DE-AC22-94PC93054--11

A Characterization and Evaluation of Coal Liquefaction Process Streams

Quarterly Report
January 1 - March 31, 1997

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Work Performed Under Contract No.: DE-AC22-94PC93054

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ABSTRACT

This is the Technical Progress Report for the eleventh quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period January 1 through March 31, 1997. Described in this report are the following activities:

- CONSOL characterized process stream samples from HTI Run ALC-2, in which Black Thunder Mine coal was liquefied using four combinations of dispersed catalyst precursors. These results are described in the Results and Discussion section of this report.

- Oil assays were completed on the HTI Run PB-05 product blend. Background information is presented in the Results and Discussion section of this report. The results are presented in Appendix 1.

- Fractional distillation of the net product oil of HTI Run POC-1 was completed. Background information is presented in the Results and Discussion section of this report. The results are presented in Appendix 2.

- CONSOL completed an evaluation of the potential for producing alkylphenyl ethers from coal liquefaction phenols. Those results are described briefly in the Results and Discussion section of this report. The full report is presented in Appendix 3.

- At the request of DOE, various coal liquid samples and relevant characterization data were supplied to the University of West Virginia and the Federal Energy Technology Center. These activities are described in Appendix 4.

- The University of Delaware is conducting resid reactivity tests and is completing the resid reaction computer model. A summary of Delaware's progress is provided in the Results and Discussion section.

- The University of Delaware was instructed on the form in which the computer model is to be delivered to CONSOL (Appendix 5).

- The University of Delaware submitted a paper on the resid reactivity work for presentation at the 213th National Meeting of the American Chemical Society, April 13-17, 1997 in San Francisco, California. The paper, "Kinetics of Hydroprocessing of Coal-Derived Vacuum Resids", is appended (Appendix 6).

TABLE OF CONTENTS

This page to be completed following DOE review

LIST OF APPENDICES

Section 1
EXECUTIVE SUMMARY

CHARACTERIZATION OF SAMPLES FROM HTI RUN ALC-2

CONSOL characterized process stream samples from HTI Run ALC-2, in which Black Thunder Mine coal was liquefied using four combinations of dispersed catalyst precursors. The major conclusions from CONSOL's analyses of samples from HTI Run ALC-2 follow.

- Oil properties were nearly constant for the four run conditions. This consistency implies stability in the operation of the new distillation system and suggests that there was little difference in performance of the four catalyst systems tested.

- Coal and oil properties provided no insight into the reasons for solids separation problems with toluene extraction and pressure filtration observed during the run.

- Solids rejected during the first condition had high Ni concentrations, the origin of which (analytical artifact or trace contamination) is unknown.

- Most toluene-extracted solids (TES) and toluene-extracted oil (TEO) samples contained more than a few percent toluene, as received by CONSOL. CONSOL characterization confirmed generally poor extraction in the early part of the run. However, extraction appeared to be moderately successful in periods 3, 9, 12, and 13.

- The tetrahydrofuran (THF)-soluble fraction of the continuous vacuum still bottoms (CVSB) sample from Condition 4, period 21, was analyzed to determine if Ni or Mo was present in oil-soluble form. The occurrence of Ni and Mo in the THF-solubles is coincident with the occurrence of a trace amount of ash; thus, the Ni and Mo are not believed to be organically associated.

- The first-stage separator overhead (SOH1) oils and reduced-pressure still overhead (RPSOH) oils had very high concentrations (perhaps 25%) of phenolics. They are potential sources of phenolic chemical feedstocks.

- The properties of the hydrotreated product oils showed that the in-line hydrotreater (HTU) was effective for removal of phenolics and most of the aromatics.

- There appeared to be a recent change, relative to characteristics observed over the past three years, in the characteristics of HTI's L-814 oil used for run start-up and slurry oil make-up.

CRUDE OIL ASSAY OF NET PRODUCTS OF HTI RUN PB-05

At DOE's request, CONSOL arranged a crude oil assay on the net products of HTI Run PB-05 (also known as Run 227-97). The crude oil assay was conducted by Inchcape (now Intertek) Testing Services Caleb Brett Laboratory (Houston, TX) on the net products obtained during operating condition 6 of Run PB-05, in which Hondo resid was coprocessed with Illinois 6 coal. The sample was obtained when the on-line hydrotreater was by-passed.

FRACTIONAL DISTILLATION OF NET PRODUCTS OF HRI RUN POC-1

Inconsistencies in distillation data generated by Conoco and Southwest Research Institute in 1995 on HTI net product oils prompted DOE to request additional tests. CONSOL provided a one-gallon sample of HTI Run POC-1 net product oil to Intertek Testing Services Caleb Brett Laboratory (Houston, TX) for fractional distillation. The results are presented in this report.

PREPARATION OF ALKYL ARYL ETHERS FROM COAL-DERIVED PHENOLS

CONSOL evaluated reactions to synthesize alkyl phenyl ethers from coal liquefaction phenols. The program included a literature review and laboratory chemical syntheses. An extensive literature search identified the Williamson Synthesis and its modifications as the preferred methods to produce mixed ethers from phenols. A variation of the Williamson Synthesis was used to produce phenetole and the ethyl derivatives of the phenolics from a caustic extract of a crude direct coal liquefaction product. Other approaches involving acid catalysts failed to produce ethers. It is recommended that the ethyl ether derivatives of coal liquefaction phenols be synthesized and characterized as a diesel fuel extender. CONSOL will develop a plan to extract phenols, synthesize the ethers and coordinate the fuel characterization upon DOE's approval.

RESID REACTIVITY

The University of Delaware completed a parametric study with two resid samples. Temperature, pressure, residence time, catalyst loading, and resid concentration were explored. Conversion leveled off with time indicating the presence of a non-convertible component. This component was isolated by successive solvent-solubility extractions and subjected to hydrotreating. Conversion of the isolated material to 454 °C$^-$ (850°F$^-$) material was only ca. 1 wt %.

The structural molecular model was completed. The computer-generated molecular representations were found to match well the experimental data. The reaction model was assembled for catalytic upgrading of coal resids and is undergoing refinement.

TECHNICAL TRANSFER

The University of Delaware submitted a paper on the resid reactivity work for presentation at the 213th National Meeting of the American Chemical Society, April 13-17, 1997, in San Francisco, CA. The paper, "Kinetics of Hydroprocessing of Coal-Derived Vacuum Resids", is appended.

Section 2
INTRODUCTION

This is the Technical Progress Report for the eleventh quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period January 1 through March 31, 1997.

CONTRACT OVERVIEW

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

CONTRACT ACTIVITIES THIS PERIOD

- CONSOL characterized process stream samples from HTI Run ALC-2, in which Black Thunder Mine coal was liquefied using four combinations of dispersed catalyst precursors. The results are described in the Results and Discussion section of this report.

- Oil assays were completed on the HTI Run PB-05 product blend. Background information is presented in the Results and Discussion section of this report. The results are presented in Appendix 1.

- Fractional distillation of the net product oil of HTI Run POC-1 was completed. Background information is presented in the Results and Discussion section of this report. The results are presented in Appendix 2.

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ACTIVITIES IN PROGRESS

- Characterization work is under way on samples from HTI Run PB-04 and work was begun on samples from PB-06.

- The development of a kinetic/mechanistic model of resid reactivity is continuing.

Section 3

RESULTS AND DISCUSSION

CHARACTERIZATION OF SAMPLES FROM HTI RUN ALC-2

RUN BACKGROUND

In HTI Run ALC-2 (Run 227-100),[1,2] the liquefaction performance of Black Thunder Mine coal was tested with four combinations of impregnated (dispersed) catalyst precursors. A new distillation system and solids separation scheme was employed during the run. Run ALC-2 consisted of 21 operating periods at four conditions. The run was carried out from November 24 through December 23, 1996. The run was planned to be made under six conditions; however, several problems occurred early in the run that decreased the number of conditions and catalysts that could be tested to four. Run conditions and yields for Run ALC-2 are provided in Table 1.[1,2] The major variable was the catalyst system used. This included differences in the active metals and molybdenum precursors used. The water-soluble catalyst precursors were impregnated on the feed coal. Sulfiding agents for the catalysts were H_2S fed to the preheater/first-stage reactor at a rate of 2% of the MF coal, and di-tertiary-nonyl polysulfide (TNPS containing 37% S) fed to the second-stage reactor at a rate equivalent to an H_2S rate of 0.5% of the MF coal. Other components in the configuration used were a coil pretreater/preheater, two forced-back mixed liquefaction reactors with an interstage vapor/slurry separator, and a direct-coupled (in-line) product hydrotreater (HTU) of increased capacity. The total recycle to MF coal ratio was approximately 1.67 (ca. 37% coal concentration). The target recycle solids to MF coal ratio was 0.20. During the run, the actual solids recycle ratio was variable, and averaged a higher value of about 0.30 for the work-up periods. To provide ash recycle, the bulk of the continuous vacuum still bottoms (CVSB) produced was recycled directly; only a fraction of the material was sent to solids separation to reject solids from the process.

HTI's results indicated that the ash balance was not good in any of the run conditions. As a result, it was concluded that operations were not at steady-state when the samples were taken and when the material balance work-ups were performed. This places uncertainty on the catalyst comparisons that are based on the run performance data. HTI reported, however, that the Mo and Ni catalyst combination provided the best overall results. They also found that catalyst choice had no effect on coal conversion and that the Mo/Ni combination seemed to provide the best resid conversion. HTI found no apparent detriment to elimination of Fe catalyst from the subbituminous coal liquefaction system. The distillation system gave satisfactory performance,

but numerous problems were encountered with solids separation. Relative to results from Condition 1 of Run ALC-1, the MAF C_4-524 °C yield in Run ALC-2 was lower by about 10% (due to about 6% lower resid conversion and 4% higher C_1-C_3 gas yields). The hydrogen consumption was also about 0.4% lower in Run ALC-2. It was thought that the high gas yields in Run ALC-2 may have been due to recycle of reduced pressure still overheads (RPSOH), an oil stream that is much lower-boiling than is desired for recycle. It became necessary to recycle RPSOH material when the preferred materials were not available.

The catalysts and active metal concentrations tested (reported on an MF coal basis) were: Condition 1 - ammonium heptamolybdate (AHM) plus ferrous sulfate (100 mg/kg as Mo, 1610 mg/kg as Fe), Condition 2 - AHM (110 mg/kg as Mo), Condition 3 - AHM plus nickel sulfate (92 mg/kg as Mo, 51 mg/kg as Ni), and Condition 4 - phosphomolybdic acid (PMA, 116 mg/kg as Mo, 3 mg/kg as P), respectively. The distillation system consisted of a continuous vacuum still (CVS) and a reduced-pressure still (RPS). Because it can be operated with a slight vacuum, it is called a "reduced pressure still". The CVS provides a vacuum gas oil at an adjustable cut point (427 °C was the cut point from Period 7 on during Run ALC-2). The RPS provides a net product distillate with a cut point that can be adjusted to higher than 343 °C. In Run ALC-2, the RPS was operated at a cut point of 316 °C (from period 7 on) to give a distillate that was predominantly 343 °C$^-$. The increase in direct-coupled hydrotreater volume from 500 cm^3 used in Run ALC-1 to 800 cm^3 in Run ALC-2 provided highly effective product hydrotreating. Nitrogen concentrations of about 40 mg/kg or less, and sulfur concentrations of about 60 mg/kg or less were obtained. The solids separation scheme was designed to avoid pressure filtration bottlenecks by using toluene extraction to recover resid and oil directly from CVS bottoms (CVSB) material. However, toluene extraction performed poorly with this material. In Condition 3, pressure filtration was used for a few days until the erratic filtration performance became unmanageable. The solids separation method was changed near the end of Condition 3 to batch vacuum distillation at 524 °C atmospheric equivalent endpoint, without toluene extraction. Solids separation was continued in this manner until the end of the run.

BRIEF DESCRIPTION OF PLANT

The run was performed in HTI's bench unit 227. Fresh feed coal was mixed batchwise with process recycle materials in a tank and transferred to a feed slurry tank that continuously fed the slurry to the liquefaction process. The feed slurry was fed to a preheater, which also conditioned the dispersed catalyst. Next, the slurry was fed to two successive stages of liquefaction. No

supported catalysts were used in the liquefaction reactors; only disposable dispersed catalysts were used. A high-pressure separator after the first reactor allows light products to be taken off and the hydrogen concentration to be increased in the second reactor. The first-stage oil, called the first-stage separator overhead oil (designated here as SOH1), is sent with second-stage light oils and light distillate to an in-line fixed-bed hydrotreater. The in-line hydrotreater (or HTU) upgrades the product using the liquefaction reactor system off gases. The second stage of liquefaction is followed by high- and low-pressure separators. The separator overheads are fed to the in-line product hydrotreater, and the separator bottoms to distillation. The distillate (ca. IBP-371 °C) is sent to the product hydrotreater, and the resid is extracted (i.e., toluene-washed) to provide a liquid for recycle and solids to reject ash. The hydrotreated product oil is called the second-stage separator overhead oil (designated here as SOH2).

Thirty-two oil samples and four feed coal samples were received from HTI for characterization. Major streams analyzed included the feed coal, the L-814 start-up oil, the unhydrotreated first-stage separator overhead (SOH1) oil, the separator bottoms (O-6 bottoms, the flashed liquefaction product), the continuous vacuum still bottoms (CVSB), the reduced-pressure still overheads (RPSOH), the reduced-pressure still bottoms (RPSB), the toluene-extracted solids (TES), the toluene-extracted oil (TEO), and the hydrotreated net product oil (SOH2).

ANALYTICAL STRATEGY

In the analytical work performed by CONSOL, an attempt was made to address the following questions:

- What caused the problems encountered in toluene extraction and pressure filtration during the run?

- What can be learned about changes in catalyst concentration on startup?

- What do sample characteristics say about :
  - Catalyst performance differences?
  - Equipment performance (e.g., distillation system)?

In order to address these questions, the characterization work was focused primarily on the feed coal, O-6 bottoms, CVSB, TES, and TEO stream samples, and on product distillate features and

differences. Specifically investigated were the treated coal characteristics, the preasphaltenes content and characteristics of the CVSB resid, and the catalyst metals in the TES samples from the first condition.

ANALYSIS OF FEED COALS

Ten-pound samples were obtained of each of the four catalyst-treated Black Thunder coals used in Run ALC-2 (L-902, L-904, L-906, and L-911). The samples, which were shipped in 5-gallon pails, were stored in plastic bags after receipt. Analyses of the feed coals from Run ALC-2 were conducted with several goals in mind. Since ultra-fine particulate matter (i.e., particles smaller than 2.5 μm diameter) was suspected to have caused the poor performance in filtration and toluene extraction, the size distribution of the feed coal was determined. Another analysis goal was to evaluate the overall characteristics of the coals, since the coals were to be used as a feedstock during agglomeration testing in preparation for Run ALC-3. Complete coal analyses were obtained, and their suitability as agglomeration feeds was evaluated.

Coal size distribution was determined by wet screen analysis. To examine the finest particles, the -325 mesh fraction from wet screening was analyzed by a Malvern laser scattering instrument. The coal size distribution (Table 2) shows that the coals are not unusually fine, and that they do not differ much in size consist. The wet screen analyses shows that the coals are 45-55% +200 mesh and 25-35% -325 mesh. There are minor differences among the samples of about 10% of the material in the +200 mesh fraction and the -325 mesh fraction. These differences may reflect treatment time in the ribbon blender, since the coals treated with Ni or Fe in addition to Mo spent additional time in the blender. The d_{50} of the -325 mesh fractions were consistent at 28-30 μm. The d_{10} and d_{50} of the -325 mesh fraction of these treated coals are similar to those of a whole Wilsonville feed (see footnote b in Table 2). Thus, there is no indication of any unusual amount of ultra-fine material in these coals.

Other coal analyses (Table 2) included proximate and ultimate analyses, heating value, and major and trace ash element analyses. The results do not indicate anything unusual about these coals and, together with the size analyses, indicate that the coals are suitable agglomeration feedstocks. CONSOL's coal analyses were compared with those reported by HTI.[1] Relative to HTI analyses for the feed coals, CONSOL obtained results that were in generally good agreement on moisture (within 0.2 wt %), MF ash (within 0.1 wt %), MF carbon (within 0.7 wt %, CONSOL typically higher by ~0.6 wt %), MF hydrogen (CONSOL was consistently ~0.32 wt % lower), MF

nitrogen (CONSOL was consistently ~0.05 wt % higher), MF sulfur (CONSOL was consistently 0.1-0.2 wt % higher); and MF oxygen by difference (CONSOL was typically ~0.5 wt % lower).

The HTI and CONSOL analyses of the catalyst element concentrations in the ash are provided in Table 3. Relative to HTI analyses,[1] CONSOL results were slightly lower for Mo (0.13-0.15 wt % for CONSOL vs. 0.15-0.18 wt % for HTI), higher for Fe (3.77-6.41 wt % for CONSOL vs. 3.18-5.25 wt % for HTI), and slightly lower for Ni (49-750 mg/kg for CONSOL vs. 49-829 mg/kg for HTI). Although there are some systematic differences in concentrations reported by CONSOL and HTI, the agreement between the CONSOL and HTI analyses was quite good. These results do not suggest a reason for the poor extraction and filtration of the product. They do indicate that the coals have normal properties and size distribution and, thus, are suitable for developmental agglomeration tests in preparation of Run ALC-3.

ANALYSIS OF CONDITION 1 TOLUENE-EXTRACTED SOLIDS FOR CATALYTIC METALS

Selected CONSOL analyses of toluene-extracted solids (TES) are presented in Table 4. Relative to CONSOL analyses for the major elemental concentrations in the ash from of the treated feed coal L-902 (ash SO_3-free), CONSOL obtained results from TES sample ash (normalized SO_3- and K_2O-free) from Condition 1 that were: high for Na, Ca, Mg, and Ti, slightly high for P, about the same for Al, quite low for Si, and not consistent for Fe. For the catalytic elements (Table 4), TES analyses varied significantly, but the averages are in the expected range for Mo and Fe. The concentration of Ni in the TES ash is much higher than in the feed coal ash. These results indicate that there is an unidentified source of Ni in the TES ash. Possible sources include vessel erosion, some other type of contamination, or analytical error. The analysis procedure is not expected to cause such an artifact, but further investigation is needed if the source of nickel contamination must be identified. Unfortunately, there are no HTI data on Ni concentrations in the continuous vacuum still bottoms (CVSB) samples from the early portion of the run (Table 3).

The concentrations of Fe measured by HTI in the CVSB sample ash (Table 3) were 28-58% higher than the concentrations in the feed coal ash for each corresponding operating condition. The concentration of Ni measured by HTI in the CVSB ash was 24% lower than the corresponding concentration measured in the feed coal ash for Condition 3. Thus, the HTI data indicate that the Ni concentration may never have reached its target in the circulating oil.

Substantial variation in Mo and Fe concentration in periods 3B and 5AB (Table 3) appeared to result from a feed disruption that occurred in period 4.

EFFICIENCY OF TOLUENE WASHING

Table 5 and Figure 1 show that the toluene content of whole TES and TEO samples, as received by CONSOL, ranged from 2 to 70%. The toluene content was measured by heating the samples in a vacuum oven at 60 °C and vacuum (ca. 5 mm Hg), until constant weight was obtained (up to several days). HTI personnel reported that these samples contained up to 8% 650 °F$^-$ oils; some of this material may have been reported as toluene using CONSOL's procedure.[2] Nevertheless, the small amount of 650 °F$^-$ oil and the generally high amount of material evaporated show that the evaporated material is predominently toluene. Table 5 and Figure 2 shows the concentrations of THF solubles, IOM, and ash measured by CONSOL on these samples, reported on a toluene-free basis. These results confirmed generally poor extraction in the early part of run, as evidenced by low concentrations of insolubles in the toluene-free TES samples. However, extraction was moderately successful in period 12, as indicated by 56% insolubles in the TES, and a low concentration of insolubles in the TEO (assuming that the period 12 TEO sample was good). Extraction also may have been moderately successful in periods 3, 9, and 13 (the TES samples contained ca. 50% or more insolubles).

CHARACTERISTICS OF O-6 BOTTOMS AND CVSB SAMPLES

Figures 3-7 and Tables 6-8 show that the characteristics of the O-6 bottoms and CVSB samples varied little between the four conditions used in Run ALC-2. Characteristics that were unchanged include microautoclave coal conversions (Table 6, ca. 82-85% in O-6 bottoms 454 °C$^-$ distillates), hydrogen distributions (Table 7 and Figures 3 and 7, e.g., ca. 31% aromatic hydrogen in the filtered whole O-6 bottoms samples, and ca. 36% aromatic hydrogen in the filtered whole CVSB samples), and phenolic -OH concentration (0.9-1.2 meq/g, Table 8 and Figure 4. The concentration of insoluble organic matter (IOM) in the CVSB and O-6 bottoms samples also was steady (6.6-8.9% in O-6 bottoms, 10.0-14.2% in CVSB). However, the Period 7 samples were low in ash concentration, and the Period 12 CVSB sample was high in ash concentration, relative to their Period 17 and Period 21 counterparts. This may be a consequence of the poor ash balances reported by HTI and LDP Associates for the run.[1,3] In the CVSB samples, the concentration of THF solubles was inversely related to the ash concentration. These results show no differences that are attributable to catalyst differences between the four run conditions represented by samples from Periods 7, 12, 17, and 21.

In order to investigate differences in preasphaltene amounts and characteristics, the THF solubles from the CVSB samples were separated by solvent fractionation into oils, asphaltenes, and preasphaltenes (Table 6 and Figure 6) using CONSOL's preparative liquid column fractionation (LCF) method. An attempt was made to characterize the collected preasphaltene fraction from one sample by proton NMR spectrometry and by FTIR spectroscopy, but there was insufficient material to obtain any useful information. Since the CVSB THF-soluble material from all four conditions consistently contained ca. 8-10% preasphaltenes, no differences were found that would be helpful in discovering the cause of the extraction and filtration problems. The only differences that were observed in these data (Figure 6, Table 6) were a higher concentration of the oils (78% vs. 67-70%), and a lower concentration of the asphaltenes (14% vs. 21-22%) in the Condition 4 CVSB THF-solubles, relative to the corresponding samples from the other conditions. Perhaps this difference was a consequence of use of the batch vacuum still for solids separation during Condition 4, since more resid may have been rejected from the process.

In general, most sample characteristics changed little over the course of the run. Thus, there are no period-to-period differences that would suggest a reason for extraction/filtration problems. Furthermore, these results provide no conclusive indication of catalyst performance differences. Combined with the distillate product characteristics, the consistent results at each condition also indicate that distillation system operations and performance were very stable.

DISTILLATE PRODUCT CHARACTERISTICS

Characteristics of the distillate and light oil streams (first-stage (unhydrotreated) SOH, second-stage (hydrotreated) SOH, RPSOH, and RPSB oils) are provided in Tables 7 and 8 and Figures 8-13. The phenolic -OH concentration and hydrogen distribution of these streams changed little over the run. This implies stability in the distillation system and provides no indication of performance differences between the catalysts used in the four run conditions.

The high phenolic -OH concentrations of the first-stage SOH and RPSOH oil samples (Table 8, Figures 8 and 11) indicate that these streams contain a significant fraction (perhaps 25%) of phenolics. The phenolics are potential sources of relatively valuable chemical feedstocks. The characteristics of the hydrotreated second-stage SOH oil samples relative to those of the unhydrotreated first-stage SOH oil samples indicate that the in-line hydrotreater effectively removes phenolic -OH and most aromatic hydrogen from the product oils (Tables 7 and 8, Figures 8-10).

NATURE OF Ni IN CONDITION 4 CVSB SAMPLE

In HTI Run ALC-2, Ni-impregnated coal was fed only during Condition 3. The Ni concentrations in the continuous vacuum still bottoms (CVSB) samples taken during the run increase throughout Condition 3, then decrease slowly (but never to baseline) during Condition 4. There was speculation that the slow rate of decline of Ni concentration could result from recycle of organically associated Ni species. To help evaluate this issue, the THF-soluble fraction of the CVSB sample from condition 4, period 21, was analyzed to determine if Ni or Mo was present in oil-soluble form. The THF-solubles were prepared from the CVSB sample by pressure filtration with THF through a Whatman 42 paper (retains particles >2.5 μm), and evaporation of the THF from the filtrate. An analysis gave 72.3% THF solubles, 11.0% IOM, and 16.7% ash. The THF-soluble material contained 6 mg/kg Ni, 4 mg/kg Mo, a total of 416 mg/kg of the oxides of Si, Al, Fe, Ca, and Mg, and less than 0.1% ash (obtained using a separate aliquot of THF-soluble material). Thus, the occurrence of Ni and Mo is coincident with the occurrence of a trace amount of ash, and the Ni and Mo are presumed to be inorganically associated. The amount of Ni or Mo in the ash of the solubles (about 1% of the ash in the CVSB THF-solubles) is higher than in the ash of the coal or ashy process streams (about 600 mg/kg or less for Ni, 0.2% for Mo).

L-814 START-UP OIL: CHANGE OF CHARACTERISTICS FROM PRIOR SAMPLES

HTI's L-814 (Tank 4) oil is used for run start-up and sometimes for make-up oil. The original inventory was a fluid catalytic cracking (FCC) decant oil. The characteristics of the inventory change over time from the exchange of oils between Tank 4 and the HTI operating units during start-up, make-up, and shut-down operations. Over the past several years, CONSOL has routinely requested a start-up oil sample from each run from which other process oils were collected for characterization. Characterization data were usually reported with data from other oils, although remarks were rarely made about the start-up oil characteristics. It was observed that the characteristics of the L-814 start-up oil sample collected from Run ALC-2 were different from those of samples collected over the prior three years.

The proton distributions of L-814 oil (Tank 4 oil) used in HTI Runs POC-2, CMSL-9, ALC-1, and ALC-2 were compared (Table 9). The most recent sample, from Run ALC-2, was less aromatic and more paraffinic than the earlier samples, The Run ALC-2 sample also was apparently lower in viscosity than the one from Run CMSL-9 that was visually inspected for this property. CONSOL requested an even more recent sample that was provided by HTI (sample ca. 6/30/97). Aromatic hydrogen content of the L-814 oils (Table 9) was 23.0% for Run POC-2, 20.4-23.3% for

Run CMSL-9, 20.6% for Run ALC-1, 14.8% for Run ALC-2, and 8.0% in the 6/30/97 sample. Alkyl beta aliphatic hydrogen content of the samples were 21.4% for Run POC-2, 23.8-25.4% for Run CMSL-9, 24.0% for Run ALC-1, 32.3% for Run ALC-2, and 38.3% in the 6/30/97 sample. The 6/30/97 sample confirms that the L-814 oil became (through replacement of the original oil by oils produced in HTI's tests) less aromatic and more paraffinic than its predecessors. Although the latest sample is the least aromatic and most paraffinic of those analyzed by CONSOL, its viscosity appears normal for this type of sample, in contrast with the Run ALC-2 sample, which had an unusually low viscosity.

CRUDE OIL ASSAY OF NET PRODUCTS OF HTI RUN PB-05

CONSOL arranged to have a crude oil assay conducted on the net products of HTI Run PB-05 (also known as Run 227-97), at DOE's request. The crude oil assay was conducted on the net products obtained during operating condition 6 of Run PB-05 in which Hondo resid was coprocessed with Illinois 6 coal and the on-line hydrotreater was by-passed.

HTI provided CONSOL with four partially-filled 1-gallon containers of separator overhead samples from HTI Run PB-05, condition 6. The individual separator overhead samples were from periods 22A, 23A, 24A, and 25A. CONSOL prepared and blended these materials to produce a large sample for crude oil assay testing. The samples were decanted and filtered over Reeve-Angel 802 filter paper to omit the small quantities of water and sediment, and then blended to produce a 12.99 kg sample (approximately 3.8 to 4 gal). The blended material was placed in a steel 5 gal can and shipped to the Inchcape (now Intertek) Testing Services Caleb Brett Laboratory in Houston, TX, for the crude oil assay testing. The analytical test plan was prepared in conjunction with P. Zhou of Burns and Roe Services Corp. A vial of the final blend was retained by CONSOL. Caleb Brett's report appears as Appendix 1.

FRACTIONAL DISTILLATION OF NET PRODUCTS OF HRI RUN POC-1

At DOE's request, CONSOL arranged to have various distillations conducted on the net products of HRI Run POC-1. DOE was interested in obtaining the distillation data on this material because of inconsistencies between the fractional distillation data generated in 1995 by Conoco[4] and Southwest Research Institute on different aliquots of the same sample of the net product of HTI Run POC-1. DOE wanted the distillations (fractional, ASTM D86, and simulated) re-checked. A one-gallon sample of the net product of HTI Run POC-1 (the whole crude oil) was recovered from the CONSOL sample bank. This sample was returned to CONSOL after Conoco conducted the crude oil assay on the material. The sample was shipped to the Inchcape (now Intertek) Testing Services Caleb Brett Laboratory in Houston, TX, for the distillation testing. The analytical test plan was prepared in conjunction with P. Zhou of Burns and Roe Services Corp. Caleb Brett's report appears as Appendix 2.

PREPARATION OF ALKYL ARYL ETHERS FROM COAL-DERIVED PHENOLS

CONSOL R&D evaluated reactions to synthesize alkyl phenyl ethers from coal liquefaction phenols. The program included a literature review and laboratory chemical syntheses. Results are briefly presented here. The full report is provided in Appendix 3.

Phenols are produced during the direct liquefaction of coal and must be removed prior to producing transportation fuels. The crude liquefaction product is commonly hydrotreated to remove the phenols and other unsaturated components. An alternative method is to extract the phenols from the crude coal liquefaction product and use them in other commercial processes. Hydrogen consumption for the hydrotreatment of the liquefaction products would be reduced. The phenolic material could be converted to alkylphenyl ethers, which may be useful as fuel extenders. If the fuel extenders can be produced using grain alcohol, the products may be entitled to special tax considerations.

An extensive literature search identified the Williamson Synthesis and its modifications as the preferred methods to produce mixed ethers from phenols. A variation of the Williamson Synthesis was used to produce phenetole and the ethyl derivatives of the phenolics from a caustic extract of a crude direct coal liquefaction product. Other approaches involving acid catalysts failed to produce ethers.

It is recommended that the ethyl ether derivatives of coal liquefaction phenols be synthesized and characterized as a diesel fuel extender. CONSOL will develop a plan to extract the phenols, synthesize the ethers, and coordinate the fuel characterization upon DOE's approval.

RESID REACTIVITY

The University of Delaware completed a parametric reaction study with two resid samples. Temperature, pressure, residence time, catalyst loading, and resid concentration were explored. The two samples chosen for the study (Wilsonville Run 260 V131B and Wilsonville Run 259 V131B) gave the highest (44.6 wt %) and lowest (33.1 wt %) resid conversions, respectively at the standard conditions of 420 °C, 30 min, 3:1 tetralin:resid and 3 wt% molybdenum naphthenate catalyst. Figure 14 shows data for two temperatures and four residence times for each of the resids. The leveling off of conversion in time is consistent with the presence of a refractory resid component, which is difficult to convert to lower-boiling product.

The refractory component was isolated by successive solvent-solubility extractions and subjected to hydrotreating. The resid was first extracted in room temperature tetralin, and placed in a Soxhlet extractor and extracted in tetralin at reflux for 48 h. The residue was dried and then hydrotreated at 440 °C, 30 min, with 3 wt % Mo, in 3:1 tetralin:residue. Conversion to 454 °C$^-$ (850°F$^-$) was only ca. 1 wt%. The unconverted material represents about 15 wt% of the 454 °C$^+$ (850 °F$^+$) resid. Elemental analyses of the successive insoluble fractions and the unconverted 454 °C$^+$ (850 °F$^+$) hydrotreated fraction are given in Table 10. The H/C molar ratio for the unconverted 454 °C$^+$ (850 °F$^+$) hydrotreated fraction is only 0.42, roughly half that of the 454 °C$^+$ (850 °F$^+$) resid.

All necessary information was determined for the Delaware set of 454 °C$^+$ (850 °F$^+$) coal resids to assemble a molecular model. The model was modified several times so that the computer-generated molecular representations match the experimental data. All properties except hydrogen:carbon ratios and the fraction of condensed aromatics are predicted within one experimental standard deviation.

A reaction model was assembled for the catalytic upgrading of coal resids. The key reaction families were identified and the most and least reactive resids for which kinetic data is being acquired (see above) will be used to optimize the rate constants. The model was coded and is being debugged and refined. The objective functions will consist of approximately eight terms. The only values used in the optimization will be the fraction of resid converted at each residence time for which experimental data were acquired. The model when completed will be able to incorporate additional analytical data to further define a unique set of rate constants. However,

the eight terms currently being used to define the objective function should be sufficient to provide an adequate unique solution.

Delaware is drafting a Final Report and will complete and submit the completed structural/reaction model, documentation which describes the software, and an operating manual.

Section 4

CONCLUSIONS

Conclusions are provided in the Executive Summary section of the report.

Section 5

REFERENCES

1. HTI portion of Advanced Direct Liquefaction Concepts for PETC Generic Units, Quarterly Technical Progress Report for Period January through March 1997, U.S. Department of Energy, Report DOE/PC 91040-80, May 30,1997.

2. J. Hu (HTI), personal communication with G. A. Robbins (CONSOL).

3. LDP Associates portion of Advanced Direct Liquefaction Concepts for PETC Generic Units, Quarterly Technical Progress Report for Period January through March 1997, U.S. Department of Energy, Report DOE/PC 91040-80, May 30,1997.

4. 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, July 1 through September 30, 1995", DOE/PC 93054-20, December 1995.

Section 6

LIST OF ABBREVIATIONS AND ACRONYMS

AHM	Ammonium heptamolybdate
ALC	Advanced liquefaction concepts
ASTM	American Society for Testing and Materials
CAS	Continuous atmospheric still
CMSL	Run designation used by HTI for catalytic multi-stage liquefaction
CVS	Continuous vacuum still
CVSOH	Continuous vacuum still overhead
CVSB	Continuous vacuum still bottoms
DOE	Department of Energy
FCC	Fluid catalytic cracking
FTIR	Fourier-transform infrared
GC-MS	Gas chromatography-mass spectrometry
HTI	Hydrocarbon Technologies, Inc.
HTU	Hydrotreater unit
IBP	Initial boiling point
IOM	Insoluble organic matter
L-814	End-of-run make-up oil in Tank 4 from HTI's POC-2 run; used as HTI start-up oil
L/O	Line-out
LCF	Liquid column fractionation
MAF	Moisture and ash free
MF	Moisture free
NIPER	National Institute for Petroleum and Energy Research
NMR	Nuclear magnetic resonance
PB	POC bench option, HTI run designation
PFC	Pressure filter cake
PFL	Pressure filter liquid
PMA	Phosphomolybdic acid
POC	Proof of concept
RPS	Reduced pressure still
RPSB	Reduced pressure still bottoms
RPSOH	Reduced pressure still overhead
SOH	Separator overhead
SOH1	First-stage SOH; a component of the HTU feed
SOH2	Second-stage SOH; the hydrotreated net product
SwRI	Southwest Research Institute
TE	Toluene extraction unit
TEO	Toluene extracted oil
TES	Toluene extracted solids
THF	Tetrahydrofuran
TNPS	Di-tertiary-nonyl polysulfide
V131B	The heavy distillate recycle oil in the Wilsonville pilot plant
VSB	Vacuum still bottoms
VSOH	Vacuum still overhead

TABLE 1

RUN CONDITIONS AND YIELDS FOR HTI RUN ALC-2 (227-100)

Date, 1996	12/8	12/13	12/18	12/22
Condition	1	2	3	4
Period (work-up was last period in each condition)	1-7	8-12	13-17	18-21
Net Normalized Yields, wt % MAF Fresh Feed				
C_1 Gases	4.32	7.03	6.01	6.71
C_2 Gases	4.11	3.97	3.36	3.83
C_3 Gases	5.14	4.89	4.21	4.84
C_4 Gases	2.86	2.67	2.45	2.51
C_5 Gases	1.93	1.47	1.57	1.44
C_6 & C_7 Gases	2.86	2.63	2.78	2.48
C_1-C_3 in Gases	13.48	15.80	13.50	15.29
C_4-C_7 in Gases	7.65	6.77	6.80	6.43
IBP-177 °C	13.27	11.00	11.94	11.74
177-260 °C	16.34	11.16	8.57	11.56
260-343 °C	18.64	16.79	16.27	17.10
343-399 °C	3.73	0.76	12.63	3.45
399-454 °C	-1.44	0.97	6.37	1.22
454-524 °C	1.58	2.98	1.59	2.33
524$^+$ °C	9.32	15.44	4.77	12.38
Unconverted Coal*	6.05	4.80	4.95	4.29
Water	13.36	13.91	15.78	14.54
CO	1.73	1.47	1.28	0.98
CO_2	5.74	4.73	3.47	5.27
NH_3	0.91	0.69	0.73	0.72
H_2S	0.13	0.07	0.31	0.14
Process Performance, wt % MAF Fresh Feed				
H_2 Consumption by Balance, SO_3 free	7.1	7.0	7.2	6.9
Coal Conversion (SO_3 Free)*	93.9	95.2	95.1	95.7
524$^+$ °C Conversion	84.6	79.8	90.3	83.3
C_4-524 °C Distillates	59.8	50.4	64.2	53.8
524$^+$ °C Resid Yield + Unconverted Coal	15.4	20.2	9.7	16.7
Catalysts (Impregnated on Coal)				
Type	AHM/Fe	AHM	AHM/Ni	PMA
Concentration, mg/kg MF Coal	Mo:100, Fe:1610	Mo:110	Mo:92, Ni:51	Mo:116, P:3

*Coal conversion and unconverted coal are calculated based on ash balance.

Common Conditions

Temperatures, °C:	Pretreater, 300; Reactor 1, 440; Reactor 2, 450; In-Line Hydrotreater, 379; RPS, 316 (period 7 on); CVS, 427; Batch Vacuum Still (Condition 4 Only), 524
Space Velocity (each reactor):	640 kg MF fresh feed/m^3 reactor volume
Inlet Pressure:	17 MPa
H_2 Rate:	20% MF coal (3270 std L/h total, 1960:1100:210 Reactor 1:Reactor 2: Separators)
Sulfiding Agents:	H_2S to Reactor 1, 2% MF coal; TNPS to Reactor 2 equivalent to H_2S dose of 0.5% MF coal

TABLE 2

CHARACTERISTICS OF CATALYST-TREATED COALS FED IN HTI RUN ALC-2

Coal Sample and Run ALC-2 Condition Number	L-902 Cond. 1	L-904 Cond. 2	L-906 Cond. 3	L-911 Cond. 4
Moisture, wt % As-Determined	12.68	13.07	10.46	11.16
Ash, wt % MF, Including SO_3	6.78	6.07	6.26	6.13
SO_3 Content Used to Correct Ash	18.95	17.11	16.73	16.86
Ash, wt % MF, SO_3-Free	5.50	5.03	5.21	5.10
Proximate, wt % MF, SO3-Free Ash Basis				
Volatile Matter	46.58	46.58	46.68	47.07
Fixed Carbon	47.92	48.39	48.11	47.83
Heating Value, Btu/lb MAF, SO3-Free Ash Basis	12627	12647	12697	12663
Ultimate, wt % MF, SO3-Free Ash Basis				
C	70.33	70.71	70.81	70.05
H	4.75	4.82	4.78	4.80
N	1.07	1.03	1.04	1.04
S, Total	0.58	0.46	0.48	0.48
O (by Difference)	17.77	17.95	17.68	18.53
Major Ash Elements, Oxide wt % of SO_3-Free Ash				
MoO_3	0.28	0.29	0.23	0.23
NiO	0.01	0.01	0.11	0.01
Na_2O	1.57	1.69	1.65	1.68
K_2O	0.47	0.54	0.54	0.49
CaO	26.67	27.58	26.68	26.83
MgO	5.43	5.60	5.58	5.65
Fe_2O_3	11.30	6.83	6.70	6.48
TiO_2	1.44	1.42	1.50	1.50
P_2O_5	1.22	1.29	1.22	1.25
SiO_2	34.62	35.84	36.17	35.37
Al_2O_3	18.10	18.13	19.01	18.50
Total	101.11	99.23	99.41	98.02
Sieve Size, Fraction wt % of Total				
+48 mesh	0.0	0.0	0.3	0.4
48 x 100 mesh	7.8	4.2	7.8	6.0
100 x 200 mesh	36.5	42.2	39.4	47.5
200 x 325 mesh	19.2	25.1	20.4	20.8
-325 mesh	36.5	28.5	32.1	25.3
Particle Size Analysis of -325 mesh Fraction (a,b), μm, vol % distribution				
d_{10}	8.08	8.14	7.88	8.97
d_{50}	28.53	27.67	28.87	30.58
d_{90}	55.85	50.12	55.43	54.47
Mo wt % of SO_3-free ash	0.19	0.19	0.16	0.16
Fe wt % of SO_3-free ash	7.90	4.78	4.69	4.53
Ni mg/kg of SO_3-free ash	60	75	901	59
Mo wt % of SO_3-containing ash	0.15	0.16	0.13	0.13
Fe wt % of SO_3-containing ash	6.41	3.96	3.90	3.77
Ni mg/kg of SO_3-containing ash	49	62	750	49

(a) By Malvern laser scattering, d_x = diameter representing xth percentile of volume distribution.

(b) For comparison, the Wilsonville Run 262 Black Thunder Mine feed coal gave d_{10} = 7 μm, d_{50} = 32 μm, and d_{90} = 72 μm when measured by the same method. The Wilsonville feed coal was prepared at the same facility used by HTI, and the data given are for the entire feed, not a size subfraction as is reported for the Run ALC-2 feeds.

TABLE 3

CONCENTRATIONS OF CATALYTIC METALS IN ASHY STREAMS FROM HTI RUN ALC-2

Sample	Cond. No.	Analyzed by	Basis	Metal Concentration in Ash		
				Mo, wt %	Fe, wt %	Ni, mg/kg
Per. 1-7 CVSB(a)	1	HTI[1]	Ash SO_3 Uncorrected	0.17	6.70	NA
Per. 8-12 CVSB	2	HTI[1]	Ash SO_3 Uncorrected	0.15-0.19	5.01-6.65	NA
Per. 13-17 CVSB	3	HTI[1]	Ash SO_3 Uncorrected	0.17-0.20	4.63-5.01	184-631
Per. 18-21 CVSB	4	HTI[1]	Ash SO_3 Uncorrected	0.16	4.59-4.75	404-565
Coal L-902	1	HTI[1]	Ash SO_3 Uncorrected	0.16	5.25	49
Coal L-904	2	HTI[1]	Ash SO_3 Uncorrected	0.18	NA	NA
Coal L-906	3	HTI[1]	Ash SO_3 Uncorrected	0.15	3.18	829
Coal L-911	4	HTI[1]	Ash SO_3 Uncorrected	0.15	3.41	67
Coal L-902	1	CONSOL	Ash SO_3 Uncorrected	0.15	6.41	49
Coal L-904	2	CONSOL	Ash SO_3 Uncorrected	0.16	3.96	62
Coal L-906	3	CONSOL	Ash SO_3 Uncorrected	0.13	3.90	750
Coal L-911	4	CONSOL	Ash SO_3 Uncorrected	0.13	3.77	49
Coal L-902	1	CONSOL	Ash SO_3-Free	0.19	7.90	60
TES Samples, Compare with Coal L-902						
Per. 2AB TES	1	CONSOL	Norm. SO_3- and K_2O- Free	0.15	7.41	258
Per. 3B TES	1	CONSOL	Norm. SO_3- and K_2O- Free	0.22	10.04	331
Per. 5AB TES	1	CONSOL	Norm. SO_3- and K_2O- Free	0.07	4.63	125
Per. 6 TES	1	CONSOL	Norm. SO_3- and K_2O- Free	0.21	8.69	135

(a) HTI analyzed only the period 7 sample.
NA = not available

TABLE 4

CHARACTERISTICS OF TOLUENE-EXTRACTED SOLIDS FROM CONDITION 1 OF HTI RUN ALC-2

Run ALC-2 Period Number	Per. 2AB	Per. 3B	Per. 5AB	Per. 6
Toluene, wt % As-Determined (By Evaporation)	10.4	2.8	15.0	25.7
Ash, wt % As-Determined, Including SO_3 (a)	7.95	25.03	10.04	10.45
Unaccounted, wt % of SO_3 -Containing Ash (b)	21.94	16.80	20.34	21.80
Ash, wt % As-Determined, Calculated, SO_3- and K_2O-Free (c)	6.21	20.82	8.00	8.17
Major and Minor Ash Elements, Oxide wt % of SO_3- and K_2O-Free Ash (c)				
MoO_3	0.22	0.34	0.10	0.32
NiO	0.03	0.04	0.02	0.02
Na_2O	2.39	2.14	2.19	2.14
CaO	33.59	30.44	33.59	36.64
MgO	7.21	6.29	7.05	7.71
Fe_2O_3	10.60	14.35	6.61	12.42
TiO_2	2.15	1.84	2.09	2.25
P_2O_5	1.48	1.43	1.43	1.68
SiO_2	23.44	25.17	27.55	18.32
Al_2O_3	18.88	17.97	19.37	18.50
Metal Concentration in SO_3- and K_2O-Free Ash				
Mo, wt %	0.15	0.22	0.07	0.21
Fe, wt %	7.41	10.04	4.63	8.69
Ni, mg/kg	258	331	125	135

(a) ASTM ash of whole sample.

(b) Weight percent of ASTM ash that was not accounted for by summing the contributions of oxides determined (SO_3 and K_2O not determined).

(c) Element concentrations were determined on an as-determined basis by digestion of the whole sample and analysis via a procedure that did not include sulfur and potassium (the digestion procedure adds potassium). Normalized SO_3- and K_2O-free ash content was obtained by summing all of the elemental concentrations in their oxide forms.

TABLE 5

COMPONENT DISTRIBUTION OF TES AND TEO SAMPLES
HTI RUN ALC-2 (227-100)

				wt % Toluene-Free Sample			
Sample	Period	Condition	Toluene, wt % of Whole Sample	THF-Solubles	IOM	Ash	Toluene, wt % of Toluene-Free Sample
TES	2AB	1	10.4	81.7	10.0	8.3	11.6
TES	3B(a)	1	2.8	32.3	42.4	25.3	2.9
TES	3B(b)	1	81.4	28.8	47.3	23.9	437.6
TES	5AB	1	15.0	78.6	9.8	11.6	17.6
TES	6	1	25.7	74.2	11.7	14.1	34.6
TES	7B	1	7.4	74.9	10.4	14.7	8.0
TES	9A/B	2	70.0	21.2	38.6	40.2	233.3
TES	12	2	43.0	42.7	25.2	32.0	75.3
TES	13	2	47.1	48.9	24.0	27.1	89.0
TEO	7	1	21.3	85.6	7.0	7.4	27.1
TEO	12	2	90.8	96.7	2.2	1.1	987.0

Toluene was determined by weight loss (to constant weight) in a vacuum oven at 60 °C and full vacuum (pressure ca. 5 mm Hg, atmospheric equivalent was less than 190 °C) for up to several days. Some 650 °F$^-$ oil may be reported as toluene by this method (cf. text).

(a) First sample received from HTI from this period; also analyzed for proton distribution and phenolic -OH concentration (reported in other tables).

(b) Second sample received from HTI from this period.

TABLE 6

MISCELLANEOUS ANALYSES OF CVSB AND O-6 BOTTOMS SAMPLES HTI RUN ALC-2 (227-100)

Condition	1	2	3	4
Period	7B	12B	17B	21B
% MAF Coal Conversion in Microautoclave Donor Solvent Assay(a)				
O-6 Btms 454 °C⁻ Distillate	82.9	85.3	84.9	82.8
Component, wt % of Whole O-6 Btms Sample				
454 °C⁻ Distillate	42.7	38.0	38.2	42.3
454 °C⁺ Resid THF Solubles	36.8	37.9	37.9	35.2
IOM	6.6	8.2	8.9	7.3
Ash	9.2	12.0	11.7	10.6
Period	7B	12	17	21
Component, wt % of Whole CVSB Sample				
Ash	13.6	19.4	16.4	16.7
IOM	10.0	14.2	12.8	11.0
THF-Solubles	76.4	66.4	70.8	72.3
Component, wt % of CVSB THF Solubles				
wt % Oils	67.2	69.5	68.9	78.2
wt % Asph.	22.4	21.1	21.8	14.1
wt % Preasph.	10.4	9.4	9.3	7.7

(a) Standard Indiana 5 test coal, modified-equilibrium test conditions: 9 g solvent, 6 g coal, 399 °C, 30 min.

TABLE 7

PROTON DISTRIBUTION OF SAMPLES BY NMR
HTI RUN ALC-2 (227-100)

Sample	Period	Condition	Proton Distribution, %						
			Cond. Arom	Uncond. Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Whole Samples									
L-814 Start-Up Oil 1/10/97 (a)		S/U	9.7	5.1	10.7	8.8	13.9	32.3	19.5
CVSB	7B	1	24.3	11.5	18.0	10.6	11.5	15.9	8.2
CVSB	12B	2	25.8	11.9	19.7	10.1	12.0	13.3	7.2
CVSB	17B	3	25.0	11.6	18.5	9.9	12.1	14.7	8.2
CVSB	21B	4	27.1	9.0	19.7	9.7	11.5	14.9	7.9
O-6 Btms	7B	1	18.8	12.2	15.4	11.4	11.9	19.2	11.1
O-6 Btms	12B	2	19.7	10.9	17.7	11.2	12.5	18.1	9.9
O-6 Btms	17B	3	19.0	12.4	16.3	10.8	12.6	18.6	10.3
O-6 Btms	21B	4	19.6	12.4	16.2	11.5	11.9	18.7	9.7
RPSOH	7B	1	8.3	12.1	13.3	13.9	14.8	24.3	13.3
RPSOH	12B	2	7.3	13.9	15.1	15.1	14.6	22.4	11.6
RPSOH	17B	3	10.2	11.9	15.1	13.5	15.1	22.6	11.6
RPSOH	21B	4	10.4	12.0	14.3	13.3	14.4	23.2	12.2
RPSB	7B	1	16.5	8.8	14.9	11.1	13.1	23.8	11.9
RPSB	12B	2	18.3	9.0	16.5	10.8	12.5	22.5	10.4
RPSB	16B	3	17.0	9.4	15.7	10.6	12.2	24.0	11.2
RPSB	17B	3	16.2	9.6	15.7	10.7	12.8	23.8	11.2
RPSB	21B	4	18.0	9.1	16.1	10.7	12.9	22.4	10.7
TES (b)	2A/B	1	25.3	12.3	16.3	11.2	10.8	15.9	8.2
TES (b)	3B	1	31.0	14.6	15.0	12.3	8.9	10.3	8.0
TES (b)	5A/B	1	24.1	12.3	16.9	10.9	11.8	15.4	8.6
TES (b)	6	1	24.5	11.5	18.3	10.7	11.1	15.0	9.0
TES	7B	1	25.9	9.8	19.4	10.6	11.9	15.3	7.2
TES	9A/B	2	22.4	5.1	15.9	7.2	12.8	17.3	19.2
TES (b)	12A/B	2	32.3	7.3	19.3	9.7	11.8	12.1	7.5
TES	13A/B	3	26.3	10.8	19.8	10.1	12.6	13.5	7.0
TEO	7	1	22.8	8.9	15.7	10.2	12.2	19.3	10.9
TEO	12	2	25.8	9.7	19.0	10.3	12.2	14.5	8.6
Stage 1 SOH	1B	1	4.4	5.1	6.3	8.9	15.0	35.4	24.8

Sample	Period	Condition	Proton Distribution, %						
			Cond. Arom	Uncond. Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Stage 1 SOH	7B	1	6.0	10.3	9.6	12.0	16.5	27.6	18.0
Stage 1 SOH	12B	2	5.8	11.2	9.7	12.1	16.4	27.8	16.9
Stage 1 SOH	13A	2-3	6.2	10.7	10.1	12.2	17.4	27.0	16.5
Stage 1 SOH	17A	3	5.3	10.8	8.9	11.7	17.1	27.8	18.5
Stage 1 SOH	21A	4	5.7	9.8	9.2	11.2	16.8	28.7	18.5
Stage 2 SOH	7A	1	0.5	2.5	3.1	4.0	23.0	36.4	30.5
Stage 2 SOH	12A	2	1.1	3.6	5.5	5.7	23.8	34.0	26.4
Stage 2 SOH	17A	3	0.9	3.2	4.7	5.3	23.6	35.4	26.9
Stage 2 SOH	17B	3	1.3	3.2	5.8	5.8	24.0	34.5	25.3
Stage 2 SOH	21A	4	0.7	2.0	2.7	4.1	24.5	35.7	30.3
Stage 2 SOH	21B	4	0.7	2.2	2.2	3.6	23.2	36.5	31.6
454 °C⁻ Distillates									
O-6 Btms	7B	1	15.9	9.2	15.1	11.7	12.9	23.4	11.7
O-6 Btms	12B	2	15.2	10.3	16.3	11.9	13.6	22.4	10.3
O-6 Btms	17B	3	13.9	11.2	15.7	12.1	13.4	22.3	11.4
O-6 Btms	21B	4	17.0	10.3	15.8	11.5	12.4	22.7	10.3
454 °C⁺ Resids									
O-6 Btms	7B	1	27.8	9.8	21.2	10.4	12.1	12.3	6.3
O-6 Btms	12B	2	27.4	9.4	20.5	10.0	11.9	13.3	7.5
O-6 Btms	17B	3	27.6	9.5	20.8	9.7	12.4	13.2	6.9
O-6 Btms	21B	4	29.3	11.4	19.9	10.2	11.4	11.8	5.9

(a) The L-814 tank is the source of start-up oil, although the date (1/10/97) of this sample suggests that it was obtained after the run. This sample appeared to be much lower in viscosity than a 1995 sample from the same tank. See text and a later table relating to comparative L-814 data over several years.

(b) These samples were dissolved in 99.96% d_5-pyridine, filtered, and integrated electronically. All other samples were dissolved in 99.96% d-$CHCl_3$ and integrated electronically.

TABLE 8

PHENOLIC -OH CONCENTRATION OF SAMPLES DETERMINED BY FTIR
HTI RUN ALC-2 (227-100)

Sample	Condition	Period	Phenolic -OH Conc., meq/g	Phenolic -OH Peak Pos., cm^{-1}	Sample	Condition	Period	Phenolic -OH Conc., meq/g	Phenolic -OH Peak Pos., cm^{-1}
Whole Sample THF Solubles					Whole Samples				
CVSB	1	7B	0.96	3295	Stage 1 SOH	1	1B	0.65	3311
CVSB	2	12B	0.91	3295	Stage 1 SOH	1	7B	1.70	3309
CVSB	3	17B	0.95	3295	Stage 1 SOH	2	12B	1.87	3309
CVSB	4	21B	0.90	3293	Stage 1 SOH	2	13A	1.90	3309
					Stage 1 SOH	3	17A	1.87	3309
TES	1	2A/B	0.83	3292	Stage 1 SOH	4	21A	1.61	3309
TES	1	3B	1.11	3292					
TES	1	5A/B	0.76	3295	Stage 2 SOH	1	7A	ND	
TES	1	6	0.88	3294	Stage 2 SOH	2	12A	ND	
TES	1	7B	0.77	3292	Stage 2 SOH	3	17A	ND	
TES	2	9A/B	0.98	3286	Stage 2 SOH	3	17B	ND	
TES	2	12A/B	1.06	3292	Stage 2 SOH	4	21A	ND	
TES	2	13A/B	1.00	3292	Stage 2 SOH	4	21B	ND	
TEO	1	7	0.70	3296	RPSOH	1	7B	1.78	3311
TEO	2	12	0.68	3296	RPSOH	2	12B	1.49	3310
					RPSOH	3	17B	1.89	3310
454 °C$^-$ Distillates					RPSOH	4	21B	1.60	3311
O-6 Bottoms	1	7B	1.02	3307					
O-6 Bottoms	2	12B	1.12	3307	RPSB	1	7B	0.81	3304
O-6 Bottoms	3	17B	1.22	3307	RPSB	2	12B	0.94	3302
O-6 Bottoms	4	21B	1.24	3307	RPSB	3	16B	0.85	3302
					RPSB	3	17B	0.91	3303
454 °C$^+$ Resid THF Solubles					RPSB	4	21B	0.85	3302
O-6 Bottoms	1	7B	0.98	3294					
O-6 Bottoms	2	12B	0.96	3294					
O-6 Bottoms	3	17B	0.93	3294					
O-6 Bottoms	4	21B	1.00	3294					

ND = None Detected

TABLE 9

PROTON DISTRIBUTIONS OF HTI L-814 START-UP OIL OVER TIME

	Proton Distribution, %						
L-814 Sample Origin	**Cond. Arom**	**Uncond. Arom**	**Cyclic Alpha**	**Alkyl Alpha**	**Cyclic Beta**	**Alkyl Beta**	**Gamma**
Recent Sample, ca. 6/30/97 (ca. 3 mo. after Run PB-07)							
Unspecified	5.0	3.0	11.0	7.2	17.2	38.3	18.4
Run ALC-2 (227-100), 1/10/97 (a)							
Per. S/U	9.7	5.1	10.7	8.8	13.9	32.3	19.5
Run ALC-1 (227-94), Spring 1996							
Per. 5	14.0	6.6	13.3	12.5	13.5	24.0	16.2
Run CMSL-9, (227-87), run ca. 5/11/95							
Per. 19	15.3	5.1	15.3	12.3	13.4	24.7	13.9
Per. 24	14.8	5.9	13.6	12.5	12.7	25.4	15.1
Per. 29	14.1	6.5	13.4	13.3	12.5	24.9	15.2
Per. 34	16.9	6.4	13.6	14.1	11.4	23.8	13.8
Per. 38	15.0	5.7	14.7	12.1	13.1	25.1	14.3
Per. 41	14.5	5.9	14.2	12.1	12.8	25.0	15.6
Run POC-2, Tank 4, ca. 6/94							
Per. 1B, Cond. L/O-1	15.9	7.1	14.6	14.6	12.2	21.4	14.1

(a) Sample date suggest that the sample may have been taken after the run was completed. Sample received by CONSOL appeared to be low in viscosity.

TABLE 10

ELEMENTAL ANALYSES OF RESIDUES

	Resid W 260 V131B(a)	Residue Of Room Temperature Tetralin Washing	Residue Of Tetralin Soxhlet Extraction	Unconverted 454 °C+ (850°F+) Residue
Ultimate, wt %				
C	82.16	65.01	52.87	44.34
H	5.93	3.21	1.83	1.56
N	0.90	1.21	1.01	0.69
S_{tot}	1.13	2.67	3.78	5.81
Ash	8.57	24.53	37.94	46.78
O (by diff)	1.31	3.37	2.57	0.82
H/C	0.87	0.59	0.42	0.42

(a) W 260 V131B = Wilsonville Run 260, Sampling location V131B (recycle stream)

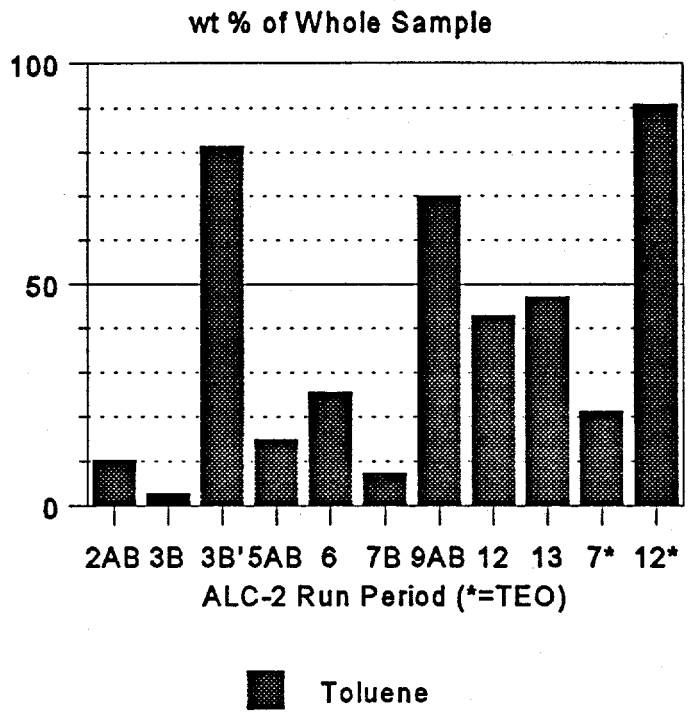


Figure 1. Toluene Concentration of As-Received TES and TEO Samples.

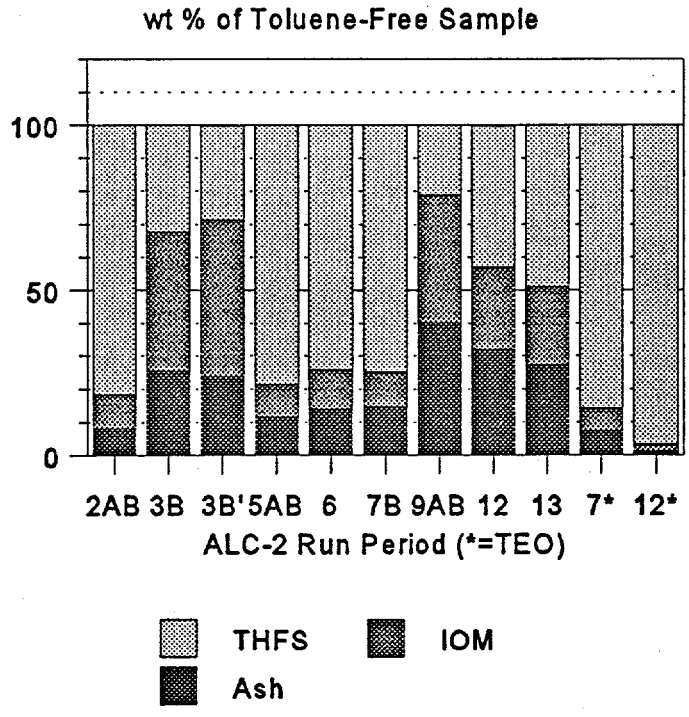


Figure 2. Composition of Toluene-Free TES and TEO Samples.

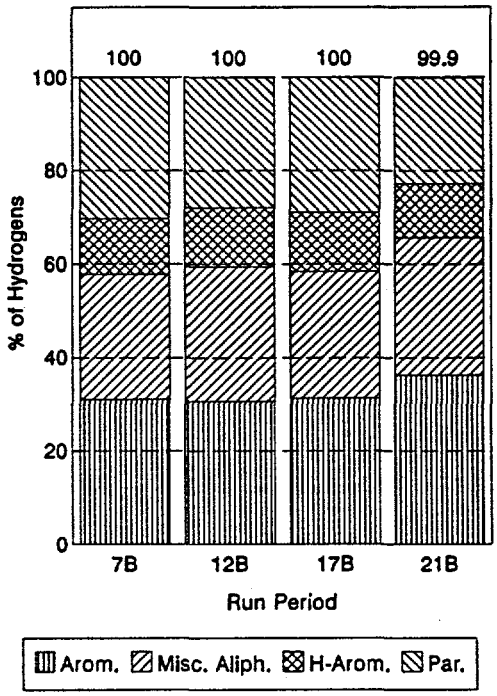


Figure 3. HTI Run ALC-2, Proton Distributions of Filtered Whole O-6 Bottoms Samples

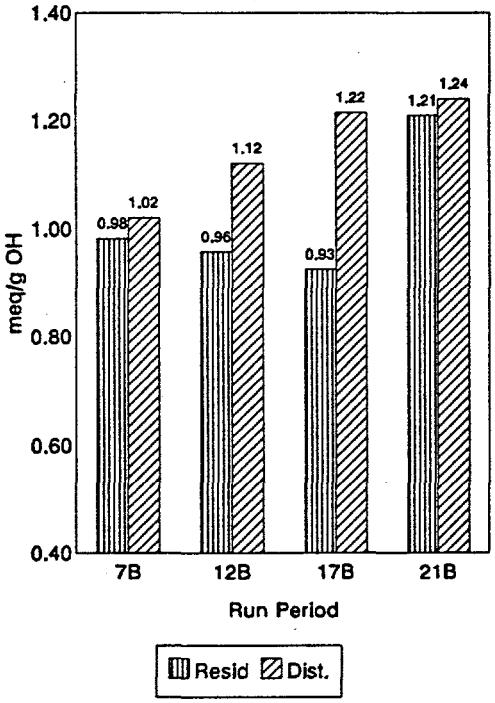


Figure 4. HTI Run ALC-2, Phenolic -OH Concentrations in O-6 Bottoms 454 °C$^-$ Distillate and 454 °C$^+$ Resid Samples.

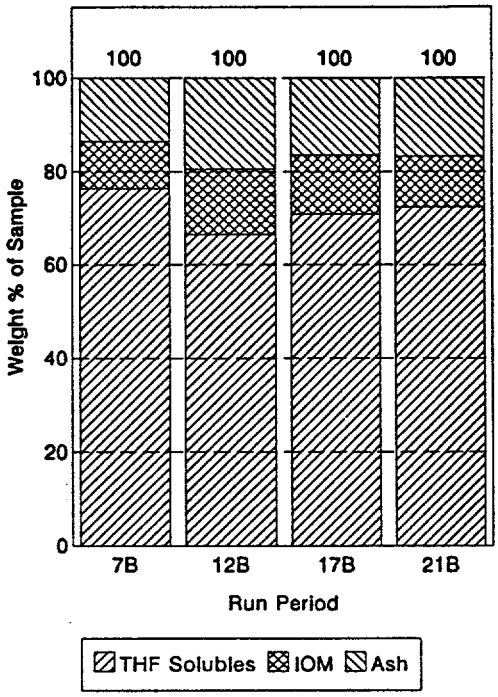


Figure 5. HTI Run ALC-2, Composition of Whole CVSB Samples.

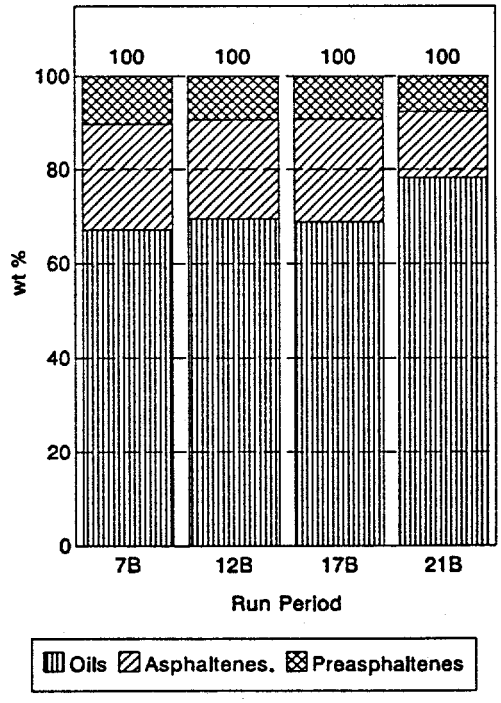


Figure 6. HTI Run ALC-2, Solubility Fractions of THF-Soluble Portion of CVSB Samples.

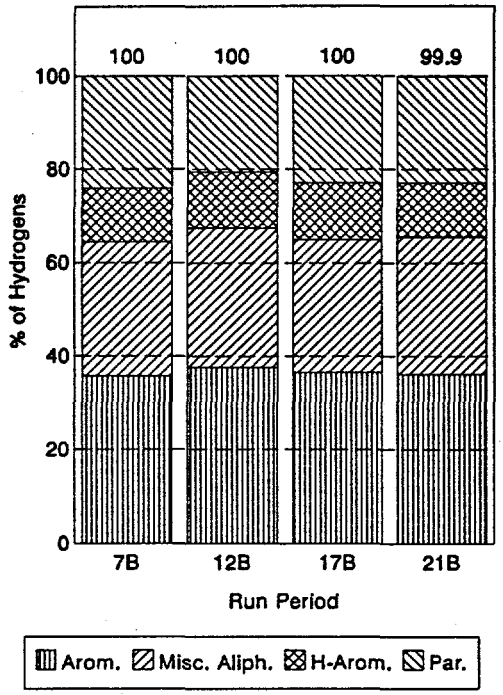


Figure 7. HTI Run ALC-2, Proton Distributions of Filtered Whole CVSB Samples.

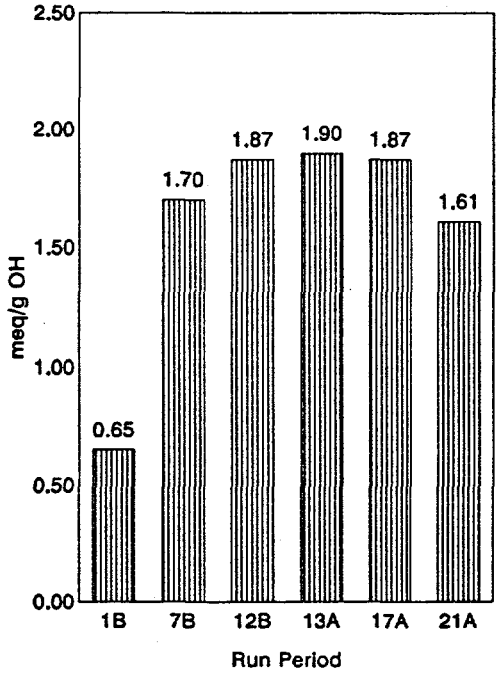


Figure 8. HTI Run ALC-2, Phenolic -OH Concentrations in First-Stage SOH Oils.

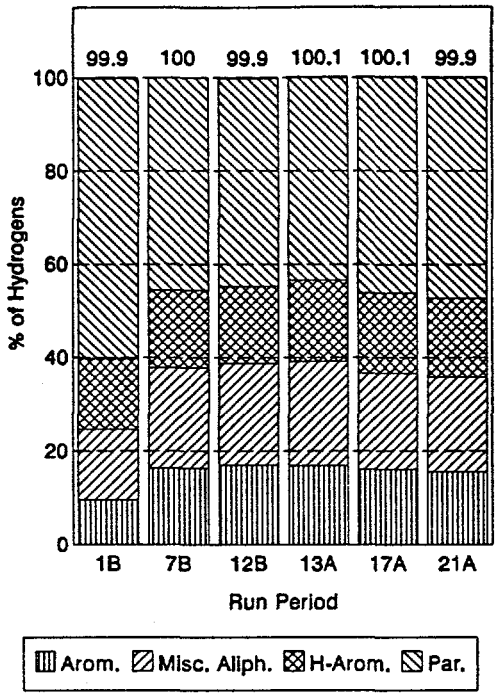


Figure 9. HTI Run ALC-2, Proton Distributions of First-Stage SOH Oils.

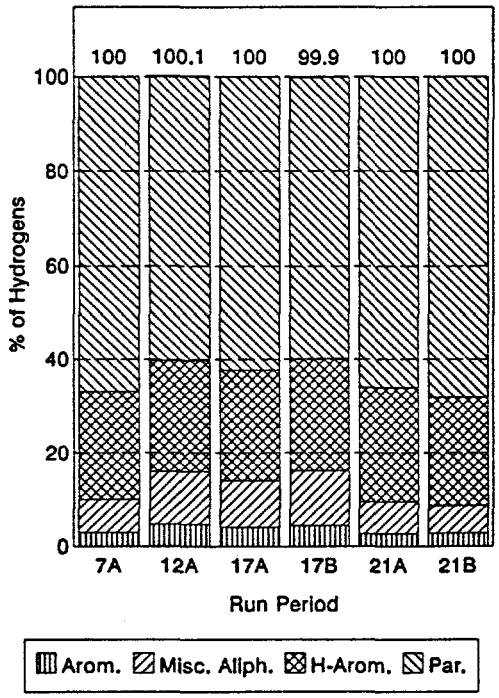


Figure 10. HTI Run ALC-2, Proton Distributions of Second-Stage SOH Oils.

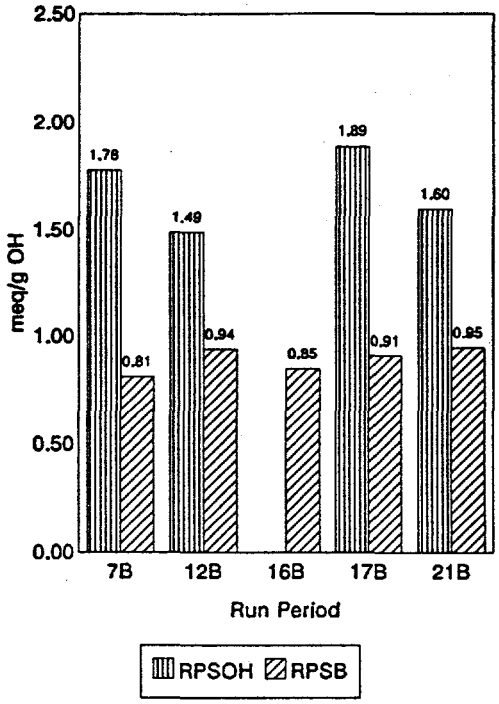


Figure 11. HTI Run ALC-2, Phenolic -OH Concentrations in RPSOH and RPSB Oils.

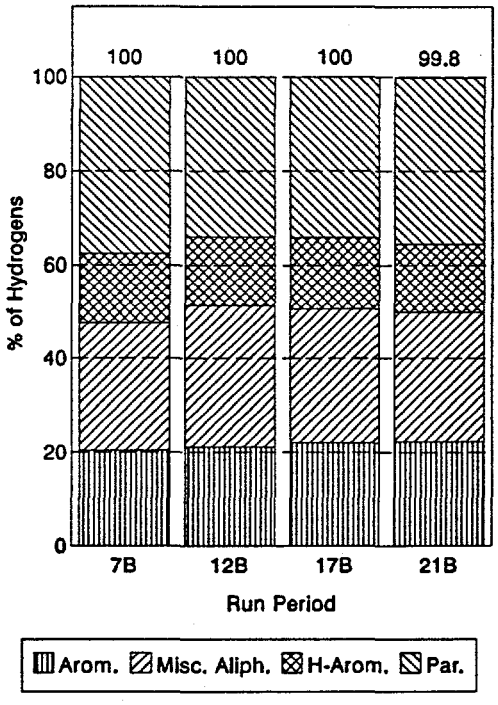


Figure 12. HTI Run ALC-2, Proton Distributions of RPSOH Oils.

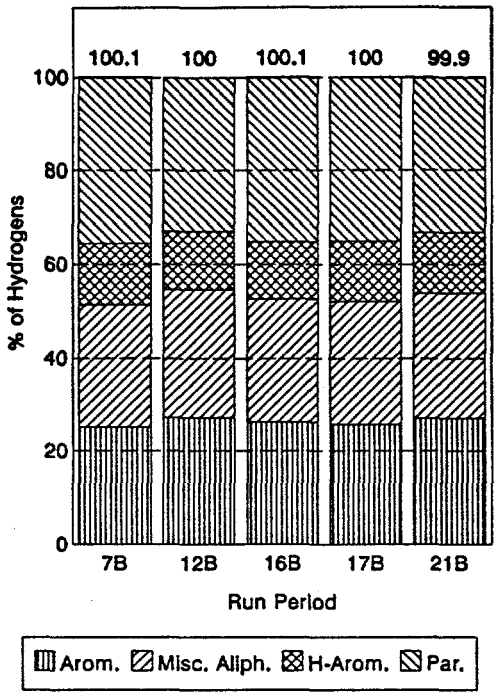


Figure 13. HTI Run ALC-2, Proton Distributions of RPSB Samples.

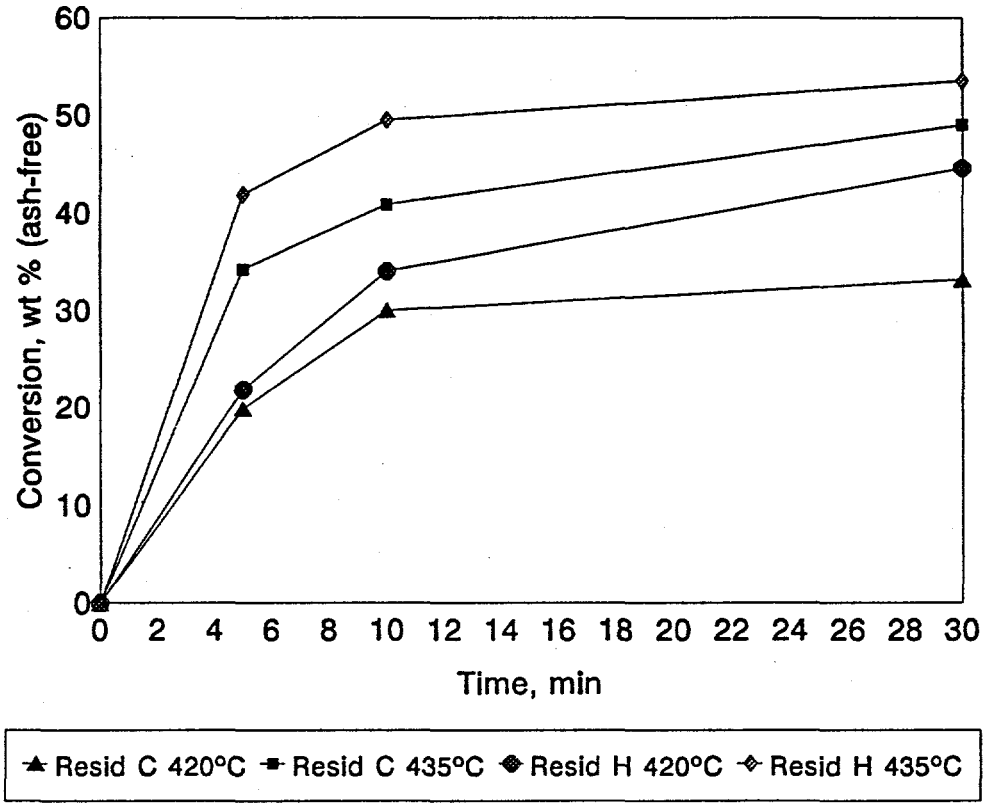


Figure 14. Conversion vs Time for the Catalyzed Hydroprocessing of Resid C and Resid H (1500 psig H_2; 3 wt % Mo; Tetralin:Resid = 3:1 wt ratio)

APPENDIX 1

CALEB BRETT REPORT ON CRUDE OIL ASSAY OF NET PRODUCTS OF HTI RUN PB-05

Intertek Testing Services
Caleb Brett

9809 Rowlett Road
Houston, TX 77075
Phone: (713) 844-3200
Fax: (713) 844-3330

Your Ref: PO# 01-001-034304

Date: 15-APR-1997

Laboratory Report No. 97-000431-0-HOUS; 1

Consol, Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129-9566

For the Attention of R.A. Winschel

SAMPLE DETAILS: 8 cut(s) from one sample received on 10-JAN-1997

SOURCE : Consol, Inc.

CUSTOMER PRODUCT DESCRIPTION :	LAB REF
"HTI PB-05-22,23,24,25 CRUDE OIL"	
Sample As Received	001-00
IBP-70 Deg. F	002-00
70-180 Deg. F	003-00
180-350 Deg. F	004-00
350-400 Deg. F	005-00
400-550 Deg. F	006-00
550-650 Deg. F	007-00
650+ Deg. F	008-00

CONTAINERS : 5 Gallon Can **SEALS :** NONE

RESULTS : SEE ATTACHED SHEETS

(TOTAL NUMBER OF PAGES 8)

Approved by: Stephen Hughes

Sample ID	Customer Product Description
	"HTI PB-05-22,23,24,25 CRUDE OIL"
97-000431-0-HOUS-001-00	Sample As Received

Test		Method	001-00
API Gravity @ 60/60 F		2-API	33.9
Specific Gravity @ 60/60 F			0.8553
Carbon	Wt. %	D5291	85.44
Hydrogen	Wt. %		11.83
Nitrogen	Wt. %		0.48
Oxygen (By Difference)	Wt. %		1.77
Sulfur Content	Wt. %	D4294	0.48
Total Nitrogen	ppm	D4629	4791.0
Ash Content for Digestion	Wt. %	D482	<0.001
Vanadium	ppm	ICP	1.2
Iron	ppm		1.2
Nickel	ppm		0.4
Freezing Point	Deg. F	D2386	Too Dark
Microcarbon Residue	Wt. %	D4530	0.40
N-Heptane Insolubles	Wt. %	D3279	0.01
Boiling Range Distribution		D2887	See Attached
Initial Boiling Point	Deg. F	D86	123
@ 5% Recovery	Deg. F		197
@ 10% Recovery	Deg. F		237
@ 20% Recovery	Deg. F		284
@ 30% Recovery	Deg. F		325
@ 40% Recovery	Deg. F		368
@ 50% Recovery	Deg. F		412
@ 60% Recovery	Deg. F		455
@ 70% Recovery	Deg. F		495
@ 80% Recovery	Deg. F		544
@ 90% Recovery	Deg. F		633
@ 95% Recovery	Deg. F		673
Final Boiling Point	Deg. F		685
Recovery	Vol. %		96.8
Residue	Vol. %		1.2
Loss	Vol. %		2.0

Sample ID	Customer Product Description
	"HTI PB-05-22,23,24,25 CRUDE OIL"
97-000431-0-HOUS-002-00	IBP-70 Deg. F

Test	Method	002-00
API Gravity @ 60/60 F	2-API	111.4
Specific Gravity @ 60/60 F		0.5826
DHA	GC-DHA	See Attached

Sample ID	Customer Product Description
	"HTI PB-05-22,23,24,25 CRUDE OIL"
97-000431-0-HOUS-003-00	70-180 Deg. F

Test		Method	003-00
API Gravity @ 60/60 F		2-API	75.0
Specific Gravity @ 60/60 F			0.6854
Carbon	Wt. %	D5291	84.28
Hydrogen	Wt. %		15.51
Nitrogen	Wt. %		0.12
Oxygen (By Difference)	Wt. %		<.01
Sulfur Content	Wt. %	D4294	0.09
Total Nitrogen	ppm	D4629	1190.0
Vapor Pressure	psi	D323	9.6
Paraffins	Vol. %	GC-PONA	63.87
Olefins	Vol. %		8.74
Naphthenes	Vol. %		24.11
Aromatics	Vol. %		3.33
Total N & A	Vol. %		27.44
Total Acid Number	mgKOH/g	D974	0.041
Corrosion 3 hrs @ 122 F		D130	4a
Existent Gum	mg/100mL	D381	5
Oxidation Stability	min.	D525	>240
Research Octane Number		D2699	70.8
Motor Octane Number		D2700	66.0
Initial Boiling Point	Deg. F	D86	100
@ 5% Evaporated	Deg. F		120
@ 10% Evaporated	Deg. F		124
@ 20% Evaporated	Deg. F		129
@ 30% Evaporated	Deg. F		134
@ 40% Evaporated	Deg. F		138
@ 50% Evaporated	Deg. F		144
@ 60% Evaporated	Deg. F		149
@ 70% Evaporated	Deg. F		155
@ 80% Evaporated	Deg. F		161
@ 90% Evaporated	Deg. F		170
@ 95% Evaporated	Deg. F		178
Final Boiling Point	Deg. F		194
Recovery	Vol. %		97.1
Residue	Vol. %		0.8
Loss	Vol. %		2.1
Benzene	Wt. %	GC	2.64

Sample ID	Customer Product Description
	"HTI PB-05-22,23,24,25 CRUDE OIL"
97-000431-0-HOUS-004-00	180-350 Deg. F

Test		Method	004-00
API Gravity @ 60/60 F		2-API	48.5
Specific Gravity @ 60/60 F			0.7862
Carbon	Wt. %	D5291	85.47
Hydrogen	Wt. %		13.18
Nitrogen	Wt. %		0.15
Oxygen (By Difference)	Wt. %		1.02
Sulfur Content	Wt. %	D4294	0.18
Total Nitrogen	ppm	D4629	1543.0
Mercaptan Sulfur Content	ppm	UOP163	516
Vapor Pressure	psi	D323	1.5
Paraffins	Vol. %	GC-PONA	41.21
Olefins	Vol. %		4.01
Naphthenes	Vol. %		30.31
Aromatics	Vol. %		24.27
Total N & A	Vol. %		54.58
Total Acid Number	mgKOH/g	D974	0.011
Corrosion 3 hrs @ 122 F		D130	3a
Existent Gum	mg/100mL	D381	16
Oxidation Stability	min.	D525	>240
Research Octane Number		D2699	66.0
Motor Octane Number		D2700	60.8
Initial Boiling Point	Deg. F	D86	196
@ 5% Evaporated	Deg. F		235
@ 10% Evaporated	Deg. F		242
@ 20% Evaporated	Deg. F		248
@ 30% Evaporated	Deg. F		255
@ 40% Evaporated	Deg. F		263
@ 50% Evaporated	Deg. F		272
@ 60% Evaporated	Deg. F		281
@ 70% Evaporated	Deg. F		291
@ 80% Evaporated	Deg. F		302
@ 90% Evaporated	Deg. F		315
@ 95% Evaporated	Deg. F		325
Final Boiling Point	Deg. F		337
Recovery	Vol. %		98.7
Residue	Vol. %		0.8
Loss	Vol. %		0.5

Sample ID	Customer Product Description
	"HTI PB-05-22,23,24,25 CRUDE OIL"
97-000431-0-HOUS-005-00	350-400 Deg. F

Test		Method	005-00
API Gravity @ 60/60 F		2-API	33.7
Specific Gravity @ 60/60 F			0.8565
Carbon	Wt. %	D5291	84.64
Hydrogen	Wt. %		11.83
Nitrogen	Wt. %		0.57
Oxygen (By Difference)	Wt. %		2.79
Sulfur Content	Wt. %	D4294	0.18
Total Nitrogen	ppm	D4629	5658.0
Mercaptan Sulfur Content	ppm	UOP163	214
Viscosity @ -20 C	cSt	D445	6.460
Viscosity @ 100 C	cSt		0.664
Freezing Point	Deg. F	D2386	-68.8
Pour Point	Deg. F	D97	<-85.0
Flash Point, TCC	Deg. F	D56	136
Vapor Pressure	psi	D323	0.1
Luminometer Number		D1740	36.0
Smoke Point	mm	D1322	15
Paraffins	Vol. %	GC-PONA	32.47
Olefins	Vol. %		6.80
Naphthenes	Vol. %		18.66
Aromatics	Vol. %		42.07
Total N & A	Vol. %		60.73
Naphthalenes	Vol. %	D1840	4.39
Total Acid Number	mgKOH/g	D974	0.04
Corrosion 3 hrs @ 122 F		D130	1a
Existent Gum	mg/100mL	D381	21
Pressure Drop	mmHg	D3241	>125.0
Oxidation Stability	min.	D525	>240
Research Octane Number		D2699	92.0
Motor Octane Number		D2700	79.2
Cetane Number		D613	19.4
Initial Boiling Point	Deg. F	D86	250
@ 5% Evaporated	Deg. F		355
@ 10% Evaporated	Deg. F		355
@ 20% Evaporated	Deg. F		357
@ 30% Evaporated	Deg. F		358
@ 40% Evaporated	Deg. F		360
@ 50% Evaporated	Deg. F		362
@ 60% Evaporated	Deg. F		364
@ 70% Evaporated	Deg. F		367
@ 80% Evaporated	Deg. F		371
@ 90% Evaporated	Deg. F		377
@ 95% Evaporated	Deg. F		382
Final Boiling Point	Deg. F		392
Recovery	Vol. %		98.7
Residue	Vol. %		1.3
Loss	Vol. %		0.0
Net Heat of Combustion	BTU/lb	D1405	18551

Sample ID	Customer Product Description
	"HTI PB-05-22,23,24,25 CRUDE OIL"
97-000431-0-HOUS-006-00	400-550 Deg. F

Test		Method	006-00
API Gravity @ 60/60 F		2-API	26.9
Specific Gravity @ 60/60 F			0.8932
Carbon	Wt. %	D5291	85.48
Hydrogen	Wt. %		11.26
Nitrogen	Wt. %		0.74
Oxygen (By Difference)	Wt. %		2.05
Sulfur Content	Wt. %	D4294	0.47
Total Nitrogen	ppm	D4629	7373.0
Basic Nitrogen	ppm	UOP269	5319
Mercaptan Sulfur Content	ppm	UOP163	262
Viscosity @ -20 C	cSt	D445	19.83
Viscosity @ 40 C	cSt		2.509
Viscosity @ 100 C	cSt		0.969
Freezing Point	Deg. F	D2386	-24.7
Pour Point	Deg. F	D97	-27.0
Aniline Point	Deg. F	D611	92.5
Flash Point, TCC	Deg. F	D56	200
Luminometer Number		D1740	22.0
Smoke Point	mm	D1322	10
Paraffins	Vol. %	GC-PONA	22.73
Olefins	Vol. %		8.60
Naphthenes	Vol. %		16.87
Aromatics	Vol. %		51.80
Total N & A	Vol. %		68.67
Naphthalenes	Vol. %	D1840	7.02
Total Acid Number	mgKOH/g	D974	0.042
Corrosion 3 hrs @ 122 F		D130	1a
Existent Gum	mg/100mL	D381	29
Pressure Drop	mmHg	D3241	>125.0
Cetane Number		D613	19.6
Initial Boiling Point	Deg. F	D86	425
@ 5% Evaporated	Deg. F		436
@ 10% Evaporated	Deg. F		438
@ 20% Evaporated	Deg. F		442
@ 30% Evaporated	Deg. F		446
@ 40% Evaporated	Deg. F		451
@ 50% Evaporated	Deg. F		458
@ 60% Evaporated	Deg. F		465
@ 70% Evaporated	Deg. F		475
@ 80% Evaporated	Deg. F		486
@ 90% Evaporated	Deg. F		500
@ 95% Evaporated	Deg. F		514
Final Boiling Point	Deg. F		525
Recovery	Vol. %		98.4
Residue	Vol. %		0.8
Loss	Vol. %		0.8
Net Heat of Combustion	BTU/lb	D1405	18294

Sample ID	Customer Product Description
	"HTI PB-05-22,23,24,25 CRUDE OIL"
97-000431-0-HOUS-007-00	550-650 Deg. F

Test		Method	007-00
API Gravity @ 60/60 F		2-API	19.8
Specific Gravity @ 60/60 F			0.9355
Sulfur Content	Wt. %	D4294	0.59
Total Nitrogen	ppm	D4629	6114.0
Carbon	Wt. %	D5291	86.62
Hydrogen	Wt. %		10.58
Nitrogen	Wt. %		0.61
Oxygene (By Difference)	Wt. %		1.6
Basic Nitrogen	ppm	UOP269	3503
Viscosity @ 40 C	cSt	D445	10.04
Viscosity @ 100 C	cSt		1.837
Pour Point	Deg. F	D97	32.0
Aniline Point	Deg. F	D611	108.0
Flash Point (Method B)	Deg. F	D93	>200
Paraffins	Vol. %	GC-PNA	25.33
Naphthenes	Vol. %		14.55
Aromatics	Vol. %		60.12
Bromine Number		D1159	16.0
Corrosion 3 hrs @ 122 F		D130	1a
Cetane Number		D613	26.9
Initial Boiling Point	Deg. F	D86	557
@ 5% Evaporated	Deg. F		573
@ 10% Evaporated	Deg. F		576
@ 20% Evaporated	Deg. F		577
@ 30% Evaporated	Deg. F		579
@ 40% Evaporated	Deg. F		580
@ 50% Evaporated	Deg. F		582
@ 60% Evaporated	Deg. F		585
@ 70% Evaporated	Deg. F		589
@ 80% Evaporated	Deg. F		594
@ 90% Evaporated	Deg. F		603
@ 95% Evaporated	Deg. F		610
Final Boiling Point	Deg. F		621
Recovery	Vol. %		97.7
Residue	Vol. %		1.1
Loss	Vol. %		1.2

Sample ID	Customer Product Description
	"HTI PB-05-22,23,24,25 CRUDE OIL"
97-000431-0-HOUS-008-00	650+ Deg. F

Test		Method	008-00
API Gravity @ 60/60 F		2-API	11.1
Specific Gravity @ 60/60 F			0.9923
Carbon	Wt. %	D5291	88.55
Hydrogen	Wt. %		9.67
Nitrogen	Wt. %		0.75
Oxygene (By Difference)	Wt. %		<.01
Sulfur Content	Wt. %	D4294	1.03
Total Nitrogen	ppm	D4629	7543.0
Basic Nitrogen	ppm	UOP269	3630
Ash Content for Digestion	Wt. %	D482	0.119
Viscosity @ 40 C	cSt	D445	34.36
Viscosity @ 100 C	cSt		4.472
Pour Point	Deg. F	D97	75.0
Aniline Point	Deg. F	D611	131.0
Flash Point (Method B)	Deg. F	D93	>200
Microcarbon Residue	Wt. %	D4530	1.80
Corrosion 3 hrs @ 122 F		D130	1b
Cetane Number		D613	* See Note *
Initial Boiling Point	Deg. F	D1160	660
@ 5% Recovery	Deg. F		673
@ 10% Recovery	Deg. F		673
@ 20% Recovery	Deg. F		681
@ 30% Recovery	Deg. F		684
@ 40% Recovery	Deg. F		689
@ 50% Recovery	Deg. F		696
@ 60% Recovery	Deg. F		706
@ 70% Recovery	Deg. F		719
@ 80% Recovery	Deg. F		738
@ 90% Recovery	Deg. F		797
@ 95% Recovery	Deg. F		873
Final Boiling Point	Deg. F		980
Recovery	Vol. %		97.0
Residue + Loss	Vol. %		3.0

* Note * The boiling point of this fraction is out of the scope of the method. (Fraction is too heavy).

CALEB BRETT HOUSTON

TID: 97-000431-0-HOUS-001-00
CID: CONSOLINC
SID: HTI PB05-22,23,24,25 CRUDE OIL/AS RECEIVED
NID: 58102 Date: 10-JAN-1997

Boiling Point Distribution

ASTM D-2887

%Off	BP(F)	BP(C)	%Off	BP(F)	BP(C)	%Off	BP(F)	BP(C)
IBP	84.2	29.0	40	384.2	195.7	80	568.5	298.1
1	91.3	32.9	41	388.4	198.0	81	573.2	300.7
2	146.0	63.3	42	390.5	199.2	82	577.0	302.8
3	158.0	70.0	43	395.3	201.8	83	584.0	306.7
4	167.8	75.4	44	399.2	204.0	84	589.9	309.9
5	181.6	83.1	45	402.6	205.9	85	596.8	313.8
6	191.3	88.5	46	409.0	209.4	86	600.8	316.0
7	205.5	96.4	47	415.2	212.9	87	607.9	319.9
8	209.8	98.8	48	416.9	213.8	88	615.4	324.1
9	214.7	101.5	49	422.0	216.7	89	622.2	327.9
10	224.5	106.9	50	426.6	219.2	90	630.0	332.2
11	228.5	109.2	51	430.9	221.6	91	638.3	336.8
12	235.0	112.8	52	434.4	223.6	92	646.2	341.2
13	239.5	115.3	53	437.2	225.1	93	654.7	345.9
14	253.0	122.8	54	443.2	228.4	94	667.5	353.1
15	255.7	124.3	55	448.1	231.2	95	677.5	358.6
16	265.3	129.6	56	452.4	233.6	96	691.9	366.6
17	268.3	131.3	57	455.2	235.1	97	712.4	378.0
18	272.8	133.8	58	459.4	237.4	98	738.8	392.7
19	273.6	134.2	59	463.2	239.6	99	810.1	432.3
20	277.0	136.1	60	467.8	242.1	FBP	1238.2	670.1
21	284.4	140.2	61	471.3	244.1			
22	288.5	142.5	62	475.3	246.3			
23	297.9	147.7	63	479.4	248.6			
24	300.3	149.1	64	481.7	249.8			
25	309.2	154.0	65	485.2	251.8			
26	314.4	156.9	66	490.8	254.9			
27	319.5	159.7	67	497.2	258.4			
28	326.6	163.7	68	501.9	261.1			
29	329.2	165.1	69	509.0	265.0			
30	336.1	168.9	70	513.7	267.6			
31	340.5	171.4	71	518.5	270.3			
32	344.3	173.5	72	524.1	273.4			
33	351.2	177.3	73	529.7	276.5			
34	355.4	179.7	74	534.6	279.2			
35	362.2	183.4	75	541.4	283.0			
36	364.7	184.8	76	545.4	285.2			
37	366.3	185.7	77	551.2	288.4			
38	374.4	190.2	78	557.6	292.0			
39	379.4	193.0	79	562.5	294.7			

Start Time: 0.2 minutes
End Time: 44.7 minutes
Area: 124898168.0
Slice Width: 0.80 sec
Baseline Subtracted: C:\TC4\SD6890\0312BA

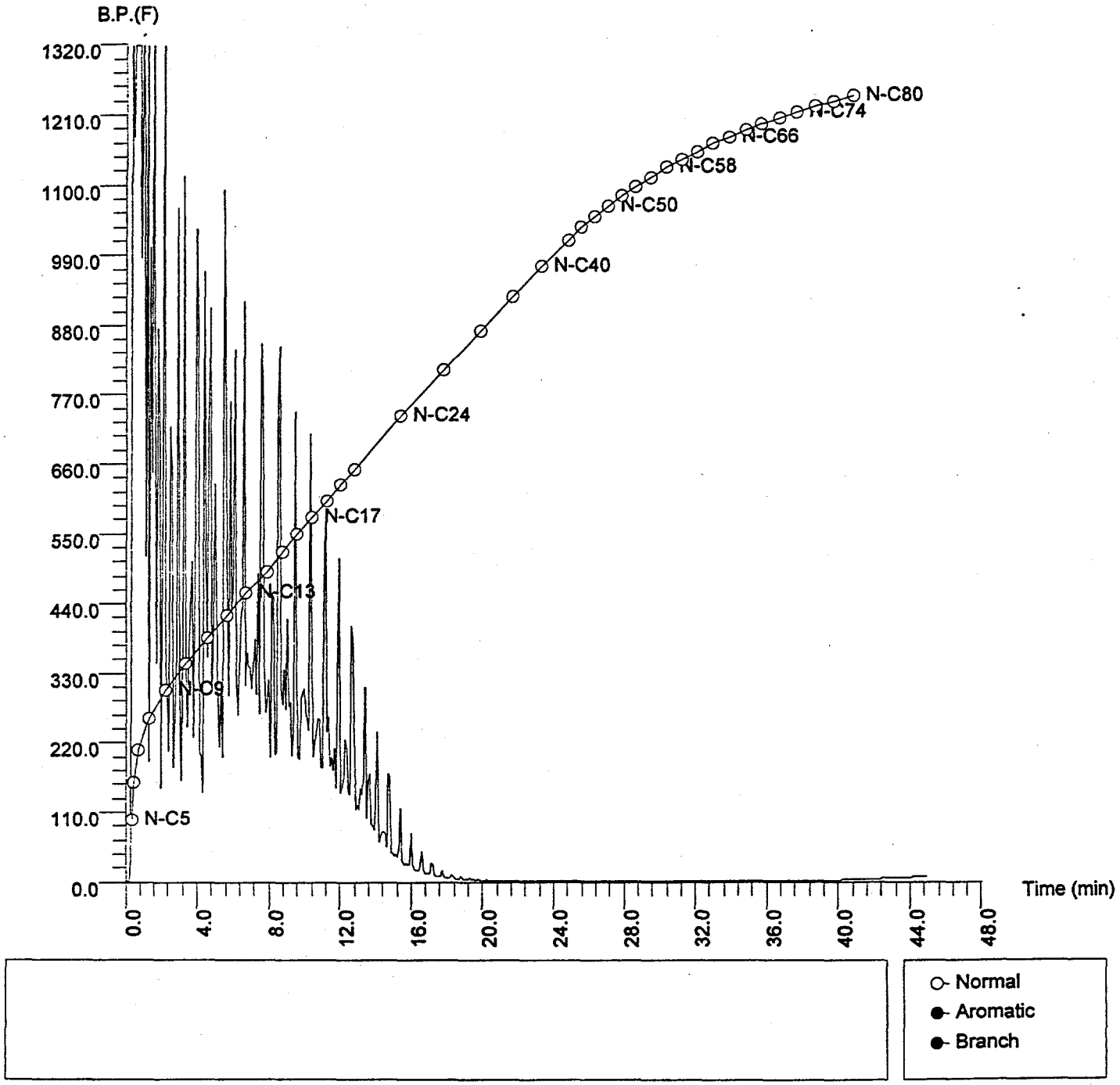
Sample Offset: 8908.0
Baseline Offset: 8422.0
Calibration File: 0312rtaa
Calibration Date: 03/13/97

CALEB BRETT HOUSTON

TID: 97-000431-0-HOUS-001-00
CID: CONSOLINC
SID: HTI PB05-22,23,24,25 CRUDE OIL/AS RECEIVED
NID: 58102 Date: 10-JAN-1997

Calibration Plot

ASTM D-2887



Standard Practice for			SAMPLE :	97-431-2								
Interconversion of Analysis of C5 and Lighter Hydrocarbons to												
Gas-Volume, Liquid-Volume, or Weight Basis												
ASTM D 2421-89												
	Conversion of Weight % to Gas or Liquid Volume %						Gas Vol%	Gas Vol%				
	Enter wt%		Liq.vol.1ml	Rel.dens.	Liq vol %	Liq Vol%	(mole %)	(mole %)	Vapor Pr.	Vapor Pr.	Sp.gravity	
	result here	Mol. wt.	idl.gas 60/760	60/60(vac)	Unnorm	Norm	Unnorm	Norm	psig	Tot. psig	Average	
Methane	0	16.04	0.00226	0.3	0	0	0	0	4985.3	0	0	Methane
Ethane	0.74	30.07	0.003566	.0.3562	2.077485	1.210329	0.024609	1.440148	700	8.472301	0.004311	Ethane
Acetylene	0	26.04	0.00263	0.418	0	0	0	0		0	0	Acetylene
Ethylene	0	28.05	0.0032	0.37	0	0	0	0		0	0	Ethylene
Propane	14.24	44.1	0.003675	0.507	28.08679	16.36317	0.322902	18.89646	174	28.47192	0.082961	Propane
Propylene	0	42.08	0.003413	0.521	0	0	0	0	213	0	0	Propylene
Propadiene	0	40.06	0.00282	0.6	0	0	0	0		0	0	Propadiene
Methylacetylene	0	40.06	0.00273	0.621	0	0	0	0		0	0	Methylacet
n-Butane	30.81	58.12	0.004205	0.584	52.75685	30.73579	0.53011	31.02237	37	11.37224	0.179497	n-Butane
Isobutane	10.84	58.12	0.004362	0.5629	19.25742	11.21924	0.186511	10.91472	58	6.507161	0.063153	Isobutane
1-Butene	0	56.11	0.003944	0.6011	0	0	0	0	47.4	0	0	1-Butene
trans-2-Butene	5.1	56.11	0.003887	0.61	8.360656	4.870862	0.090893	5.319109	35.24	1.716492	0.029712	trans-2-But
cis-2-Butene	5.64	56.11	0.00378	0.6272	8.992347	5.238881	0.100517	5.882308	31.25	1.63715	0.032858	cis-2-Buten
Isobutylene	10.57	56.11	0.003949	0.6004	17.60493	10.25651	0.18838	11.02411	48.94	5.019538	0.06158	Isobutylene
1,2-Butadiene	0	54.09	0.00347	0.658	0	0	0	0	21.8	0	0	1,2-Butadie
1,3-Butadiene	0.01	54.09	0.003643	0.6272	0.015944	0.009289	0.000185	0.010819	44.7	0.004152	5.83E-05	1,3-Butadie
Ethylacetylene	0	54.09	0.00328	0.696	0	0	0	0		0	0	Ethylacetyl
n-Pentane	6.43	72.15	0.00483	0.6311	10.18856	5.935787	0.08912	5.215351	0.875	0.051938	0.037461	n-Pentane
Isopentane	10.75	72.15	0.004879	0.6247	17.20826	10.02542	0.148995	8.719289	5.744	0.57586	0.062629	Isopentane
Neopentane	0.23	72.15	0.005108	0.5967	0.385453	0.224563	0.003188	0.186552	21.96	0.049314	0.00134	Neopentan
1-Pentene	0.44	70.13	0.004589	0.6457	0.681431	0.396997	0.006274	0.367162	4.417	0.017535	0.002563	1-Pentene
trans-2-Pentene	0.28	70.13	0.004537	0.653	0.42879	0.24981	0.003993	0.233649		0	0.001631	trans-2-Pen
cis-2-Pentene	0.14	70.13	0.004482	0.6611	0.211768	0.123375	0.001996	0.116824		0	0.000816	cis-2-Pente
2-Methyl-1-Butene	0.17	70.13	0.004519	0.6557	0.259265	0.151046	0.002424	0.141858		0	0.00099	2-Methyl-1-
3-Methyl-1-Butene	0.01	70.13	0.004684	0.6325	0.01581	0.009211	0.000143	0.008345		0	5.83E-05	3-Methyl-1-
2-Methyl-2-Butene	0.16	70.13	0.00447	0.663	0.241327	0.140596	0.002281	0.133513		0	0.000932	2-Methyl-2-
Cyclopentane	0.43	70.13	0.003948	0.7505	0.572951	0.333798	0.006131	0.358817		0	0.002505	Cyclopenta
Isoprene	0.01	68.12	0.004195	0.6861	0.014575	0.008491	0.000147	0.008591		0	5.83E-05	Isoprene
1-trans-3-Pentadiene	0	68.12	0.004224	0.6815	0	0	0	0		0	0	1-trans-3-P
1-cis-Pentadiene	0	68.12	0.004133	0.6964	0	0	0	0		0	0	1-cis-Penta
1,2-Pentadiene	0	68.12	0.004125	0.6976	0	0	0	0		0	0	1,2-Pentadi
C6+	3	85		0.7	4.285714	2.496829					0.017478	C6+
Total	100				171.6463	100	1.708799	100		63.89561	0.582593	
Calculated Vapor Pressure		63.89561										
		0.582593										

CALEB BRETT HOUSTON

TID: 97-000431-0-HOUS-002-00
CID: CONSOLINC
SID: HTI PB05-22,23,24,25 CRUDE OIL/IBP-70 F
NID: 58159 Date: 10-JAN-1997

Analyzed: 1/29/97 9:49 AM
Reported: 01-29-1997 11:45:10
Normalized to 100.00%

Comments:

Components Listed in Chromatographic Order

Min.	INDEX	Component	Wt%	Vol%	Mol%
6.592	182.7	ethylene	0.002	0.004	0.004
6.656	200.0	ethane	0.735	1.246	1.401
7.086	300.0	propane	14.236	16.394	18.504
7.677	347.6	?	0.016	0.018	0.021
7.777	353.3	?	0.008	0.010	0.011
8.088	368.5	i-butane	10.835	11.208	10.685
8.729	392.3	isobutylene	10.570	10.237	10.798
8.988	400.0	n-butane	30.807	30.678	30.380
9.438	414.7	t-butene-2	5.104	4.869	5.214
9.525	417.3	2,2-dimethylpropane	0.225	0.220	0.179
9.779	424.5	?	0.006	0.006	0.005
9.946	428.9	c-butene-2	5.641	5.233	5.762
10.302	437.7	?	0.001	0.001	0.001
11.129	455.2	ethanol	0.006	0.004	0.007
11.411	460.5	3-methylbutene-1	0.403	0.371	0.330
12.479	478.1	i-pentane	10.750	10.000	8.540
13.321	489.9	pentene-1	0.440	0.396	0.360
13.481	491.9	i-propanol	0.005	0.003	0.004
13.582	493.2	?	0.006	0.004	0.006
13.775	495.6	2-methylbutene-1	0.170	0.151	0.139
14.138	500.0	n-pentane	6.430	5.918	5.108
14.353	504.1	isoprene	0.006	0.005	0.005
14.607	508.9	t-pentene-2	0.281	0.250	0.230
14.948	515.0	3,3-dimethylbutene-1	0.001	0.001	0.001
15.112	517.9	c-pentene-2	0.138	0.121	0.113
15.437	523.4	2-methylbutene-2	0.159	0.138	0.130
16.437	539.2	2,2-dimethylbutane	0.008	0.007	0.005
17.504	554.4	O6	0.066	0.059	0.054
17.647	556.3	cyclopentene	0.046	0.034	0.038
18.017	561.2	4-methylpentene-1	0.021	0.018	0.014
18.084	562.0	3-methylpentene-1	0.008	0.007	0.006
18.419	566.3	cyclopentane	0.429	0.332	0.351
18.613	568.7	2,3-dimethylbutane	0.061	0.053	0.040
18.751	570.4	4-methyl-c-pentene-2	0.003	0.002	0.002
18.895	572.1	?	0.006	0.005	0.004
19.001	573.4	2-methylpentane	0.831	0.733	0.553
19.120	574.8	4-methyl-t-pentene-2	0.018	0.015	0.012
20.020	585.1	3-methylpentane	0.233	0.202	0.155
20.449	589.8	2-methylpentene-1	0.014	0.012	0.010
20.532	590.6	hexene-1	0.017	0.014	0.011
21.440	600.0	n-hexane	0.478	0.418	0.318
21.643	602.6	c-hexene-3	0.007	0.006	0.005
21.699	603.3	?	0.002	0.002	0.001

File: 431-2.DHA Sample: 97-431-2 p. 1

Components Listed in Chromatographic Order

Min.	INDEX	Component	Wt%	Vol%	Mol%
21.848	605.2	?	0.014	0.012	0.009
22.042	607.6	2-methylpentene-2	0.021	0.018	0.015
22.264	610.3	3-methylcyclopentene	0.004	0.003	0.003
22.356	611.4	O13	0.002	0.002	0.002
22.603	614.4	O14	0.007	0.006	0.005
23.137	620.7	3-methyl-t-pentene-2	0.005	0.004	0.003
23.428	624.0	2,2-dimethylpentane	0.001	0.001	0.000
23.582	625.8	methylcyclopentane	0.246	0.189	0.167
24.003	630.5	2,4-dimethylpentane	0.023	0.020	0.013
25.065	641.8	?	0.000	0.000	0.000
25.528	646.5	?	0.001	0.001	0.001
25.738	648.6	1-methylcyclopentene	0.005	0.004	0.004
25.867	649.9	benzene	0.012	0.008	0.009
26.325	654.4	5-methylhexene-1	0.000	0.000	0.000
26.429	655.4	?	0.001	0.001	0.001
26.683	657.9	cyclohexane	0.135	0.100	0.092
27.310	663.8	4-methylhexene-1	0.001	0.000	0.000
27.571	666.2	4-methyl-t/c-hexene-2	0.001	0.000	0.000
27.720	667.5	2,3-dimethylpentane	0.012	0.010	0.007
27.865	668.8	5-methyl-t-hexene-2	0.005	0.004	0.003
28.139	671.3	1,1-dimethylcyclopentane	0.002	0.001	0.001
28.415	673.7	cyclohexene	0.007	0.005	0.005
28.663	675.9	3-methylhexane	0.014	0.011	0.008
29.351	681.8	1c,3-dimethylcyclopentane	0.007	0.005	0.004
29.676	684.5	1t,3-dimethylcyclopentane	0.006	0.005	0.004
29.842	685.9	3-ethylpentane	0.001	0.001	0.000
30.001	687.2	1t,2-dimethylcyclopentane	0.010	0.008	0.006
30.200	688.8	heptene-1	0.000	0.000	0.000
31.429	698.5	t-heptene-3	0.001	0.000	0.000
31.622	700.0	n-heptane	0.012	0.010	0.007
32.929	709.0	3-methyl-t-hexene-2	0.000	0.000	0.000
34.319	718.0	methylcyclohexane	0.014	0.011	0.008
34.768	720.9	*1,1,3-trimethylcyclopentane	0.001	0.000	0.000
35.373	724.6	?	0.127	0.098	0.065
36.110	729.1	ethylcyclopentane	0.001	0.001	0.001
37.525	737.3	1c,2t,4-trimethylcyclopentane	0.001	0.001	0.000
38.788	744.4	1t,2c,3-trimethylcyclopentane	0.001	0.001	0.001
40.178	751.8	toluene	0.028	0.019	0.018
42.621	764.2	?	0.001	0.001	0.001
44.212	771.9	3-methylheptane	0.000	0.000	0.000
44.496	773.2	1c,2t,3-trimethylcyclopentane	0.001	0.001	0.000
44.904	775.1	1t,4-dimethylcyclohexane	0.000	0.000	0.000
47.825	788.1	2t-ethylmethylcyclopentane	0.001	0.000	0.000
49.008	793.0	?	0.001	0.001	0.000
50.711	800.0	n-octane	0.002	0.001	0.001
55.086	817.2	?	0.034	0.028	0.017
59.275	832.3	?	0.001	0.001	0.001
61.050	838.3	2,5-dimethylheptane	0.001	0.001	0.000
65.933	853.9	I4	0.001	0.001	0.000
69.237	863.8	N14	0.001	0.001	0.001
76.400	883.5	I6	0.001	0.001	0.000

CALEB BRETT HOUSTON

TID: 97-000431-0-HOUS-002-00
CID: CONSOLINC
SID: HTI PB05-22,23,24,25 CRUDE OIL/IBP-70 F
NID: 58159 Date: 10-JAN-1997

Analyzed: 1/29/97 9:49 AM
Reported: 01-29-1997 11:45:10
Normalized to 100.00%

Comments:

Composite Report
Totals by Group Type & Carbon Number
(in Weight Percent)

	Paraffins:	I-paraffins:	Aromatics:	Naphthenes:	Olefins:	Total:
C1:	0.000	0.000	0.000	0.000	0.000	0.000
C2:	0.735	0.000	0.000	0.000	0.002	0.737
C3:	14.236	0.000	0.000	0.000	0.000	14.236
C4:	30.807	10.835	0.000	0.000	21.315	62.957
C5:	6.430	10.975	0.000	0.429	1.711	19.545
C6:	0.478	1.132	0.012	0.381	0.139	2.142
C7:	0.012	0.050	0.028	0.041	0.008	0.138
C8:	0.002	0.000	0.000	0.005	0.000	0.007
C9:	0.000	0.002	0.000	0.001	0.000	0.004
C10:	0.000	0.000	0.000	0.000	0.000	0.000
C11:	0.000	0.000	0.000	0.000	0.000	0.000
C12:	0.000	0.000	0.000	0.000	0.000	0.000
C13:	0.000	0.000	0.000	0.000	0.000	0.000
C14:	0.000	0.000	0.000	0.000	0.000	0.000
Total:	52.700	22.995	0.040	0.856	23.173	99.765

Oxygenates: 0.011 Total C14+: 0.000 Total Unknowns: 0.225
Grand Total: 100.000

Molecular Weight and Relative Density Data

Group:	Ave. Mw.:	Ave. Rel. Density:
C1:	0.000	0.000
C2:	30.064	0.340
C3:	44.097	0.501
C4:	57.425	0.583
C5:	71.919	0.626
C6:	85.615	0.676
C7:	97.749	0.737
C8:	112.832	0.745
C9:	127.536	0.744
C10:	0.000	0.000
C11:	0.000	0.000
C12:	0.000	0.000
C13:	0.000	0.000
C14:	0.000	0.000
Total Sample:	57.184	0.575

File: 431-2.DHA

CALEB BRETT HOUSTON

TID: 97-000431-0-HOUS-002-00
CID: CONSOLINC
SID: HTI PB05-22,23,24,25 CRUDE OIL/IBP-70 F
NID: 58159 Date: 10-JAN-1997

Analyzed: 1/29/97 9:49 AM
Reported: 01-29-1997 11:45:10
Normalized to 100.00%

Comments:

Composite Report
Totals by Group Type & Carbon Number
(in Volume Percent)

	Paraffins:	I-paraffins:	Aromatics:	Naphthenes:	Olefins:	Total:
C1:	0.000	0.000	0.000	0.000	0.000	0.000
C2:	1.246	0.000	0.000	0.000	0.004	1.250
C3:	16.394	0.000	0.000	0.000	0.000	16.394
C4:	30.678	11.208	0.000	0.000	20.339	62.224
C5:	5.918	10.220	0.000	0.332	1.526	17.996
C6:	0.418	0.995	0.008	0.289	0.116	1.826
C7:	0.010	0.042	0.019	0.031	0.006	0.108
C8:	0.001	0.000	0.000	0.003	0.000	0.005
C9:	0.000	0.002	0.000	0.001	0.000	0.003
C10:	0.000	0.000	0.000	0.000	0.000	0.000
C11:	0.000	0.000	0.000	0.000	0.000	0.000
C12:	0.000	0.000	0.000	0.000	0.000	0.000
C13:	0.000	0.000	0.000	0.000	0.000	0.000
C14:	0.000	0.000	0.000	0.000	0.000	0.000
Total:	54.665	22.467	0.027	0.656	21.990	99.806

Oxygenates: 0.008 Total C14+: 0.000 Total Unknowns: 0.187
Grand Total: 100.000

(in Mole Percent)

	Paraffins:	I-paraffins:	Aromatics:	Naphthenes:	Olefins:	Total:
C1:	0.000	0.000	0.000	0.000	0.000	0.000
C2:	1.401	0.000	0.000	0.000	0.004	1.405
C3:	18.504	0.000	0.000	0.000	0.000	18.504
C4:	30.380	10.685	0.000	0.000	21.774	62.840
C5:	5.108	8.719	0.000	0.351	1.399	15.577
C6:	0.318	0.753	0.009	0.259	0.095	1.434
C7:	0.007	0.029	0.018	0.024	0.004	0.081
C8:	0.001	0.000	0.000	0.002	0.000	0.003
C9:	0.000	0.001	0.000	0.001	0.000	0.002
C10:	0.000	0.000	0.000	0.000	0.000	0.000
C11:	0.000	0.000	0.000	0.000	0.000	0.000
C12:	0.000	0.000	0.000	0.000	0.000	0.000
C13:	0.000	0.000	0.000	0.000	0.000	0.000
C14:	0.000	0.000	0.000	0.000	0.000	0.000
Total:	55.719	20.187	0.026	0.637	23.277	99.846

Oxygenates: 0.012 Total C14+: 0.000 Total Unknowns: 0.142
Grand Total: 100.000

File: 431-2.DHA

CALEB BRETT HOUSTON

TID: 97-000431-0-HOUS-002-00
CID: CONSOLINC
SID: HTI PB05-22,23,24,25 CRUDE OIL/IBP-70 F
NID: 58159 Date: 10-JAN-1997

Analyzed: 1/29/97 9:49 AM
Reported: 01-29-1997 11:45:10
Normalized to 100.00%

Comments:

Boiling Point Distribution Data

	Wt. Percent Off: deg.C.:	deg.F.:	Vol. Percent Off: deg.C.:	deg.F.:
IBP (0.5%)	-88.60	-127.48	-88.60	-127.48
5.0%	-42.04	-43.67	-42.04	-43.67
10.0%	-42.04	-43.67	-42.04	-43.67
15.0%	-11.72	10.90	-42.04	-43.67
20.0%	-11.72	10.90	-11.72	10.90
25.0%	-11.72	10.90	-11.72	10.90
30.0%	-6.25	20.75	-6.25	20.75
35.0%	-6.25	20.75	-6.25	20.75
40.0%	-0.50	31.10	-0.50	31.10
45.0%	-0.50	31.10	-0.50	31.10
50.0%	-0.50	31.10	-0.50	31.10
55.0%	-0.50	31.10	-0.50	31.10
60.0%	-0.50	31.10	-0.50	31.10
65.0%	-0.50	31.10	-0.50	31.10
70.0%	0.88	33.58	0.88	33.58
75.0%	3.72	38.70	3.72	38.70
80.0%	27.84	82.11	9.50	49.10
85.0%	27.84	82.11	27.84	82.11
90.0%	36.06	96.91	27.84	82.11
95.0%	36.06	96.91	36.06	96.91
FBP (99.5%)	71.80	161.24	71.80	161.24

Research Octane Number =108.61
(Calculated from Individual Component Values)

Contribution to Total by:

Paraffins:	57.15
Iso-paraffins:	24.97
Aromatics:	0.05
Naphthenes:	0.75
Olefins:	25.53
Oxygenates:	0.01

File: 431-2.DHA

Intertek Testing Services
Caleb Brett

WinAssay '95

Version 1.00

Final Reports

Client Name:	**Consol Inc.**
Sample ID:	**HTI PB-05-22,23,24,25**
Laboratory ID:	**97-000431**
Date:	**02/14/97**
Operator:	**Robert Kelly**

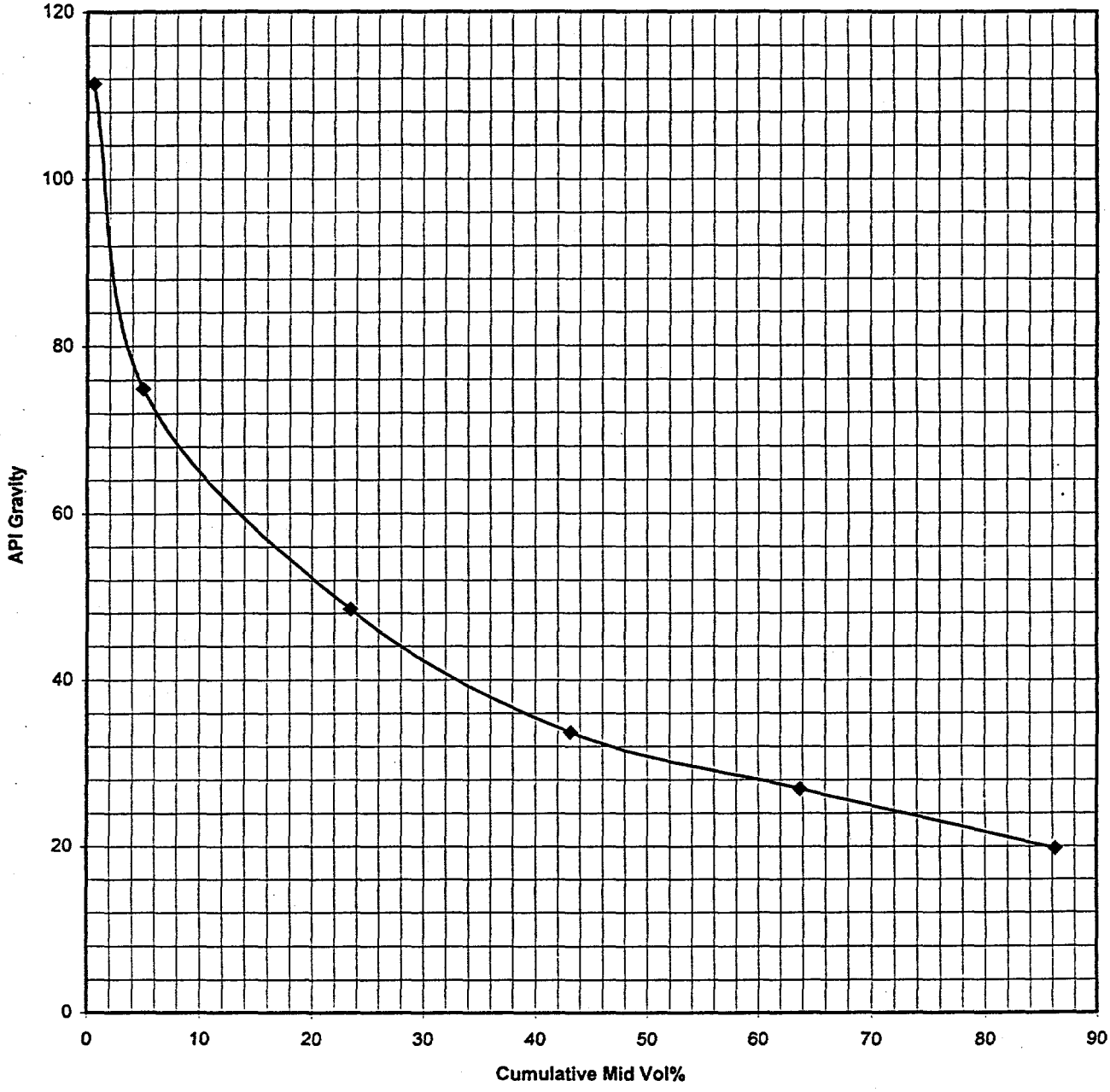
Prepared For: Consol Inc.
Sample ID: HTI PB-05-22,23,24,25
Date: 02/14/97

Cut Temp	Degrees F TO	DUMP WT(g)	Specific Gravity	MLS	LIQ VOL%	CUM. LIQ VOL%	WT%	CUM WT%	API GRAVITY	MID LIQ VOL%
ASTM D2892 Distillation Yields										
IBP	70	82.40	0.5826	141.43	1.19	1.19	0.81	0.81	111.38	0.60
70	180	616.20	0.6854	899.04	7.57	8.76	6.07	6.88	74.95	4.98
180	350	2743.70	0.7862	3489.82	29.38	38.14	27.01	33.89	48.48	23.45
350	400	1014.80	0.8565	1184.82	9.98	48.12	9.99	43.88	33.71	43.13
400	550	3320.10	0.8932	3717.08	31.30	79.42	32.68	76.56	26.92	63.77
550	650	1526.30	0.9355	1631.53	13.74	93.16	15.03	91.59	19.76	86.29
650+		854.50	0.9923	861.13	7.25	100.41	8.41	100.00	11.10	

WinAssay '95 Quality Control Applications

Cum. Mid Vol% v. API Gravity

HTI PB-05-22,23,24,25

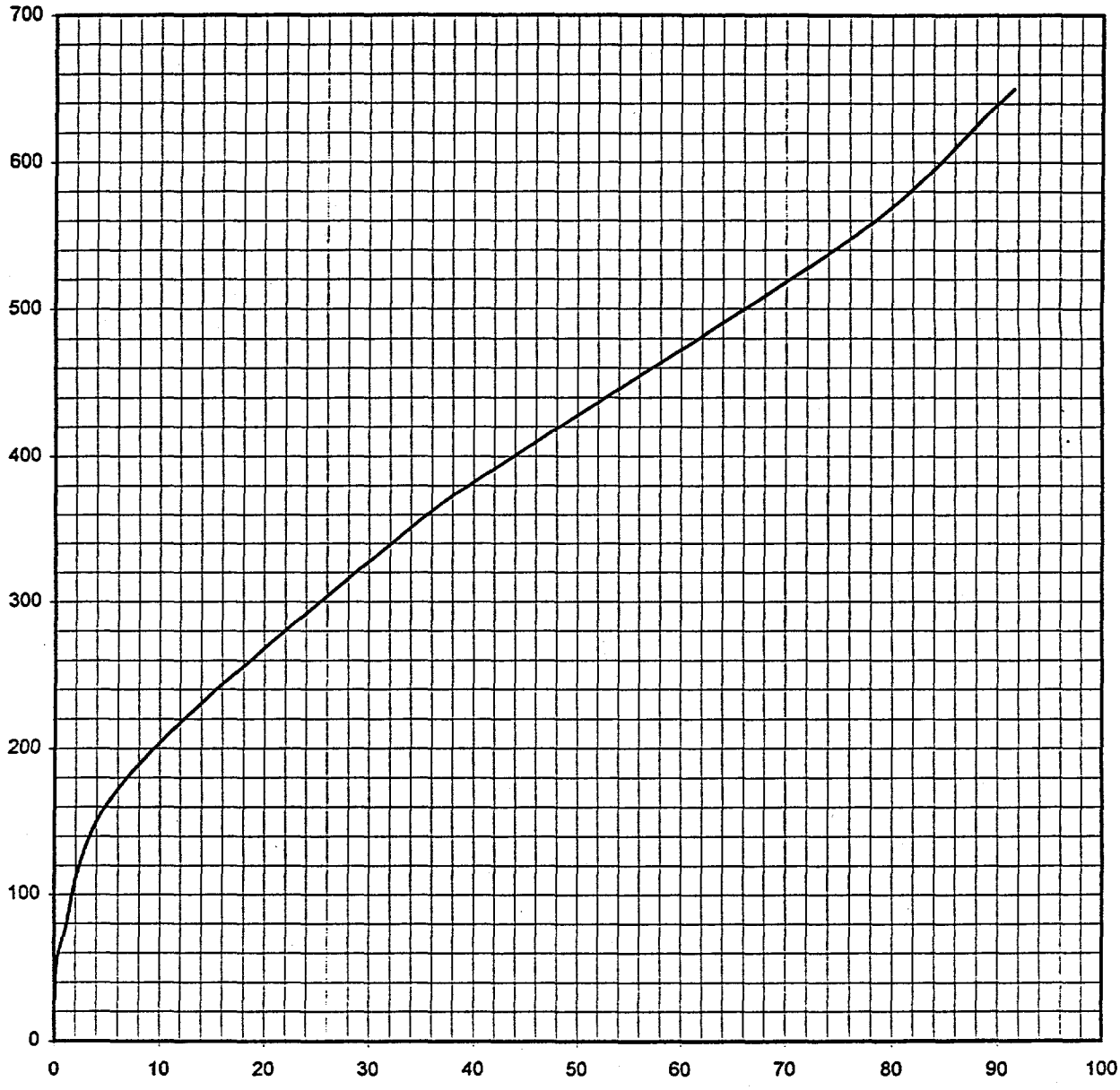


API CURVE Chart 1

WinAssay '95
True Boiling Point Curve
Vaporline Temperature v. Cumulative Wt% Yield

Sample ID

HTI PB-05-22,23,24,25

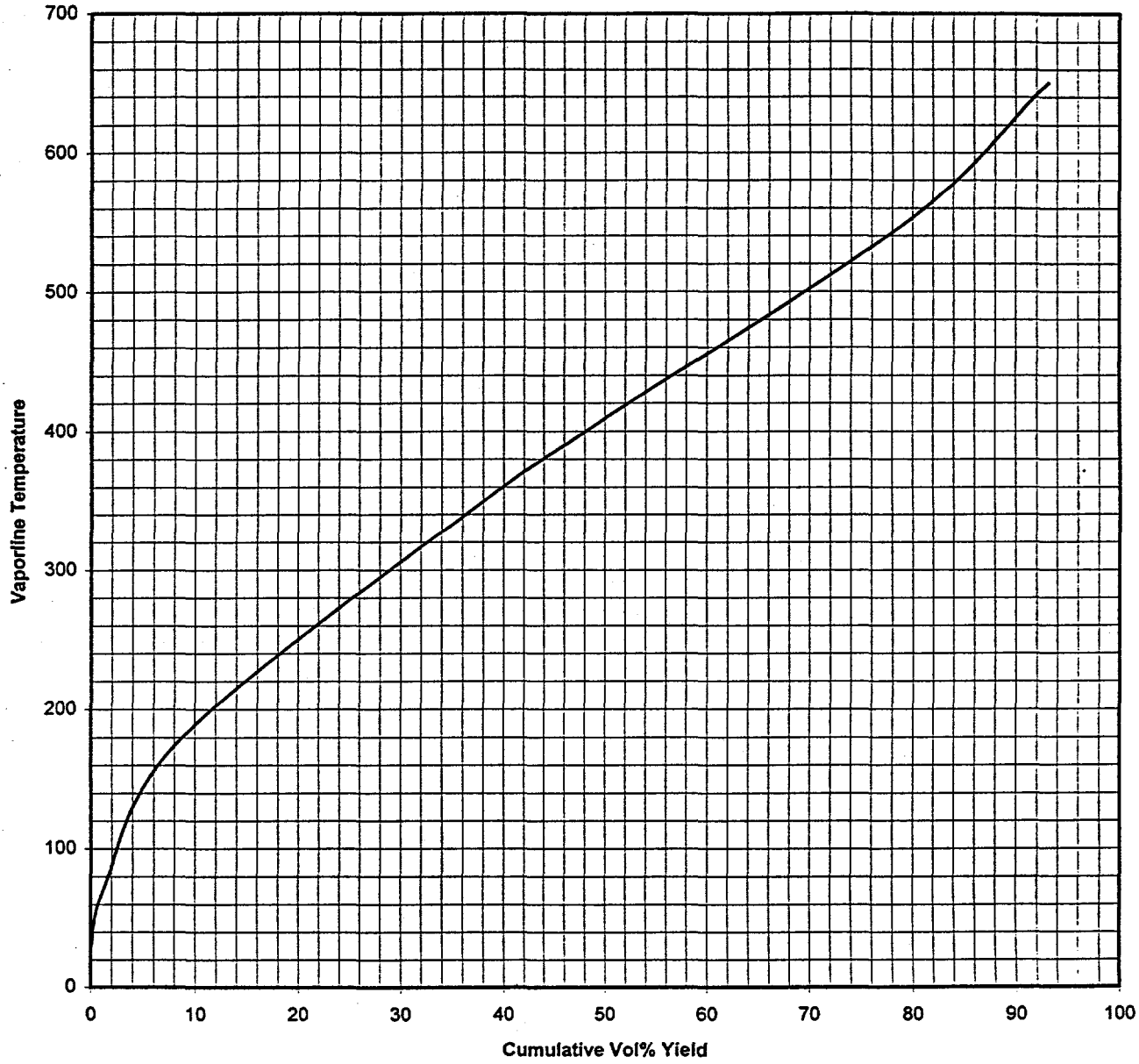


Wt Curve Chart 1

WinAssay '95
True Boiling Point Curve vs Cumulative Vol% Yield

Sample ID

HTI PB-05-22,23,24,25



TBP CURVE Chart 1

ASTM D2892/D5236 CHARGE INFORMATION

Lab ID:	97-000431
Client Name:	Consol Inc.
Sample ID:	HTI PB-05-22,23,24,25
Date:	02/14/97

Operator: Robert Kelly

Charge Mass D2892(g):	10158.0
Charge S.G D2892 (60/60F):	0.8553
Charge Mass D5236(g):	0.0
Charge S.G. D5236 (60/60F):	0.0000

Water Weight Removed (g):	0.0
Initial Vapor Temp:	26
Whole Crude Sulfur Wt%:	

WinAssay '95
ASTM TBP And Potstill Distillation

Quality Control Report

Sample ID:	HTI PB-05-22,23,24,25		
Lab ID:	97-000431		
Client:	Consol Inc.	Date:	02/14/97

Material Balance Parameters:

ASTM D2892 Distillation

D2892 Material Balance:	100.00	Passes Material Balance Per D2892

API Balance Parameters:

D2892 Measured API:	33.9 °	
D2892 Calc API:	34.6 °	
API Delta (Meas-Calc):	-0.7 °	Passes API Test

Note: Review the API vs Mid-Vol% Plot For Outliers along the curve. Points lying off the curvature should be reviewed for accuracy in density determination.

Intertek Testing Services
Caleb Brett

Temperature Readings At 10% (Volume) Increments

Date: February 14,1997

Sample Description: HTI PB-05-22,23,24,25

****NOTE**** The following data was estimated during the ASTM D2892 Distillation Process and actual 10% readings may vary, refer to ASTM D2892 Distillation Summary Report for more precise data.

% Volume	Temperature (Deg.F)
10	187
20	249
30	310
40	357
50	406
60	455
70	501
80	551
90	624

APPENDIX 2

CALEB BRETT REPORT ON FRACTIONAL DISTILLATION OF NET PRODUCTS OF HTI RUN POC-1

Intertek Testing Services
Caleb Brett

9809 Rowlett Road
Houston, TX 77075
Phone: (713) 844-3200
Fax: (713) 844-3330

Your Ref: PO# 01-001-034304

Date: 15-APR-1997

Laboratory Report No. 97-000432-0-HOUS; 1

Consol, Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129-9566

For the Attention of R.A. Winschel

SAMPLE DETAILS: 2 cut(s) from one sample received on 10-JAN-1997

SOURCE : Consol, Inc.

CUSTOMER PRODUCT DESCRIPTION :	**LAB REF**
"HTI POC 1 CRUDE OIL"	
Sample As Received	001-00
IBP-70 Deg. F	002-00

CONTAINERS : 1 Gallon Can **SEALS** : NONE

RESULTS : SEE ATTACHED SHEETS

(TOTAL NUMBER OF PAGES 2)

Approved by: Stephen Hughes

Sample ID	Customer Product Description
	"HTI POC 1 CRUDE OIL"
97-000432-0-HOUS-001-00	Sample As Received

Test		Method	001-00
Initial Boiling Point	Deg. F	D86	174
@ 5% Evaporated	Deg. F		220
@ 10% Evaporated	Deg. F		242
@ 20% Evaporated	Deg. F		300
@ 30% Evaporated	Deg. F		374
@ 40% Evaporated	Deg. F		440
@ 50% Evaporated	Deg. F		483
@ 60% Evaporated	Deg. F		520
@ 70% Evaporated	Deg. F		558
@ 80% Evaporated	Deg. F		590
@ 90% Evaporated	Deg. F		650
Final Boiling Point	Deg. F		655
Recovery	Vol. %		93.0
Residue	Vol. %		6.5
Loss	Vol. %		0.5
Boiling Range Distribution		D2887	See Attached

Sample ID	Customer Product Description
	"HTI POC 1 CRUDE OIL"
97-000432-0-HOUS-002-00	IBP-70 Deg. F

Test	Method	002-00
Detailed Hydrocarbon Analysis	GC	See Attached

Intertek Testing Services
Caleb Brett

WinAssay '95

Version 1.00

Final Reports

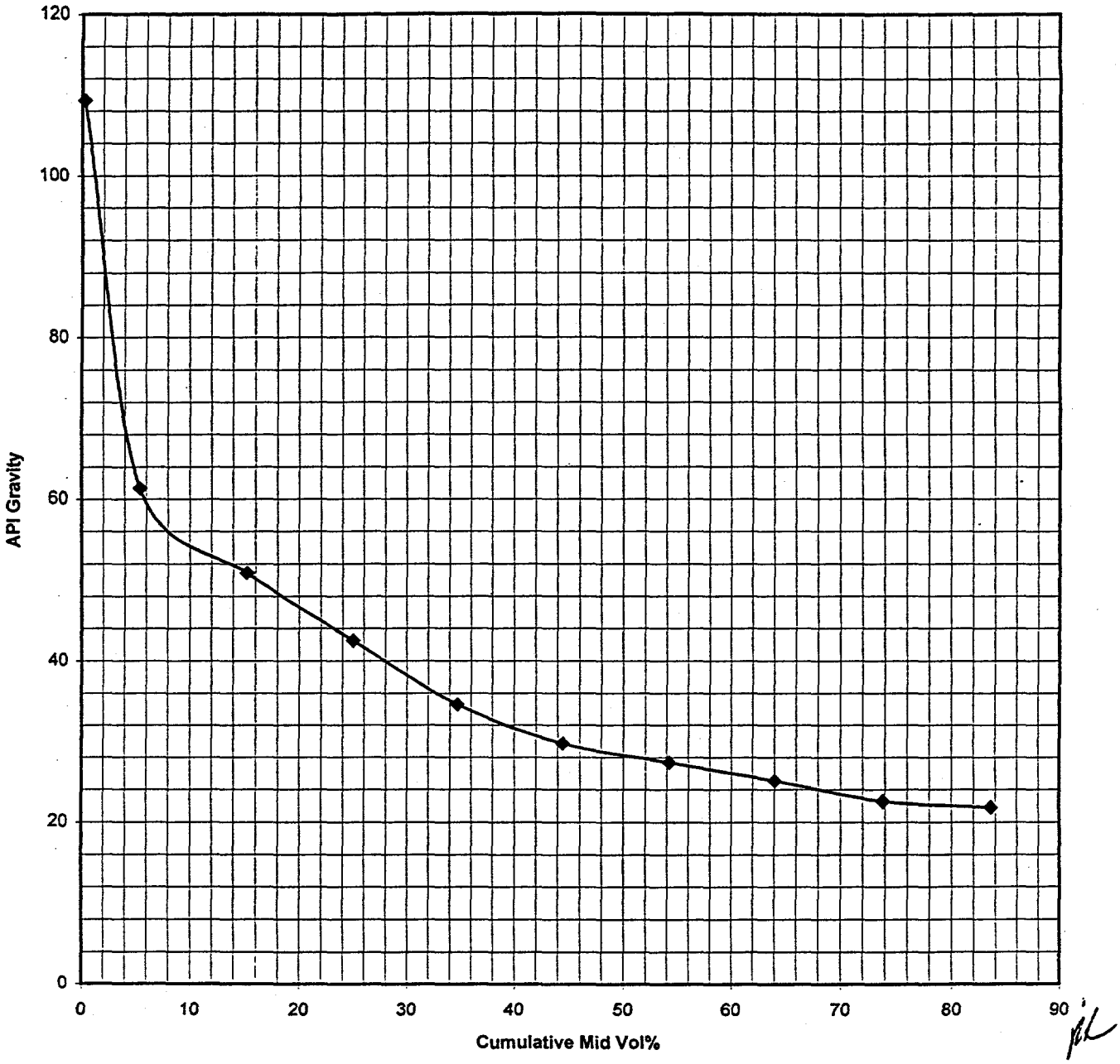
Client Name:	**Consol Inc.**
Sample ID:	**HTI POC 1**
Laboratory ID:	**97-000432**
Date:	**02/14/97**
Operator:	**Robert Kelly**

Prepared For: Consol Inc.
Sample ID: HTI POC 1
Date: 02/14/97

Cut Temp TO	Degrees F	DUMP WT(g)	Specific Gravity	MLS	LIQ VOL%	CUM. LIQ VOL%	WT%	CUM WT%	API GRAVITY	MID LIQ VOL%
ASTM D2892 Distillation Yields										
IBP	70	5.60	0.5876	9.53	0.53	0.53	0.36	0.36	109.31	0.27
70	206	128.10	0.7339	174.55	9.78	10.32	8.31	8.67	61.31	5.43
206	280	135.80	0.7758	175.05	9.81	20.13	8.81	17.48	50.89	15.23
280	347	141.00	0.8132	173.39	9.72	29.85	9.15	26.63	42.50	24.99
347	407	148.10	0.8520	173.83	9.74	39.60	9.61	36.24	34.58	34.72
407	452	152.50	0.8778	173.73	9.74	49.34	9.89	46.13	29.70	44.47
452	499	155.30	0.8907	174.36	9.77	59.11	10.07	56.20	27.36	54.22
499	538	158.50	0.9037	175.39	9.83	68.94	10.28	66.48	25.08	64.03
538	570	159.60	0.9185	173.76	9.74	78.68	10.35	76.84	22.56	73.81
570	612	161.70	0.9228	175.23	9.82	88.51	10.49	87.32	21.84	83.59
612+		195.40	0.9355	208.87	11.71	100.21	12.68	100.00	19.76	

Cum. Mid Vol% v. API Gravity

HTI POC 1

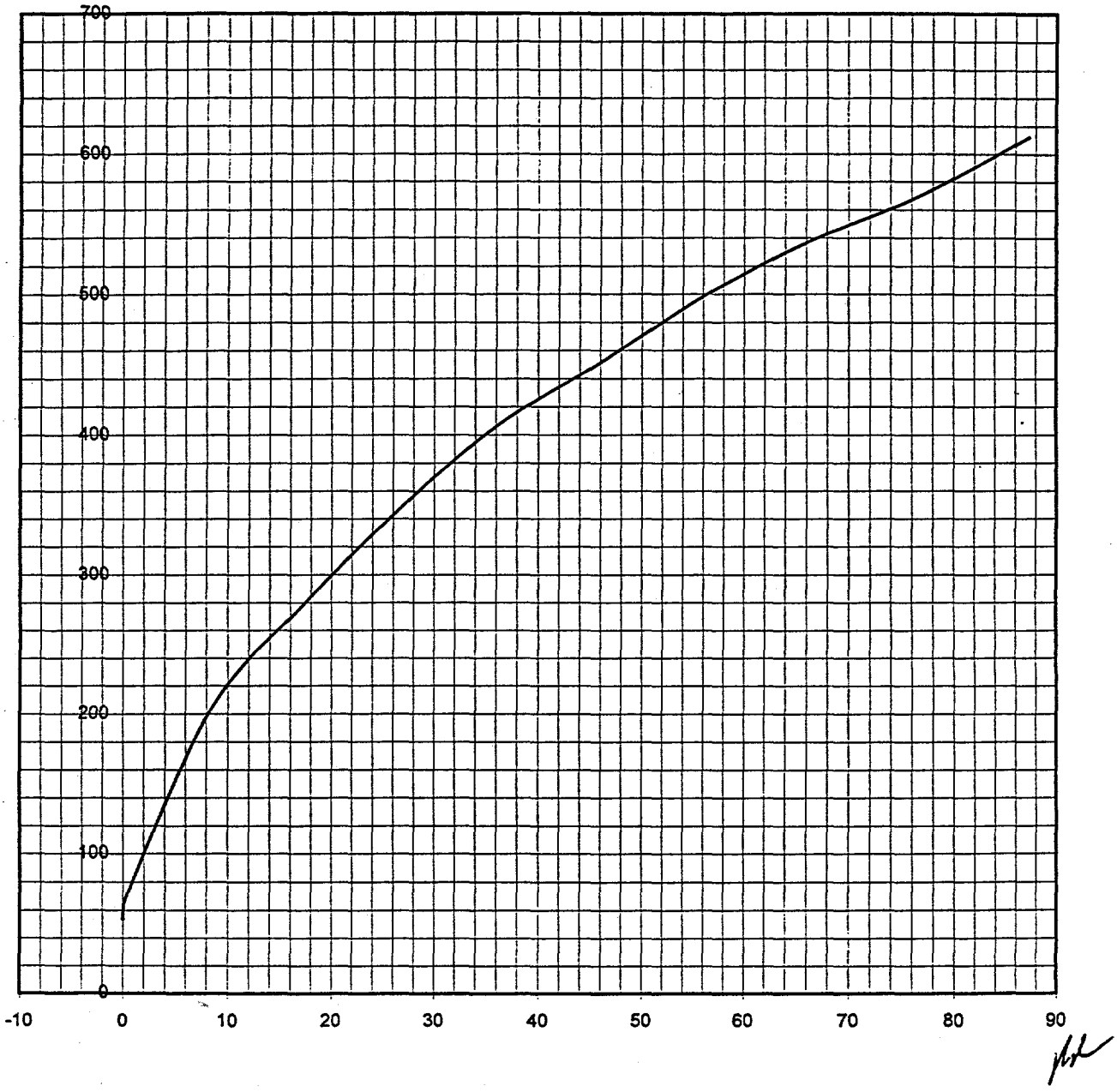


API CURVE Chart 1

WinAssay '95
True Boiling Point Curve
Vaporline Temperature v. Cumulative Wt% Yield

Sample ID

HTI POC 1

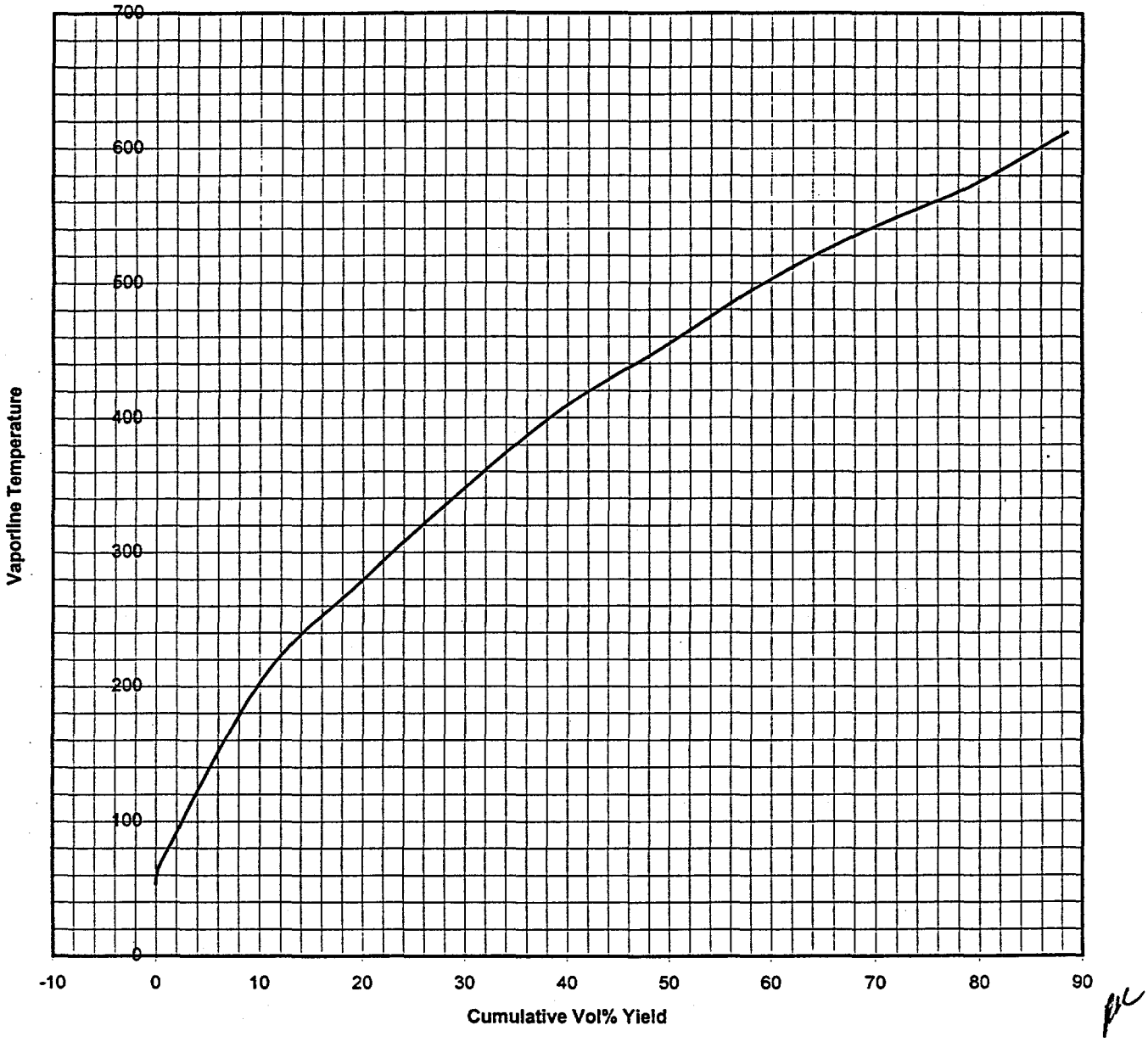


Wt Curve Chart 1

WinAssay '95
True Boiling Point Curve vs Cumulative Vol% Yield

Sample ID

HTI POC 1



TBP CURVE Chart 1

ASTM D2892/D5236 CHARGE INFORMATION

Lab ID:	97-000432
Client Name:	Consol Inc.
Sample ID:	HTI POC 1
Date:	02/14/97

Operator: Robert Kelly

Charge Mass D2892(g):	1541.6
Charge S.G D2892 (60/60F):	0.8642
Charge Mass D5236(g):	0.0
Charge S.G. D5236 (60/60F):	0.0000

Water Weight Removed (g):	0.0
Initial Vapor Temp:	54
Whole Crude Sulfur Wt%:	

WinAssay '95
ASTM TBP And Potstill Distillation

Quality Control Report

Sample ID:	**HTI POC 1**		
Lab ID:	**97-000432**		
Client:	**Consol Inc.**	**Date:**	**02/14/97**

Material Balance Parameters:

ASTM D2892 Distillation

D2892 Material Balance:	**100.00**	**Passes Material Balance Per D2892**

API Balance Parameters:

D2892 Measured API:	**32.2** °	
D2892 Calc API:	**32.6** °	
API Delta (Meas-Calc):	**-0.4** °	**Passes API Test**

Note: **Review the API vs Mid-Vol% Plot For Outliers along the curve. Points lying off the curvature should be reviewed for accuracy in density determination.**

CALEB BRETT HOUSTON

TID: 97-000432-0-HOUS-001-00
CID: CONSOLINC
SID: HTI POC 1 CRUDE OIL/AS RECEIVED
NID: 58261 Date: 10-JAN-1997

Boiling Point Distribution

CRUDE EXT_STD HI-TEMP

ASTM D2887

%Off	BP(F)	BP(C)	%Off	BP(F)	BP(C)	%Off	BP(F)	BP(C)
IBP	65.0	18.3	40	426.6	219.2	80	580.5	304.7
1	99.0	37.2	41	432.3	222.4	81	583.9	306.6
2	155.4	68.6	42	439.5	226.4	82	587.6	308.7
3	169.6	76.4	43	443.7	228.7	83	591.1	310.6
4	183.2	84.0	44	446.8	230.4	84	594.5	312.5
5	194.4	90.2	45	451.5	233.1	85	598.5	314.7
6	204.2	95.7	46	455.6	235.3	86	601.8	316.6
7	211.3	99.6	47	460.2	237.9	87	605.7	318.7
8	215.9	102.2	48	464.0	240.0	88	609.9	321.1
9	220.8	104.9	49	468.6	242.6	89	614.2	323.4
10	226.7	108.2	50	472.9	244.9	90	619.0	326.1
11	234.6	112.6	51	477.6	247.6	91	623.9	328.8
12	244.4	118.0	52	482.7	250.4	92	627.9	331.1
13	253.4	123.0	53	487.3	252.9	93	633.3	334.1
14	262.6	128.1	54	490.1	254.5	94	639.4	337.4
15	268.6	131.4	55	493.7	256.5	95	645.8	341.0
16	274.7	134.8	56	497.0	258.3	96	652.2	344.6
17	285.5	140.8	57	501.4	260.8	97	659.3	348.5
18	293.2	145.1	58	505.0	262.8	98	667.6	353.1
19	301.5	149.7	59	508.6	264.8	99	677.5	358.6
20	308.6	153.7	60	512.5	266.9			
21	313.5	156.4	61	516.1	268.9			
22	320.5	160.3	62	519.6	270.9			
23	330.3	165.7	63	523.2	272.9			
24	334.8	168.2	64	527.2	275.1			
25	340.6	171.4	65	531.0	277.2			
26	347.6	175.3	66	534.6	279.2			
27	354.9	179.4	67	538.0	281.1			
28	359.0	181.7	68	541.7	283.2			
29	365.0	185.0	69	545.8	285.4			
30	372.0	188.9	70	548.3	286.8			
31	378.0	192.2	71	550.6	288.1			
32	383.4	195.2	72	553.3	289.6			
33	389.9	198.8	73	557.3	291.8			
34	397.5	203.1	74	561.1	293.9			
35	402.5	205.8	75	564.0	295.6			
36	405.6	207.6	76	567.9	297.7			
37	410.4	210.2	77	572.2	300.1			
38	416.5	213.6	78	575.2	301.8			
39	421.6	216.4	79	577.7	303.2			

Start Time: 0.1 minutes
End Time: 23.1 minutes
Area: 346915328.0
Slice Width: 0.66 sec
Baseline Subtracted: c:\tc4\hitemp\0327hbf

Sample Offset: 17520.0
Baseline Offset: 18314.0
Calibration File: 0331hrt
Calibration Date: 04/04/97

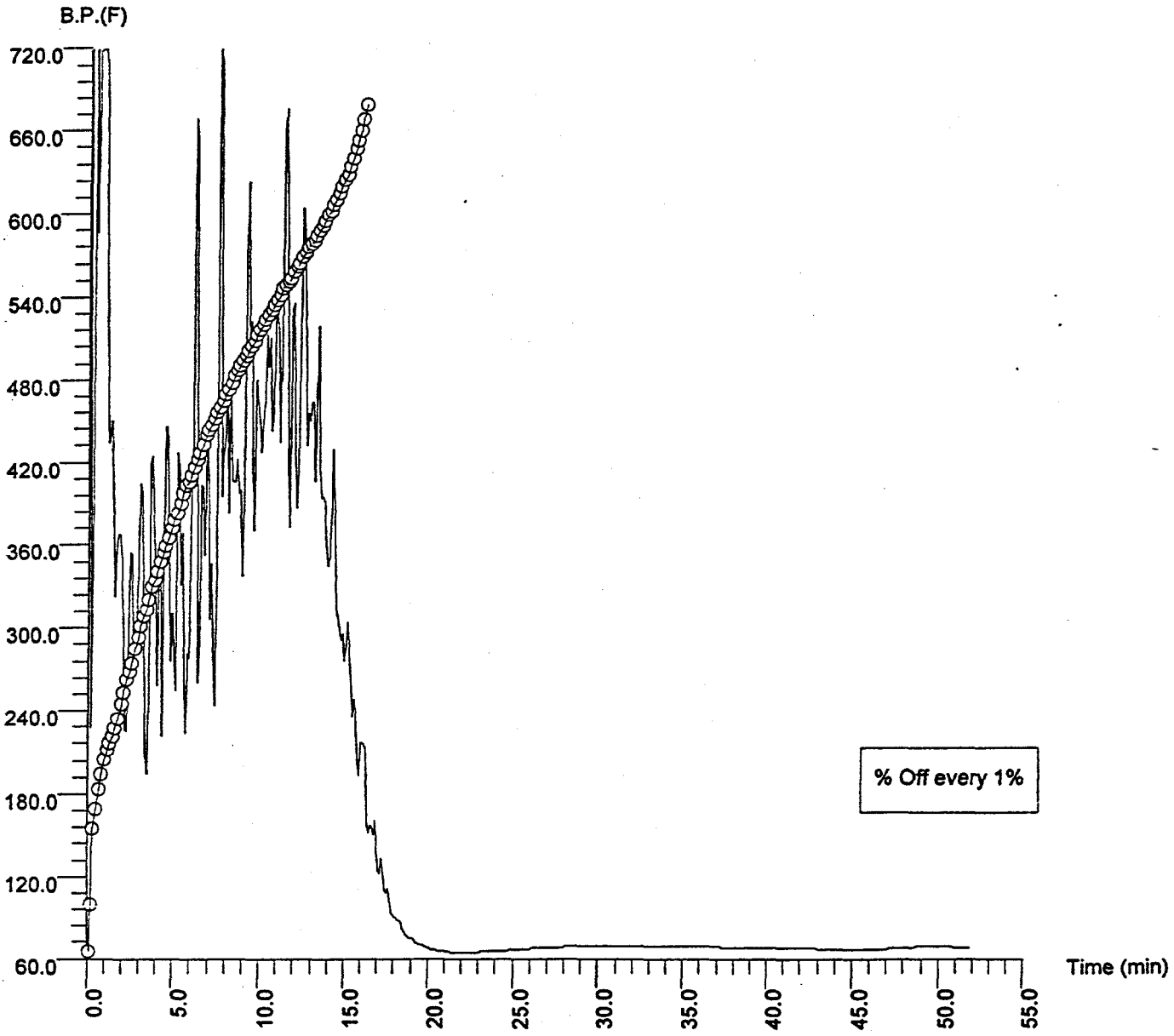
Residue: -99.0 at 859.2 F (459.5 C)
Concentration: 0.019435
Standard File: rgo0325h
Standard Date: 03/27/97

CALEB BRETT HOUSTON

TID: 97-000432-0-HOUS-001-00
CID: CONSOLINC
SID: HTI POC 1 CRUDE OIL/AS RECEIVED
NID: 58261 Date: 10-JAN-1997

SimDis Plot

CRUDE EXT_STD HI-TEMP



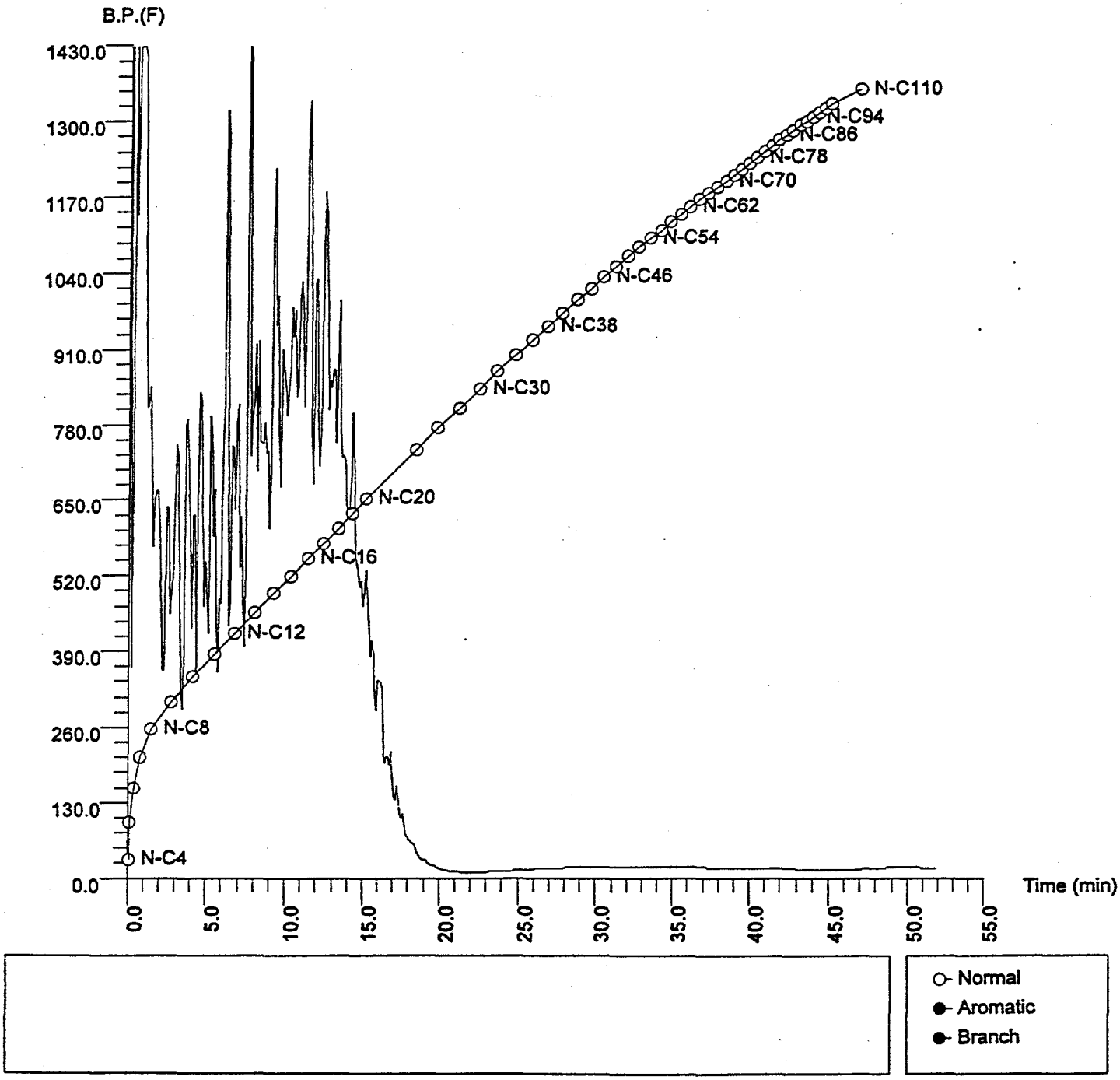
CALEB BRETT HOUSTON

TID: 97-000432-0-HOUS-001-00
CID: CONSOLINC
SID: HTI POC 1 CRUDE OIL/AS RECEIVED
NID: 58261 Date: 10-JAN-1997

APR 01, 1997 - 16:45:26
SIMDIS EXPERT V5.0
Page 1

Calibration Plot

CRUDE EXT_STD HI-TEMP



Standard Practice for			SAMPLE :	97-432-2								
Interconversion of Analysis of C5 and Lighter Hydrocarbons to												
Gas-Volume, Liquid-Volume, or Weight Basis												
ASTM D 2421-89												
	Conversion of Weight % to Gas or Liquid Volume %						Gas Vol%	Gas Vol%				
	Enter wt%		Liq.vol.1ml	Rel.dens.	Liq vol %	Liq Vol%	(mole %)	(mole %)	Vapor Pr.	Vapor Pr.	Sp.gravity	
	result here	Mol. wt.	idl.gas 60/760	60/60(vac)	Unnorm	Norm	Unnorm	Norm	psig	Tot. psig	Average	
Methane	0	16.04	0.00226	0.3	0	0	0	0	4985.3	0	0	Methane
Ethane	0.03	30.07	0.003566	0.3562	0.084222	0.049493	0.000998	0.059822	700	0.34645	0.000176	Ethane
Acetylene	0	26.04	0.00263	0.418	0	0	0	0		0	0	Acetylene
Ethylene	0	28.05	0.0032	0.37	0	0	0	0		0	0	Ethylene
Propane	8.8	44.1	0.003675	0.507	17.357	10.19975	0.199546	11.96514	174	17.74756	0.051713	Propane
Propylene	0.21	42.08	0.003413	0.521	0.403071	0.236862	0.00499	0.299238	213	0.504517	0.001234	Propylene
Propadiene	0	40.06	0.00282	0.6	0	0	0	0		0	0	Propadiene
Methylacetylene	0	40.06	0.00273	0.621	0	0	0	0		0	0	Methylacetylene
n-Butane	49.19	58.12	0.004205	0.584	84.22945	49.49697	0.846352	50.74872	37	18.31388	0.289062	n-Butane
Isobutane	9.59	58.12	0.004362	0.5629	17.03677	10.01157	0.165003	9.893885	58	5.806708	0.056355	Isobutane
1-Butene	3.8	56.11	0.003944	0.6011	6.321743	3.714938	0.067724	4.060852	47.4	1.76088	0.02233	1-Butene
trans-2-Butene	1.33	56.11	0.003887	0.61	2.180328	1.281258	0.023703	1.421298	35.24	0.451515	0.007816	trans-2-Butene
cis-2-Butene	0.98	56.11	0.00378	0.6272	1.5625	0.918195	0.017466	1.047272	31.25	0.286936	0.005759	cis-2-Butene
Isobutylene	0	56.11	0.003949	0.6004	0	0	0	0	48.94	0	0	Isobutylene
1,2-Butadiene	0	54.09	0.00347	0.658	0	0	0	0	21.8	0	0	1,2-Butadiene
1,3-Butadiene	0.4	54.09	0.003643	0.6272	0.637755	0.374773	0.007395	0.443422	44.7	0.167524	0.002351	1,3-Butadiene
Ethylacetylene	0	54.09	0.00328	0.696	0	0	0	0		0	0	Ethylacetylene
n-Pentane	10.92	72.15	0.00483	0.6311	17.30312	10.16808	0.151351	9.075283	0.875	0.088971	0.064171	n-Pentane
Isopentane	10.53	72.15	0.004879	0.6247	16.85609	9.905389	0.145946	8.751166	5.744	0.568966	0.061879	Isopentane
Neopentane	0.26	72.15	0.005108	0.5967	0.43573	0.256054	0.003604	0.216078	21.96	0.05623	0.001528	Neopentane
1-Pentene	0.56	70.13	0.004589	0.6457	0.867276	0.50965	0.007985	0.478804	4.417	0.022511	0.003291	1-Pentene
trans-2-Pentene	0.23	70.13	0.004537	0.653	0.352221	0.20698	0.00328	0.196652		0	0.001352	trans-2-Pentene
cis-2-Pentene	0.1	70.13	0.004482	0.6611	0.151263	0.088889	0.001426	0.085501		0	0.000588	cis-2-Pentene
2-Methyl-1-Butene	0.3	70.13	0.004519	0.6557	0.457526	0.268863	0.004278	0.256502		0	0.001763	2-Methyl-1-Butene
3-Methyl-1-Butene	0.2	70.13	0.004684	0.6325	0.316206	0.185816	0.002852	0.171002		0	0.001175	3-Methyl-1-Butene
2-Methyl-2-Butene	0.23	70.13	0.00447	0.663	0.346908	0.203859	0.00328	0.196652		0	0.001352	2-Methyl-2-Butene
Cyclopentane	0.74	70.13	0.003948	0.7505	0.986009	0.579423	0.010552	0.632706		0	0.004349	Cyclopentane
Isoprene	0	68.12	0.004195	0.6861	0	0	0	0		0	0	Isoprene
1-trans-3-Pentadiene	0	68.12	0.004224	0.6815	0	0	0	0		0	0	1-trans-3-Pentadiene
1-cis-Pentadiene	0	68.12	0.004133	0.6964	0	0	0	0		0	0	1-cis-Pentadiene
1,2-Pentadiene	0	68.12	0.004125	0.6976	0	0	0	0		0	0	1,2-Pentadiene
C6+	1.6	85		0.7	2.285714	1.343187					0.009402	C6+
Total	100				170.1709	100	1.667731	100		46.12265	0.587644	
Calculated Vapor Pressure		46.12265										
		0.587644										

CALEB BRETT HOUSTON

TID: 97-000432-0-HOUS-002-00
CID: CONSOLINC
SID: HTI POC 1 CRUDE OIL/IBP-70 F

NID: 58262 Date: 10-JAN-1997

Analyzed: 2/4/97 6:43 PM
Reported: 02-05-1997 02:19:24
Normalized to 100.00%

Comments:

Composite Report
Totals by Group Type & Carbon Number
(in Weight Percent)

	Paraffins:	I-paraffins:	Aromatics:	Naphthenes:	Olefins:	Total:
C1:	0.000	0.000	0.000	0.000	0.000	0.000
C2:	0.033	0.000	0.000	0.000	0.000	0.033
C3:	8.803	0.000	0.000	0.000	0.210	9.013
C4:	49.185	9.586	0.000	0.000	6.105	64.876
C5:	10.924	10.792	0.000	0.740	2.110	24.567
C6:	0.256	0.416	0.034	0.646	0.110	1.461
C7:	0.000	0.026	0.000	0.008	0.012	0.045
C8:	0.000	0.000	0.000	0.000	0.000	0.000
C9:	0.000	0.000	0.000	0.000	0.000	0.000
C10:	0.000	0.000	0.000	0.000	0.000	0.000
C11:	0.000	0.000	0.000	0.000	0.000	0.000
C12:	0.000	0.000	0.000	0.000	0.000	0.000
C13:	0.000	0.000	0.000	0.000	0.000	0.000
C14:	0.000	0.000	0.000	0.000	0.000	0.000
Total:	69.201	20.820	0.034	1.394	8.547	99.995

Oxygenates: 0.000 Total C14+: 0.000 Total Unknowns: 0.005
Grand Total: 100.000

Molecular Weight and Relative Density Data

Group:	Ave. Mw.:	Ave. Rel. Density:
C1:	0.000	0.000
C2:	30.070	0.340
C3:	44.048	0.501
C4:	57.928	0.578
C5:	71.868	0.628
C6:	84.902	0.710
C7:	99.323	0.703
C8:	0.000	0.000
C9:	0.000	0.000
C10:	0.000	0.000
C11:	0.000	0.000
C12:	0.000	0.000
C13:	0.000	0.000
C14:	0.000	0.000
Total Sample:	59.337	0.582

File: 233-02.DHA

CALEB BRETT HOUSTON

TID: 97-000432-0-HOUS-002-00
CID: CONSOLINC
SID: HTI POC 1 CRUDE OIL/IBP-70 F

NID: 58262 Date: 10-JAN-1997

Analyzed: 2/4/97 6:43 PM
Reported: 02-05-1997 02:19:24
Normalized to 100.00%

Comments:

Composite Report
Totals by Group Type & Carbon Number
(in Volume Percent)

	Paraffins:	I-paraffins:	Aromatics:	Naphthenes:	Olefins:	Total:
C1:	0.000	0.000	0.000	0.000	0.000	0.000
C2:	0.056	0.000	0.000	0.000	0.000	0.056
C3:	10.245	0.000	0.000	0.000	0.242	10.487
C4:	49.499	10.021	0.000	0.000	5.916	65.436
C5:	10.162	10.158	0.000	0.578	1.882	22.780
C6:	0.226	0.369	0.022	0.489	0.093	1.199
C7:	0.000	0.022	0.000	0.006	0.010	0.037
C8:	0.000	0.000	0.000	0.000	0.000	0.000
C9:	0.000	0.000	0.000	0.000	0.000	0.000
C10:	0.000	0.000	0.000	0.000	0.000	0.000
C11:	0.000	0.000	0.000	0.000	0.000	0.000
C12:	0.000	0.000	0.000	0.000	0.000	0.000
C13:	0.000	0.000	0.000	0.000	0.000	0.000
C14:	0.000	0.000	0.000	0.000	0.000	0.000
Total:	70.188	20.570	0.022	1.074	8.143	99.996

Oxygenates: 0.000 Total C14+: 0.000 Total Unknowns: 0.004
Grand Total: 100.000

(in Mole Percent)

	Paraffins:	I-paraffins:	Aromatics:	Naphthenes:	Olefins:	Total:
C1:	0.000	0.000	0.000	0.000	0.000	0.000
C2:	0.065	0.000	0.000	0.000	0.000	0.065
C3:	11.846	0.000	0.000	0.000	0.296	12.142
C4:	50.214	9.787	0.000	0.000	6.457	66.458
C5:	8.984	8.876	0.000	0.626	1.797	20.284
C6:	0.176	0.286	0.026	0.456	0.078	1.021
C7:	0.000	0.015	0.000	0.005	0.007	0.027
C8:	0.000	0.000	0.000	0.000	0.000	0.000
C9:	0.000	0.000	0.000	0.000	0.000	0.000
C10:	0.000	0.000	0.000	0.000	0.000	0.000
C11:	0.000	0.000	0.000	0.000	0.000	0.000
C12:	0.000	0.000	0.000	0.000	0.000	0.000
C13:	0.000	0.000	0.000	0.000	0.000	0.000
C14:	0.000	0.000	0.000	0.000	0.000	0.000
Total:	71.285	18.964	0.026	1.087	8.635	99.997

Oxygenates: 0.000 Total C14+: 0.000 Total Unknowns: 0.003
Grand Total: 100.000

File: 233-02.DHA

CALEB BRETT HOUSTON

TID: 97-000432-0-HOUS-002-00
CID: CONSOLINC
SID: HTI POC 1 CRUDE OIL/IBP-70 F

NID: 58262 Date: 10-JAN-1997

Analyzed: 2/4/97 6:43 PM
Reported: 02-05-1997 02:19:24
Normalized to 100.00%

Comments:

Boiling Point Distribution Data

	Wt. Percent Off: deg.C.:	deg.F.:	Vol. Percent Off: deg.C.:	deg.F.:
IBP (0.5%)	-42.04	-43.67	-42.04	-43.67
5.0%	-42.04	-43.67	-42.04	-43.67
10.0%	-11.72	10.90	-42.04	-43.67
15.0%	-11.72	10.90	-11.72	10.90
20.0%	-6.25	20.75	-11.72	10.90
25.0%	-0.50	31.10	-0.50	31.10
30.0%	-0.50	31.10	-0.50	31.10
35.0%	-0.50	31.10	-0.50	31.10
40.0%	-0.50	31.10	-0.50	31.10
45.0%	-0.50	31.10	-0.50	31.10
50.0%	-0.50	31.10	-0.50	31.10
55.0%	-0.50	31.10	-0.50	31.10
60.0%	-0.50	31.10	-0.50	31.10
65.0%	-0.50	31.10	-0.50	31.10
70.0%	-0.50	31.10	-0.50	31.10
75.0%	27.84	82.11	0.88	33.58
80.0%	27.84	82.11	27.84	82.11
85.0%	27.84	82.11	27.84	82.11
90.0%	36.06	96.91	36.06	96.91
95.0%	36.06	96.91	36.06	96.91
FBP (99.5%)	80.72	177.30	71.80	161.24

Research Octane Number =106.66
(Calculated from Individual Component Values)

Contribution to Total by:

Paraffins:	73.18
Iso-paraffins:	22.64
Aromatics:	0.03
Naphthenes:	1.22
Olefins:	9.58
Oxygenates:	0.00

File: 233-02.DHA

CALEB BRETT HOUSTON

TID: 97-000432-0-HOUS-002-00
CID: CONSOLINC
SID: HTI POC 1 CRUDE OIL/IBP-70 F

NID: 58262 Date: 10-JAN-1997

Analyzed: 2/4/97 6:43 PM
Reported: 02-05-1997 02:19:24
Normalized to 100.00%

Comments:

Components Listed in Chromatographic Order

Min.	INDEX	Component	Wt%	Vol%	Mol%
6.657	200.0	ethane	0.033	0.056	0.065
7.110	293.7	propylene	0.210	0.242	0.296
7.166	300.0	propane	8.803	10.245	11.846
8.104	366.2	i-butane	9.586	10.021	9.787
8.736	391.4	butene-1	3.802	3.721	4.021
9.004	400.0	n-butane	49.185	49.499	50.214
9.355	411.9	t-butene-2	1.325	1.277	1.401
9.447	414.7	2,2-dimethylpropane	0.261	0.258	0.215
9.894	427.5	c-butene-2	0.979	0.918	1.035
11.392	460.6	3-methylbutene-1	0.204	0.190	0.173
12.383	477.3	i-pentane	10.531	9.900	8.661
12.478	478.8	1,4-pentadiene	0.397	0.350	0.346
13.299	490.5	pentene-1	0.556	0.506	0.470
13.755	496.4	2-methylbutene-1	0.300	0.269	0.254
14.051	500.0	n-pentane	10.924	10.162	8.984
14.586	510.1	t-pentene-2	0.230	0.207	0.194
15.098	519.1	c-pentene-2	0.103	0.092	0.087
15.423	524.5	2-methylbutene-2	0.230	0.202	0.194
16.426	540.2	2,2-dimethylbutane	0.003	0.003	0.002
17.638	557.1	cyclopentene	0.090	0.068	0.078
18.008	561.9	4-methylpentene-1	0.016	0.014	0.012
18.073	562.8	3-methylpentene-1	0.009	0.008	0.007
18.399	566.8	cyclopentane	0.740	0.578	0.626
18.599	569.3	2,3-dimethylbutane	0.043	0.038	0.030
18.734	570.9	4-methyl-c-pentene-2	0.009	0.007	0.006
18.962	573.6	2-methylpentane	0.248	0.221	0.171
19.105	575.3	4-methyl-t-pentene-2	0.015	0.013	0.010
20.002	585.4	3-methylpentane	0.121	0.106	0.084
20.439	590.1	2-methylpentene-1	0.007	0.006	0.005
20.521	591.0	hexene-1	0.014	0.012	0.010
21.408	600.0	n-hexane	0.256	0.226	0.176
21.629	602.8	c-hexene-3	0.009	0.008	0.006
21.836	605.4	t-hexene-2	0.005	0.004	0.004
22.050	608.1	2-methylpentene-2	0.004	0.004	0.003
22.069	608.3	?	0.005	0.004	0.003
22.252	610.6	3-methylcyclopentene	0.001	0.001	0.001
22.343	611.7	O13	0.002	0.002	0.002
22.592	614.7	O14	0.002	0.002	0.001
23.125	620.9	3-methyl-t-pentene-2	0.002	0.002	0.001
23.562	625.9	methylcyclopentane	0.190	0.148	0.134
23.988	630.6	2,3,3-trimethylbutene-1	0.007	0.006	0.004
25.725	648.8	1-methylcyclopentene	0.005	0.004	0.004
25.878	650.3	benzene	0.034	0.022	0.026

File: 233-02.DHA Sample: 97-233-2 p. 1

Components Listed in Chromatographic Order

Min.	INDEX	Component	Wt%	Vol%	Mol%
26.663	657.9	cyclohexane	0.456	0.341	0.321
27.705	667.6	2,3-dimethylpentane	0.011	0.010	0.007
27.850	668.9	5-methyl-t-hexene-2	0.005	0.004	0.003
28.401	673.8	cyclohexene	0.008	0.006	0.006
28.650	675.9	3-methylhexane	0.014	0.012	0.008
29.334	681.8	1c,3-dimethylcyclopentane	0.008	0.006	0.005

APPENDIX 3

REPORT ON PREPARATION OF ALKYL ARYL ETHERS FROM COAL DRIVED PHENOLS

By: G. W. Heunisch

PREPARATION OF ALKYL ARYL ETHERS FROM COAL-DERIVED PHENOLS

G. W. Heunisch
CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 5129

INTRODUCTION AND SUMMARY

CONSOL R&D evaluated reactions to synthesize alkyl phenyl ethers from coal liquefaction phenols. The program included a literature review and laboratory chemical syntheses.

Phenols are produced during the direct liquefaction of coal and must be removed prior to producing transportation fuels. The crude liquefaction product is commonly hydrotreated to remove the phenols and other unsaturated components. An alternative method is to extract the phenols from the crude coal liquefaction product and use them in other commercial processes. Hydrogen consumption for the hydrotreatment would be reduced, and the phenolic material could be converted to alkylphenyl ethers. Alkylphenyl ethers may be useful as fuel extenders. If the fuel extenders can be produced using grain alcohol, the products may be entitled to special tax considerations.

An extensive literature search identified the Williamson Synthesis and its modifications as the preferred methods to produce mixed ethers from phenols. A variation of the Williamson Synthesis[1,2,3] was used to produce phenetole and the ethyl derivatives of the phenolics from a caustic extract of a crude direct coal liquefaction product. The methyl derivatives of similar coal derived phenolic material were synthesized and characterized earlier at Gulf Research.[4] Other approaches involving acid catalysts failed to produce ethers.

RECOMMENDATION

The ethyl ether derivatives of coal liquefaction phenols should be synthesized and characterized as a diesel fuel extender. CONSOL R&D will develop a plan to extract and synthesize the ethers and coordinate the fuel characterization upon DOE's approval.

DISCUSSION

Literature Search

A literature search was conducted to identify commercial processes which produce alkylphenyl ethers. The Williamson Synthesis and its modifications are the methods commonly used to produce mixed ethers from phenols, although other innovative laboratory methods were identified. The DOE-FETC library, the NIOSH (formerly the Bureau of Mines) library, and the extensive electronic data base of Dialog, Inc. of Knight-Ridder, Inc. were searched. A former Gulf Research employee who prepared and tested methylphenyl ethers as gasoline additives was consulted.

Williamson Synthesis

Phenetole. Phenetole, ethylphenyl ether, was prepared to verify the chemical procedure and the analytical techniques. A variation of the Williamson Synthesis was used to prepare the ether. Phenol was reacted with diethylsulfate in the presence of sodium hydroxide under reflux conditions. On cooling, an organic liquid phase separated from the aqueous solution. An ^{1}H-NMR analysis (Figure 1a) of the isolated organic phase indicated a mixture of phenetole and residual diethylsulfate. An analysis of the organic phase showed 11.9% sulfur, which indicates 57% diethylsulfate. The diethylsulfate was removed by hydrolysis of the mixture in warm water. Figure 1b shows an ^{1}H-NMR spectrum of the purified phenetole. The infrared spectrum shows the characteristic absorption for the ether linkage at 1250 cm^{-1} and 1025 cm^{-1},[5] and the organic product was identified by GC/MS as phenetole with trace impurities. The yield was 40-50% of the theoretical yield. The yield can be improved by optimizing the experimental conditions. The phenolic -OH concentration in the product was determined by an FTIR procedure to be 0.001 meq/g, indicating the absence of phenol.

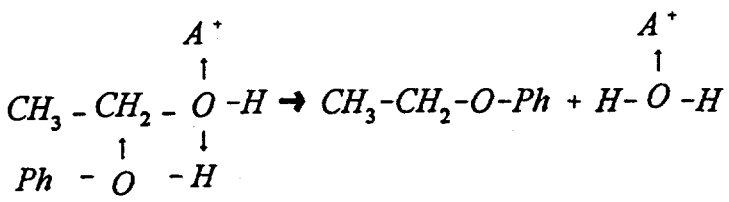
Ethylated Coal Liquid. The phenols extracted from the IBP-380 °F distillate fraction of the crude coal liquid from Black Thunder coal was treated with diethylsulfate under the same experimental conditions used to prepare phenetole. The source of the coal liquid is identified in the Experimental Section. The ^{1}H-NMR spectrum of the organic mixture showed the diethylsulfate impurity, and an analysis gave 10.0% sulfur. The liquid was hydrolyzed to remove the diethylsulfate. The hydrolyzed product contained 0.2% sulfur.

A comparison of the ^{1}H-NMR spectra of the original phenolic fraction and the ethylated product is presented in Figure 2. The spectra show the disappearance of the phenol group at 6.6 ppm, splitting of the side chain methyl groups, and an ethyl group bound to an electronegative component at 1.3 and 3.9 ppm; e.g., oxygen. The infrared spectrum shows characteristic ether linkage absorptions at 1250 cm^{-1} and 1025 cm^{-1}. GC/MS identified phenetole, dimethylphenetole, and other methyl and/or ethyl substituted phenetoles. The concentration of phenolic -OH was <0.2 meq/g, indicating zero or trace residual phenol.

The phenols extracted from the 380 °-510 °F fraction of the Black Thunder coal liquids were also treated with diethylsulfate under the same conditions. The ^{1}H-NMR spectrum of the product is shown in Figure 3 and is analogous to that of the IBP-380°F derived material. The GC/MS chromatogram shows alkyl substituted phenetoles corresponding to the starting phenols. Ethers with side chains containing up to four carbon atoms were identified. The characteristic ether absorption was observed at 1250 cm^{-1} and 1025 cm^{-1} in the infrared spectrum. The absorptions are not observed in the starting phenols.

Acid Catalyzed Syntheses

p-Toluenesulfonic Acid. Based on a conversation with G. Singerman, formerly of Gulf Research, methanol and ethanol were reacted with phenol under reflux in the presence of p-toluenesulfonic acid. The etherification reaction is expected to proceed as shown below:



The comparison of ^{1}H-NMR spectra shown in Figure 4 indicate that no reaction occurred in the acid solution. Figure 4a shows the ^{1}H-NMR spectrum of the methanol/phenol/p-toluenesulfonic acid reaction product. Figure 4b is a spectrum of 50% phenol in methanol solution. Figures 4a and 4c are analogous spectra for phenol with ethanol. The spectra of the reaction products do not show the characteristic shifts attributed to anisole or phenetole and are indistinguishable from a solution of phenol in the appropriate alcohol. The peak at 6.7 ppm in Figures 4a and 4c is attributed to the phenolic -OH, which is protonated in the acid solution.

The same reagents were reacted in the presence of 15% sulfuric acid solution. Again, only the starting materials were observed by ^{1}H-NMR in the reaction product.

Attempts to react alcohols and phenol were unsuccessful in the presence of hydrated boron trifluoride, a Lewis acid. The ^{1}H-NMR spectra showed only the starting materials. GC/MS shows phenol as the major component. No ethers were observed.

EXPERIMENTAL

Phenetole Preparation

Phenetole was prepared by reacting reagent grade phenol and diethylsulfate in basic sodium hydroxide solution. The phenol (10.05g) was placed in a 250-mL round bottom flask fitted with a single standard taper ground glass joint. The phenol was dissolved in 50 mL of 10% sodium hydroxide solution with stirring. Diethylsulfate (12.1g) was added slowly with continued stirring, and a condenser was connected to the ground glass joint. The reaction mixture was refluxed for three hours with stirring. The apparatus was confined to a chemical ventilation hood. The solution was cooled, and 5 mL of 25% sodium hydroxide solution were added to decompose excess diethylsulfate. The two-phase mixture was transferred to a 200-mL separatory funnel and the aqueous layer was separated and discarded. The organic layer was washed twice with 25 mL aliquots of 10% NaOH/10% NaCl solution. The washed organic product was analyzed using ^{1}H-NMR, GC/MS, and infrared spectroscopy. To decompose and remove the excess diethylsulfate, the mixture was warmed with an equal volume of deionized water for two hours. The diethylsulfate destruction was confirmed by ^{1}H-NMR and GC/MS.

Etherification of Coal Liquid Phenols

The procedure described above was used to prepare and purify the O-ethylated derivatives of the phenols derived from coal liquefaction. The phenols extracted from the IBP-380 °F and the 380 °F-510 °F distillation fractions from Black Thunder coal liquids were reacted with diethylsulfate and the products were analyzed by ^{1}H-NMR, GC/MS, and infrared spectroscopy. The IBP-380 °F distillate fraction, after reaction with diethylsulfate, yielded 7.3g of ethylated product. The 380 °F-510 °F fraction yielded 8.6g of recovered product.

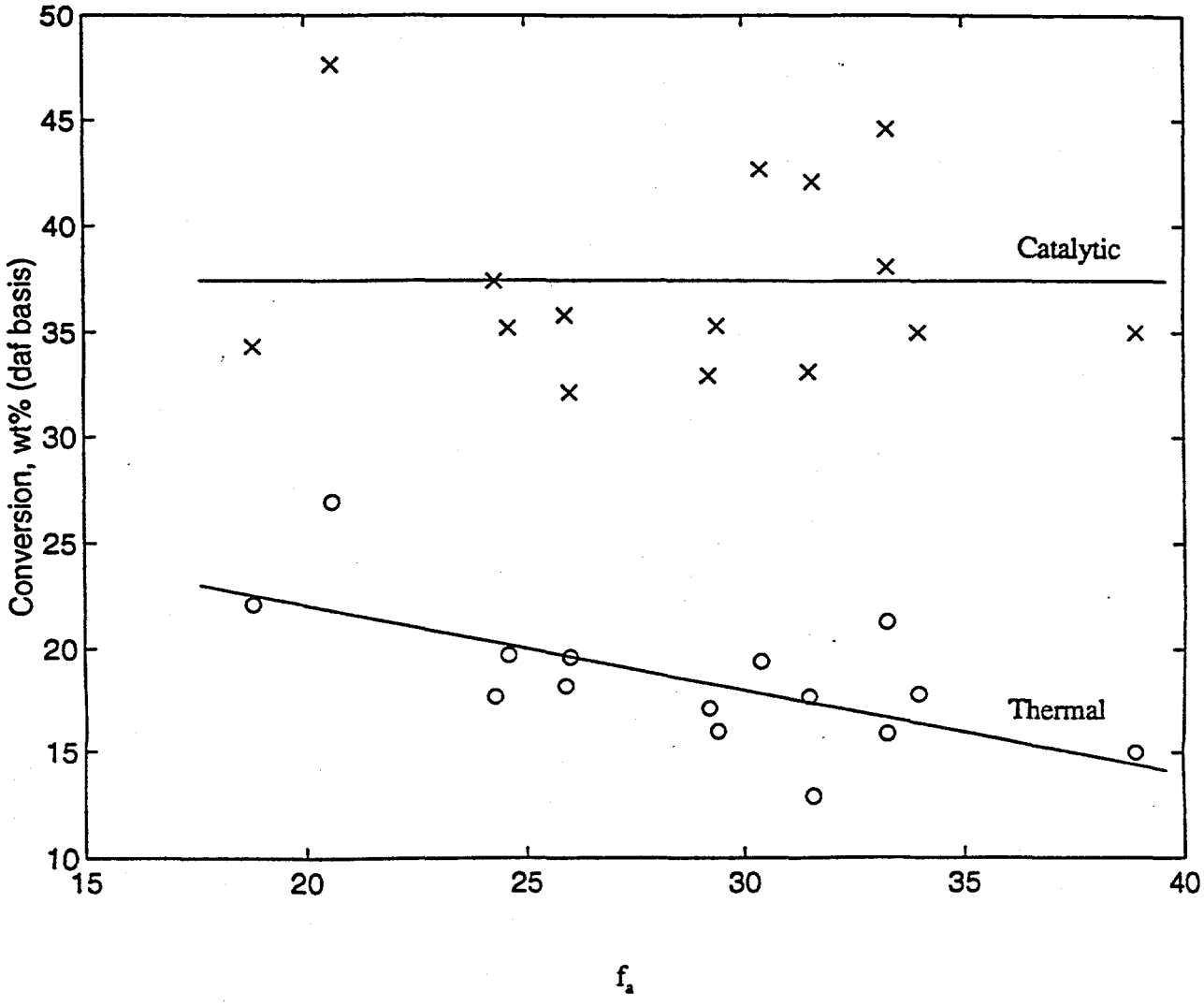


Figure 3 Thermal and catalyzed hydroprocessing conversions vs f_a of the resids

Reaction of Phenol and Alcohols in Acid Media

p-Toluenesulfonic acid (99%), sulfuric acid (reagent grade), and hydrated boron trifluoride (96% $BF_3 \cdot 2H_2O$) were evaluated as catalysts. The phenol was placed in a 250-mL round bottom flask and dissolved in the methyl or ethyl alcohol. After addition of the acid catalyst (4-8%), the flask was fitted with a condenser. The reaction mixture was refluxed for 2.5 hours, cooled, and the total product mixture was analyzed for the appropriate ether.

The quantities of the reactants using p-toluenesulfonic acid are given in the table below:

Reactant Alcohol	Quantity		
	Phenol, g	Alcohol, mL	p-TSA,g
Methyl	22.03	14	2.06
Ethyl	21.95	15	2.05

The quantities of the reactants using 15% sulfuric acid are given in the following table:

Reactant Alcohol	Quantity		
	Phenol, g	Alcohol, mL	15% H_2SO_4, mL
Methyl	-	-	-
Ethyl	19.92	20	20

The boron trifluoride catalyzed reaction mixtures produced precipitates, which were determined by infrared spectroscopy and ^{19}F-NMR to be silicon compounds etched from the flask. The quantities of the reactants are given in the following table:

Reactant Alcohol	Quantity		
	Phenol, g	Alcohol, mL	$BF_3 \cdot 2H_2O$, mL
Methyl	22.34	11	5
Ethyl	20.08	13	6

None of the reactions in acid media produced a two-phase mixture. The crude reaction product was analyzed for the ether.

EQUIPMENT AND CHEMICALS

Nuclear Magnetic Resonance (^{1}H-/^{19}F-NMR)

The NMR spectra were obtained using a Varian Model EM360L NMR Spectrometer. Samples were dissolved in $CDCl_3$ and referenced to tetramethylsilane.

Gas Chromatography/Mass Spectrometry (GC/MS)

The GC/MS data were obtained using a Hewlett-Packard Model 5890, Series II, Gas Chromatograph equipped with a Hewlett-Packard Model 5970 Mass Selective Detector and a phenylmethylpolysiloxane column. Identifications were based on a search of the Wiley/NBS library of mass spectra.

Infrared Spectroscopy

The infrared spectra were obtained using a Nicolet Model 550 Magna-IR Spectrometer, Series II. A 0.2 cm NaCl cell was used for the liquid samples. The phenolic -OH concentration in solution was determined using this instrument.

Sulfur Determination

The concentration of sulfur in the reaction mixtures was determined using a LECO Model SC-432 Sulfur Determinator.

Coal-Derived Phenols

The coal liquid phenols were obtained from a direct coal liquefaction product sample from HTI Run CC-15. Black Thunder Coal was the feedstock. The crude product was distilled and the IBP-380 °F and 380 °F-510 °F distillate fractions were extracted with caustic to isolate the corresponding phenolic fraction by the National Institute for Petroleum and Energy Research (6).

REFERENCES

1. Encyclopedia of Chemical Technology, H. E. Mark, J. J. McKetta, Jr., D. F. Othmer, Editors, Vol. 5, 2nd Ed., Interscience Publishers, Inc., NY, 1965.

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3. Encyclopedia of Science and Technology, McGraw-Hill Book Co., NY, 1971.

4. Singerman, G. M., "Methyl Aryl Ethers from Coal Liquids as Gasoline Extenders and Octane Improvers", Gulf Research and Development Co., Report DOE/CE/50022-1, November 1980.

5. Spectrometric Identification of Organic Compounds, R. M. Silverstein and G. C. Bassler, John Wiley & Sons, Inc., NY, 1963.

6. Sturm, G. P., Jr., Kim, J., Shay, J., "Coal Liquefaction Process Streams Characterization and Evaluation/Analysis of Coal-Derived Synthetic Crude from HRI CTSL Run CC-15 and HRI Run CMSL-2", Report DOE/PC89883-92, January 1994.

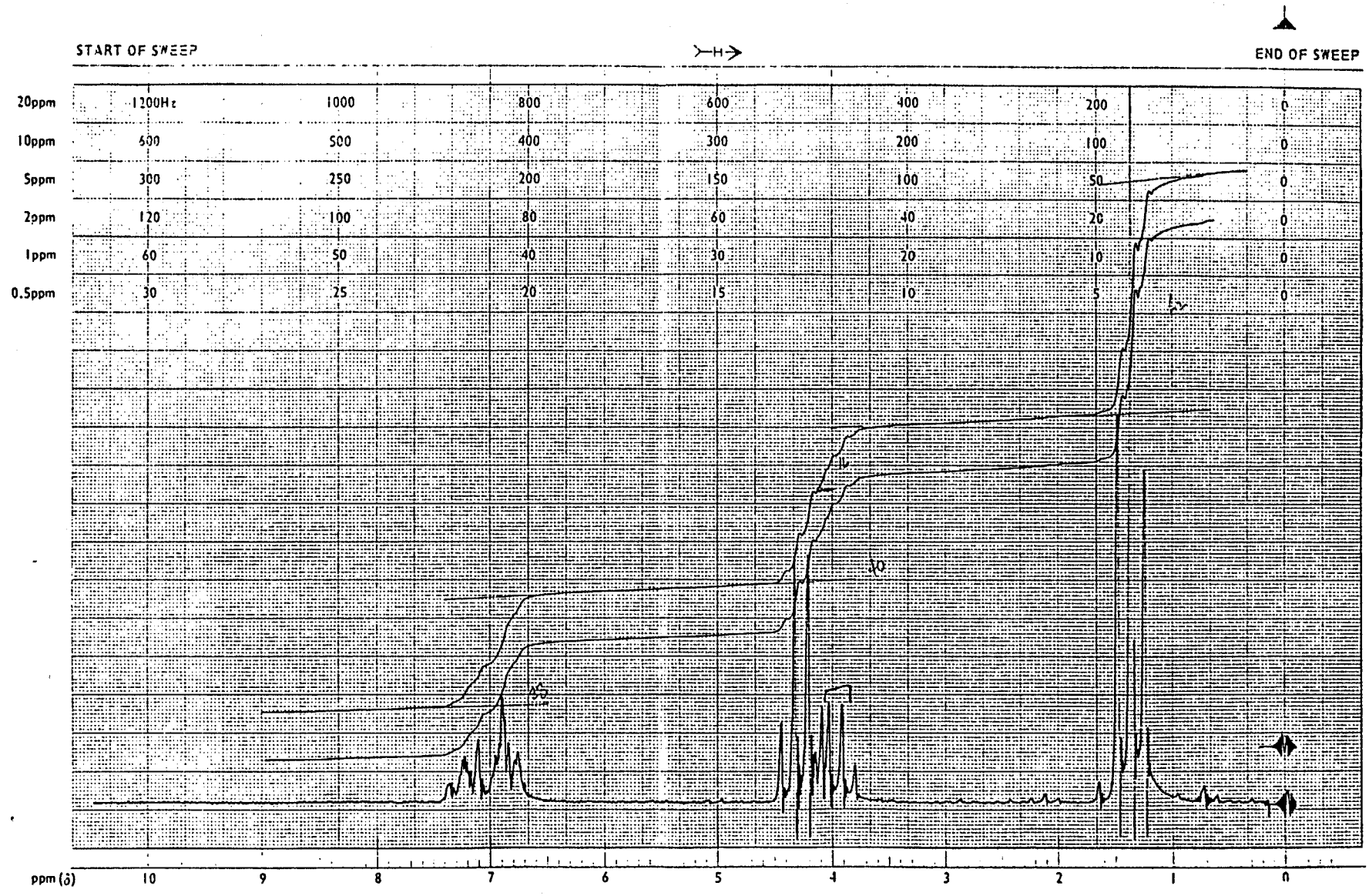
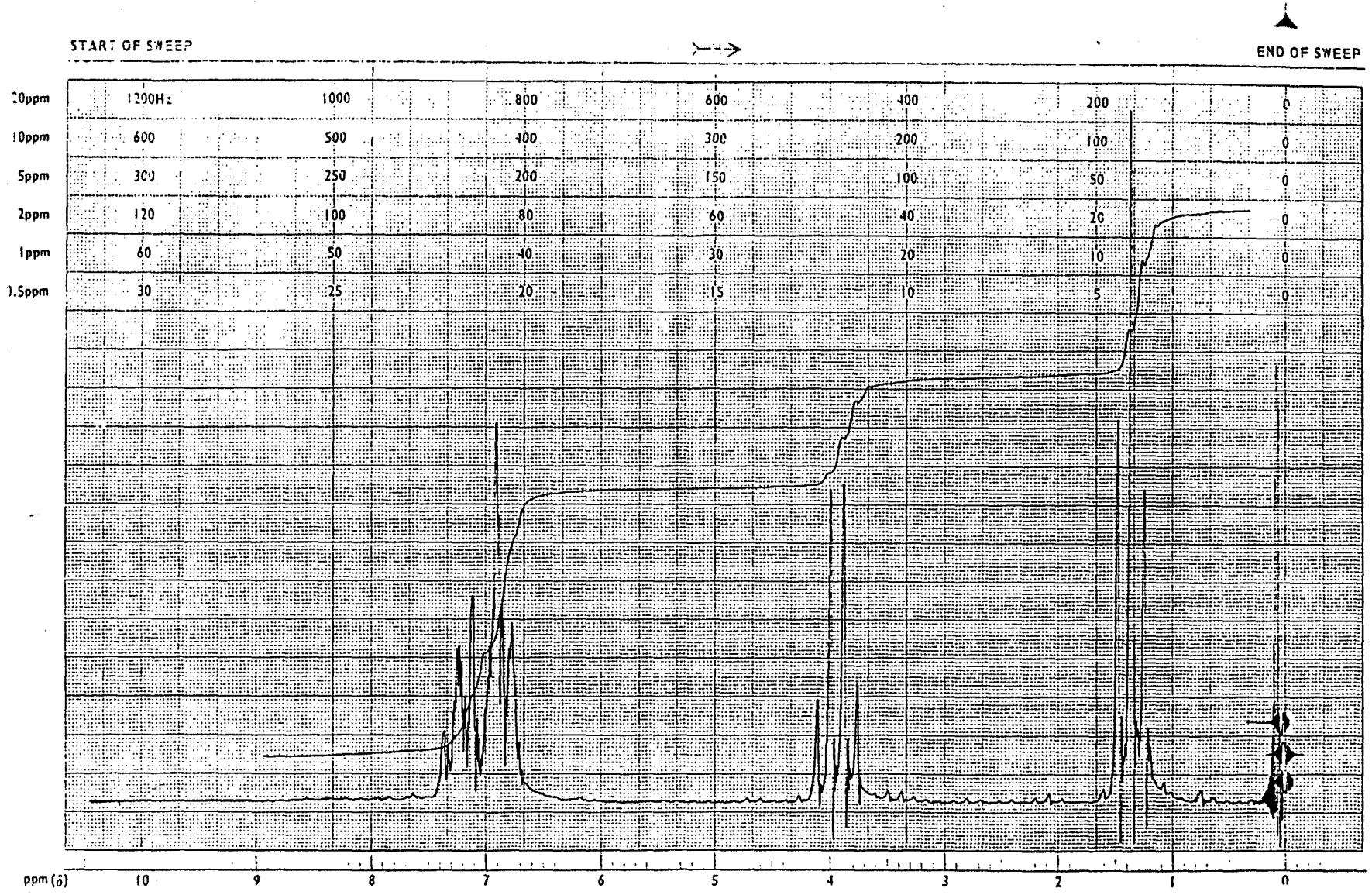
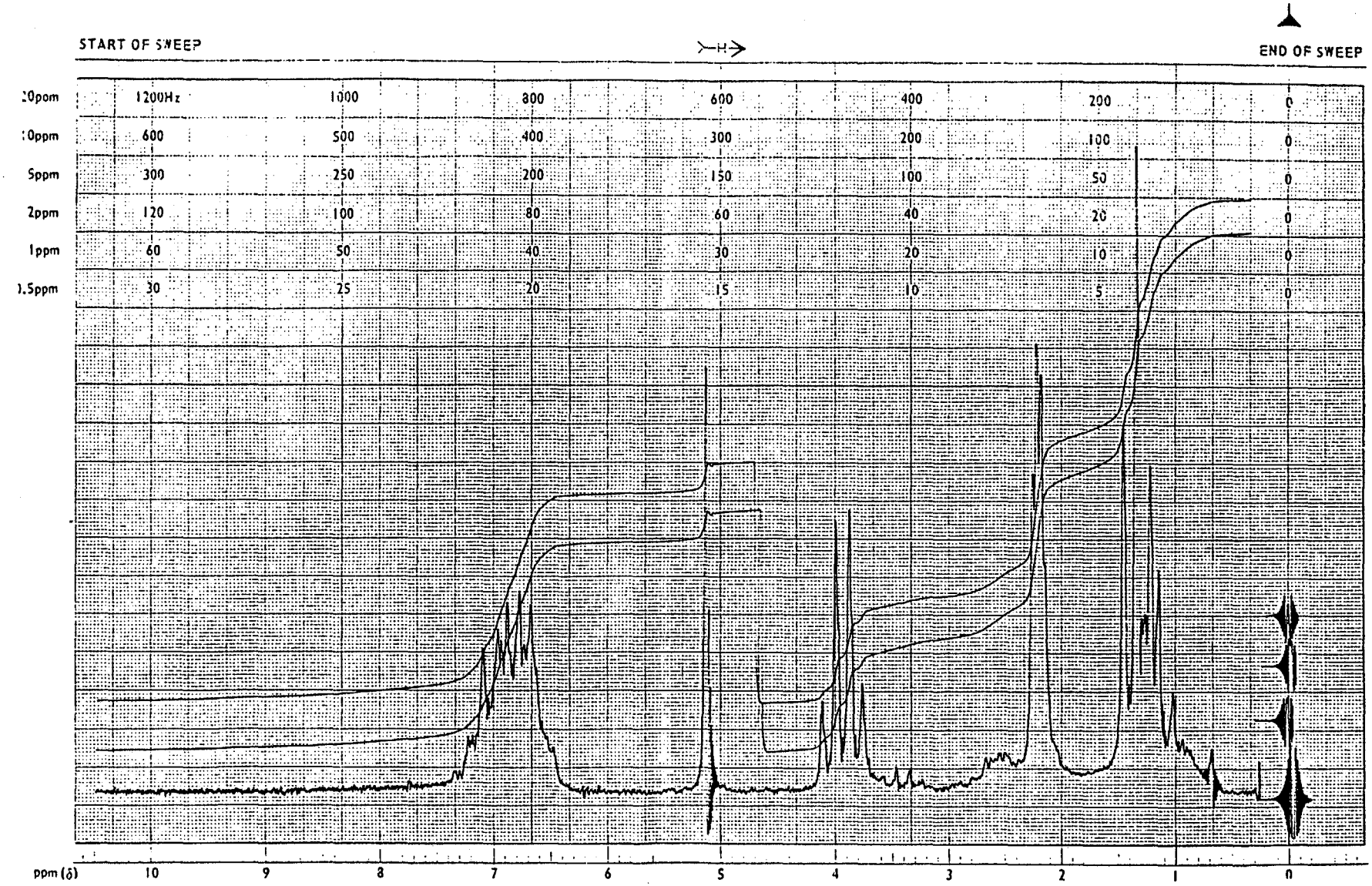


Figure 1A. NMR Spectra of Phenol/Ethanol Reaction Mixtures: Phenetole with Residual Diethylsulfate.



EM-360 60 MHz NMR SPECTROMETER

Figure 1B. NMR Spectra of Phenol/Ethanol Reaction Mixtures: Purified Phenetole Product.



EM-360 60 MHz NMR SPECTROMETER

Figure 2A. NMR Spectra of IBP-380 °F/Ethanol Reaction Mixture: Purified Ether Product.

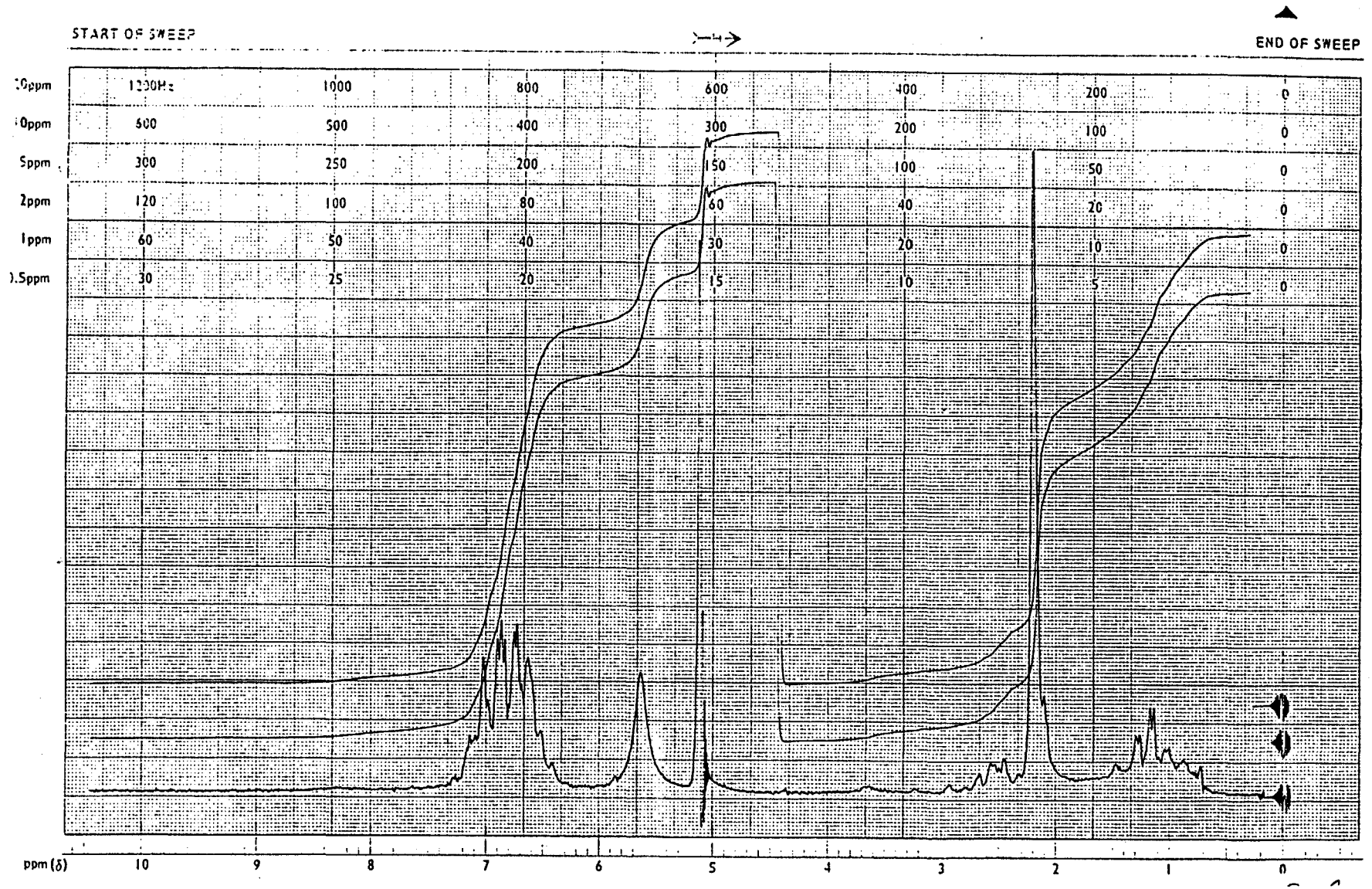
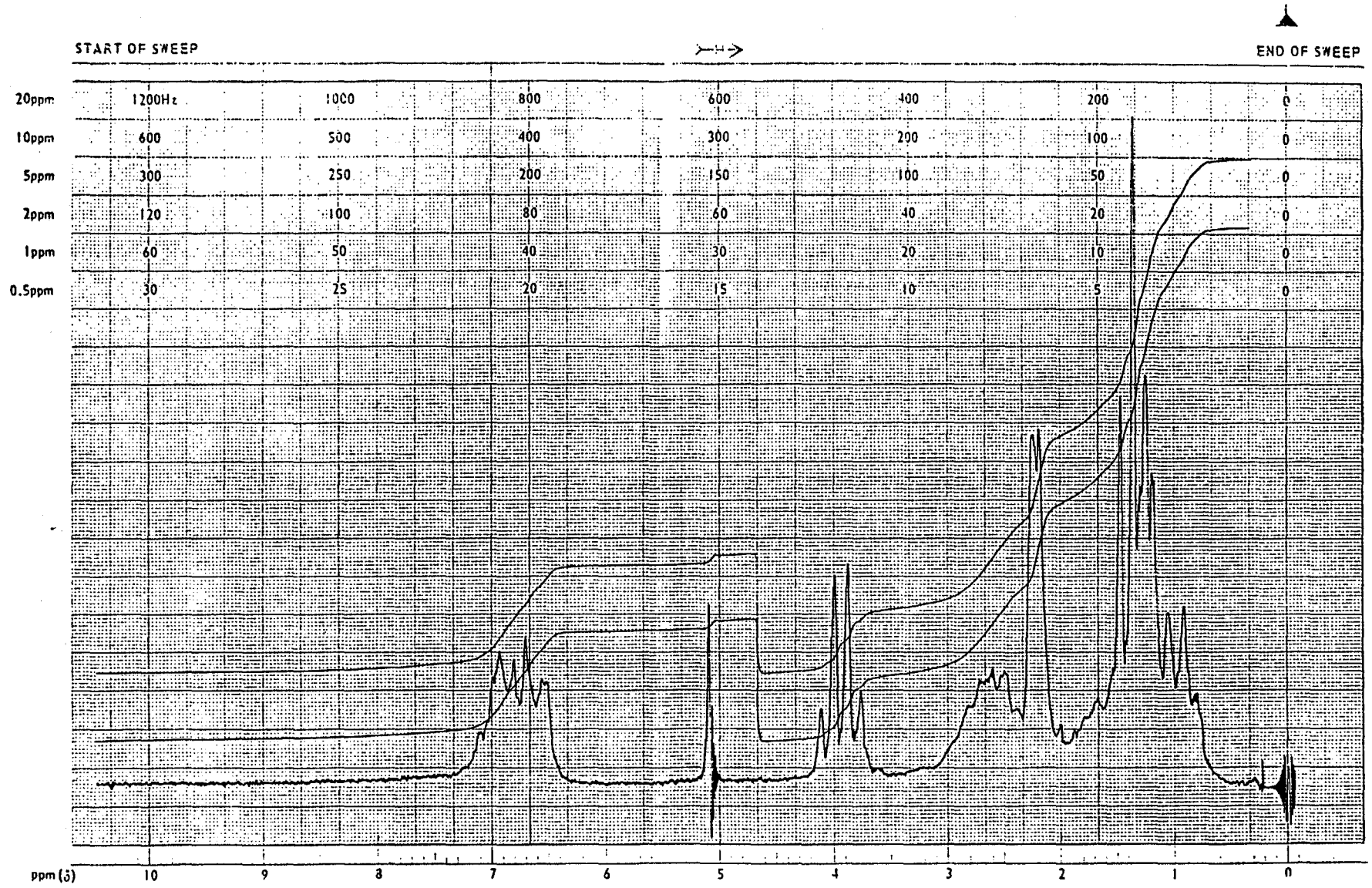
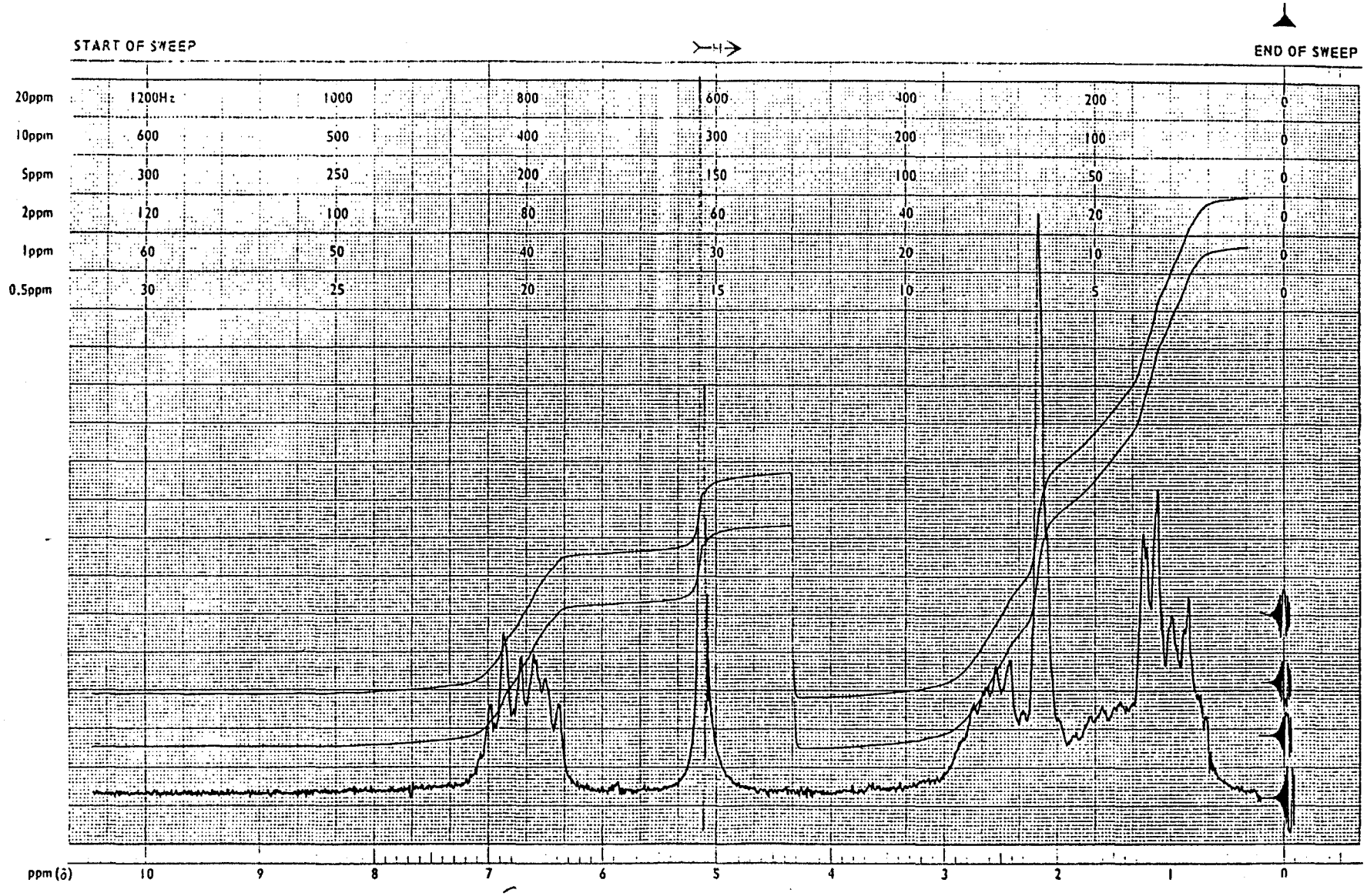


Figure 2B. NMR Spectra of IBP-380 °F/Ethanol Reaction Mixture: Unreacted Phenolic Fraction.



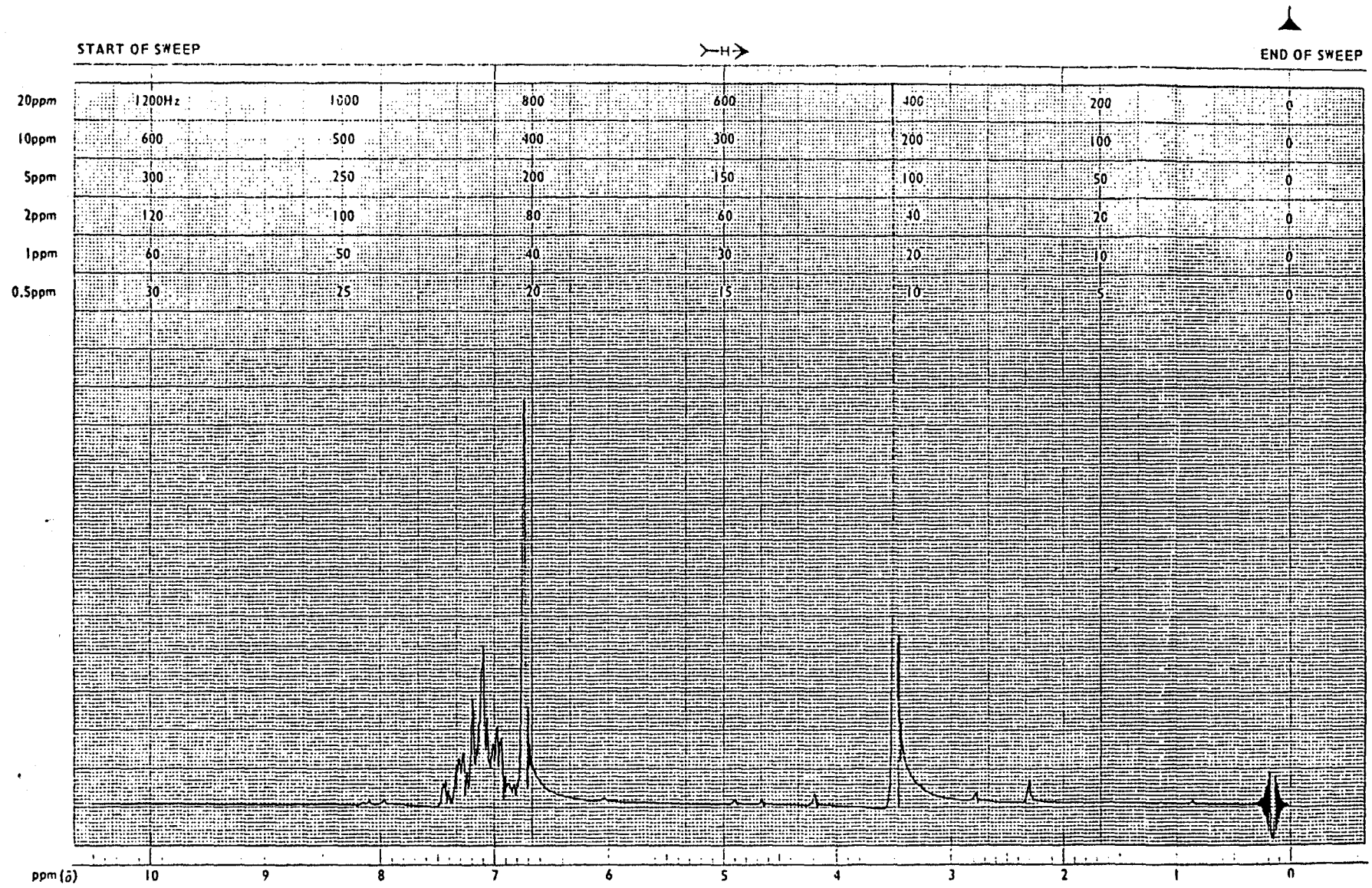
EM-360 60 MHz NMR SPECTROMETER

Figure 3A. NMR Spectra of 380 °F-510 °F/Ethanol Reaction Mixture: Purified Ether Product.



EM-360 60 MHz NMR SPECTROMETER

Figure 3B. NMR Spectra of 380 °F-510 °F/Ethanol Reaction Mixture: Unreacted Phenolic Fraction.



EM-360 60 MHz NMR SPECTROMETER

Figure 4A. NMR Spectra of Phenol/Alcohol Mixtures: Phenol/Methanol/p-Toluenesulfonic Acid Reaction Product.

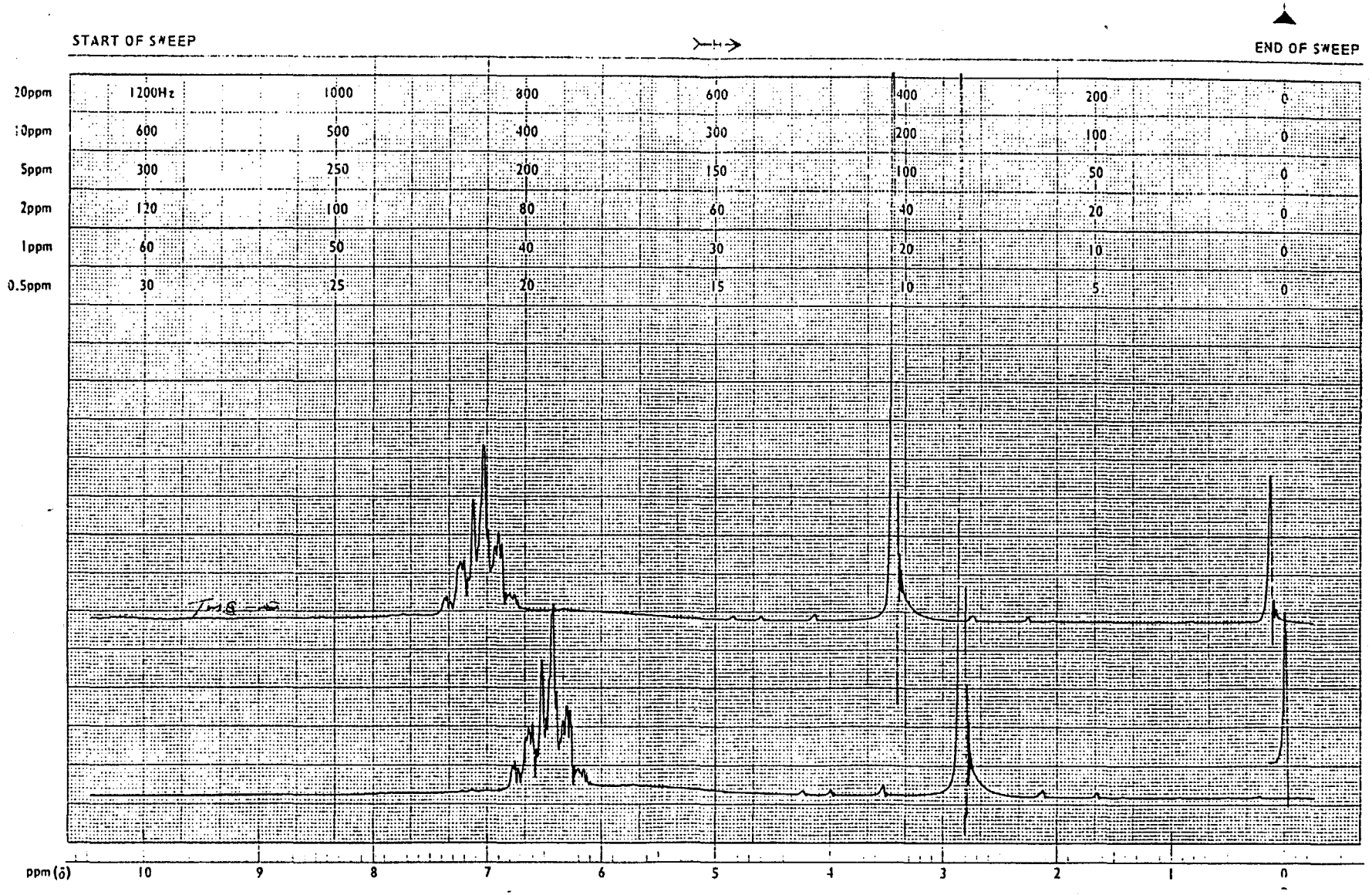
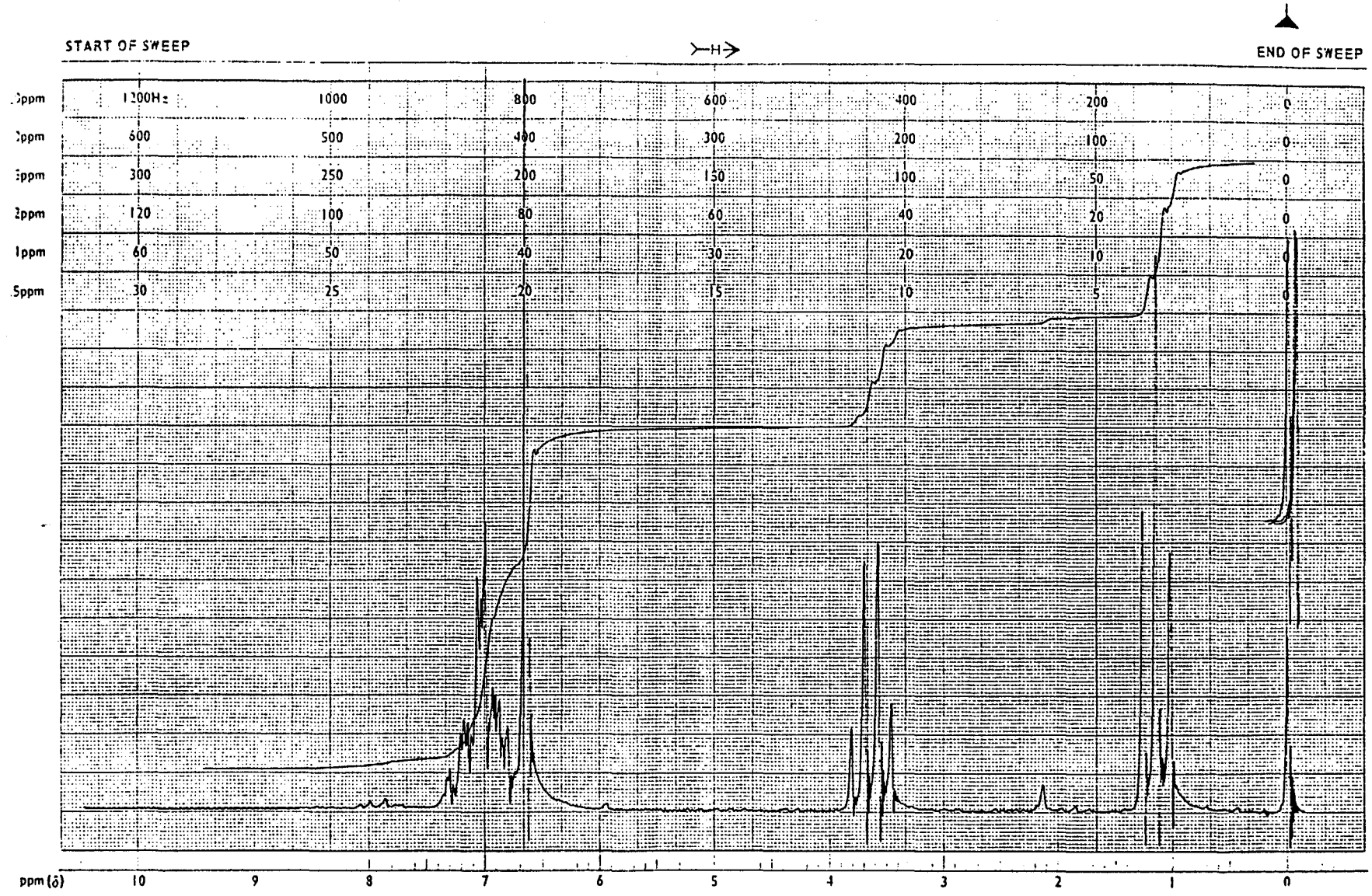


Figure 4B. NMR Spectra of Phenol/Alcohol Mixtures: 50% Phenol in Methanol.

EM-360 60 MHz NMR SPECTROMETER



EM-360 60 MHz NMR SPECTROMETER

Figure 4C. NMR Spectra of Phenol/Alcohol Mixtures: Phenol/Ethanol/p-Toluenesulfonic Acid Reaction Product.

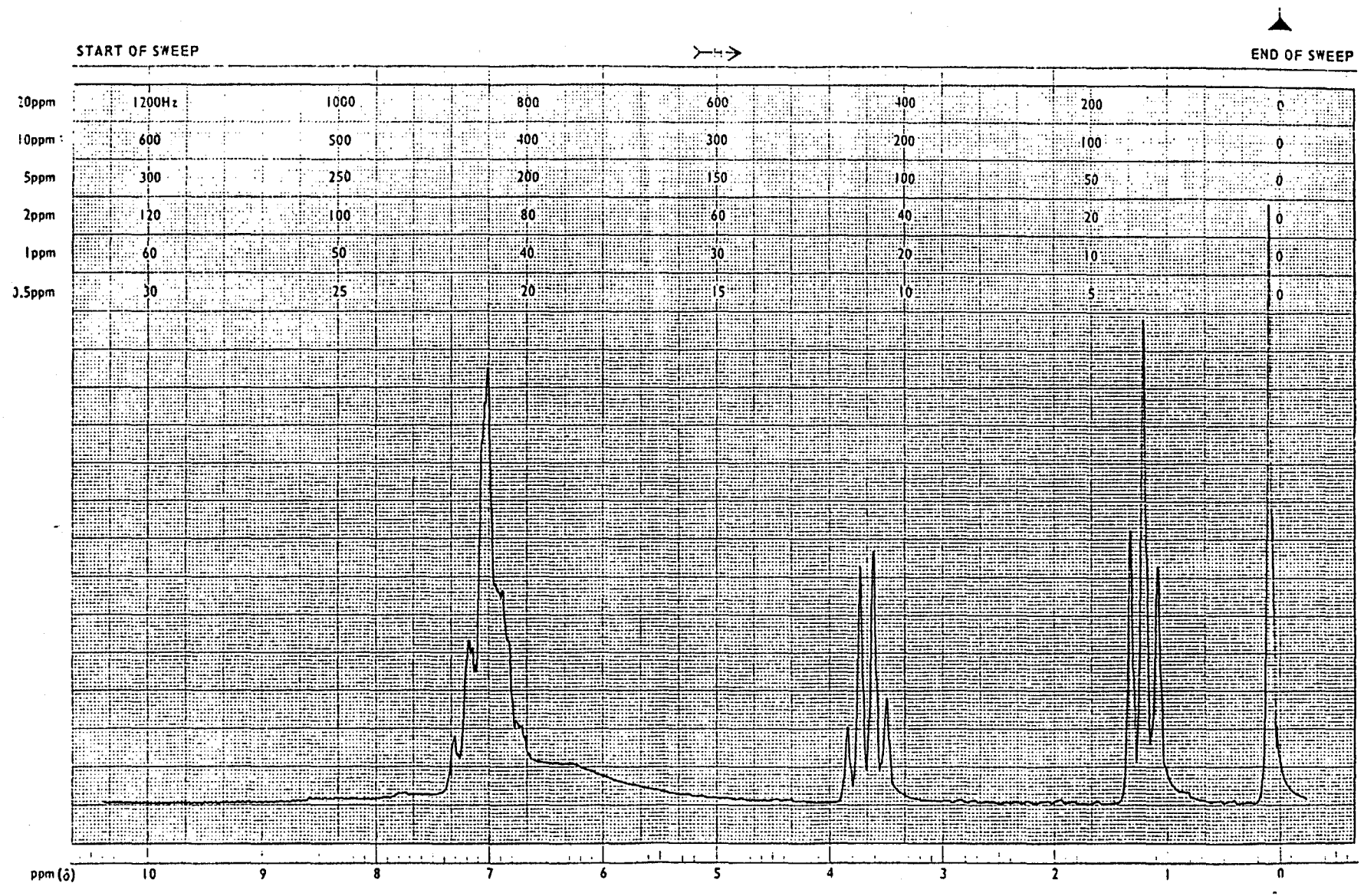


Figure 4D. NMR Spectra of Phenol/Alcohol Mixtures: 50% Phenol in Ethanol Solution.

EM-360 60 MHz NMR SPECTROMETER

APPENDIX 4

SAMPLES SUPPLIED TO OTHER DOE PROJECTS

CONSOL Inc.
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412-854-6683

December 12, 1996

Dr. John Zondlo
Department of Chemical Engineering
West Virginia University
P. O. Box 6101
Morgantown, WV 26506-6101

Dear Dr. Zondlo:

Dr. Michael A. Nowak of DOE/FETC asked if I could provide you with a coal liquefaction material for possible use in making anodes. I am shipping you a 4 oz jar of a material labeled "Kerr-McGee Light Phase" for your inspection. I have a 55 gal drum of this material and one drum of a similar material. What follows is my best attempt to reconstruct the source of this material; be aware that I am uncertain of many details. I believe the material was produced at the Wilsonville, AL, Solvent Refined Coal (SRC) pilot plant. The Kerr-McGee critical Solvent Deasher (CSD, later called the ROSE-SR unit) was a device that deashed the raw SRC product of the liquefaction section of the plant. The CSD unit produced an "ash concentrate" stream and "light SRC" and "heavy SRC" streams. The light and heavy SRC streams were sometimes combined and sometimes left separate. I believe this material is the light SRC stream produced in about 1979 from a Wilsonville run made with an Illinois Basin bituminous coal. Our laboratory recently obtained the following elemental analysis of the sample:

	wt %
C	85.71
H	6.73
N	1.80
S	0.68

We also obtained a ^{1}H- nuclear magnetic resonance spectrum of the sample; 38.5% of the hydrogen is aromatic.

An MSDS is enclosed with the sample. Please call me to discuss the sample origins or to request a drum of the material.

Sincerely,

R. A. Winschel
Research Group Leader

/ls

cc: M. A. Nowak
R. M. Statnick

CONSOL Inc.
Research & Development
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412-854-6568

January 24, 1997

Dr. John Zondlo
Department of Chemical Engineering
West Virginia University
P. O. Box 6101
Morgantown, WV 26506-6101

Dear Dr. Zondlo:

Dr. Michael A. Nowak of DOE-FETC informed me that a sample sent to you in December 1996 by Dick Winschel of CONSOL R&D was found by you to be inappropriate for the production of carbon anodes. Mike requested that I supply you with another sample that would be representative of a "typical" two-stage direct coal liquefaction process stream.

The sample I have chosen to send is a composite of individual samples taken over extended periods of Run 259 made in 1990 at the Wilsonville integrated two-stage coal liquefaction pilot plant. Wilsonville Run 259 was made in a two-stage continuous unit with catalyst in both reactors. The feed coal was Ireland Mine, Pittsburgh seam bituminous coal. The sampling point from which the individual samples were obtained is called "Interstage" and was located between the first and second reactors. The sample designator for these samples is R1235. Each individual sample was distilled to an atmospheric equivalent boiling point of 850 °F. Approximately half of the 850 °F$^+$ fractions were then combined to make the composite sample. An analysis of the composite is attached.

I shipped to you, under separate cover, 50 g of the composite sample. We retained an additional limited quantity. Please contact me or Dick Winschel (412-854-6683) if you wish to obtain more of this sample or other samples. Please let me know if I can otherwise help by providing additional information. We welcome any comments you wish to make on the progress of your work with this sample.

Sincerely,

S. D. Brandes
Sr. Research Engineer

/ls

cc: R. M. Statnick
R. A. Winschel
G. A. Robbins
M. A. Nowak - DOE/FETC

Sample Analysis

Plant	Wilsonville Pilot Plant
Run No.	259
Sample Location	Interstage
Feed Coal	
Mine	Ireland
Seam	Pittsburgh
Ultimate	
Ash, wt%, as det.	8.74
C, wt% MAF	90.12
H, wt% MAF	6.19
N, wt% MAF	1.15
S, wt% MAF	1.50
O, (diff) wt% MAF	1.04
Ash Elementals (%)	
Na_2O	0.52
K_2O	1.63
CaO	2.62
MgO	0.84
Fe_2O_3	20.87
TiO_2	0.91
P_2O_5	0.15
SiO_2	44.30
Al_2O_3	24.77
SO_3	1.46
Unaccounted	2.13
Proton Distribution of Tetrahydrofuran-Solubles, %	
Condensed Aromatics	30.7
Uncondensed Aromatics	2.6
Cyclic Alpha	20.9
Alkyl Alpha	10.2
Cyclic Beta	13.8
Alkyl Beta	13.4
Gamma	8.4
Carbon Distrib. of Tetrahydrofuran-Solubles, % (a)	
Aromatic Carbon	63.35
Aliphatic Carbon	26.77
Phenolic -OH Concentration of Tetrahydrofuran-Solubles, meq/g	0.92
Molecular Weight, Da (b)	
M_n	610
M_w	710

a) Carbon distribution determined by Western Research Institute using solid-state ^{13}C-NMR
b) Molecular weight data determined by SRI International using field ionization mass spectrometry (FIBS)

CONSOL Inc.
Research & Development
4000 Brownsville Road
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412-854-6683

April 18, 1997

Mr. Richard Sprecher
U.S. Department of Energy
Federal Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236-0940

Subject: DOE Contract DE-AC22-94PC93054

Dear Rich:

This is to document the samples you picked up on April 18 from CONSOL. The eleven samples were contained in 20 mL vials. These samples are aliquots of the materials returned to CONSOL from Caleb Brett. Caleb Brett, under subcontract to CONSOL, conducted crude oil assays on two net products of HTI Run PB-03. The one product, HTI PB-03-6,7,8 was produced with the hydrotreater on line. The second product, HTI Run PB-03-9,10,11 was produced while the hydrotreater was by-passed. As part of the crude oil assay, Caleb Brett fractionally distilled both samples. One of the crude oils and most of the fractions were not completely consumed in the assay tests. I provided you with samples of the available crude and all available fractions, as listed below.

Sample	Fraction Boiling Point, °F
HTI PB-03-6,7,8	70-180
"	180-350
"	400-550
"	550-650
"	650+
HTI PB-03-9,10,11	crude oil
"	70-180
"	180-350
"	400-550
"	550-650
"	650+

My understanding is that you will analyze these materials by high resolution mass spectrometry to determine the susceptibility of various nitrogen-compound types to hydrotreating. This should be a good set of samples for that purpose, as long as your method has the sensitivity to handle the low nitrogen contents of the hydrotreated fractions. Details of CONSOL's and Caleb Brett's

work with these materials, including detailed analyses, can be found in the quarterly Technical Progress Report for June through September 1996 under the subject contract. Please contact Gary Robbins if you would like a copy of the draft report.

Sincerely,

R. A. Winschel
Research Group Leader
Exploratory Research Group

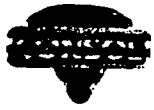
/ls

cc: M. A. Nowak
F. P. Burke
R. M. Statnick
P. Zhou - BRSC

APPENDIX 5

FORMAT REQUEST FOR SOFTWARE OF KINETIC/MECHANISTIC MODEL OF RESID REACTIVITY

Letter from S. D. Brandes to the University of Delaware



CONSOL Inc.
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4000 Brownsville Road
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412-854-6568

March 6, 1997

Darin Campbell
Department of Chemical Engineering
Colburn Laboratory
University of Delaware
Newark, DE 19716-3110

Subject: Subcontract Under DOE Contract DE-AC22-94PC93054

Dear Darin:

I spoke with Mike Nowak, our DOE contracting officer's representative, concerning the form in which the kinetic/mechanistic model of resid reactivity you are developing is to be delivered to DOE.

The following items are to be submitted: 1) an electronic copy of the model either on disc or tape; 2) a hard copy printout of the code; 3) documentation which describes the software; specifically, what it is intended to do and how it is expected to do it; and 4) an operating manual that is sufficiently detailed that a knowledgeable individual can use the model.

I believe, based on our conversation, that items 1 and 2 should be easily accomplished. I suggest that you keep item 3 to a maximum length of a page or two. Item 4 is important and may require more space.

When you are ready to deliver the software, please contact me. I will put you in touch with one of our systems analysis engineers who will be able to tell you the formats, etc. we are capable of employing.

If you have any questions, feel free to call me. Dick Winschel and I will be at Delaware on April 30th and look forward to a demonstration of the model at that time.

Sincerely,

S.D. Brandes
Sr. Research Engineer

/ls

cc: F. P. Burke
R. M. Statnick
R. A. Winschel
W. H. Calkins - University of Delaware
M. T. Klein - University of Delaware
M. A. Nowak - DOE/PETC

APPENDIX 6

"KINETICS OF HYDROPROCESSING OF COAL-DERIVED VACUUM RESIDS"

By: Shaojie Wang, He Huang, Keyu Wang, M. T. Klein and W. H. Calkins
University of Delaware
Department of Chemical Engineering
Newark, DE 19716

KINETICS OF HYDROPROCESSING OF COAL-DERIVED VACUUM RESIDS

Shaojie Wang, He Huang, Keyu Wang, M.T. Klein and W.H. Calkins*
Department of Chemical Engineering
University of Delaware
Newark, DE 19716

Key words: coal-derived resid, hydroprocessing, kinetics

Introduction

The direct liquefaction of coal produces a substantial amount of high boiling, non-distillable residuum, whose amount depends upon a number of factors such as the coal type, the hydrogen donor strength of the solvent, activity of the catalyst, and the conditions under which the direct liquefaction was run. Because of its high boiling point and potential thermal instability, this material is not suitable for processing in a conventional petroleum refinery. In a commercial liquefaction process as visualized today, therefore, this material would be recycled to the process to recover its energy value and to provide some of the solvent needed for the coal liquefaction process itself. Furthermore, this recycle oil has been shown to have a beneficial effect (i.e. increased oil yield) in the liquefaction process (1,2). Thus, it became important to determine the rates of conversion of these residual materials to products boiling in the fuel range (e.g. $<850°F$) and to know whether these high boilers will build up or be rapidly broken down in the recycling process. It was to follow the rates of resid breakdown (resid reactivity) under conditions approximating the conditions in the liquefaction process that this program was undertaken. Knowing the rates of resid condensation as well as breakdown are also important as retrograde processes reduce product yields and foul catalysts and equipment. This required the use of a reactor system capable of measuring hydroprocessing rates at very short contact times and the development of analytical methods for measuring the conversion and boiling ranges of the products. Resid conversion rates (both condensation and breakdown) would be correlated with composition data obtained by other analytical methods (e.g. TGA, NMR, elemental analysis etc.)

Experimental Section

Apparatus. The design and operation of the Short Contact Time Batch Reactor (SCTBR) system have been described in detail elsewhere (3). In operation, both the empty 30 cm^3 reactor and the preheater and precooler are immersed in a fluidized sand bath and brought up to reaction temperature. High pressure hydrogen gas provided the driving force to deliver the reaction mixture of solvent, coal and catalyst from a blow case into the reactor at reaction temperature in of the order of 0.3 seconds, eliminating the heat up limitations in kinetic measurements. Discharging and quenching of the reaction mixture was carried out in the similar time frame. Hydrogen bubbled through the reactor from the bottom provided the necessary agitation. Temperature control was within $\pm$ 2°C. Reaction times as short as 5 seconds could be measured with considerable precision.

Materials Studied. Thirteen resid samples (boiling above 850°F) from coal liquefaction runs made at the Wilsonville pilot plant and two resid samples from Hydrocarbon Research Institute bench scale unit were prepared and supplied by CONSOL Inc. The feed coals for the resids produced at the Wilsonville pilot plant were Wyodak-Anderson, Illinois #6 and Pittsburgh coals. Selected properties, such as elemental analysis and the ^{13}C NMR patterns obtained by CONSOL Inc., of each resid are shown in Table 1.

Resid Conversion Reactions. All reactions were run as mixtures of tetralin T (the donor solvent) and resid R over a range of T/R ratios, temperatures and catalyst. For each reactor run, 5 - 10 grams of resid were used together with added tetralin to make up the desired T/R ratio. Holdup of material prevented complete recovery of the reaction products. Recoveries varied from 75 to 85 wt%, depending upon the T/R ratio used. The determination of conversion and subsequent analytical results were therefore based on representative aliquots. Molybdenum naphthenate was used as the catalyst and was sulfided *in-situ* using methyldisulfide.

Reaction Product Workup Procedure. The reaction products were worked up by separating the solids from the liquids by filtration (Figure 1). The solid filter cake was washed with methylene chloride which went into the filtrate with the product liquids. The filtrate was then distilled at low temperatures (45°C) to remove the methylene chloride. The resulting solid cake and the filtrate were analyzed separately.

Analytical Methods - Conversion. The conversion to liquid was determined using thermogravimetric analysis (TGA) on the solid cake by an ash balance calculation.

The tetralin content of the methylene chloride-free filtrate was determined by gas chromatography using an added 1-methylnaphthalene internal standard.

To determine the amount of liquid product boiling above and below 850°F (454 °C), a boiling range method, SimDis TG, was developed based on TGA (4).

The conversion of resid to the material boiling below 850 °F was estimated by Equation 1:

$$Conversion\ (< 850\ ^\circ F) = TSF \times \left(1 - \frac{850\ ^\circ F^{+}}{RSF}\right) \qquad (1)$$

where TSF is the Tetralin Soluble Fraction of the resid (daf basis) determined by ash content in the solid resid after resid hydroprocessing; RSF is the Resid Soluble Fraction in tetralin and 850 °F^{+} is the fraction boiling above 850 °F.

Analytical Methods - Resid Characterization. The resids studied were characterized by thermogravimetric analysis at 10°C/min in nitrogen from room temperature to 600 °C. This was followed by combustion of the remaining organic material at 100 °C/min to 850 °C in air. The derivative DTG curves, Volatile Matter (VM), Fixed Carbon (FC), and ash were determined. These TGA parameters as well as the peak temperatures and peak heights from the DTG curves are also included in Table 1.

Results and Discussion

As discussed in a previous section of this paper, conversion has been determined in part by an ash balance. Efforts to carry out hydroprocessing of resids using the Ni/Mo on alumina catalyst used in Wilsonville, however, resulted in unreliable conversions data because of the large amount of ash in the catalyst. In addition, it was found that the supported catalyst changed

as the hydroprocessing progressed, making the calculations of conversion unreliable. Sulfided molybdenum catalyst, on the other hand, contributed little ash (which can be corrected for) to the system and gave very reproducible results. Preliminary experiments using a range of sulfided molybdenum naphthenate catalyst concentrations from 0.9 wt% to 5.0 wt% showed that 0.9 wt% catalyst resulted in only a barely detectable increase in conversion over uncatalyzed runs. However, 3 to 5 wt% (based on the resid) gave significant conversion to lower boiling products.

After considerable experimentation to determine appropriate reaction conditions, all 15 resids were hydroprocessed for 30 minutes at 420°C in 3 to 1 tetralin to resid weight ratio and 1500 psig hydrogen with and without sulfided molybdenum naphthenate catalyst (as 3 wt% molybdenum based on the resid charged). Each resid was also run at ambient temperature for comparative purposes.

Tables 2 and 3 show the conversions to material boiling below 850°F for the thermal and catalyzed hydroprocessed resids, respectively. It is to be noted that significant conversion to lower boiling material occurs even in the absence of catalyst. However, in the presence of the molybdenum catalyst, conversion to the lower boiling material was at least doubled. To attain as much as 30 to 40% conversion requires a significant amount of catalyst.

As Tables 2 and 3 show, there is considerable variation among the resids in terms of their reactivity and convertability to lower boiling products. Plots of the thermal and catalyzed conversions of the resids vs the feed coal types are shown in Figure 2. In the thermal hydroprocessing, there appears to be a correlation with the coal type used in the liquefaction, i.e., the lower rank coal produced resid which gave higher conversion on hydroprocessing in the absence of catalyst. On the other hand, if a catalyst is used, the resids from the three coals studied showed little or no difference in conversion under the conditions used. It will be noted in Figure 3 and Tables 1, 2 and 3 that those resids having high DTG peaks and high aromatic carbon content (by ^{13}C NMR) generally show low conversions under the thermal hydroprocessing conditions while lower aromatic carbon containing resids show higher conversions in thermal hydroprocessing. Use of a strong catalyst apparently compensates in part for the high aromaticity.

SimDis TGA on the solid filter cake showed that, whereas there is considerable solubility of the resid in tetralin, up to 80 wt%, the solids themselves are not degraded to lower boiling material. Therefore, the resid must be solubilized in the recycle solvent for the resid breakdown to occur.

Summary and Conclusions

With the appropriate catalyst and conditions approximating coal liquefaction, high boiling coal-derived resids do break down to lower boiling products as they are recycled to the coal liquefaction process.

Coal-derived resids vary widely in their reactivity toward breakdown to lower boiling products under both thermal and catalytic conditions.

High catalyst activity appears to be necessary to convert these refractory materials to lower boiling materials.

Solubilization of the resid in the processing solvent is necessary for the molecular breakdown.

Acknowledgements

The support of various portions of this work by the Department of Energy and CONSOL Inc. under subcontract DE-AC22-94PC93054 is acknowledged. The guidance and assistance of Drs F.P. Burke, R.A. Winschel and S.D. Brandes in providing samples, analytical data and other assistance were also major factors in the progress of this project.

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Table 1 Selected properties of the resids

Resid	Feed Coal	Number	Stream*	f_a	VM wt%	FC wt%	Ash wt%	Tpeak °C	Peak Height wt%/min (daf)
Resid L	Wyodak-Anderson	4	V 1067	34.0	51.3	48.7	19.1	470.7	4.59
Resid K	Black Thunder	5	R 1235	24.6	53.6	46.4	17.2	464.8	4.60
Resid H		6	V 131B	33.3	57.1	42.9	15.2	475.3	4.67
Resid F		10	V 1067	24.3	55.2	44.8	17.5	461.5	4.36
Resid E		11	R 1235	26.0	53.4	46.6	15.6	454.4	4.24
Resid G		12	V 131B	25.9	55.7	44.3	15.9	462.2	5.02
Resid I	Illinois No. 6	7	V 1067	30.4	61.5	38.5	15.9	480.1	6.44
Resid M	Burning Star No. 2	8	R 1235	29.4	59.7	40.3	13.7	481.8	6.16
Resid D		9	V 131B	29.2	70.9	29.1	9.9	490.5	6.83
Resid J	Pittsburgh	1	V 1067	31.6	57.6	42.4	10.2	490.1	7.20
Resid B	Ireland	2	R 1235	33.3	61.1	38.9	8.7	493.6	7.43
Resid C		3	V 131B	31.5	61.0	39.0	8.5	490.2	6.23
Resid A				38.9	51.8	48.2	17.0	472.1	4.75
Resid N				20.6			0.4		
Resid O				18.8			4.1		

*

V 1067 = interstage stream

R 1235 = 2nd stage product stream

V 131B = recycle stream

Table 2 Conversion of thermal hydroprocessing of resid

Resid			Solid Residue		Liquid Residue			Conversion to 850 F-
Sample	Name	Ash	Ash	TSF	Tetralin	SRF	850 F+	
Resid A	W258V-131B	17.0	50.1	79.7	88.2	11.8	9.6	15.0
Resid B	W259R-1235	8.7	33.5	81.0	88.0	12.0	9.6	15.9
Resid C	W259V-131B	8.5	35.0	82.7	86.2	13.8	10.8	17.7
Resid D	W261V-131B	9.9	45.8	87.1	87.9	12.1	9.7	17.1
Resid E	W262R-1235	15.6	43.5	76.0	88.4	11.6	8.6	19.6
Resid F	W262V-1067	17.5	47.8	76.9	87.4	12.6	9.7	17.7
Resid G	W262V-131B	15.9	46.5	78.3	88.7	11.3	8.7	18.2
Resid H	W260V-131B	15.2	46.6	79.5	87.7	12.3	9.0	21.3
Resid I	W261V-1067	15.9	50.8	81.8	88.9	11.1	8.5	19.4
Resid J	W259V-1067	10.2	38.7	82.0	86.4	13.6	11.5	12.9
Resid K	W260R-1235	17.2	49.0	78.4	86.9	13.1	9.8	19.7
Resid L	W260V-1067	19.1	51.3	77.6	89.2	10.8	8.3	17.8
Resid M	W261R-1235	13.7	45.6	81.1	90.1	9.9	7.9	16.0
Resid N	HTI POC-01, O-43	0.4	33.0	99.2	80.6	19.4	14.1	27.0
Resid O	HTI POC-02, O-43	4.1	38.0	93.1	70.6	29.4	22.4	22.1
Thermal: 420 C; 30 min; 1500 psig H2								
Catalytic: 420 C; 30 min; 1500 psig H2; 3 wt% Mo								
Control: 25 C; 10 min; 1500 psig H2								
TSF: Tetralin Soluble Fraction of resid, wt% (daf basis)								
RSF: Resid Soluble Fraction in tetralin, wt%								
850 F+: fraction of boiling above 850 F								

Table 3 Conversion of catalytic hydroprocessing of resid

Resid			Solid Residue		Liquid Residue			Conversion
Sample	Name	Ash	Ash	SF	Tetralin	SR in Tetralin	850 F+	
Resid A	W258V-131B	17.0	51.5	80.7	82.5	17.5	9.9	35.0
Resid B	W259R-1235	8.7	40.0	85.6	79.8	20.2	11.2	38.1
Resid C	W259V-131B	8.5	41.4	86.8	81.4	18.6	11.5	33.1
Resid D	W261V-131B	9.9	54.9	91.0	77.9	22.1	14.1	32.9
Resid E	W262R-1235	15.6	44.2	76.6	80.6	19.4	11.3	32.1
Resid F	W262V-1067	17.5	49.4	78.3	79.6	20.4	10.7	37.4
Resid G	W262V-131B	15.9	48.3	79.8	79.2	20.8	11.5	35.8
Resid H	W260V-131B	15.2	50.9	82.7	75.6	24.4	11.3	44.6
Resid I	W261V-1067	15.9	56.6	85.5	76.2	23.8	11.9	42.7
Resid J	W259V-1067	10.2	43.8	85.4	76.5	23.5	11.9	42.1
Resid K	W260R-1235	17.2	52.1	80.8	78.1	21.9	12.4	35.2
Resid L	W260V-1067	19.1	53.5	79.5	79.1	20.9	11.7	35.0
Resid M	W261R-1235	13.7	53.7	86.3	80.2	19.8	11.7	35.3
Resid N	HTI POC-01, O-43	0.4	36.4	99.3	67.9	32.1	16.7	47.6
Resid O	HTI POC-02, O-43	4.1	48.3	95.4	70.2	29.8	19.1	34.3
Thermal: 420 C; 30 min; 1500 psig H2								
Catalytic: 420 C; 30 min; 1500 psig H2; 3 wt% Mo								
Control: 25 C; 10 min; 1500 psig H2								
TSF: Tetralin Soluble Fraction, wt% (daf basis)								
RSF: Resid Soluble Fraction in tetralin, wt%								
850 F+: fraction of boiling above 850 F								

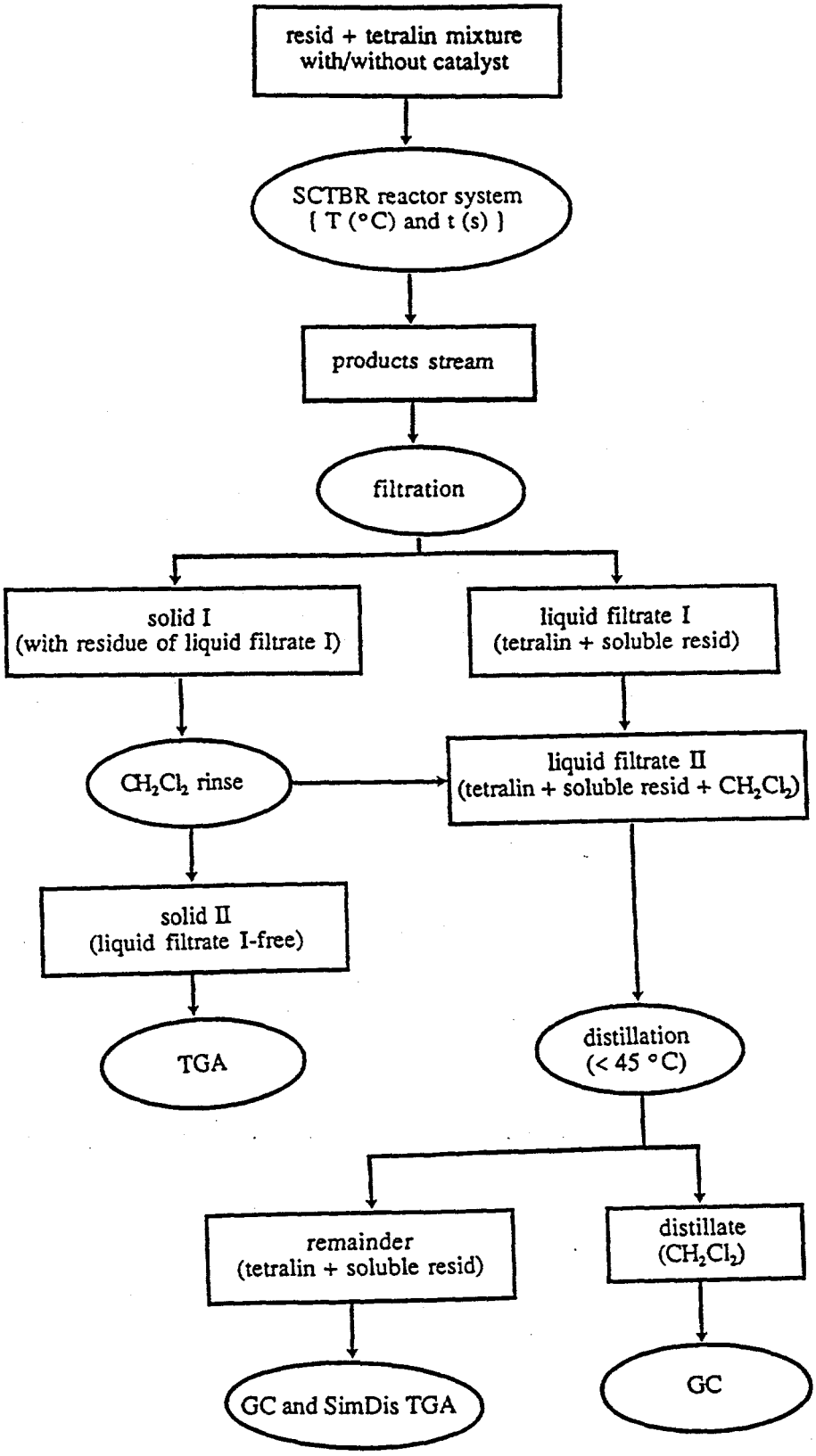

Figure 1 Scheme of the reaction product workup procedure

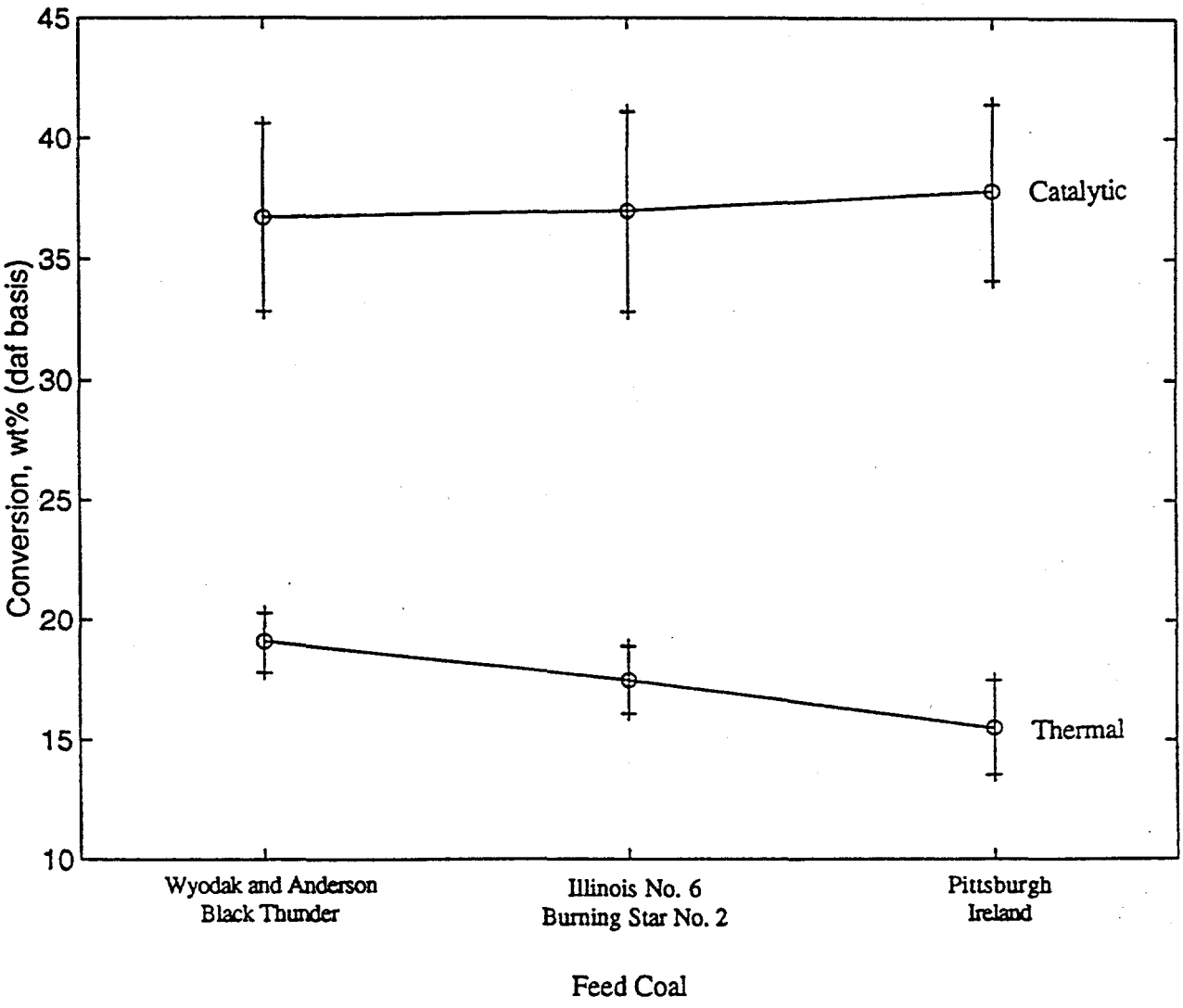

Figure 2 Thermal and catalyzed hydroprocessing conversions of the resids vs feed coal type

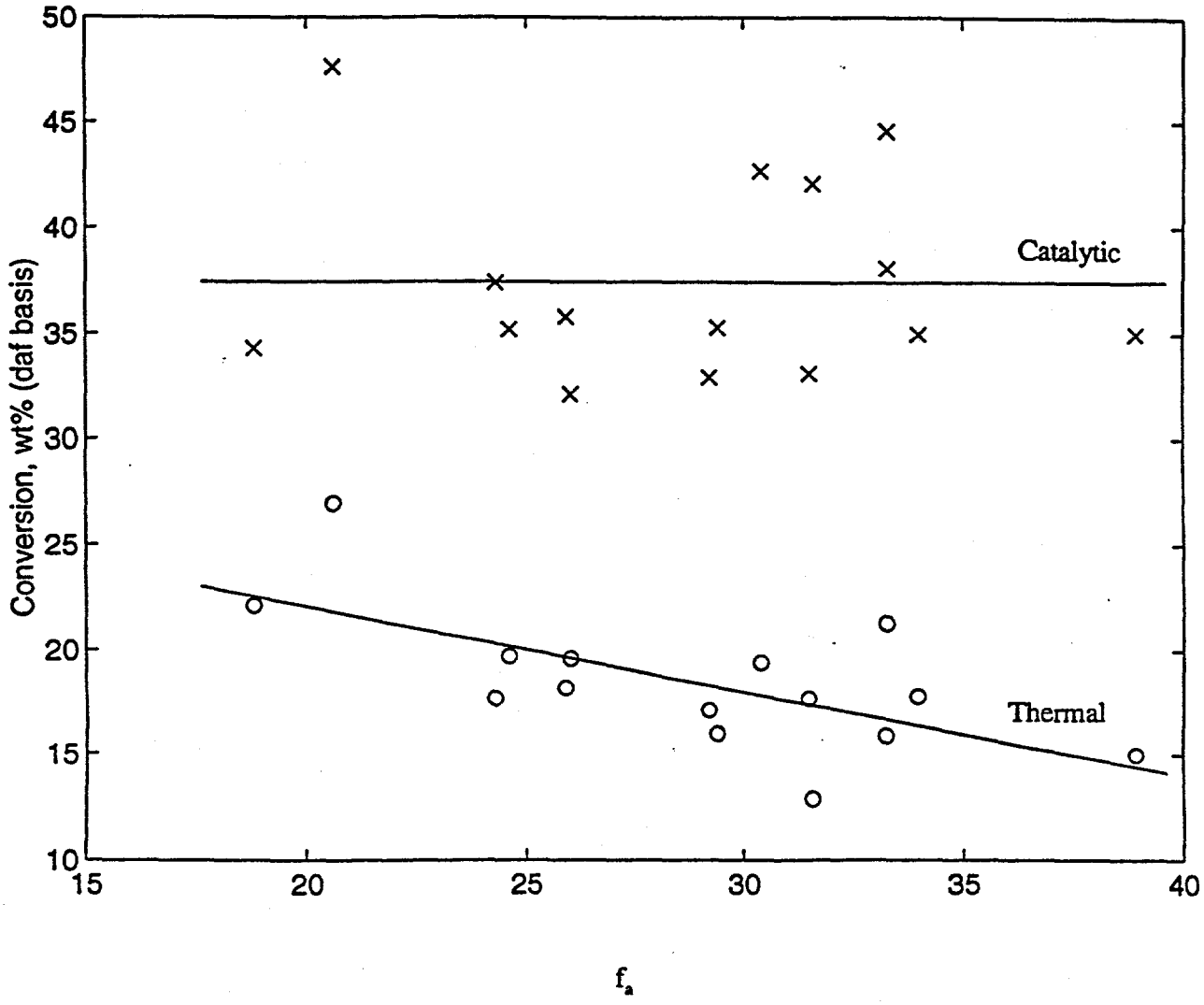

Figure 3 Thermal and catalyzed hydroprocessing conversions vs f_a of the resids