629 bottoms product". The oil is quite different than those produced by current catalytic two-stage liquefaction processes. The 80% of the sample that is distillable at 850 °F has a composition (composed primarily of unalkylated aromatics and the homologous hydroaromatics, low concentration of n-paraffins) like that of a recycle oil that is not too far evolved from hydrogenated anthracene oil, rather than like that expected of a recycle solvent generated at equilibrium at process conditions. The 11% of the sample that is 850 °F$^+$ THF-soluble resid has properties (e.g., H and O contents) in between those of lignite and soluble resids produced in current two-stage liquefaction (TSL) processes.

UNIVERSITY OF DELAWARE - RESID CONVERSION STUDIES

The University of Delaware continues to make progress in the resid conversion studies in the short-time batch reactor. The fourteen remaining samples in the sample set were sent to Delaware to begin reactivity testing.

UNIVERSITY OF DELAWARE - TECHNOLOGY TRANSFER

The University of Delaware presented three papers at the 211th National Meeting of the American Chemical Society, March 24-28, 1996, in New Orleans, LA. The papers are appended.

Section 2

INTRODUCTION

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

<u>CONTRACT OVERVIEW</u>

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 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 are being evaluated. The data obtained from this study is used to help guide current 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 resids toward hydrocracking at liquefaction conditions (i.e., resid reactivity) is being 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.

<u>CONTRACT ACTIVITIES THIS PERIOD</u>

- In order to recover and characterize incompletely converted high-density polyethylene (HDPE), and to determine its concentration in ashy liquefaction stream samples, CONSOL developed an analytical procedure for HDPE in the ashy stream samples. The method is based on extraction of HDPE from the sample using hot (150 °C) decalin (decahydronaphthalene), in which the HDPE is soluble. The method (provided in Appendix 1), verification tests, and application to Run CMSL-8 and Run CMSL-9 sample characterization are described in this report.

- Samples for characterization were requested from HTI Run PB-03 (Appendix 2) and HTI Run ALC-1 (Appendix 3).

- At DOE's request, CONSOL characterized a sample of process oil from the University of North Dakota liquefaction program. Characterization results are provided in this report, and sample background information is appended (Appendix 4).

3

- Three microautoclave tests were made by CONSOL to aid in deciding which catalyst (homogeneous Mo-naphthanate or heterogeneous Shell 324, Ni/Mo on alumina) will be used for the remainder of the resid reactivity program. The liquid products were sent to the University of Delaware for further analysis.

- A meeting was held with Drs. Calkins and Huang of the University of Delaware on March 24 in New Orleans to discuss the current status of their subcontract. A report of that meeting is appended to this document (Appendix 5).

- The University of Delaware Quarterly Report is appended to this report (Appendix 6).

- University of Delaware researchers presented three papers at the 211th American Chemical Society National Meeting. These papers are appended (Appendix 7).

ACTIVITIES IN PROGRESS

- We began characterization of samples from HTI Run CMSL-11.

- We are working toward arranging a complete suite of light oil assay tests on hydrotreated and unhydrotreated products from HTI Run PB-03.

- We began work to recalibrate our phenolic -OH measurement method for the new FTIR system.

4

Section 3

RESULTS AND DISCUSSION

UNCONVERTED HDPE EXTRACTION METHOD AND APPLICATION

INTRODUCTION

In several coal/plastics liquefaction runs performed by Hydrocarbon Technologies, Inc. (HTI), a substantial amount of incompletely converted high-density polyethylene (HDPE) was present in the ash-free recycle resid streams when either the ROSE-SR unit was used in Run POC-2, or the pressure filter unit was used in Runs CMSL-8 and CMSL-9. This indicates that the HDPE is less reactive than coal at the liquefaction conditions used.[1,2,3] In these ash-free streams, there is no interfering coal-derived solid organic or inorganic material, and the incompletely converted HDPE can be recovered by a simple extraction and filtration with tetrahydrofuran (THF) at room temperature. The HDPE (or HDPE-like material, which could also consist of heavy waxes) is recovered as the THF-insoluble material. However, in ashy streams, there are both inorganic ("ash") and organic (unconverted coal) components present from liquefaction of the coal that interfere with an easy and clean separation of the HDPE from the coal/plastics liquefaction stream sample. Therefore, to better recover and characterize the HDPE, and to determine its concentration in ashy liquefaction stream samples, we developed an analytical procedure to isolate the HDPE from the ashy stream samples. The method is based on extraction of HDPE from the sample using hot (150 °C) decalin (decahydronaphthalene), in which the HDPE is soluble. The decalin extraction is both preceded and succeeded by extractions and washes with THF at room temperature, to remove the coal-derived components from the sample. The procedure requires about four hours to perform, with several hours of additional unattended time required for solvent removal from the extracted fractions. The method, verification tests, and application to Run CMSL-8 and Run CMSL-9 sample characterization are described here. This method permits an authentic determination of HDPE conversion during these runs, since it provides data from ashy streams, which were not available for use in an earlier estimate of HDPE conversion during Run CMSL-8.

DEVELOPMENT AND VERIFICATION TESTS

HDPE Solubility and Filtration Tests

The first tests were performed to determine whether the HDPE feedstock used in HTI Runs POC-2, CMSL-8, and CMSL-9 could be dissolved in hot cresol or decalin, filtered and recovered, and at what temperature this operation could be performed. The HDPE has been described elsewhere;[4] briefly, it is a virgin material, consisting of clear pellets, supplied to HTI by Amco plastics, manufactured by BASF, mp 275 °F, and density 0.96 g/cc. It is essentially devoid of ash, sulfur, nitrogen, and

5

oxygen.[1] The decahydronaphthalene (decalin; anhydrous, >99% purity) was obtained from Aldrich Chemical Co., consisting of a mixture of cis- and trans- isomers, and with b.p. 189-191 °C.

Experiment 1 - Test of Cresol as a Potential Solvent

2.08 g of HDPE and 25 mL of mixed cresol were placed into a 250 mL beaker and gradually heated on a hot plate to 155 °C, with occasional stirring with a glass rod. Although the plastic became pliable at ca. 100 °C, it never dissolved, even at 155 °C.

Experiment 2 - Test of Decalin as a Potential Solvent

2.37 g of HDPE and 50 mL of decahydronaphthalene (decalin) were placed into a 250 mL beaker and gradually heated on a hot plate to 125 °C. At 105 °C, the plastic began to melt and dissolve. The mixture was heated with stirring to 125 °C, after which the HDPE was completely dissolved, forming a clear colorless solution with the decalin. When a portion of the solution was allowed to cool, a white precipitate formed, coating the glass stirring rod and beaker with a soft, white mass. The HDPE-decalin solution at 125 °C was pressure-filtered through a Whatman no. 42 paper in a pressure filtration device wound with resistance wire and insulation for electrical heating, with control provided through a potentiostat, and temperature measurement provided by a thermocouple readout. The filtration apparatus was heated to 145 °C. About 7 psig of nitrogen gas was used, and the solution filtered readily. Hot decalin was used to rinse the beaker and filter paper, but some precipitated HDPE adhered to the beaker. After the filtrate cooled to room temperature, it was pressure-filtered through Whatman no. 42 paper and washed with fresh decalin. The filtrate was clear, and slightly yellow in color. The filter cake was dried in a vacuum oven at 60 °C under full vacuum overnight. After drying, it still had a faint decalin odor. 91.6% of the HDPE was recovered as a hard white solid.

Tests of Extraction Sequence

HDPE is completely insoluble in THF at room temperature; therefore, a THF wash could be used to distinguish HDPE from other materials that may be extracted in hot decalin. However, it was uncertain whether it was better to apply the decalin extraction directly to the sample, or rather to apply the decalin extraction to the sample after THF-extraction to remove coal-derived components. A test was conducted in which aliquots of one sample were extracted using both test sequences. Those results are shown in Table 3. In the decalin-first procedure (Experiment 3): the sample was extracted and filtered with hot decalin, the decalin extract was cooled to room temperature, the precipitated solid HDPE was filtered and dried, the tan-colored filter cake was washed with THF, and all fractions were dried in the vacuum oven to remove solvent.

In the THF-first procedure (Experiment 4): the sample was extracted and filtered with THF at room temperature, the sample was extracted and filtered with hot decalin, the decalin extract was cooled to room temperature, the precipitated solid HDPE was filtered and dried, the off-white-colored filter cake was washed with THF, and all fractions were dried in the vacuum oven to remove solvent. In this method, both the THF-soluble fractions obtained prior to and after decalin extraction were combined before solvent removal.

The results obtained using the two sequences are quite similar (Table 3). The similarity of the results provided overall validation of the hot decalin approach, and indicated that either sequence probably was adequate for HDPE determination. HDPE products from both extractions had a similar coarse powdery appearance. FTIR spectra (Figure 1) show that the recovered HDPE fractions obtained by the two extraction sequences are similar to each other, and to the feed HDPE. Thus, these recovered decalin solubles appear to be essentially pure HDPE (or heavy n-paraffins, which may be indistinguishable from HDPE). The THF-first procedure is preferred because it minimizes the possibility of interferences and because the HDPE product was cleaner in appearance. The THF-first procedure requires an additional extraction step, but the total time required for both extraction steps is only about four hours.

METHOD DETAILS

The specific procedure used for routine tests is attached as Appendix 1, and a flow diagram of the method is shown in Figure 2. The method is easy to perform in a routine manner. Combined recoveries of the three fractions (THF solubles, HDPE, and THF/decalin insolubles) ranged from 98.0% to 104.6%, averaging 102.1% in 19 tests using the method (this includes the decalin-first test described above and the application tests described later). It is presumed that recoveries are biased high because of the difficulty in removing solvents (THF or decalin) from the recovered fractions. For routine use, the fraction percentages are reported on a normalized basis.

APPLICATION TO RUN CMSL-8

This method was previously applied to selected samples from HTI Run CMSL-9, for the purposes of characterization of the samples, and exploration of issues relating to the fate of HDPE.[3] The data were used primarily for four specific purposes: 1) to determine the amount of HDPE in the pressure filter cake (PFC) samples from periods in which coal and plastics were fed, 2) to determine the degree of analytical interference from HDPE-like material produced from the coal, 3) to determine the HDPE conversion for each of the periods of coal/plastics operation, and 4) to develop a HDPE material balance around the solids separation unit (vacuum still or pressure filter, depending on run period).[3] It was found for Run CMSL-9 data that the material balances for HDPE ranged from poor

to excellent, but that poor results also were obtained when our conventional work-up data were used to calculate material balances for 850 °F⁻ distillate, 850 °F⁺ resid THF solubles, unconverted coal, and ash as individual components.

Corresponding extraction data and material balances around the plant solids-separation system (pressure filtration) for samples from HTI Run CMSL-8 obtained from the HDPE extraction method and conventional work-up (distillation and THF extraction) are given in Tables 4 and 5. In samples of resid from continuous atmospheric still bottoms (CASB) and of pressure-filter cake (PFC) from the coal-only period of Run CMSL-8, only 0.06 to 0.30 wt % of each sample reported as "HDPE", showing that little coal-derived material reports as "HDPE" using this method (Table 4). Similarly, corresponding samples from coal-only operation in Run CMSL-9 previously showed only 0.17 to 0.32 wt % of each sample reporting as "HDPE".[3] Extraction results from the coal/plastics operating periods show that with pressure filtration, little HDPE exits the process in the PFC stream; instead, most of the HDPE is recycled in the pressure-filter liquid (PFL) stream (Table 4). During coal/plastics periods of Run CMSL-8, there was a concentration of about 5 wt % HDPE in the PFC stream, and 16 to 37 wt % HDPE in the PFL stream. Similarly, during coal/plastics periods of Run CMSL-9, there was a concentration of about 2 wt % HDPE in the PFC stream, and about 23 wt % HDPE in the PFL stream.[3]

When we used the data derived from the HDPE determination procedures to conduct a HDPE material balance in Run CMSL-8 around the solids separation unit (pressure filter), we found that the results for HDPE were poor (Table 4). The corresponding data from our conventional work-up provided individual balances of 850 °F⁻ distillate, 850 °F⁺ resid THF solubles, unconverted coal, and ash that ranged from poor to excellent (Table 5). For example, the ash balances in coal/plastics periods ranged from 132% to 854% (Table 5). In order to identify the reasons for such poor material balances, we examined the percent total THF insolubles (THFI) obtained from the THF/decalin extraction of the CASB resid, and compared it with percent total THFI obtained from THF extraction of the CASB resid, and with percent total THFI obtained from THF extraction of the whole CASB. If the extraction procedures are robust, then the THFI contents determined by different extraction procedures on the same sample should agree well, regardless of which specific extraction method was used. The THFI value is the sum of THF/DI (THF and decalin insolubles) and HDPE fraction weight percentages from the decalin extraction method (Method 1). For the THF extraction procedure (Method 2, our normal work-up procedure for liquefaction samples), this value is the sum of IOM and ash component weight percentages. As shown in Figure 3, the amount of THF insolubles obtained by the two methods (Method 1 and Method 2) on two sample types (CASB 850 °F⁺ resid and whole CASB), shows considerable scatter for samples representing a particular run condition.

8

We have found some CASB samples from coal/plastics periods of both Runs CMSL-8 and CMSL-9 whose integrity were considered suspect, because they contained only trace amounts of ash. The data shown in Figure 3 thus suggest that a major problem may lie in obtaining good data from the CASB samples from coal/plastics operations in general. However, we find that percent THF insolubles obtained by Method 1 (the decalin extraction method) of VSB and PFC are very similar to those obtained by Method 2 (THF extraction) of the same samples (Figure 4). These results indicate that there is no problem with use of the decalin extraction data obtained from the VSB and PFC samples. Calculations of overall HDPE conversion depend on determinations of HDPE in the PFL product, and in the PFC or VSB product. Calculations of single-pass HDPE conversion depend on determination of HDPE in the CASB, and thus are more questionable. However, it is possible to calculate single-pass conversion by substituting appropriate proportions of PFL and PFC for CASB in the calculations.

REVISION OF HDPE CONVERSION ESTIMATES FOR RUN CMSL-8

Our original procedure for estimating HDPE conversions employed the simplifying assumption that the PFC contained no unconverted HDPE.[2] This assumption was made because, at the time, we had no way of measuring the concentration of unconverted HDPE in solids-containing streams. We can now make these measurements directly with the hot decalin extraction procedure. The HDPE extraction results presented above for Run CMSL-8, and previously presented for Run CMSL-9,[3] generally validate the approximation that the PFCs contain no HDPE, because little HDPE (1 to 6 wt %) was found in the PFC samples. When the unconverted HDPE in the PFCs and CAS bottoms samples is included, the calculated overall HDPE conversions for Run CMSL-8 (Table 6) are 39% to 76% (reduced about 5% from our previous estimate).[3] The corresponding single-pass conversions are 8% to 27%. We discovered a mathematical error in the single-pass conversion results for period CMSL-8-22 originally reported.[2] The revised value is 27% to 34% (depending on the calculation basis and inclusion of the HDPE in the PFC or CAS bottoms or both). It is much closer to those of other periods of Run CMSL-8.

Both overall and single-pass conversions of HDPE are determined by the following equation:

Conversion = [Mass of HDPE In - Mass of HDPE Out] x 100% / [Mass of HDPE In],

where the masses of HDPE in and out are defined differently for overall conversion than for single-pass conversion. For overall conversion, the mass of HDPE in is the HDPE in the fresh feed, and the mass of HDPE out is summed from HDPE in any net product streams, such as PFL and PFC or VSB. For single-pass conversion, the mass of HDPE in is the sum of HDPE in the fresh feed and

9

all recycle streams (such as CASB, PFL, and PFC or VSB), and the mass of HDPE out is the sum of HDPE in all of the gross product streams (such as CASB, PFL, and PFC or VSB). The results presented here for Run CMSL-8 differ from those given previously,[2] in that HDPE can be accounted for in more streams, whereas previously it could only be accounted in the fresh feed and PFL streams. Note that CASB can be accounted directly (if the HDPE content of CASB is measured), or it can be accounted as both PFL and PFC (or as VSB). Thus, it is possible to measure single-pass HDPE conversion with CASB as a recycle or product stream, even if the HDPE content of the CASB is not measured directly. Problems described above with use of the CASB data suggests that it may be better to use the PFL/PFC accounting approach, since the HDPE concentrations of PFC samples seem to be more reliable than those of CASB samples.

In Figure 5, the overall and single-pass conversions of HDPE in each period of Runs CMSL-8 and 9 that were evaluated are compared. The overall conversion of HDPE ranged from 69-86% during Run CMSL-9, comparable to those obtained for periods Conditions 8-2, 8-4, and 8-5. This was accomplished in Run CMSL-9 in spite of operation at a higher space velocity and without benefit of supported catalyst, but at higher liquefaction temperatures, relative to conditions used in Run CMSL-8. A high space velocity led to operating problems and low HDPE conversion in Condition 8-3. Higher conversion of HDPE in Condition 9-7, in which vacuum distillation and ashy recycle were used, relative to Conditions 9-8 and 9-9, in which pressure filtration and ash-free recycle were used, suggests that use of ashy recycle may increase HDPE conversion. In Figure 6, the overall HDPE conversions based on CONSOL's direct measurement method for Run CMSL-9 periods are compared with those estimated by HTI[6] based on measured total feed conversions, and assumed fixed conversions of 88% for the coal, and 100% for all of the non-HDPE plastics.[6] These two sets of results show good agreement for the overall run and for individual periods. HTI's model assumptions thus appear to apply to the combination of coal and plastics tested in Run CMSL-9.

FUTURE WORK

The HDPE concentration data provided by the hot decalin extraction method can provide a basis for consideration of kinetics of HDPE conversion, and in development of improved processing strategies. Conversion data from Run CMSL-9 have provided an indication that ashy recycle may improve HDPE conversion.

In runs following CMSL-9, HTI's feedstocks for co-liquefaction have included municipal solid waste (MSW) plastics and petroleum resid, in various combinations with and without coal. The HDPE extraction method provides a potential means to determine HDPE concentration in mixed MSW feeds. Potential difficulty for the method would be interference from other polyolefins or petroleum

resid, since other polyolefins and heavy waxes may behave like HDPE in terms of solubilities in decalin and THF. Our intent is to continue to apply this characterization method to samples from appropriate streams in HTI runs in which HDPE is fed.

CHARACTERIZATION OF UNIVERSITY OF NORTH DAKOTA LIQUEFACTION OIL

INTRODUCTION AND SUMMARY

At DOE's request, CONSOL characterized a sample of process oil from the University of North Dakota liquefaction program identified as "N-629 bottoms product". A detailed description of the production of the oil appears in a letter from J. R. Rindt of the University of North Dakota (Appendix 4) and additional information on the process can be found in Reference 7. The oil is quite different than those produced by current catalytic two-stage liquefaction processes. The 80% of the sample that is distillable at 850 °F has a composition (composed primarily of unalkylated aromatics and the homologous hydroaromatics, low concentration of n-paraffins) like that of a recycle oil that is not too far evolved from hydrogenated anthracene oil, rather than like that expected of a recycle solvent generated at equilibrium at process conditions. The 11% of the sample that is 850 °F$^+$ THF-soluble resid has properties (e.g., H and O contents) in between those of lignite and soluble resids produced in current two-stage liquefaction (TSL) processes.

METHODS

The 300 g sample was shipped from North Dakota on November 29, 1995. CONSOL's characterization included: vacuum distillation of the oil at 850 °F (equivalent) to recover a distillate and a resid; extraction of the resid with freshly distilled tetrahydrofuran to recover THF soluble resid and THF insolubles; elemental analysis and phenolic -OH determination on the distillate and THF-soluble resid; elemental, ash and ash SO_3 analysis of the THF insolubles; microautoclave solvent quality assay at the modified equilibrium conditions with Old Ben Mine No. 1 coal of the distillate and whole oil; and gas chromatography/mass spectroscopy analysis (GC/MS) of the distillate. GC/MS analyses employed an HP 5970B instrument equipped with a 30 m x 0.25 mm DB-5 column (0.25 μm film thickness). The carrier gas was 20 psig He. Samples were injected in the splitless mode as 1% solutions into a 300 °C injection port. GC conditions were 5 min at 35 °C, 35 °C/min to 100 °C, 4 °C/min to 320 °C, 20 min hold. The mass spectrometer was scanned from 33 to 300 amu. Peak identifications were based on searches of the Wiley/NBS mass spectral library and retention times. ^{1}H-nuclear magnetic resonance spectra were recorded for the whole oil, THF-soluble resid (both in C_5D_5N, whole oil filtered), and distillate (in $CDCl_3$) with a Varian EM-360L instrument. Solubility fractionation analysis of the THF-soluble resid was accomplished by the liquid column fractionation (LCF) method.

RESULTS

Analytical data appear in Table 7. The GC/MS chromatogram of the distillate is shown in Figure 8. The analyzed material is a black, viscous oil with a coal-tar-like odor. The oil contains 79.7% 850 °F$^-$ distillate, 11.0% THF-soluble resid, 4.4% insoluble organic matter (IOM), and 2.6% SO_3-free ash.

The whole oil is very aromatic (55% aromatic H) and, unlike most coal liquids we have examined, the distillate is more aromatic than the THF-soluble resid (58% vs. 45% aromatic H). The low concentration of paraffinic alkyl beta protons (<11% in the whole oil and its fractions) and the lack of prominent n-paraffin peaks in the GC/MS analysis is uncharacteristic of low-rank coal liquids, except perhaps for those produced at temperatures higher than those typically employed in liquefaction. The THF-soluble resid has a much higher concentration of total O by difference (7.5%) than typical 850 °F+ THF-soluble resids produced from low-rank coals in the TSL process (less than 3% total O by difference). The concentration of phenolic -OH in the THF-soluble resid is at the high end of that observed in typical 850 °F+ THF-soluble resids produced from low-rank coals at 1.1 meq/g phenolic -OH. The hydrogen content of the soluble resid, 6.5%, is considerably higher than that of most North Dakota lignites, ca. 4.5 to 5% on a moisture and SO_3-free ash free basis, but lower than that of most two-stage liquefaction (TSL) soluble resids, 7 to 8%. The initial boiling point appears to be ca. 535 °F, on the basis of the first-eluting prominent compound (acenaphthene). The prominent GC/MS peaks represent unalkylated aromatics and their hydroaromatic analogues. The whole oil and its distillate fraction are good to excellent hydrogen donor solvents, giving 86% and 91% conversion in the modified equilibrium microautoclave test.

DISCUSSION

The oil characterized is quite different than those produced by current catalytic two-stage liquefaction (TSL) processes, such as those developed at the Wilsonville pilot plant or the HTI facility. For comparison, shown in Table 8 are selected properties[8] of a heavy recycle distillate (V-1074) and a deashed recycle resid (V-130) from Wilsonville Run 262E, which was a TSL run made with subbituminous coal. These liquids provide a reasonable represention of low-rank coal TSL liquids, although other low-rank coal TSL liquids have somewhat different properties. The Wilsonville oils were fractionated in the plant to an approximate equivalent cut-point of 1050 °F, not 850 °F as used for the sample of interest and the initial boiling point of the Wilsonville distillate is higher than the sample of interest. Nevertheless, the comparison is instructive.

The primary components of the 850 °F- distillate, which is about 80% of the oil, are unalkylated aromatics and hydroaromatics (Table 7 and Figure 9), rather than the alkylated aromatics and hydroaromatics and paraffins typical of a TSL liquid (Table 8). The distillate is highly aromatic, yet is an excellent donor solvent because many of the aromatics are partially hydrogenated. Our judgement is that the distillate does not represent a steady-state process-derived liquefaction recycle oil. Its composition resembles that of a recycle oil that is not too far evolved from a start-up hydrogenated anthracene oil.

13

The 11% of the oil that is THF-soluble resid also has properties different than TSL products. However, rather than resembling a coal tar product as does the distillate, the soluble resid has properties in between those of lignite and highly processed TSL resids. For example, the hydrogen and oxygen contents of the THF soluble resid (Table 7) are intermediate between those of lignite and typical TSL soluble resids (Table 8).

If it is assumed that the 850 °F$^+$ THF-soluble resid/IOM/ash ratio of the sample is representative of that in the product, and that the feed coal has an SO$_3$-free ash content of 4.5% MF (typical for Freedom Mine lignite), then ash balance calculations indicate that this sample represents about 92% lignite conversion to THF solubles and about 72% lignite conversion to 850 °F$^-$ products. Of course, the accuracy of the calculated values depends on the accuracy of the two assumptions.

Section 4
EXPERIMENTAL

Experimental details are described, where appropriate, in the Discussion section of this report. Details of the other analytical techniques used in this work were reported previously.[5,6]

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, May 1995.

2. 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, April 1 through June 30, 1995", DOE/PC 93054-18, September 1995.

3. 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, 1995", DOE/PC 93054-25, May 1996.

4. Comolli, A. G. "Results of Recent POC Run at HRI on Waste/Coal Coprocessing", Proceedings of the PETC/DOE Workshop "Waste/Coal Coprocessing", Pittsburgh, PA, September 9, 1994.

5. Burke, F. P.; Winschel, R. A.; Robbins, G. A. "Recycle Slurry Oil Characterization Final Report, October 1980 through March 1985", DOE/PC 30027-61, March 1985.

6. Winschel, R. A.; Robbins, G. A.; Burke, F. P. "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report, July 1985 through September 1985", DOE/PC 70018-13, December 1985.

7. Hetland, M. D.; Rindt, J. R. "Solvent Recyclability In A Multistep Direct Liquefaction Process", in Proceedings of the DOE Coal Liquefaction and Gas conversion Contractors Review Conference, Pittsburgh, PA, August 1995, p. 147.

8. Technical Progress Reports For July Through September 1992 and October Through December 1992, Report Nos. 91040-17 and 91040-21, DOE Contract DE-AC22-91PC91040, November 1992 and February 1993.

TABLE 1

RESID REACTIVITY TEST CONDITIONS

Test Number	RR-5	RR-6	RR-7a*
Resid(a), g	2.54	2.52	2.50
Tetralin, g	5.02	5.01	5.04
Catalyst	none	molybdenum naphthanate	Shell 324, presulfided, washed with THF, and ground to -60 mesh
Catalyst, g	-	0.44	2.51
Sulfiding agent	-	dimethyldisulfide	-
Sulfiding agent, g	-	0.55	-
TOTAL IN, g	**7.56**	**8.52**	**10.05**
H_2 cold, psig	1200	1200	1200
Reaction Temperature, °C	434	436	435
Residence time, min	30	30	30
Final gas pressure, psig	1000	720	750
Gas, g	0.24	0.63	0.30(b)
Unrecovered from reactor, g	0.77	0.79	0.30
TOTAL NON-GASEOUS PRODUCT OUT, g	**6.55**	**7.10**	**9.52(c)**

* Run RR-7A was made to replace Run RR-7 which was lost in shipment to Delaware

(a)   Wilsonville Run 258, V131B composite 850°F$^+$ resid
(b)   value higher than previously reported
(c)   includes washings from reactor

17

TABLE 2

RESID REACTIVITY TESTS
PRODUCT GAS ANALYSIS

Component	Test Number	Volume Percent		
		RR-5	RR-6(a)	RR-7(a)
propane		0.054	0.132	0.190
propylene		0.013	0.010	0.002
isobutane		0.007	0.009	0.010
n-butane		0.019	0.025	0.118
isobutene		0.007	0.002	0.002
trans-2-butene		0.007	0.003	0.002
cis-2-butene		0.008	0.001	0.002
isopentene		0.004	0.006	0.007
n-pentane		0.008	0.004	0.003
hydrogen		98.268	89.192	95.961
carbon dioxide		0.102	0.132	0.039
ethylene		0.014	0.000	0.002
ethane		0.126	0.257	0.375
oxygen		0.038	0.021	0.042
nitrogen		0.688	0.760	1.887
methane		0.540	9.248	1.356
carbon monoxide		0.098	0.204	0.050

(a)   average of two determinations

TABLE 3

TEST OF THF AND DECALIN EXTRACTION SEQUENCE

Fraction	Fraction Wt % of Sample (850 °F$^+$ Resid from CAS Bottoms Sample, Period 38 of Run CMSL-9)	
	Decalin Extraction First - Unnormalized (Normalized)	THF Extraction First - Unnormalized (Normalized)
THF/Decalin Insolubles	2.91 (2.77)	3.59 (3.46)
THF Solubles	61.0 (58.2)	64.3 (62.1)
Decalin Solubles/THF Insolubles (HDPE)	40.9 (39.0)	35.7 (34.4)
Recovery	104.8 (100.0)	103.6 (100.0)

TABLE 4

HDPE-EXTRACTION RESULTS AND MATERIAL BALANCES FOR SELECTED SAMPLES FROM HTI RUN CMSL-8

Balances from HDPE Extraction Experiments								
Sample	Sample wt % of Whole CAS Btms	Analysis, wt % of Sample			wt % of Whole CAS Btms			
		THFS	THF/DI	HDPE	THFS	THF/DI	HDPE	Total
Condition 1, Period 6 (Coal)								
CASB Resid	45.90	84.13	15.82	0.06	92.72	7.26	0.03	100.00
PFL	85.90	100.00		0.00	85.90	0.00	0.00	85.90
PFC	12.69	41.72	57.98	0.30	5.29	7.36	0.04	12.69
Sums					91.20	7.36	0.04	98.59
Balances					98.36	101.33	138.24	98.59
Condition 2, Period 11 (Coal/Mixed Plastics)								
CASB Resid	55.00	73.72	2.19	27.60	85.55	1.20	15.18	101.93
PFL	89.44	79.70		20.30	71.28	0.00	18.16	89.44
PFC	7.77	31.96	63.51	4.53	2.48	4.93	0.35	7.77
Sums					73.76	4.93	18.51	97.20
Balances					86.23	409.56	121.92	95.36
Condition 3, Period 16 (Coal/Mixed Plastics)								
CASB Resid	60.90	79.33	8.55	14.86	87.41	5.21	9.05	101.67
PFL	89.67	62.60		37.40	56.13	0.00	33.54	89.67
PFC	6.69	28.31	67.27	4.42	1.89	4.50	0.30	6.69
Sums					58.03	4.50	33.83	96.36
Balances					66.38	86.39	373.85	94.78
Condition 4, Period 20 (Coal/Mixed Plastics)								
CASB Resid	67.30	5.00	54.82	40.18	36.07	36.89	27.04	100.00
PFL	92.04	83.50		16.50	76.86	0.00	15.19	92.04
PFC	5.69	20.86	73.29	5.85	1.19	4.17	0.33	5.69
Sums					78.04	4.17	15.52	97.74
Balances					216.40	11.31	57.40	97.74
Condition 5, Periods 22/23 (Coal/HDPE)								
CASB Resid	76.80	37.15	1.04	61.81	51.73	0.80	47.47	100.00
PFL	92.72	84.20		15.80	78.07	0.00	14.65	92.72
PFC	7.18	22.41	72.32	5.28	1.61	5.19	0.38	7.18
Sums					79.68	5.19	15.03	99.90
Balances					154.03	650.36	31.66	99.90

TABLE 5

CONVENTIONAL THF-EXTRACTION RESULTS AND MATERIAL BALANCES FOR SELECTED SAMPLES FROM HTI RUN CMSL-8

Balances of Normal Workup Components										
Sample	Sample wt % of Whole CAS Btms	Analysis, wt % of Sample				wt % of Whole CAS Btms					
		850 °F⁻ Dist.	850 °F⁺ Resid	IOM	Ash	850 °F⁻ Dist.	850 °F⁺ Resid	THFS	IOM	Ash	Total
Condition 1, Period 6 (Coal)											
CASB Resid	45.90	53.40	38.50	2.10	5.30	53.40	38.50	91.90	2.10	5.30	99.30
PFL	85.90	55.00	43.90	0.20	0.00	47.25	37.71	84.96	0.17	0.00	85.13
PFC	12.69	0.00	41.20	14.20	44.60	0.00	5.23	5.23	1.80	5.66	12.69
Sums						47.25	42.94	90.19	1.97	5.66	97.82
Balances						88.48	111.53	98.14	93.99	106.79	98.51
Condition 2, Period 11 (Coal/Mixed Plastics)											
CASB Resid	55.00	44.80	32.90	21.70	0.40	44.80	32.90	77.70	21.70	0.40	99.80
PFL	89.44	39.70	39.00	20.30	0.00	35.51	34.88	70.39	18.16	0.00	88.54
PFC	7.77	0.00	30.70	25.60	44.00	0.00	2.38	2.38	1.99	3.42	7.79
Sums						35.51	37.27	72.77	20.14	3.42	96.33
Balances						79.26	113.27	93.66	92.83	854.42	96.53
Condition 3, Period 16 (Coal/Mixed Plastics)											
CASB Resid	60.90	38.20	42.50	16.10	2.30	38.20	42.50	80.70	16.10	2.30	99.10
PFL	89.67	35.00	25.50	37.40	0.00	31.38	22.87	54.25	33.54	0.00	87.79
PFC	6.69	0.00	28.10	26.60	45.30	0.00	1.88	1.88	1.78	3.03	6.69
Sums						31.38	24.75	56.13	35.32	3.03	94.47
Balances						82.16	58.22	69.55	219.35	131.71	95.33
Condition 4, Period 20 (Coal/Mixed Plastics)											
CASB Resid	67.30	32.30	46.40	20.20	0.70	32.30	46.40	78.70	20.20	0.70	99.60
PFL	92.04	27.60	54.80	16.50	0.10	25.40	50.44	75.84	15.19	0.09	91.12
PFC	5.69	0.00	31.10	26.90	42.00	0.00	1.77	1.77	1.53	2.39	5.69
Sums						25.40	52.21	77.61	16.72	2.48	96.82
Balances						78.65	112.52	98.62	82.77	354.80	97.21
Condition 5, Periods 22/23 (Coal/HDPE)											
CASB Resid	76.80	23.00	55.50	21.30	0.00	23.00	55.50	78.50	21.30	0.00	99.80
PFL	92.72	17.50	65.30	15.80	0.00	16.23	60.55	76.77	14.65	0.00	91.42
PFC	7.18	0.00	24.90	27.50	47.60	0.00	1.79	1.79	1.98	3.42	7.18
Sums						16.23	62.33	78.56	16.62	3.42	98.60
Balances						70.55	112.31	100.08	78.05	ERR	98.80

TABLE 6

HDPE CONVERSION IN HTI RUN CMSL-8 (REVISED TO INCLUDE NON-PFL CONTRIBUTION)

Overall Conversion of HDPE*							
Period	HDPE in, wt % Dry Feed	PFL Product, wt % Dry Feed	wt % HDPE in PFL	PFC Product, wt % Dry Feed	wt % HDPE in PFC	HDPE Product, wt % Dry Feed	Overall Conv., %
11	12.5	12.02	20.0	14.59	4.5	3.1	75.5
16	12.5	22.74	30.4	14.83	4.4	7.6	39.4
20	16.5	32.30	14.5	14.67	5.9	5.5	66.4
22/23	33.0	46.33	18.6	15.09	5.3	9.4	71.5

Single-Pass Conversion of HDPE*									
		Based on PFC and PFL Only				wt % HDPE in CASB	Based on CASB, PFC and PFL		
Period	Fresh HDPE Feed, g/h	Recycle HDPE In, g/h	Total HDPE In, g/h	HDPE Out, g/h	1-Pass Conv., %		Recycle HDPE In, g/h, w/CASB	Total HDPE In, g/h, w/CASB	HDPE Out, g/h	1-Pass Conv., %
11	118.5	306.0	424.5	332.4	21.7	15.2	306.0	424.5	332.4	21.7
16	156.2	700.7	856.9	787.4	8.1	9.1	700.7	856.9	787.4	8.1
20	159.3	295.1	454.4	343.7	24.4	27.0	295.1	454.4	343.7	24.4
22/23	312.9	359.7	672.7	443.8	34.0	47.5	525.5	838.5	609.6	27.3

* Using THF insolubles in whole PFL as estimate for HDPE in PFL.

TABLE 7

ANALYSIS OF UNIVERSITY OF NORTH DAKOTA LIQUEFACTION OIL

Component Distribution	
	Yield, wt %
850 °F⁻ Distillate	79.7
THF-Soluble Resid	11.0
Insoluble Organic Matter	4.4
SO₃-Free Ash	2.6
Distillation Hold-Up and Loss	2.3

	Proton Distribution, %							Phenolic -OH Concentration, meq/g
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	
Whole Oil	47.1	8.3	15.2	8.3	9.4	8.1	3.6	-
850 °F⁻ Distillate	49.0	9.1	14.1	7.9	9.1	7.1	3.7	0.29
THF-Soluble Resid	36.1	9.0	18.9	9.5	10.0	10.5	5.9	1.10

	Ultimate Analysis, wt %					SO₃-Free Ash
	C	H	N	S	O (diff)	
850 °F⁺ Resid	74.7	4.4	1.2	1.2	4.3	14.2
THF-Soluble Resid	84.1	6.5	1.2	0.7	7.5	-
850 °F⁻ Distillate	91.0	7.0	0.4	0.2	1.4	-

	Microautoclave Solvent Quality Assay, Coal Conversion, wt % MAF (a)
Whole Oil	85.7
850 °F⁻ Distillate	90.7

(a)   Mod-EQ Conditions With Old Ben No. 1 Mine Coal.

	LCF Solubility Fractionation Analysis of THF-Soluble Resid (b), wt %
Oils	47.4
Asphaltenes	30.6
Preasphaltenes	22.0

(b)   Average Response Factors Used.

23

TABLE 8

ANALYSES OF
WILSONVILLE RUN 262E MATERIALS

	Proton Distribution, %							Phenolic -OH Concentration, meq/g
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	
V-1074 (1050°F· Dist.)	11.3	3.6	14.7	7.6	15.8	34.6	12.3	0.44
V-130 (Deashed Resid)	22.7	4.9	19.3	9.3	14.7	19.3	9.7	0.90

	C	H	N	S	O (diff)	Ash
V-1074 (1050°F· Dist.)	88.9	9.9	0.4	<0.1	0.8	-
V-130 (Deashed Resid)	89.8	7.3	0.9	<0.1	1.3	0.7

	Microautoclave Solvent Quality Assay, Coal Conversion, wt % MAF (a)
V-1074 (1050°F· Dist.)	63.8

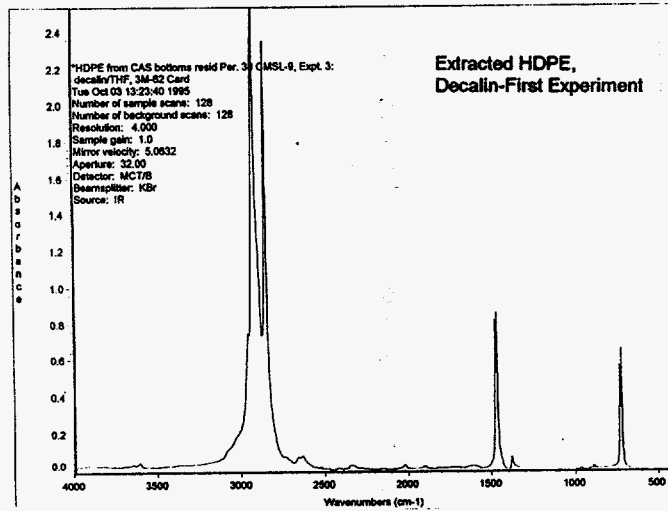(a)   Mod-EQ Conditions With Old Ben No. 1 Mine Coal.

Source: Reference 8

24

HDPE Feed

HTI Feed HDPE to CMSL-9 & Prev. runs, as film - thinnest
Tue Oct 03 15:56:43 1995
Number of sample scans: 128
Number of background scans: 128
Resolution: 4.000
Sample gain: 1.0
Mirror velocity: 5.0632
Aperture: 32.00
Detector: MCT/B
Beamsplitter: KBr
Source: IR

Extracted HDPE,
THF-First Experiment

*HDPE from CAS bottoms resid Per. 30 CMSL-9, Expt. 4:
THF/decalin, 3M-52 Card
Tue Oct 03 10:11:49 1995
Number of sample scans: 128
Number of background scans: 128
Resolution: 4.000
Sample gain: 1.0
Mirror velocity: 5.0632
Aperture: 32.00
Detector: MCT/B
Beamsplitter: KBr
Source: IR

Extracted HDPE,
Decalin-First Experiment

*HDPE from CAS bottoms resid Per. 30 CMSL-9, Expt. 3:
decalin/THF, 3M-52 Card
Tue Oct 03 13:23:40 1995
Number of sample scans: 128
Number of background scans: 128
Resolution: 4.000
Sample gain: 1.0
Mirror velocity: 5.0632
Aperture: 32.00
Detector: MCT/B
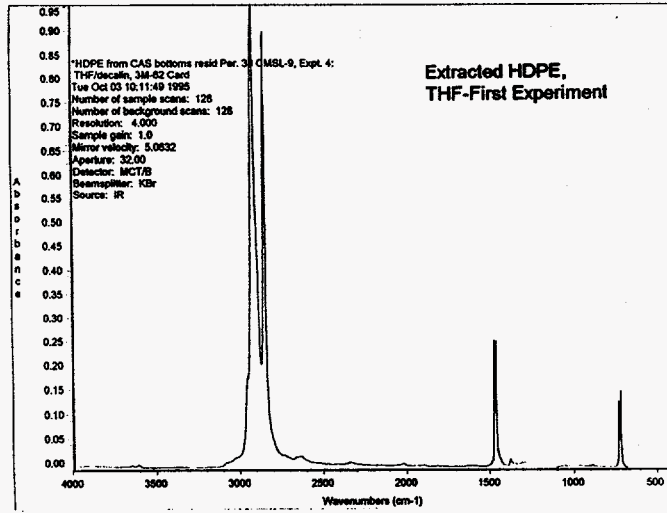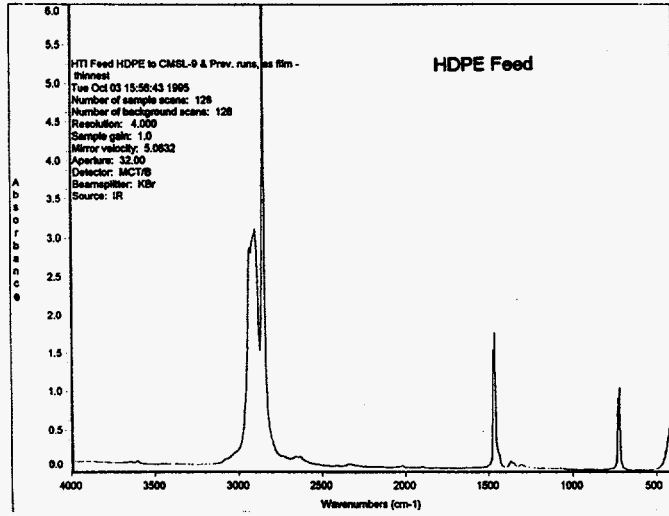Beamsplitter: KBr
Source: IR

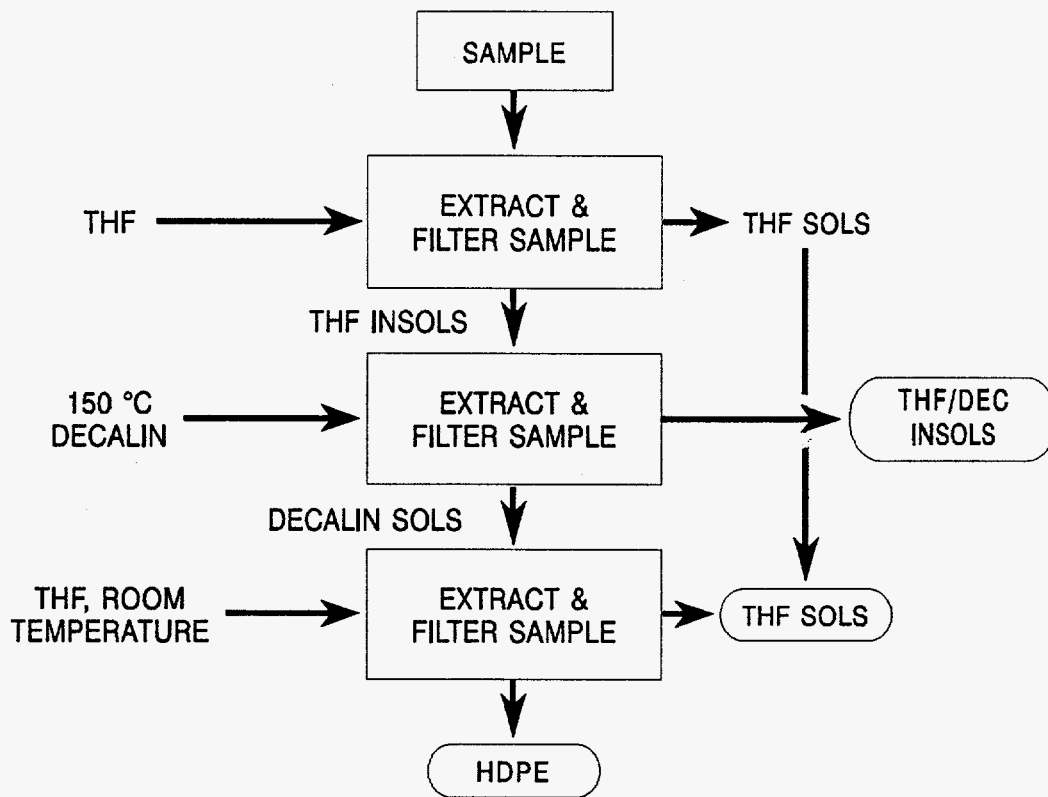Figure 1. FTIR Spectra of Feed HDPE and HDPE from Extraction Order Test.

Figure 2. Flow Chart of Hot Decalin Extraction Method to Recover HDPE
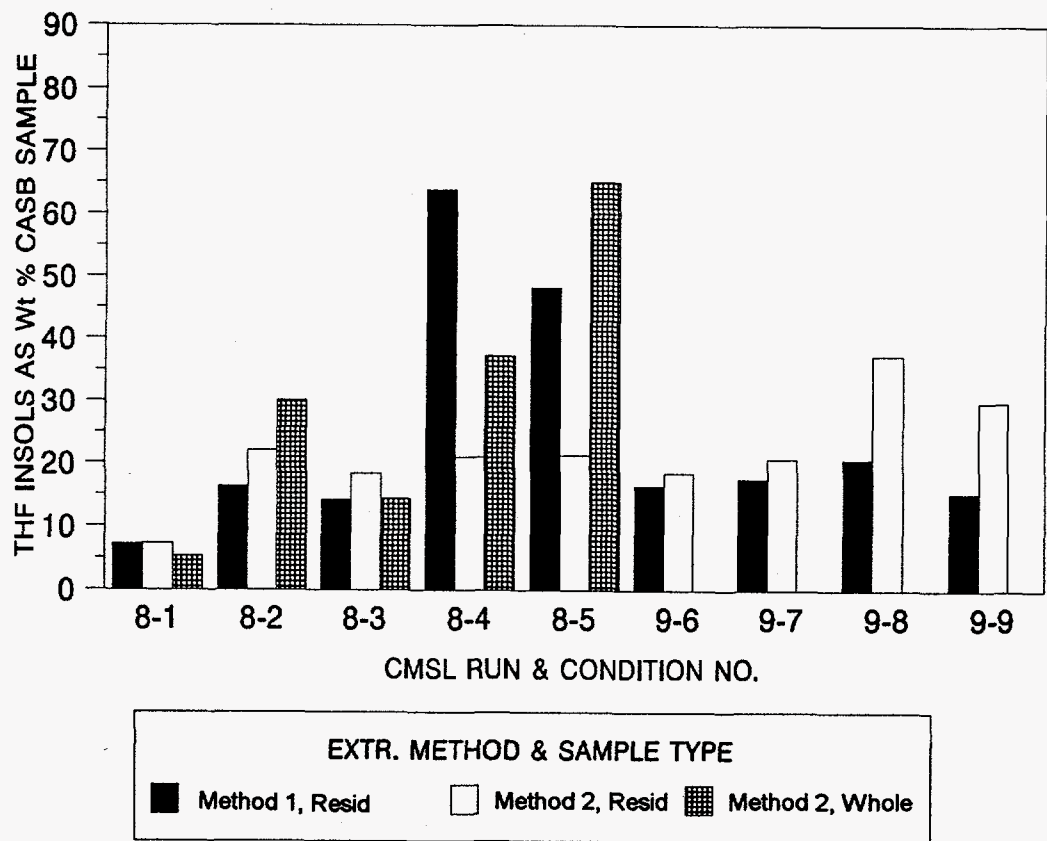from Coal/Plastics Co-Liquefaction Samples.

Figure 3. THF Insolubles Concentration in CAS Bottoms Samples from HTI Runs CMSL-8 and CMSL-9 as Measured by Two Extraction Procedures, Showing Poor Agreement.
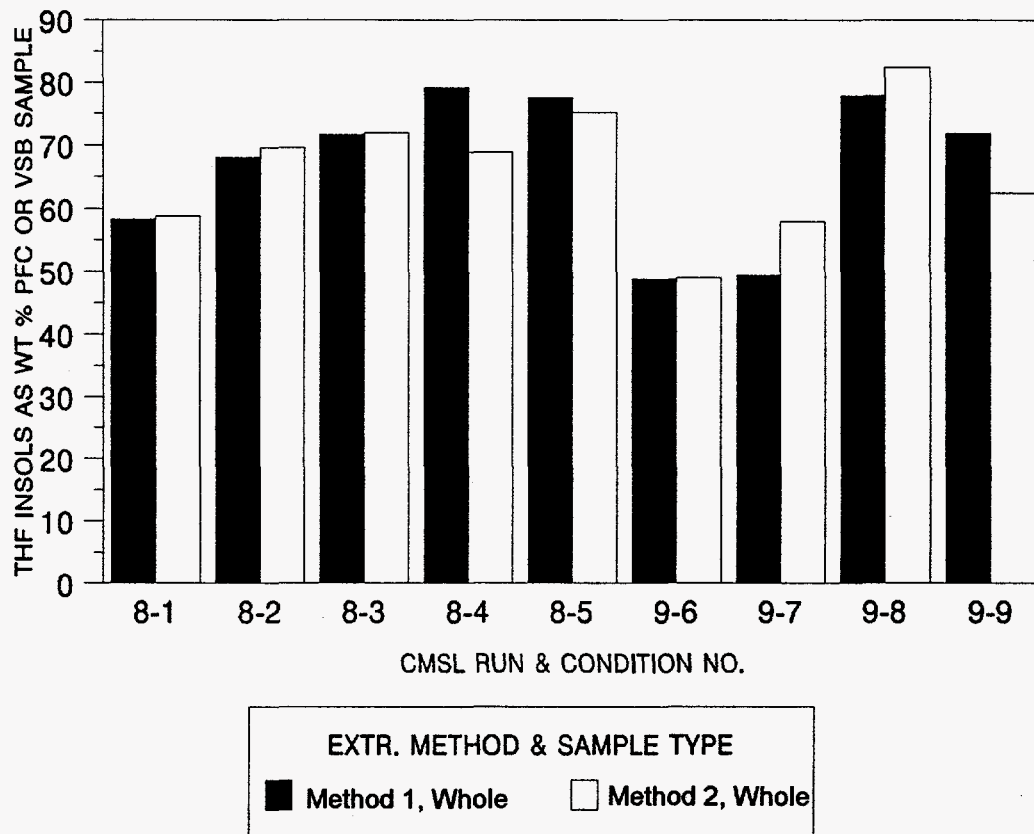
Figure 4. THF Insolubles Concentration in PFC and VSB Samples from HTI Runs CMSL-8 and CMSL-9 as Measured by Two Extraction Procedures, Showing Good Agreement.
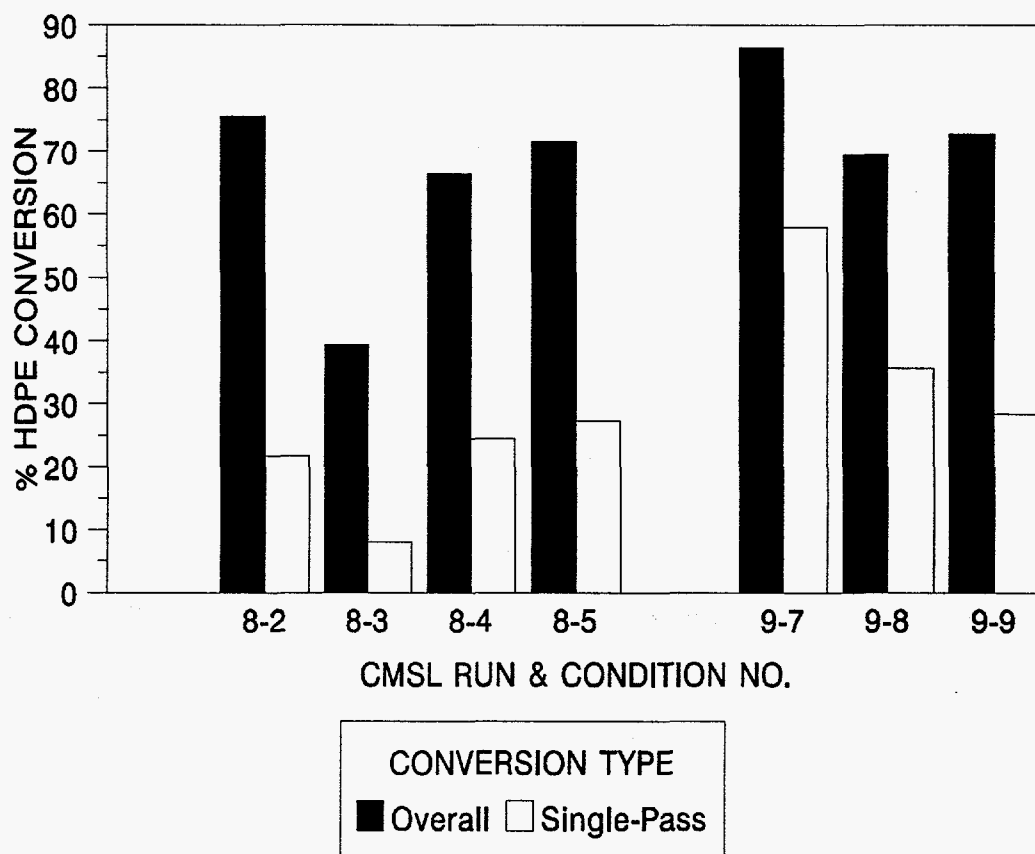
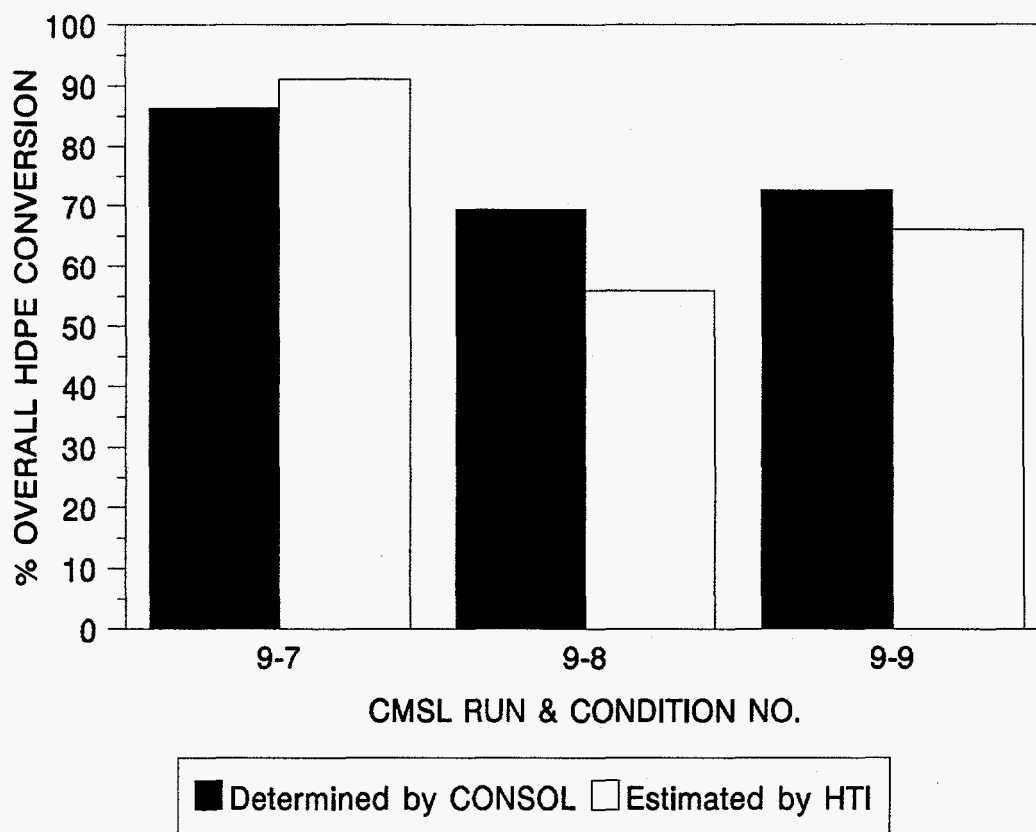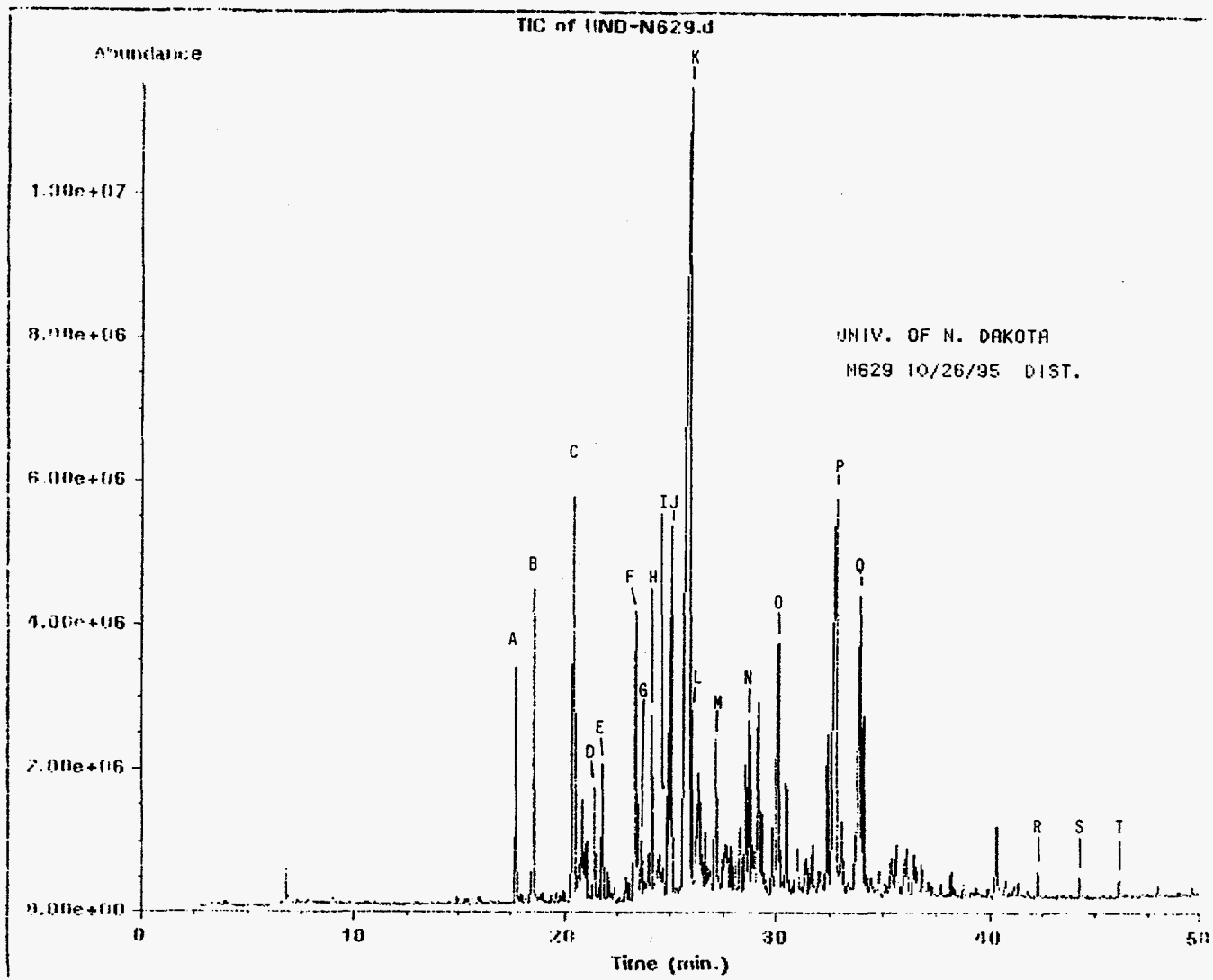Figure 5. Overall and Single-Pass Conversion of HDPE in HTI Runs CMSL-8 and CMSL-9.

Figure 6. A Comparison of CONSOL (Determined) and HTI (Estimated) Overall
Conversion of HDPE in HTI Run CMSL-9.

Key

A = acenaphthene
B = dibenzofuran
C = fluorene
D = methyldibenzofuran
E = methyldibenzofuran
F = dihydrophenanthrene
G = octahydrophenanthrene/anthracene
H = tetrahydrophenanthrene/anthracene
I = tetrahydrophenanthrene/anthracene
J = phenanthrene

K = phenanthrene
L = anthracene
M = carbazole
N = methylphenanthrene/anthracene
O = tetrahydrofluoranthene
P = fluoranthene
Q = pyrene
R = n-pentacosane
S = n-hexacosane
T = n-heptacosane

Figure 7. Gas Chromatography/Mass Spectrometry Chromatogram
University of North Dakota Liquefaction Oil.
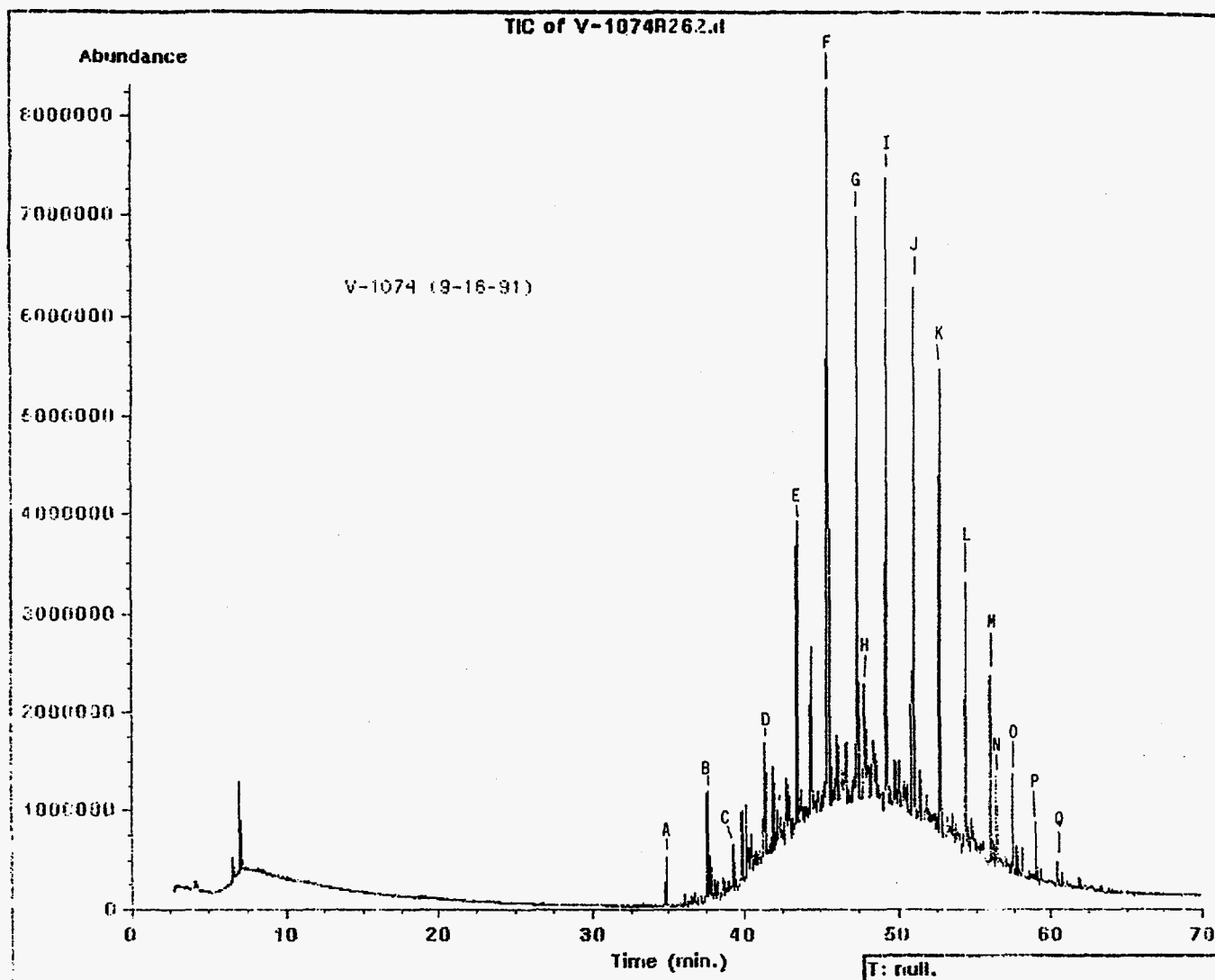
Key

A = pyrene
B = methylpyrene
C = n-C_{23}
D = n-C_{24}
E = n-C_{25}
F = n-C_{26}
G = n-C_{27}
H = C_2 - chrysene isomer
I = n-C_{28}

J = n-C_{29}
K = n-C_{30}
L = n-C_{31}
M = n-C_{32}
N = $C_{22}H_{12}$ isomer
O = n-C_{33}
P = n-C_{34}
Q = n-C_{35}

Figure 8. Gas Chromatography/Mass Spectrometry Chromatogram,
Wilsonville Subbituminous Coal Liquefaction Oil (Run 262G V-1074 Distillate).

APPENDIX 1

METHOD FOR EXTRACTION OF HDPE FROM COAL/PLASTICS CO-LIQUEFACTION SAMPLES USING HOT DECALIN

THF/DECALIN EXTRACTION OF ASHY LIQUEFACTION SAMPLES

By: D. L. Olson

PROCEDURE

1. Grind sample with a mortar and pestle and weigh approximately 5 g into a 250 mL beaker. (Obtain a tare weight for the empty beaker and record the weight of the sample.)

2. Add distilled THF and stir with a stir bar for approximately 5 min.

3. Filter this mixture over a 9 cm No. 42 Whatman filter paper in a pressurized filtration unit under nitrogen pressure into a 500 mL evaporation flask. (Obtain tare weights for the filter paper and flask.)

4. Extract with additional THF until the filtrate is light straw-colored, then rotary evaporate to dryness. Save the THF solubles for later use.

5. Collect the dried THF-insoluble filter cake by turning the filtration unit upside down on a piece of aluminum foil and removing the filter paper. Transfer the collected insolubles to an 80 mL beaker and reuse the filter paper, this time installing it on the heated filtration unit. Heat this unit to 150 °C.

6. Add decalin to the 80 mL beaker containing the collected THF insolubles, and gradually bring the mixture to 150 °C on a hot plate, while stirring with a glass rod from time to time. When the unit and the mixture are at temperature, add the hot mixture to the filtration unit, filter under ca. 7 psig nitrogen, and collect the filtrate in a tared beaker. Add more hot clean decalin (100 mL) to the unit and filter into the same beaker. Cool the filtrate to room temperature and refilter using a new tared filter paper, rinsing with distilled THF. Collect this filtrate into the evaporation flask containing the original THF-solubles. Rotary evaporate the THF-decalin filtrate to dryness and put the evaporation flask into a 60 °C vacuum oven under vacuum overnight and weigh.

7. Collect the filter-cake containing the plastics by removing the filter paper from the filter unit and place in a 60 °C vacuum oven overnight under vacuum. Weigh dried filter cake.

Recovery equals the sum of fraction weights of:

      THF/decalin-insoluble fraction, plus
      THF/decalin-soluble fraction, plus
      the recovered plastic filter cake fraction,
      divided by the initial sample weight.

APPENDIX 2

REQUEST FOR SAMPLES FROM HTI RUN PB-03

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

February 13, 1996

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 PB-03 is described below. We are requesting material in sufficient quantities to allow for sample distribution to other research groups, as needed. We understand that you cannot always provide the requested amounts, and we can work with smaller quantities.

We would like to receive from each run condition: 1) 250 g of separator overhead (SOH); 2) 250 g of atmospheric still overhead (ASOH) and any other hydrotreater feed stream which may be available; 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; and 6) 350 g of interstage sample (first-stage product). Please also include: 7) 350 g of the start-up/make-up oil from the beginning of the run; 8) 250 g samples of SOH and ASOH liquids from any bypass periods of the in-line hydrotreater; and 9) a fresh 300 g sample of the feed coal.

We have not yet received any of the plastic feedstocks used in Runs CMSL-11 and PB-01, or resid feedstock used in Run PB-01. We expect to receive samples from Run PB-02 in the near future. Also, we would like to obtain material balance data and reports on Runs CMSL-11, PB-01, and PB-02 (when available), and material balance data for Run CMSL-10.

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

Sincerely,

G. A. Robbins
Sr. Research Chemist

/ls

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

APPENDIX 3

REQUEST FOR SAMPLES FROM HTI RUN ALC-1

March 8, 1996

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

Dear Theo:

Our revised sample request for Run ALC-1 is described below. We have cut back amounts requested for internal streams to 50-150 g in order to minimize any impact of sampling on internal oil inventory. We are requesting much more distillate product, however.

We would like to receive from each run condition: (1) 2 gal of hydrotreated separator overhead (SOH) oil; (2) 250 g of separator overhead (SOH) water; (3) 50 g of atmospheric still overhead (ASOH); (4) 50 g of in-line hydrotreater feed; (5) 150 g of continuous atmospheric still (CAS) bottoms; (6) 150 g of interstage sample (first-stage product); (7) 200 g of feed slurry; (8) 150 g of pressure-filter liquid (PFL); (9) 150 g of pressure-filter cake (PFC); (10) 100 g of vacuum still overheads (VSOH); (11) 100 g of vacuum still bottoms (VSB). Please also include: (12) 350 g of wax produced in each run condition in which dewaxing is used; (13) 100 g of dewaxed VSOH produced in each run condition in which dewaxing is used; (14) 100 g of hydrotreated dewaxed VSOH produced in each run condition in which dewaxing and hydrotreating are used; and (15) 200 g of the 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). Note that whenever both pressure filtration and vacuum distillation are used, samples of products from both separation devices should be included.

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

Sincerely,

G. A. Robbins

/ls

cc: A. G. Comolli - HTI
        M. A. Nowak - PETC
        E. B. Klunder - PETC
        E. N. Givens - CAER
        M. Peluso - LDP Associates
        J. Miller - Sandia

APPENDIX 4

BACKGROUND ON UNIVERSITY OF NORTH DAKOTA LIQUEFACTION OIL

January 23, 1996

Mr. Richard Winschell
CONSOL, Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129-9566

Dear Mr. Winschell:

The sample sent to you earlier was produced during a "cascading" test scheme. Because of this, you may find a general test description of the multistep tests to be useful. The purpose of the research was to determine the recyclability of the solubilization solvent. The task consisted of 10 multistep, "cascading" tests. In the first test, Freedom mine lignite and a composite solubilization solvent (consisting of cresylic acid and certain fractions of hydrogenated coal-derived anthracene oil) were pretreated for 60 minutes at 150°C under 1000 psi (cold) CO in the presence of H_2S. The pretreated slurry was solubilized at 375°C under 1000 psi (cold) CO and H_2S for 60 minutes. The product of the solubilization step was polished with additional solvent at 430°C under approximately 1000 psi (cold) H_2 for 20 minutes. The polished product slurry was combined with a hydrogen-donor vehicle solvent. Water was removed and the organics distilled to separate solubilization solvent (equal to the amount added in the polishing step) and oxygenated light coal-derived liquids (CDLs). The bottoms from this step would have been hydrotreated, if this task had included hydrotreatment. The light CDLs and the solubilization solvent were recycled as the feed solvent for the pretreatment step of the next multistep test.

The sample sent to you was produced during the distillation of the eighth multistep test. The solubilization solvent had essentially been through the process seven times. During the eighth test, approximately 232 g of moisture- and ash-free Freedom lignite were slurried with 456 g recycle solvent. The slurry was cold-charged to the autoclave with CO and H_2S. The pretreatment was performed at 148°C and 1000 psig (cold) for 30 min. Solubilization was performed at 374°C and 1000 psig (cold) for 60 min. The product was recovered after the reaction was quenched. The material balance for the two integrated steps was 99.7%.

The solubilized slurry was then charged to a preheated autoclave containing 114 g recycle solvent and H_2. The average polishing conditions were 443°C and 3987 psig for 20 min. The reaction was quenched and the product recovered. An overall material balance of 98.9% was achieved for the polishing step.
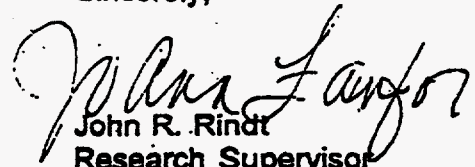
The polished slurry was combined with 51 g vehicle solvent and distilled. Water was removed from the organics and the distillation performed at the end-point conditions of 1.09 psig and 222°C pot temperature to separate the light oil fraction from the heavier fraction. The light oil fraction was recycled for use as the feed solvent for Multistep Test 9. The sample sent to Consol consists of the heavier fraction (i.e., hydrotreatment feed).

I hope that this description of the sample contains the information that you need. Should you have any questions, please feel free to call either John Rindt or Randy Sauer at (701) 777-3378.

Sincerely,

John R. Rindt
Research Supervisor
Advanced Technologies Group

JRR/jaf

APPENDIX 5

UNIVERSITY OF DELAWARE
MEETING REPORT

Trip Report: Meeting with University of Delaware Representatives

Date: March 25, 1996

Principal Contact: Dr. W. H. Calkins
                          Phone: (302) 831-2213

Attendees: University of Delaware
                          Bill Calkins
                          He Huang

                          CONSOL
                          Susan Brandes

Subject: Trip Report - Meeting with Dr. W. H. Calkins and Dr. He Huang (University
                          of Delaware) March 25, 1996, New Orleans, LA, Re: Subcontract with
                          University of Delaware Under DOE Contract DE-AC22-94PC93054

I met with Bill Calkins and He Huang to discuss progress and current status on the subject subcontract.

We clarified one point from the Delaware 10/16/95-1/15/96 Quarterly Report and one from the 1/16/96-2/15/96 monthly report. The value m_{lost} referred to in the quarterly report accounts for losses reported to Delaware by CONSOL for the samples CONSOL prepared and sent to Delaware. These losses arose from adherence of material to the microautoclave reactor walls; no solvent was used in the transfer of material from the reactor to sample vials. In the most recent monthly report, Delaware reported having difficulty in closing a material balance with these samples. They consistently obtain sample weights higher (0.1-0.6 g) than those which CONSOL reported to them. They have decided to use the CONSOL samples only to perfect analytical techniques and not for conversion calculations.

Delaware has decided to use cold CH_2Cl_2 rather than tetralin for the filtration of the STBR products.   .
He Huang said he can obtain a clean separation between the CH_2Cl_2 used for the filtration, the tetralin used as solvent for the reaction, and the coal products in the TGA.
The TGA work for analysis of the filter cakes is now being done in a cylindrical high-capacity (70-90 mg) TGA pan. He loads the pan usually half full and finds this to be working well.

I addressed the question of the work-up of the solid catalyst-containing products (catalyst: resid = 1:1) which Delaware had made a number of months ago. With these runs, they obtained 80% recovery of feed. Now that they have decided to use CH_2Cl_2 for filtration, they will filter these samples and use the solid filter cake to check their recoveries by using an ash balance. They will attempt to determine conversion to solubles just based on the filtrate. They intend to do this work soon.

Work was initiated on the 14 resid samples which comprise the set of samples that will be the basis for the kinetic model. They intend to do a time-temperature study with each resid looking for maximum conversion before moving on to the next resid. They will concentrate their efforts using Mo-naphthanate catalyst. They expect to report some data in the next monthly report. Depending on their findings with the supported catalyst samples, work may be done with supported catalyst and the 14 resid samples. However, a much lower catalyst:resid ratio will be used.

Concerning the long time it is taking to obtain a complete set of molecular weight measurements by VPO on the SARA fractions, Bill could only say that the equipment had to be moved a number of times during the building renovations, and that two part-time student workers were now responsible for generating the data. He will check with Darin Campbell and pass on my concerns about the long time it is taking and the possible degradation of the samples.

I discussed scheduling with Bill. The period of performance for the subcontract is 8/15/94-4/30/97. He does not know how long it will take the modeling group to complete their work once he turns over his results to them. We agreed that the last month of their contract would probably be taken up with preparing a final report and presenting the model in a reportable form. If the modeling group requires more than five months (11/1/96-3/31/97), Bill feels he will be pressed for time. Bill will discuss this issue with Mike Klein and Darin Campbell. Bill and He agree that the bottleneck in their work is instrument time on the TGA. They are considering leasing or renting another instrument to complete this project in a timely fashion. They, of course, would be interested in donation of a machine if one could be found. Bill is starting to investigate this possibility.

APPENDIX 6

UNIVERSITY OF DELAWARE QUARTERLY REPORT

April 30, 1996

Dr. F.P. Burke
Director, Applied Research
CONSOL, Inc.
4000 Brownsville Road
Library, PA 15129-9566

Dear Frank:

Attached is our Quarterly Report for the period 1/15/96 through 4/15/96 on subcontract DE-AC22-94PC93054. When you, Dick and Sue have had a chance to study it, we should have a conference call regarding the present status of the project and particularly concerning the use of the solid Shell catalyst and the methods of calculation of conversion to 850°F- material. We hope that we can agree on the catalyst system(s) to use and the procedure for the hydroprocessing all of the 15 resids we have on hand.

Sincerely,

Bill

W.H. Calkins
Research Professor

Enclosure
c.c. S.D.Brandes, CONSOL, Inc.
    D. Campbell, U.of D.
    He Huang, U.of D.
    M.T.Klein, U.of D.
    R.A.Winschell, CONSOL,Inc.
    Research Office, U.of D.
    M Yarnell, U.of D.

THE KINETICS OF COAL LIQUEFACTION DISTILLATION
RESID CONVERSION

QUARTERLY REPORT
1/15/96-4/15/96

Michael T. Klein
Principal Investigator

William H. Calkins
Co-Principal Investigator

He Huang
Research Associate

and

Shaojie Wang
Visiting Scientist

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

Date Published
April 30, 1996

EXECUTIVE SUMMARY

Hydroconversion experiments on two Wilsonville resids (258 and 259) using 3 wt % sulfided molybdenum naphthenate catalyst at 410 °C showed 36 to 38 % conversion in 30 minutes to material boiling below 850°F. This can be compared to uncatalyzed hydroconversion of the same materials of 18 - 19 wt % under the same conditions. Previous work using a different work up procedure showed that 0.9 wt % sulfided molybdenum naphthenate at the same times and temperature showed only a slight increase in conversion over the uncatalyzed system.

Hydroconversion experiments using Shell Ni/Mo catalyst are still indeterminate pending solution of the method of conversion determination. Reduced concentrations of the Shell catalyst (20 wt%) were tried where the ash contributed by the catalyst was smaller and should increase the total recovery from the reactor. However, we have experienced difficulties in obtaining representative sampling of the reactant mixtures which is the basis for calculating conversion. This is being explored experimentatlly. We are also running hydroconversion experiments with the Shell catalyst (20 wt %) where the reaction mixture is totally recovered by subsequent solvent washes to better understand the sampling process.

The molecular modelling work is proceeding satisfactorily and the algorithm for the resid structure is in place. Necessary analytical work on the VPO molecular weights is being expedited.

QUARTERLY REPORT

Work up Procedure for Hydroprocessing Experiments

Up until recently, resids hydroprocessed in the SCTBR reactor have been worked up by filtering the products into two components: a solid filter cake and a liquid filtrate. The filter cake was washed with cold tetralin and then dried in a vacuum oven. Little material was removed in the tetralin wash, but considerable tetralin remained with the filter cake. Cold tetralin was used for washing the filter cake in order not to remove hydrocracked products or mineral matter. We had had indications from previous work that methylene chloride may remove some mineral matter from the filter cake, thereby interfering with the use of the ash tracer method to follow the conversion of the resids.

Further and more recent experiments have now shown that mineral matter present in the resids we have tested is not extracted by methylene chloride. This has prompted us to change the work up procedure. We now filter the reaction products into a filter cake and filtrate as before. The filter cake is then washed with cold methylene chloride. The methylene chloride is then distilled out of the filtrate at low temperature (below 45°C), thereby effecting removal of the methylene chloride rapidly and easily. The methylene chloride distilled out is quite pure as shown by gas chromatography with only traces of tetralin (about 0.5 wt%)(see Table 1). The methylene chloride remaining in the filtrate amounts to about 0.5 wt % (see also Table 1). The filtrate, which consists of tetralin and cracking products of the resid, and the filter cake are each subjected to our SimDis TG methods to determine the amount of material that is volatile below 850°F. The tetralin remaining in the filtrate is determined by gas chromatography. We are now in the process of hydroprocessing the 15 coal derived resids from CONSOL,Inc using sulfided molybdenum naphthenate catalyst and working them up by the above procedure.

Calculation of conversion to 850°F- products was described in the previous quarterly report. Reactor runs performed using this new work up procedure are shown in Table 2.

Hydroconversion of Resid Without Catalyst and Using Sulfided Molybdenum Naphthenate Catalyst.

Table 3 shows results of hydroconversion of Resids 258 and 259 without catalyst and with 3 wt % sulfided molybdenum naphthenate catalyst to 850°F- product for 30 minutes at 410°F. Previous work had shown that with 0.9 wt % molybdenum as sulfided molybdenum naphthenate under the same conditions, only barely measurable changes in conversion of the resid to lower boiling material occurred compared to uncatalyzed resid. After trying a range of naphthenate concentrations up to 5 wt %, we selected 3 wt % as a reasonable compromise between practical economics and measurable results (see Table 3). We conclude from this work, that these resids are very refractory and hydroconversion of them is difficult, requiring high concentrations of catalyst. Further work will be needed to confirm this observation, and

2

to indicate whether all the resid samples we plan to study are so refractory.

Hydroconversion of Resid Using the Solid Shell Ni/Mo Catalyst

Since we have not yet found a satisfactory way to determine resid conversion when hydroconversion is done using large amounts of Shell Ni/Mo catalyst, we ran some hydroconversion runs using only 20 wt % Shell catalyst. These runs went satisfactorily in terms of material recovery (over 80 %). However, to determine conversion we had to find a basis for determining the residual ash contributed by the Shell catalyst itself.

To establish a control run with Shell catalyst, a number of experiments were tried. Catalyst alone run in the TGA showed a large amount of weight loss with several different weight loss processes occurring depending on the time and temperature (see Figure 1). Shell catalyst was also exposed to tetralin at room temperature and at 410 °C and the TGA determined on the methylene chloride washed catalyst residue (see Figure 2). It became obvious from these experiments that the catalyst was undergoing considerable changes during the hydroconversion process. We were reluctant to base our calculations on corrected ash figures from these results as they appear to be changing during the run.

The conversion results using 20 wt% of the Shell catalyst did not appear to be reasonable. There may be a question of representative sampling of the catalyst from the reactor. This was supported by an experiment where we prepared a mixture of Shell catalyst and resid and put it through the reactor at room temperature. The TGA results on the recovered product did not correspond to the expected ash values. We are now running hydroconversion runs in the SCTBR with 20 wt % Shell catalyzed resid where we are recovering essentially all of the reaction product by solvent wash at the end of a run and will compare those results with the ones described above. This work is still in progress.

Modeling

An algorithm for the construction of a resid structure is now in place. Carbon, hydrogen and sulfur atoms are included and the incorporation of nitrogen and oxygen is being investigated. Structure tests will begin shortly when vapor phase osmometer (VPO) results for the preasphaltene fraction becomes available. Each molecule is considered to be a juxtaposition of attributes (e.g. number of aromatic rings, number of naphthenic rings, etc.) and the attribute values are associated with probability density functions (pdf's). The pdf is a function that provides the quantitative probability of finding the value (or less) of a given attribute. By stochastically sampling these pdf's a representation of approximately 10,000 molecules can be constructed which accurately represents a selected resid.

Once the molecular weights of the preasphaltene fractions have been determined, the pdf values will be optimized for each resid. The optimization varies the pdf parameters so that the

3

representative resid matches as closely as possible the key analytical properties experimentally determined for a selected resid.

The information contained within the pdf's allow the construction of a reaction model by solving a set of material balance ordinary differential equations (ODE's). These ODE's are the mass balances of the reactive attributes (e.g. alkyl side chains) and can be solved quickly (1 CPU second). At any desired reaction time, a molecular representation can be constructed for comparison with analytical properties to experimental results of an actual reaction mixture. Currently this reaction model is being updated to include heteroatom attributes.

To date, molecular weights (VPO's) have been determined for each of the aromatic fractions and several of the saturate, resin and asphaltene fractions. Dichlorobenzene has been used as solvent for the aromatics, resins, and asphaltene fractions and toluene is used for the saturate fractions. Tetrahydrofuran (THF) is used for the preasphaltene fractions, and the osmometer is being conditioned for this solvent. Since only about a little over a third of these measurements are finished, the time of the part time technician assigned to the VPO measurements is being increased. Other methods using SimDis and density measurements are also being investigated for molecular weight determination of the lighter fractions (saturates, aromatics and resins) in an effort to accelerate these measurements. The VPO results obtained to date are shown in Table 4.

Table 1 Tetralin concentrations in the distilled methylene chloride and methylene chloride concentrations in the resid filtrate

Sample	Tetralin, wt%	CH2Cl2, wt%
	in distillate	in liquid filtrate
C079	0.48%	0.67%
C080	0.45%	0.59%
C081	0.54%	0.39%
C082	0.26%	0.61%
C084	0.61%	0.56%
C085	0.42%	0.49%
C086	0.53%	0.35%
C087	0.58%	0.58%
C088	0.40%	0.41%
C089	0.51%	0.52%
C090	0.32%	0.52%

Table 2 Reactor runs of the resid hydroconversion in tetralin (1500 psig H2)

Run	Resid	T C	time min	Catalyst type	Catalyst loading	SA* g
C078	258	415	30	None	None	None
C079	258	417	30	None	None	None
C080	258	415	30	None	None	None
C081	258	413	30	Mo-naph	3.0 wt%	3
C082	258	413	30	Mo-naph	3.0 wt%	3
C083	258	410	30	Mo-naph	3.0 wt%	3
C084	259	400	30	None	None	None
C085	259	407	30	None	None	None
C086	259	405	30	Mo-naph	3.0 wt%	3
C087	259	408	30	Mo-naph	3.0 wt%	3
C088	258	412	30	Ni/Mo Shell	20 wt%	None
C089	258	408	30	Ni/Mo Shell	20 wt%	None
C090	258	411	30	Ni/Mo Shell	20 wt%	None
C091	258	21	30	None	None	None
C092	258	21	30	Ni/Mo Shell	20 wt%	None
C093	None	411	30	Ni/Mo Shell	100 wt%	None

*SA: sulfiding agent - methyl disulfide

Table 3 Hydroconversion of resids

Sample	Soluble Fraction wt%	850 F+ in liquid	Tetralin in liquid determined by GC	Conversion wt%
C079	65.2%	10.3%	85.6%	18.5%
C080	65.9%	9.4%	86.8%	19.0%
C081	67.8%	10.9%	76.7%	36.0%
C082	68.0%	9.7%	77.9%	38.0%
C083	67.9%	10.0%	78.1%	36.9%
C084	72.1%	10.0%	88.4%	9.9%
C085	70.6%	10.6%	87.4%	11.1%
C086	81.4%	13.1%	78.3%	32.4%
C087	80.8%	13.1%	75.8%	37.1%

Table 4 VPO results

Sample Number	Saturate MW	Aromatic M W	Resin MW	Asphaltene M W	Pre-Asphaltene M W
1	288	320	676	1620	
2	270	274	613	1533	
3	295	319	568	1472	
4	305	362	718	1736	
5	443	493	789	1827	
6	347	420			
7		348			
8		425			
9		323			
10		430			
11		386			
12		413			
13		336			
14		356			
15		345		-	

Figure 1

Sample: Shell Catalyst
Size: 87.3380 mg
Method: Resid Processing, Solid
Comment: 10 °C/min to 600 °C, gas 2, 100°/min to 850 °C

TGA

File: C: SHELLCAT.001
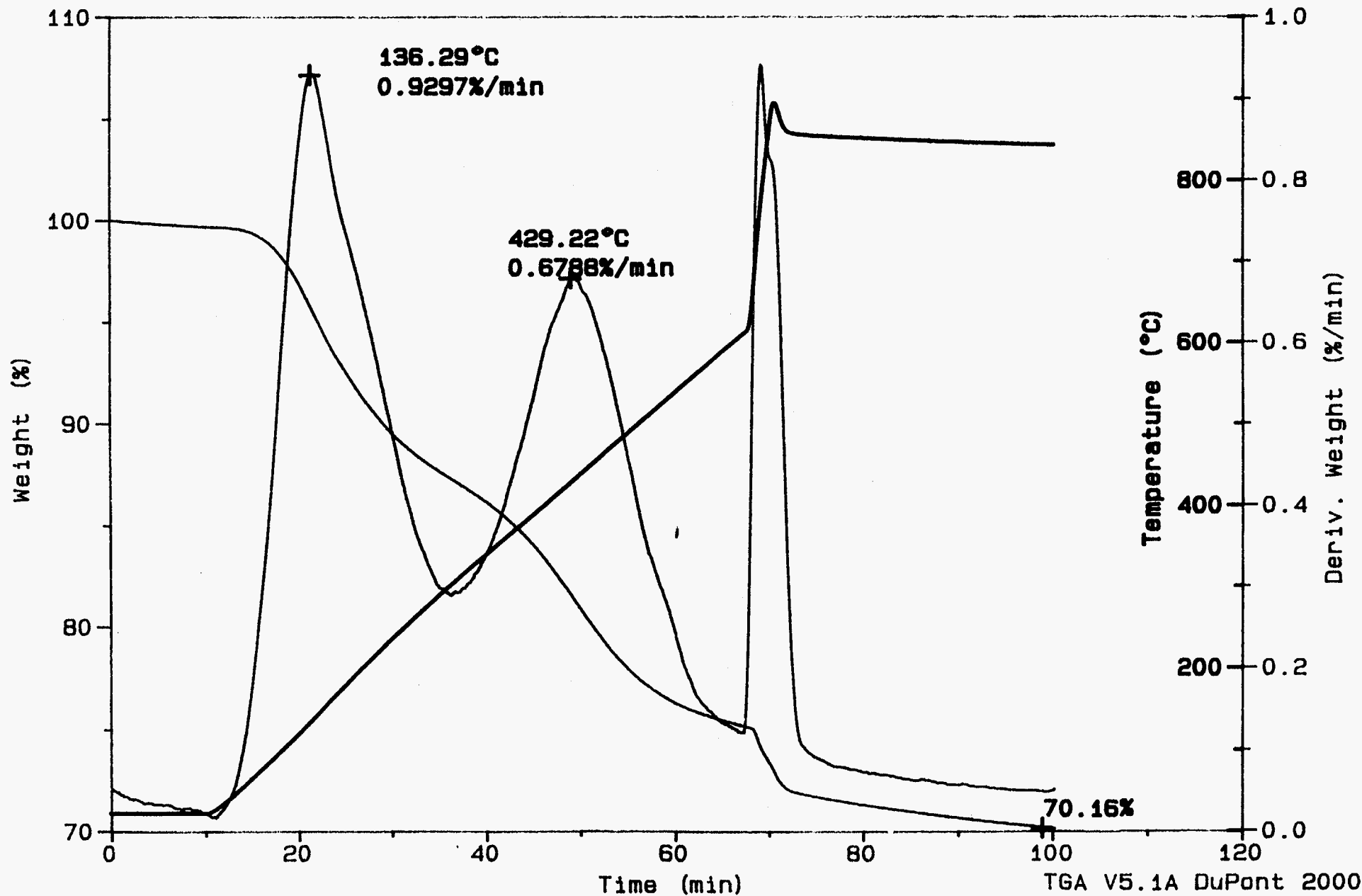Operator: Keyu Wang
Run Date: 27-Apr-96 03: 44

136.29°C
0.9297%/min

429.22°C
0.6788%/min

70.16%

TGA V5.1A DuPont 2000
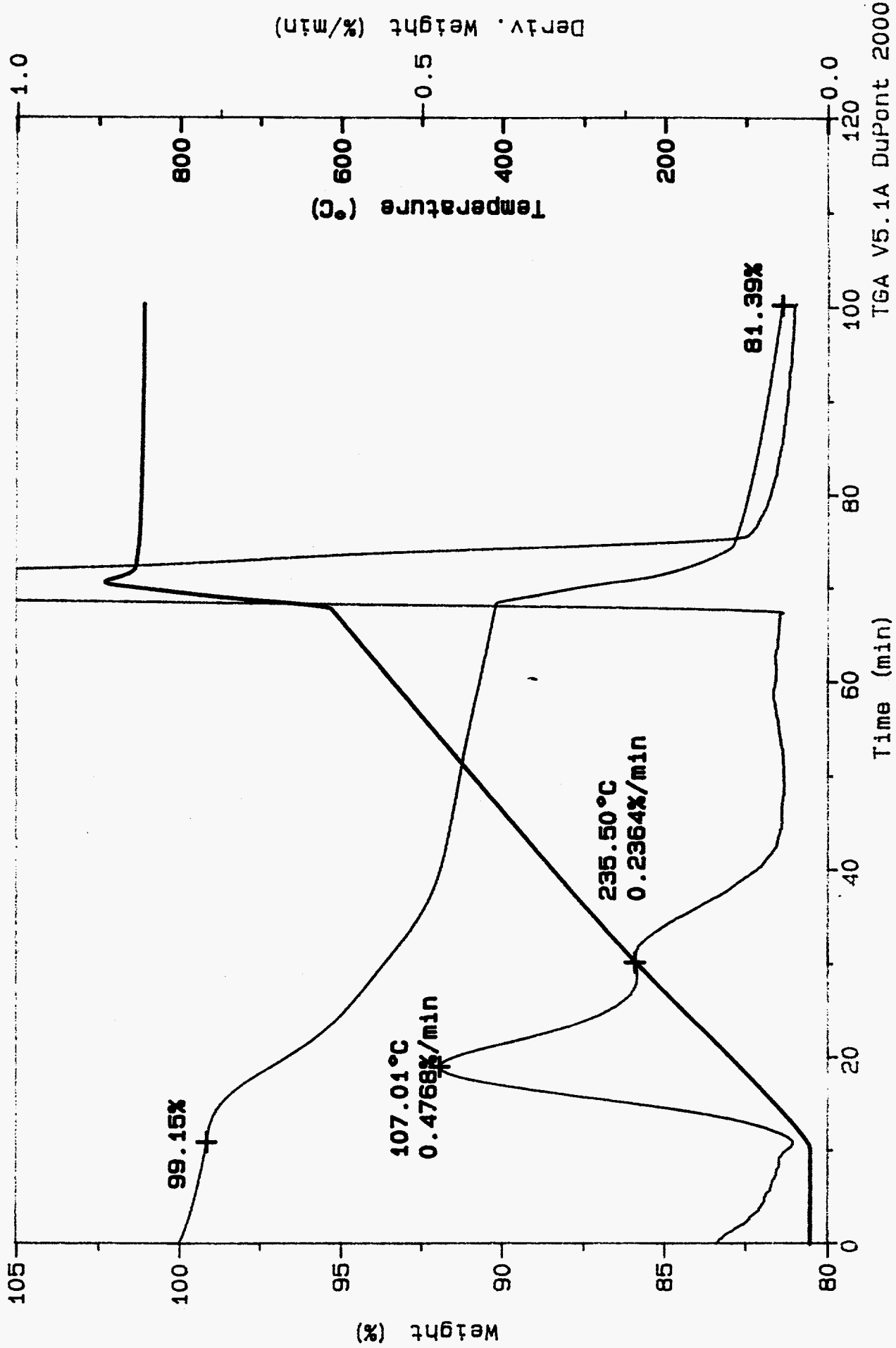
Figure 2

TGA

Sample: CO93S
Size: 65.5430 mg
Method: Resid Processing, Solid
Comment: 10 °C/min to 600 °C, Gas 2, 100 °C/min to 850 °C

File: C:CO93S.001
Operator: Keyu Wang
Run Date: 30-Apr-96 00:56

99.15%

107.01°C
0.4768%/min

235.50°C
0.2364%/min

81.39%

Weight (%)

Temperature (°C)

Deriv. Weight (%/min)

Time (min)

TGA V5.1A DuPont 2000

APPENDIX 7

UNIVERSITY OF DELAWARE PAPERS

**(Presented at the 211th National Meeting of the American Chemical Society,
March 24-28, 1996, New Orleans, LA)**

Papers removed for separate copling

Huang, H.;Wang, K.; Wang, S.; Klein, M. T.; Calkins, W. H. "Distillation of Liquid Fuels by Thermogravimetry"

Wang, K; Wang, S.; Huang, H; Klein, M. T.; Calkins, W. H. "A Novel Smoothing Routine for the Data Processing in Thermogravimetric Analysis.

Huang, H.; Wang, K.; Wang, S.; Klein, M. T.; Calkins, W. H. "Applications of the Thermogravimetric Analysis in the Study of Fossil Fuels"