

**A Characterization and Evaluation of  
Coal Liquefaction Process Streams**

**Quarterly Technical Progress Report  
April 1 through June 30, 1996**

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March 1997



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## Section 1

### EXECUTIVE SUMMARY

#### **CHARACTERIZATION OF SAMPLES FROM HTI RUN CMSL-11**

CONSOL completed characterization of 17 samples from HTI Run CMSL-11 (227-89), in which Black Thunder Mine subbituminous coal was fed, alone (Conditions 1 and 2) and with municipal solid waste (MSW) plastics (Conditions 3A and 3B). Dispersed catalysts were used in all four conditions. Highlights of CONSOL's characterization results are provided below.

- The effect of feeding MSW plastics with coal (MF feed was 25% plastics/75% coal) was examined by comparing characteristics of samples at conditions 3B and 2, in which the reactor temperatures were the same, but solvent/feed ratios differed.
- The donor solvent qualities of the whole pressure filter liquid (PFL), the PFL 850 °F distillate, and separator bottoms distillate were significantly lower in Condition 3B than in the corresponding samples from Condition 2. It appears that the lower solvent quality of these samples is due to increased paraffinic H content produced when MSW plastic and coal were fed. The aromatic H content of the pressure filter cake (PFC) increased by a few percent with the addition of MSW plastics.
- The PFL samples from coal-only Conditions 1 and 2 contained several percent of tetrahydrofuran- (THF) insoluble organic matter (IOM) and ash, even though HTI's intent was to operate with solids-free PFL as recycle. Apparently, the IOM and ash resulted from HTI's remedial measures to prevent filtration bottlenecks by allowing some unfiltered material into the PFL stream. No ash was found in the PFL from Condition 3B, in which filtration was improved and these measures were not needed. The IOM found in the PFL from Condition 3B is presumed to be unconverted plastic, as was observed in Runs CMSL-8 and CMSL-9.
- The separator bottoms and PFC samples from Condition 3B had higher IOM and lower ash contents than did the corresponding Condition 2 samples. This suggests lower feed conversion in Condition 3B. This may result partly from recycle of both IOM and ash in the PFL in Condition 2 (poor filter operation), and recycle of only IOM (unconverted plastics) in the PFL in Condition 3B. In contrast, HTI results based on

nearly equal MAF feed conversion in the two periods. The use of hot quinoline may dissolve the IOM and indicate that all of the plastic was converted.

- It is estimated from decreases in phenolic -OH concentration that occurred in some samples when plastics were fed that ca. 37% of the heavy liquid recycle solubles are plastic-derived material.
- The hot decalin extraction method developed for detecting unconverted high-density polyethylene (HDPE) was used to determine the concentration of unconverted polypropylene (PP) + HDPE poly(olefins) in the separator bottoms sample, and to characterize the feed slurry from a coal/plastics period of the run, a composite sample of the feed MSW plastics, and various virgin poly(olefins) that represent possible components of the feed MSW plastics.
  - Virgin polymer results show that the low-density polyethylene (LDPE) tested does not respond to the analysis procedure as do PP and HDPE. Most of the LDPE solubilized in hot decalin remains soluble in decalin or THF at room temperature.
  - A homogenized composite sample of feed MSW plastic was prepared and found to respond essentially like PP and HDPE to the hot decalin extraction procedure. The results indicate about 94% PP+HDPE in the feed.
  - Inconsistencies between concentrations of both ash and PP+HDPE components between the MSW plastics sample and the feed slurry sample suggests that some problem exists with the measurements in one or both samples, perhaps from non-representative sampling. Analysis of the ash content of the feed MSW plastic was 1.6%, whereas an indirect estimate based on the feed slurry gave 9.7% ash in the feed MSW plastic. The 8 wt % fresh + unconverted recycled PP+HDPE measured in the feed slurry appears to be too low a concentration.
  - The unconverted PP+HDPE fraction in the samples from Condition 3B was determined to be 5.5% of the separator bottoms, 1.5% in the pressure-filter cake (PFC), and 6.5% in the pressure-filter liquid (PFL). These values are at the low end

of, or are lower than, the concentrations observed in corresponding samples from Runs CMSL-8 and CMSL-9.

- Based on gas chromatography-mass spectrometry (GC-MS) analysis of the product separator overheads (SOH) oil and results with virgin polymers, the feed MSW is estimated to contain about 2 wt % polystyrene (PS).
- Based on the gas chromatography-mass spectrometry (GC-MS) data, n-paraffins constitute approximately 36% of the product SOH oil obtained from coal/MSW plastics operation in Condition 3B. Several individual n-paraffins each constitute 2% or more of the SOH.
- From Condition 1 to Condition 2, the increase in reactor temperature and addition of 50 ppm more Mo catalyst precursor, incorporated in HTI's Fe catalyst precursor, had little or no impact on characteristics of the streams analyzed by CONSOL.
- The distillation resid from coal/plastics processing separated into two phases that were plastic-like and coal resid-like in nature. This is similar to behavior previously observed in samples from Runs CMSL-8 and CMSL-9. However, distinct particles of material recovered in the THF-insolubles did not melt at 100 °C, as was previously observed.

### **RESID REACTIVITY**

The University of Delaware is continuing to evaluate fourteen resid samples in the Delaware sample set for relative resid reactivity. The kinetic model is nearly ready to accept chemical data of the 15 resids in the sample set.

### **TECHNOLOGY TRANSFER**

A paper was submitted for presentation at the 212th National Meeting of the American Chemical Society, and for presentation at the DOE First Joint Power and Fuel Systems Contractors Conference. The paper "Determination of Unconverted HDPE in Coal/ Plastics Co-Liquefaction Stream Samples", by G. A. Robbins, R. A. Winschel, and F. P. Burke appears as Appendix 3.

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## **Section 2**

### **INTRODUCTION**

This is the Technical Progress Report for the eighth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period April 1 through June 30, 1996.

#### **CONTRACT OVERVIEW**

The objectives of this project are to support the DOE direct coal liquefaction process development program and to improve the useful application of chemical analyses to direct coal liquefaction process development. This project builds on work performed during 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 will be constructed. Such a model will provide insights to improve process performance and the economics of direct coal liquefaction.

#### **CONTRACT ACTIVITIES THIS PERIOD**

- CONSOL completed characterization of 17 samples from HTI Run CMSL-11 (227-89). The run consisted of 17 days of operation at four run conditions. Black Thunder Mine subbituminous coal was fed alone and with municipal solid waste (MSW) plastics. Only dispersed catalysts were used.
- Ten samples from HTI Run CMSL-10 and 27 samples from HTI Run PB-01 were provided to the DOE/PETC in-house research program.
- Sets of samples were requested from HTI Run PB-04 (Appendix 1).



- Plans were made to initiate a series of microautoclave tests using the fifteen resids in the Delaware sample set. Resid conversions and product analyses will be forwarded to Delaware for use in the resid reactivity model.
- The University of Delaware Quarterly Report is appended to this report (Appendix 2).
- A paper was submitted for presentation at the 212th National Meeting of the American Chemical Society and at the DOE First Joint Power and Fuel Systems Contractors Conference. The paper "Determination of Unconverted HDPE in Coal/Plastics Co-Liquefaction Stream Samples", by G. A. Robbins, R. A. Winschel, and F. P. Burke appears as Appendix 3.

#### **ACTIVITIES IN PROGRESS**

- Characterization work is under way on samples from HTI Run ALC-1.
- We continued recalibration of our phenolic -OH measurement method for the new FTIR system.
- CONSOL is arranging a complete suite of light oil assay tests for hydrotreated and unhydrotreated net products from HTI Run PB-03. Five to six gallons of the two samples are on hand. The analytical test plan provided by Burns and Roe Services was forwarded to National Institute for Petroleum and Energy Research, and a cost quote was requested.

### Section 3

## RESULTS AND DISCUSSION

### CHARACTERIZATION OF SAMPLES FROM HTI RUN CMSL-11

#### INTRODUCTION

CONSOL characterized 17 samples from HTI Run CMSL-11 (227-89). The run consisted of 17 days of operation at four run conditions. Operating conditions, yields, and performance data are provided in Table 1.<sup>1-3</sup> Black Thunder Mine subbituminous coal was fed alone and with municipal solid waste (MSW) plastics. Only dispersed catalysts were used. Previous runs fed virgin plastics with coal.

In Condition 1, coal was fed with 50 ppm Mo (MF coal basis, Molyvan A was the catalyst precursor). Other operating conditions included 5000 ppm Fe catalyst precursor (HTI's sulfated hematite catalyst) and use of a coil pretreater (essentially a preheater) that operated at 575 °F and preceded the liquefaction reactors. The in-line hydrotreater for distillate product was used for Conditions 1 through 3. The hydrotreater used Criterion 411 supported catalyst, and was operated at 714 °F. The reactor temperatures were 825/840 °F in the first/second liquefaction stages for Condition 1. The solvent/MF-feed ratio was 1.0 during Conditions 1 and 2. The H<sub>2</sub>S feed rate throughout the run was 3 wt % of the MF coal. Throughout the run, space velocity was ca. 42 lb MF feed/h/ft<sup>3</sup> each reactor, and pressure filtration was used for solids separation, with (nominally) solids-free recycle from the PFL stream.

During Condition 2, coal was fed with a total Mo concentration of 100 ppm (MF coal basis); 50 ppm Mo was from the Molyvan A precursor and 50 ppm additional Mo was from Mo incorporated into HTI's Fe catalyst. In this condition and Conditions 3A and 3B, the reactor temperatures were increased to 840/860 °F. HTI lists the relative severity as 1.00 in Condition 1, and about 1.15 in Conditions 2, 3A and 3B (Table 1).

In Conditions 3A and 3B, coal and MSW plastics were fed at a ratio of 67/33 (Condition 3A) or 75/25 (Condition 3B). The solvent/feed ratio was increased from 1 in Conditions 1 and 2 to 1.5 in Conditions 3A and 3B.

HTI attempted to feed color regrinds of HDPE, PP, and high-impact polystyrene (a different source of recycled plastic) with coal after Condition 2, but the slurry viscosities were too high. Therefore, MSW plastic and coal were fed for the remainder of the run.<sup>3</sup>

HTI obtained the MSW plastics from Monmouth Plastics Recycling, Monmouth County, New Jersey. The material consisted of waste plastic collected from curbside recycling. It was supplied to HTI as a bale of HDPE, other polyethylenes, polypropylene (PP), high impact polystyrene (PS), polyvinyl chloride (PVC), and contaminants.<sup>2</sup> HTI removed by hand the non-plastic (e.g., food, metal, paper) contaminants and prepared the plastics for feeding to the liquefaction unit.<sup>1,2</sup> DOE/PETC researchers characterized by FTIR spectroscopy a sample of the feed plastics that was hand-sorted by color and plastic type. They found the prepared feed plastic to contain ca. 95% HDPE, 3% PP, and 2% other plastics, including polycarbonate (PC).<sup>4</sup> However, differences have been found in the MSW feed prepared for different HTI runs, and the material characterized may not represent the composition of plastics actually fed to the unit. HTI reported that the MSW plastic contained <0.1% chlorine, and contained 50% HDPE, 33% PP, and 27% PS.<sup>3</sup>

HTI's process performance data (Table 1) indicate that when plastics and coal were fed in Conditions 3A and 3B, the yield of C<sub>4</sub>-524 °C distillate was high. The hydrogen consumption and C<sub>1</sub>-C<sub>3</sub> gas yield were much lower, relative to the conditions in which coal only was fed (Conditions 1 and 2). The distillate produced when plastics were fed was higher boiling than that made from coal alone. The reader is referred to HTI's run report for additional information regarding run objectives, run results, process performance results, and analyses of feed and product samples.<sup>3</sup>

#### **EFFECT OF INCREASED MO CATALYST CONCENTRATION AT HIGHER TEMPERATURE**

Between Condition 1 (Period 5) and Condition 2 (Period 10), the temperature of each liquefaction reaction was increased about 10 °C, and 50 ppm additional Mo catalyst precursor (incorporated with the HTI Fe catalyst precursor) was added. Data presented in Figures 1-6 and Tables 2-7 show that most characteristics of the coal liquids change little from Condition 1 (Period 5) to Condition 2 (Period 10). CONSOL's results show (Table 2, Figure 1) that the 850 °F<sup>-</sup> distillate content of the PFL and separator bottoms samples from Condition 2 increased by about 6% compared to the Condition 1 samples. It is possible that this small increase resulted primarily from the increase in severity. The additional Mo could be responsible. There were changes in other characteristics, such as aromatic H content of the continuous atmospheric still bottoms (CASB) and its resid fraction, and in the PFL donor solvent quality. These changes, however,

were about 5% absolute in magnitude, or lower. The results indicate that the temperature increase and the Mo catalyst precursor feed rate increase had little or no impact on the characteristics of the streams analyzed by CONSOL. HTI found the process performance in Condition 1 to be similar to that obtained in Condition 2.<sup>3</sup>

#### **EFFECT OF 850 °F+ RESID ON DONOR SOLVENT QUALITY**

PFL or CASB distillates were typically 8-12% higher in solvent quality (as measured by microautoclave solvent quality assay, Table 6) than the corresponding whole sample. This indicates that the resid was consistently lower in solvent quality than the corresponding distillate. This is generally consistent with similar all-dispersed catalyst runs at HTI (Runs CMSL-8 and CMSL-9).<sup>5,6</sup> This may reflect depletion of donors, or less effective hydrogenation to create donors, in the resid fraction produced with dispersed catalyst. A different effect of resid on solvent quality has been observed when supported catalyst was present in the reactors.<sup>7</sup>

#### **UNUSUAL SAMPLE CHARACTERISTICS**

As was observed in some samples from Runs CMSL-8<sup>5</sup> and CMSL-9<sup>6</sup>, the 850 °F+ distillation resid from the Condition 3B separator bottoms sample (equivalent to the CAS bottoms sample) separated into two phases on cooling. The upper phase was lighter in color and plastic-like, and the lower phase was darker in color and more friable.

The THF insolubles from Period 3B distillation resid contained gray and tan particles. The particles did not melt at 100 °C, unlike materials similar in appearance from earlier HTI runs with plastic feedstocks. The MSW feed may contain plastics that did not convert to lighter materials as readily as did the four virgin polymers, which HTI processed in prior runs.

#### **SOH CHARACTERISTICS**

The SOH received from Condition 1, period 5, consisted of two phases: an aqueous phase and an oil phase. The analyses reported here are only those of the oil phase. Samples received from periods 10 and 17, Conditions 2 and 3B, appear to consist of a single oil phase. The Condition 1 SOH sample contains little or no sediment, whereas the presence of sediment was apparent in the SOH sample from Condition 2. The SOH sample from Condition 3B was so dark that it was not possible to visually determine the presence or absence of sediment. No further work was performed to isolate or characterize sediments that may have been present in the SOH oils.

The SOH from Condition 3B (coal/MSW plastics) was characterized by proton NMR spectroscopy and gas chromatography-mass spectrometry (GC-MS). From the total ion chromatogram presented in Figure 7, it is apparent that n-paraffins are major components. The identifiable n-paraffins were found to comprise approximately 36.4 wt % of the SOH (Table 7, estimate based on area percent). Several individual n-paraffins constitute 2 wt % or more of the SOH, based on the area percent. The concentrations of ethylbenzene and cumene (Table 7, retention times of 15.8 and 20.9 minutes) are 1.35 wt % and 0.20 wt %, respectively. Prior work<sup>6-7</sup> indicated that about 50-70% of the PS fed was found in these two components of the SOH product. Since ethylbenzene and cumene are minor components, it indicates that the feed MSW contained minor amounts of polystyrene (PS). In earlier tests, cumene was found to represent 10-16% of the PS fed (10% of the PS fed with in-line hydrotreating, and 16% of the PS fed without in-line hydrotreating). Assuming that the SOH product is 45 wt % of the MF feed (a representative value from the earlier runs), that the non-hydrotreated case based on cumene alone is appropriate, and using the 25 wt % MSW plastic in the MF feed, it is possible to estimate the PS concentration as about 0.6% of the MF total feed, or about 2% of the MSW plastics feed. The maximum PS concentration in the MF feed is about 2.5% (about 4.5% of the MSW plastics feed). Based on SOH product GC-MS data and past results with virgin polymers, the feed MSW contains about 2 wt % PS. This is consistent with the DOE/PETC characterization of the MSW feed, which indicated about 2 wt % polycarbonate and other polymers (not HDPE or PP) were present.<sup>4</sup> The PS constitutes a smaller percentage of the MSW plastic than the 27% expected by HTI.<sup>3</sup>

The proton distributions of the SOH samples from Condition 1 and Condition 2 were nearly identical (Table 3). However, there was significantly less hydroaromatic proton content in the Condition 3B SOH relative to the SOHs from the prior conditions. This is probably due to a lack of in-line hydrotreating during Condition 3B, although the primary objective of hydrotreating is generally geared toward reduction of heteroatom content, rather than hydrogenation of aromatics.

#### **EFFECT OF FEEDING MSW PLASTICS WITH COAL**

The effect of feeding MSW plastics with coal (MF feed was 25% plastics/75% coal) can be examined by comparing characteristics of stream samples from Condition 3B (Period 17) with those of the earlier conditions, particularly Condition 2 (Period 10). Reactor temperatures were the same in these two conditions; however, the solvent/feed ratio was increased from 1.0 to 1.5.

The donor solvent qualities of the PFL, and the PFL 850 °F<sup>-</sup> distillate were significantly lower in Condition 3B (Period 17) samples than in corresponding samples from the earlier conditions (Figure 6). This observation also applies to the separator bottoms sample distillate from Condition 3B (Period 17). It appears that the lower solvent quality of these samples is a consequence of the increased paraffinic H content (Figures 4 and 5) of the samples produced during Condition 3B (Period 17) when MSW plastic and coal were fed. The separator bottoms sample from Condition 3B (Period 17) had the same solvent quality as the corresponding samples from Conditions 1 and 2 (Periods 5 and 10) (Figure 6). It is not clear why the separator bottoms sample did not show lower microautoclave conversion in Condition 3B (Period 17).

The aromatic H content of the PFC (Figure 2) increased by a few percent from Condition 2 (Period 10) to Condition 3B (Period 17). The proton distributions are obtained from filtered samples, and represent the hydrogen distribution in the pyridine-soluble portion of each sample. The data presented in the figures for aromatic and paraffinic H content are summarized from proton data presented in Tables 3 to 5.

Phenolic -OH concentrations (Table 6A) of 850 °F<sup>-</sup> distillates and THF-soluble 850 °F<sup>+</sup> resids from separator bottoms and PFLs from Period 17 were lower than those of corresponding samples from Periods 5 and 10. This is attributable to the presence of non-phenolic material derived from the MSW plastic in the Period 17 samples. If we assume that the decrease in phenolic -OH concentration from Period 10 to Period 17 is a measure of amount of plastic-derived material present in a sample, then the composition of both the separator bottoms liquids (i.e., non-ash and non-IOM) and the PFL liquids can be estimated as about 37% plastic-derived.

The PFL samples from Conditions 1 and 2 contained several percent of IOM and ash (Table 2), even though HTI's intent was to operate with solids-free PFL as recycle<sup>3</sup>. The filtration rate was slow during these conditions, and HTI's standard procedure in such cases is to make a hole in the paper filter to increase the filtration flow rate. However, this allows some unfiltered ashy material into the PFL stream. The filtration rate improved when the plastics were fed during Condition 3B; no ash was observed in the PFL (Table 2). The IOM found in the PFL from Condition 3B (Table 2) is presumed to be unconverted plastic.

The separator bottoms sample from Condition 3B had a higher IOM content and lower ash content than did the corresponding Condition 2 sample (Table 2). Since the Condition 3 sample

ash content is lower than expected due to the change in feed ash content, the results suggest that the percent conversion of the feed was lower in Condition 3B. In contrast, HTI results based on hot quinoline solubility (Table 1) show nearly equal MAF feed conversion in the two periods. The HTI method may result in all plastic being considered as converted material. The difference in IOM and ash contents in the Condition 3B sample in CONSOL's data may be related to the recycle of both IOM and ash in the PFL in Condition 2, but recycle of only IOM in the PFL in Condition 3B (Table 2). The PFC data (Table 2) also show relatively more IOM in the Condition 3B sample, but the ash content is not as drastically different as in the separator bottoms sample.

## **DETERMINATION OF POLY(OLEFIN) CONTENT OF SAMPLES**

### **Virgin Plastic Feed Components**

The hot decalin extraction procedure,<sup>8</sup> was applied to HDPE and PP feeds used by HTI and an LDPE sample obtained from Dr. Christine Curtis at Auburn University. Although it had previously been determined that over 90% of the virgin HDPE tested could be recovered by hot extraction and filtration using decalin, the HDPE had not been subjected to the full analytical procedure used on process samples. The specific samples tested may not be generally representative of PP or LDPE behavior in the test, but these results are at least indicative of the behavior that might be observed on extraction of other similar polymers. In general, polymers of the same type could vary significantly in MW distribution, crystallinity, degree of crosslinking, etc., not to mention additives such as colorants, fillers, and plasticizers. Some difficulty was encountered in applying the extraction method to some of these feed-related samples (e.g., viscous, gooey consistency of dissolved sample; slow or clogged filtration).

The results of the extraction test performed on the three virgin polymers are presented in Table 8. PP reports to the same analytical fraction (hot-decalin-soluble/tetrahydrofuran-insoluble, THFI/DS, the "plastic" fraction ) as the virgin HDPE. Therefore, any unconverted PP in the liquefaction samples would be extracted like HDPE. Only 13% of the LDPE sample reported to the THFI/DS "plastic" fraction; most of the sample remained soluble in cold decalin and THF. This behavior is likely with lower molecular weight or lower crystallinity polymers than the HDPE. This behavior might be expected in some polymers after liquefaction. Thus, the extraction method developed for unconverted HDPE detects unconverted PP+HDPE or unconverted poly(olefins).

Additional samples of HDPE, PP, and LDPE should be tested to determine the range of responses to the extraction method. The response of other poly(olefins), such as linear low-

density polyethylene (LLDPE), or cross-linked high-density polyethylene (XLPE), to the extraction method perhaps would be useful. The contribution of such polymers to the typical consumer plastics waste stream, such as was fed in Run CMSL-11, is not known at this time.

### **Feed MSW Plastic**

A sample assumed to be representative of the feed MSW plastic was obtained by the following procedure. About 1 kg of the chipped feed MSW plastic sample (ca. 1/4 x 3/8 in. particle size) was riffled to produce a 137 g sample. This material was melted with about 323 g decalin at 150 °C, and stirred to produce a uniform sample (medium gray and fairly uniform in color). The appearance of white streaks during or after cooling may be related to evaporation of decalin. About 5 g of this material was sliced from the homogenized mass, placed in a vacuum oven to remove decalin, and dried to a weight of 1.88 g. The sample was extracted with hot decalin for characterization (Table 8). The homogenized, composite sample of feed MSW plastic was 93.7% THFI/DS "plastic", which is similar to the fraction reported by the method for pure virgin PP or HDPE. It is preferable to report that the feed MSW contains 93.7% PP + HDPE (rather than 100% PP + HDPE), because of uncertainty in the possible contribution of plasticizers and lower molecular weight components, to any of these extraction results. This result is similar to the DOE/PETC results, described above (95% HDPE), although they reported an additional 3% PP, and 2% other plastics.<sup>4</sup> CONSOL's extraction method reports insolubles separately, whereas the handpicking method used at DOE/PETC would not separately measure inorganics, such as pigments, since they are an integral part of the plastic chips.

### **Feed Slurry**

The feed slurry from Condition 3B of CMSL-11 was found by the extraction procedure to contain about 8% unconverted PP + HDPE (Table 8). Since there is nominally 10% fresh MSW plastic in the feed slurry, and a few percent recycled unconverted PP + HDPE, this quantity seems to be too low, but the results are reproducible. The low value may be due to melted and dissolved plastic in the feed slurry that may not report as unconverted material by the extraction procedure. The feed slurry ash content was measured as 2.77% MF (Table 8 footnote). The MF feed slurry consists (nominally) of 30% fresh MF coal, 10% fresh MSW plastic, and 60% recycle PFL. Based on the HTI coal analysis, if the MF coal ash content is assumed to be 6.0%, the ash contribution to the feed slurry from the MSW plastic is 0.97%. This suggests that the plastic contains 9.7% ash. An independent determination of the ash content of the feed MSW plastic gave an ash content of 1.55% (as-determined, Table 8 footnote). The differences may be the result of non-



representative sampling, though it is unclear as to which stream or sample is most seriously affected.

### **Other Stream Samples**

The unconverted PP+HDPE concentrations in the separator bottoms and pressure-filter cake samples from Condition 3B, as measured by the hot decalin extraction procedure, are presented in Table 8. The tetrahydrofuran- (THF) insoluble fraction (listed as "IOM" in Table 2) of the corresponding PFL also is considered to represent unconverted poly(olefins), such as PP and HDPE. The value of the 1.5% PP + HDPE for the PFC is quite low, and is similar to that seen in PFC samples from Runs CMSL-8 and CMSL-9 (Reference 8 and the paper appearing as Appendix 3). The PFL concentration (6.5%) is low, compared to 16-37% in the PFLs in Runs CMSL-8 and CMSL-9 (Reference 8 and Appendix 3). Similarly, the value of 10.1% in the separator bottoms 850 °F+ resid (5.5% of the whole separator bottoms) is at the low end of values observed in samples from Runs CMSL-8 and CMSL-9. These differences may be the result of different reactivities of the virgin polymers fed in CMSL-8 and CMSL-9 and the MSW.

The concentration of total THF insolubles (THFI) in a sample can be obtained both from results of conventional analyses (Table 2) and from the decalin extraction procedure (Table 8). Both methods were used on the separator bottoms and PFC samples from Period 17. The conventional analysis THFI results were obtained as the sum of IOM and ash concentrations in Table 2. These results gave 12.3% THFI in the separator bottoms and 74.1% THFI in the PFC sample. From the decalin extraction results (Table 8), THFI concentration is the sum of THFI-DS (the unconverted plastic) and THFI/DI concentrations. These were 27.3% THFI in the separator bottoms and 87.0% THFI in the PFC. For unknown reasons, the decalin extraction procedure gave THFI concentrations that were 13-15% higher than the other method. Analytical and/or sampling problems could contribute to the observed THFI concentration differences.

## **Section 4**

### **EXPERIMENTAL**

The experimental procedures used to produce results presented in this report have been described previously.<sup>8-10</sup>

## Section 5

### REFERENCES

1. Personal communication of author with V. Pradhan of HTI.
2. Letter from A. G. Comolli to H. Chambers, 8/1/95, describing run plan for Run CMSL-11
3. Draft internal HTI report on Run CMSL-11.
4. Personal communication of author with K. S. Rothenberger, 5/24/96.
5. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "A Characterization and Evaluation of Coal Liquefaction Process Streams, Quarterly Technical Progress Report, April 1 through June 30, 1995", DOE/PC 93054-18, September 1995.
6. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "A Characterization and Evaluation of Coal Liquefaction Process Streams, Quarterly Technical Progress Report, October 1 through December 31, 1995", DOE/PC 93054-25, May 1996.
7. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "A Characterization and Evaluation of Coal Liquefaction Process Streams, Quarterly Technical Progress Report October 1 through December 31, 1994", DOE/PC 93054-10, May 1995.
8. 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 January 1 through March 31, 1996", DOE/PC 93054-29, July 1996.
9. Burke, F. P.; Winschel, R. A.; Robbins, G. A. "Recycle Slurry Oil Characterization Final Report, October 1980 through March 1985", DOE/PC 30027-61, March 1985.
10. Winschel, R. A.; Robbins, G. A.; Burke, F. P. "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report, July 1985 through September 1985", DOE/PC 70018-13, December 1985.

TABLE 1

**HTI OPERATING CONDITIONS AND PROCESS PERFORMANCE RESULTS  
FROM RUN CMSL-11 (227-89)**

| Condition<br>Period No.                    | 1<br>1-5 | 2<br>7B-10 | 3A<br>13-16 | 3B<br>17 |
|--------------------------------------------|----------|------------|-------------|----------|
| Dispersed Catalyst ppm                     |          |            |             |          |
| Fresh Mo                                   | 50       | 100*       | 100*        | 100*     |
| Fresh Fe                                   | 5000     | 5000       | 5000        | 5000     |
| Plastics Feed, wt %                        | 0        | 0          | 33          | 25       |
| SV, Kg MF Feed hr/m <sup>3</sup>           | 703      | 671        | 687         | 662      |
| SV, lb MF Feed hr/ft <sup>3</sup>          | 43.9     | 41.9       | 42.9        | 41.3     |
| Solvent/MF Feed                            | 1.0      | 1.0        | 1.5         | 1.5      |
| Temperatures, °C                           |          |            |             |          |
| Pretreater Coil                            | 302      | 302        | 302         | 302      |
| First Stage                                | 441      | 450        | 450         | 447      |
| Second Stage                               | 449      | 459        | 459         | 461      |
| Product Hydrotreater                       | 379      | 379        | 379         | **       |
| Relative Process Severity                  | 1.00     | 1.15       | 1.14        | 1.14     |
| Material Balance, % (gross)                | 96.65    | 102.82     | 99.37       | 95.63    |
| Estimated Normalized Yields, wt % Dry Feed |          |            |             |          |
| C <sub>1</sub> -C <sub>3</sub> in Gases    | 14.76    | 17.17      | 8.29        | 7.09     |
| C <sub>4</sub> -C <sub>7</sub> in Gases    | 4.84     | 8.07       | 4.61        | 3.73     |
| IBP-177 °C in Liquids                      | 14.88    | 12.41      | 11.63       | 9.08     |
| 199-260 °C in Liquids                      | 13.51    | 11.66      | 9.71        | 10.49    |
| 260-343 °C in Liquids                      | 18.62    | 14.41      | 14.15       | 14.47    |
| 343-454 °C in Liquids                      | 8.34     | 10.49      | 19.13       | 21.32    |
| 454-524 °C in Liquids                      | 0.68     | 2.27       | 5.19        | 5.57     |
| 524 °C <sup>+</sup>                        | 3.72     | 5.68       | 10.95       | 10.68    |
| Unconverted Feed                           | 4.22     | 4.58       | 4.54        | 5.1      |
| Water                                      | 9.31     | 7.28       | 9.33        | 11.14    |
| CO <sub>x</sub>                            | 6.97     | 6.38       | 2.80        | 1.9      |
| NH <sub>3</sub>                            | 0.97     | 0.92       | 0.51        | 0.58     |
| H <sub>2</sub> S                           | -0.02    | -0.57      | -0.92       | -0.74    |
| Hydrogen Consumption                       | 6.53     | 6.51       | 3.85        | 4.73     |
| Process Performance, wt % MAF Feed         |          |            |             |          |
| Coal Conversion                            | 95.5     | 95.1       | 95.3        | 94.7     |
| C <sub>4</sub> -524 °C Distillate Yield    | 64.6     | 62.9       | 67.0        | 67.6     |
| 524 °C <sup>+</sup> Conversion             | 91.5     | 89.1       | 83.9        | 83.5     |

Note: H<sub>2</sub>S Rate - 3 wt % MF Coal

\*The additional 50 ppm Mo supplied was incorporated in the Fe catalyst; the baseline Mo source was Molyvan A.

\*\*Off-line due to plugging problems.

**TABLE 2**  
**COMPONENT DISTRIBUTION OF WHOLE SAMPLES**  
**HTI Run 227-89, CMSL-11**

| Sample Type           | Period | Component wt % of Sample |                         |        |      |       |
|-----------------------|--------|--------------------------|-------------------------|--------|------|-------|
|                       |        | 850 °F-<br>Dist          | THF<br>Soluble<br>Resid | IOM    | Ash  | Total |
| PFL                   | 5B     | 50.6                     | 40.3                    | 3.5    | 4.9  | 99.3  |
| PFL                   | 10B    | 56.8                     | 33.3                    | 3.9    | 6.1  | 100.1 |
| PFL                   | 17B    | 58.7                     | 34.7                    | 6.5(a) | <0.1 | 99.9  |
| CAS Bottoms           | 5B     | 50.5                     | 37.9                    | 4.3    | 7.3  | 100.0 |
| Separator Bottoms     | 10B    | 55.1                     | 31.5                    | 3.9    | 9.3  | 99.8  |
| Separator Bottoms (b) | 17B    | 54.9                     | 32.7                    | 8.1    | 4.2  | 99.2  |
| PFC                   | 5B     | N/A                      | 43.2(c)                 | 16.5   | 40.3 | 100.0 |
| PFC                   | 10B    | N/A                      | 38.2(c)                 | 17.8   | 44.0 | 100.0 |
| PFC                   | 17B    | N/A                      | 25.9(c)                 | 36.9   | 37.2 | 100.0 |

- (a) Assumed to represent unconverted plastic (probably PP + HDPE).  
(b) Two phases were observed in the cooled 850 °F+ material after distillate.  
(c) By difference

TABLE 3

**PROTON DISTRIBUTION OF WHOLE SAMPLES**  
**HTI Run 227-89, CMSL-11**

| Sample Type       | Period | Condition | Proton Distribution, % of Protons |             |              |             |             |            |       |
|-------------------|--------|-----------|-----------------------------------|-------------|--------------|-------------|-------------|------------|-------|
|                   |        |           | Cond Arom                         | Uncond Arom | Cyclic Alpha | Alkyl Alpha | Cyclic Beta | Alkyl Beta | Gamma |
| Feed Slurry       | 5B     | 1         | 23.2                              | 6.3         | 19.0         | 10.0        | 12.4        | 19.0       | 10.4  |
| Feed Slurry       | 10B    | 2         | 22.7                              | 6.6         | 17.8         | 10.2        | 12.8        | 18.7       | 11.2  |
| Feed Slurry       | 17B    | 3B        | 25.2                              | 3.8         | 16.4         | 10.2        | 11.5        | 22.9       | 10.0  |
| SOH               | 5B     | 1         | 8.8                               | 4.9         | 7.7          | 6.9         | 21.9        | 29.4       | 20.4  |
| SOH               | 10B    | 2         | 9.4                               | 4.2         | 6.7          | 6.4         | 22.1        | 30.0       | 21.2  |
| SOH               | 17B    | 3B        | 7.6                               | 8.4         | 7.9          | 9.7         | 12.6        | 32.6       | 21.0  |
| PFL               | 5B     | 1         | 25.5                              | 8.9         | 17.9         | 11.5        | 11.3        | 16.5       | 8.4   |
| PFL               | 10B    | 2         | 24.3                              | 9.4         | 17.6         | 10.9        | 11.7        | 17.0       | 9.2   |
| PFL               | 17B    | 3B        | 23.8                              | 7.6         | 14.5         | 10.4        | 10.0        | 23.4       | 10.4  |
| PFC               | 5B     | 1         | 32.4                              | 3.9         | 19.4         | 10.2        | 11.6        | 14.8       | 7.8   |
| PFC               | 10B    | 2         | 30.9                              | 4.1         | 19.0         | 10.6        | 12.1        | 15.5       | 7.8   |
| PFC               | 17B    | 3B        | 35.9                              | 4.6         | 17.4         | 10.4        | 9.4         | 14.9       | 7.4   |
| CAS Bottoms       | 5B     | 1         | 24.3                              | 9.8         | 17.2         | 11.2        | 11.5        | 17.2       | 8.8   |
| Separator Bottoms | 10B    | 2         | 22.3                              | 11.6        | 16.3         | 11.8        | 11.5        | 17.7       | 8.9   |
| Separator Bottoms | 17B    | 3B        | 23.1                              | 8.0         | 14.4         | 10.4        | 9.6         | 24.9       | 9.6   |
| Interstage        | 5B     | 1         | 29.2                              | 8.9         | 16.5         | 11.5        | 9.7         | 15.9       | 8.2   |
| CAS Overhead      | 5B     | 1         | 10.1                              | 11.4        | 13.7         | 13.7        | 14.3        | 23.8       | 13.1  |

**TABLE 4**

**PROTON DISTRIBUTION OF DISTILLATE SAMPLES  
HTI Run 227-89, CMSL-11**

| Sample Type       | Period | Proton Distribution, % of Protons |             |              |             |             |            |       |
|-------------------|--------|-----------------------------------|-------------|--------------|-------------|-------------|------------|-------|
|                   |        | Cond Arom                         | Uncond Arom | Cyclic Alpha | Alkyl Alpha | Cyclic Beta | Alkyl Beta | Gamma |
| PFL               | 5B     | 19.7                              | 9.5         | 15.7         | 11.8        | 12.3        | 20.6       | 10.3  |
| PFL               | 10B    | 21.7                              | 8.4         | 17.6         | 12.0        | 12.7        | 19.6       | 7.9   |
| PFL               | 17B    | 20.7                              | 6.4         | 13.7         | 10.6        | 10.3        | 27.3       | 11.0  |
| CAS Bottoms       | 5B     | 21.0                              | 8.2         | 17.3         | 11.8        | 12.8        | 19.5       | 9.3   |
| Separator Bottoms | 10B    | 19.2                              | 9.9         | 15.8         | 12.2        | 12.3        | 20.3       | 10.4  |
| Separator Bottoms | 17B    | 19.5                              | 6.6         | 14.0         | 10.9        | 11.0        | 27.3       | 10.6  |

**TABLE 5**

**PROTON DISTRIBUTION OF RESID SAMPLES  
HTI Run 227-89, CMSL-11**

| Sample Type       | Period | Proton Distribution, % of Protons |             |              |             |             |            |       |
|-------------------|--------|-----------------------------------|-------------|--------------|-------------|-------------|------------|-------|
|                   |        | Cond Arom                         | Uncond Arom | Cyclic Alpha | Alkyl Alpha | Cyclic Beta | Alkyl Beta | Gamma |
| PFL               | 5B     | 38.2                              | 5.8         | 19.7         | 9.8         | 10.8        | 9.8        | 5.8   |
| PFL               | 10B    | 39.3                              | 8.4         | 17.9         | 9.6         | 10.2        | 8.8        | 5.8   |
| PFL               | 17B    | 39.9                              | 5.6         | 17.8         | 10.5        | 9.8         | 9.4        | 7.1   |
| CAS Bottoms       | 5B     | 38.9                              | 3.6         | 21.6         | 9.5         | 11.1        | 9.5        | 5.9   |
| Separator Bottoms | 10B    | 40.6                              | 5.3         | 20.3         | 9.3         | 10.2        | 8.7        | 5.6   |
| Separator Bottoms | 17B    | 40.3                              | 7.4         | 18.0         | 10.5        | 9.2         | 9.3        | 5.3   |

TABLE 6

**MICROAUTOCLAVE SOLVENT QUALITY ASSAYS OF  
WHOLE AND DISTILLATE SAMPLES  
HTI Run 227-89, CMSL-11**

| Sample Type       | Period | Conversion, % MAF |                    |
|-------------------|--------|-------------------|--------------------|
|                   |        | Whole Sample      | 850 °F- Distillate |
| PFL               | 5B     | 79.1              | 87.5               |
| PFL               | 10B    | 74.9              | 86.0               |
| PFL               | 17B    | 60.3              | 75.0               |
| CAS Bottoms       | 5B     | 75.5              | 86.6               |
| Separator Bottoms | 10B    | 75.4              | 87.4               |
| Separator Bottoms | 17B    | 77.0              | 73.2               |

**Conditions:**

Standard Old Ben No. 1 coal (Indiana V), 9 g solvent, 6 g coal, 750 °F, 30 min, conversion to THF solubles

TABLE 6A

**PHENOLIC -OH CONCENTRATIONS OF DISTILLATE AND RESID SAMPLES  
HTI Run 227-89, CMSL-11**

| Sample Type       | Period | 850 °F- Distillate |                               | 850 °F- Resid THF Solubles |                               |
|-------------------|--------|--------------------|-------------------------------|----------------------------|-------------------------------|
|                   |        | Conc., meq/g       | Pk Position, cm <sup>-1</sup> | Conc., meq/g               | Pk Position, cm <sup>-1</sup> |
| CAS Bottoms       | 5B     | 0.90               | 3303                          | 0.90                       | 3292                          |
| Separator Bottoms | 10B    | 1.05               | 3305                          | 0.95                       | 3292                          |
| Separator Bottoms | 17B    | 0.58               | 3303                          | 0.73                       | 3293                          |
| PFL               | 5B     | 0.77               | 3304                          | 0.85                       | 3291                          |
| PFL               | 10B    | 0.96               | 3305                          | 0.81                       | 3290                          |
| PFL               | 17B    | 0.52               | 3305                          | 0.65                       | 3292                          |

**Note:**

These results were obtained in THF solution by a recalibrated FTIR procedure to be described in a later report.



TABLE 7

**GC-MS RESULTS FOR SOH OIL COMPONENTS  
DERIVED PRIMARILY FROM PLASTICS**

| Sample: Run CMSL-11 Condition 3 Period 17 SOH |           |              |              |
|-----------------------------------------------|-----------|--------------|--------------|
| Peak ID                                       | Ret. time | % Total Area | Compound     |
| A                                             | 8.6       | 0.69         | Toluene      |
| B                                             | 15.8      | 1.35         | Ethylbenzene |
| C                                             | 20.9      | 0.20         | Cumene       |
| D                                             | 19.7      | 1.13         | n-paraffin   |
| E                                             | 28.0      | 0.63         | n-paraffin   |
| F                                             | 36.0      | 1.53         | n-paraffin   |
| G                                             | 36.0      | 0.35         | n-paraffin   |
| H                                             | 43.4      | 1.16         | ? n-paraffin |
| I                                             | 43.6      | 1.07         | ? n-paraffin |
| J                                             | 50.7      | 2.33         | n-paraffin   |
| K                                             | 56.0      | 2.35         | n-paraffin   |
| L                                             | 60.0      | 2.54         | n-paraffin   |
| M                                             | 63.5      | 2.61         | n-paraffin   |
| N                                             | 66.6      | 2.85         | n-paraffin   |
| O                                             | 69.4      | 2.70         | n-paraffin   |
| P                                             | 72.1      | 2.06         | n-paraffin   |
| Q                                             | 74.6      | 2.41         | n-paraffin   |
| R                                             | 77.0      | 1.98         | n-paraffin   |
| S                                             | 79.3      | 1.86         | n-paraffin   |
| T                                             | 81.4      | 1.61         | n-paraffin   |
| U                                             | 83.5      | 1.32         | n-paraffin   |
| V                                             | 85.5      | 1.08         | n-paraffin   |
| W                                             | 87.4      | 0.71         | n-paraffin   |
| X                                             | 89.2      | 0.63         | n-paraffin   |
| Y                                             | 91.0      | 0.56         | n-paraffin   |
| Z                                             | 92.8      | 0.32         | n-paraffin   |
| AA                                            | 94.4      | 0.22         | n-paraffin   |
| AB                                            | 96.0      | 0.16         | n-paraffin   |
| AC                                            | 97.6      | 0.11         | n-paraffin   |
| AD                                            | 99.2      | 0.08         | n-paraffin   |
| AE                                            | 100.6     | 0.05         | n-paraffin   |
| Total of n-paraffins                          |           | 36.41        |              |

Note: Coal-derived material contributes to an unknown degree to the toluene, ethylbenzene, and n-paraffin peaks.

TABLE 8

**RESULTS OF EXTRACTION OF PLASTICS-CONTAINING SAMPLES  
WITH HOT DECALIN AND THF**

| Sample                             | Source                                   | wt % of Sample             |                            |                            |             |
|------------------------------------|------------------------------------------|----------------------------|----------------------------|----------------------------|-------------|
|                                    |                                          | THFS/DS (a),<br>Normalized | THFI/DS (b),<br>Normalized | THFI/DI (c),<br>Normalized | % Recovered |
| HDPE                               | HTI                                      | 1.5                        | 96.3                       | 2.2                        | 97.8        |
| PP - Trial 1                       | HTI                                      | 13.2                       | 86.2                       | 0.6                        | 104.2       |
| - Trial 2                          |                                          | 9.5                        | 90.4                       | 0.1                        | 101.2       |
| LDPE (d)                           | Auburn                                   |                            |                            |                            |             |
| - Trial 1                          |                                          | 86.3                       | 13.0                       | 0.7                        | 96.1        |
| - Trial 3                          |                                          | 89.6                       | 10.0                       | 0.4                        | 102.8       |
| Composite MSW<br>Plastic Feed (e)  | Composited<br>from HTI<br>Feed<br>Sample | 4.5                        | 93.7                       | 1.8                        | 97.1        |
| Period 17 Feed Slurry<br>(f)       | HTI                                      |                            |                            |                            |             |
| - Trial 1                          |                                          | 55.6                       | 8.1                        | 36.3                       | 100.3       |
| - Trial 2                          |                                          | 60.8                       | 7.8                        | 31.4                       | 102.1       |
| Period 17 Separator<br>Bottoms     | HTI                                      | 72.7                       | 10.1                       | 17.2                       | 104.2       |
| Period 17 Pressure-<br>Filter Cake | HTI                                      | 13.0                       | 1.5                        | 85.5                       | 101.7       |

- (a) THF soluble/decalin solubles.  
 (b) THF insoluble/decalin solubles, the unconverted plastic fraction.  
 (c) THF insoluble/decalin insolubles.  
 (d) Filter clogging was encountered in Trial 2, and the results differed significantly from those listed for THFS/DS and THFI/DS in Trials 1 and 3.  
 (e) Ash content was measured as 1.53% and 1.57% in separate determinations (average 1.55%).  
 (f) As-determined moisture content was 3.95%, ash content was measured as 2.56% and 2.76% as-determined in separate determinations (average was 2.66% as-determined, 2.80% MF).

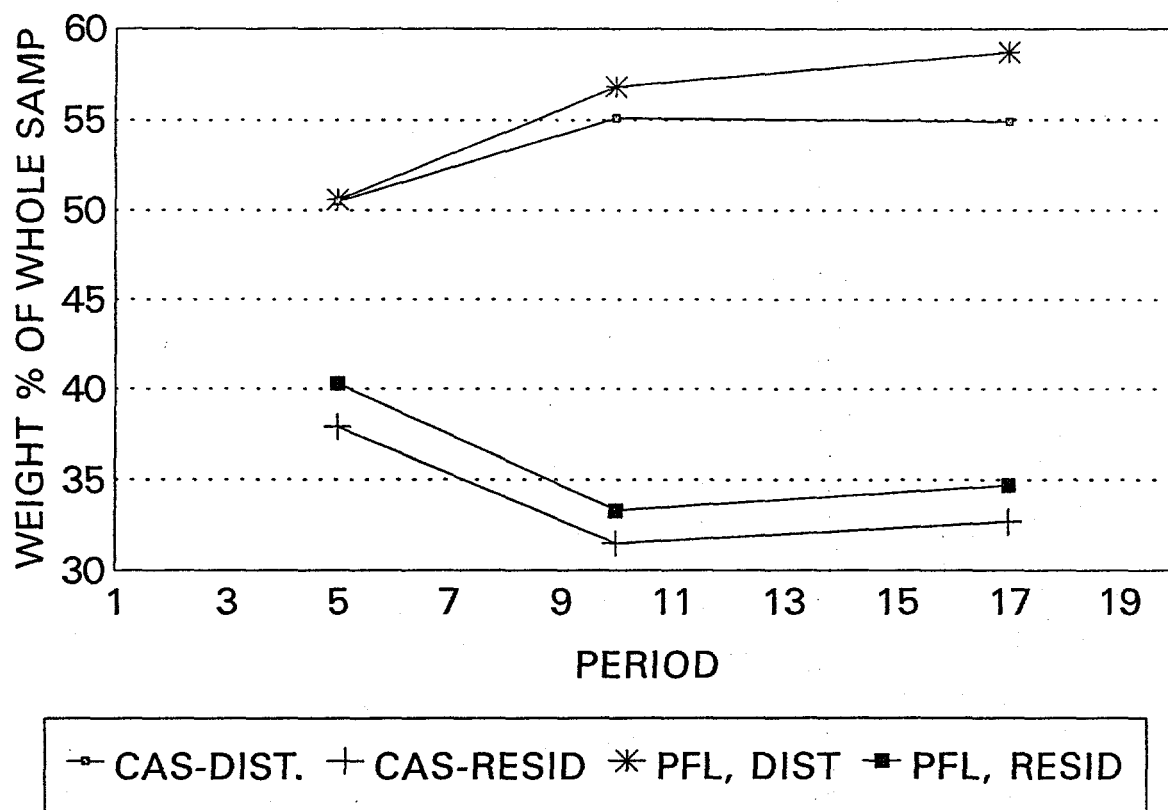


Figure 1. Distillate and Resid Content of Selected Process Streams During HTI Run CMSL-11.

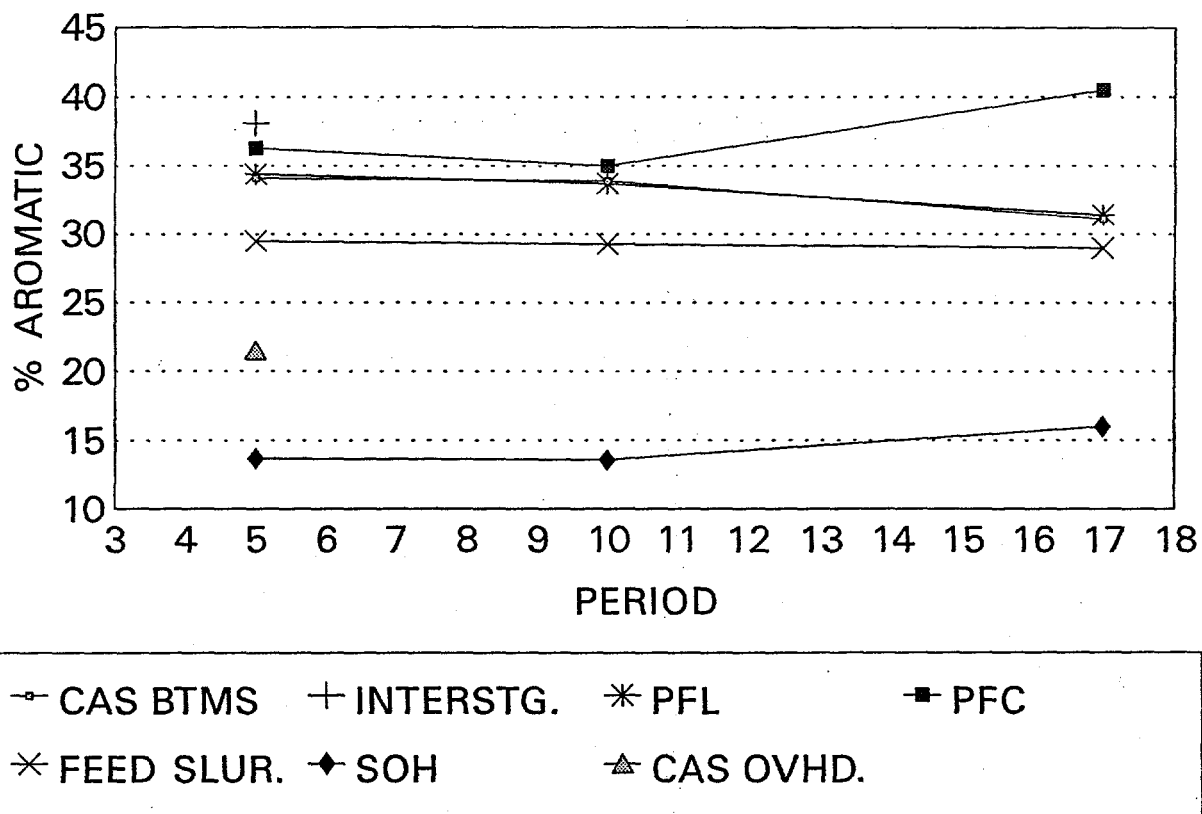


Figure 2. Proton Aromaticity of Whole Process Stream Samples During HTI Run CMSL-11.

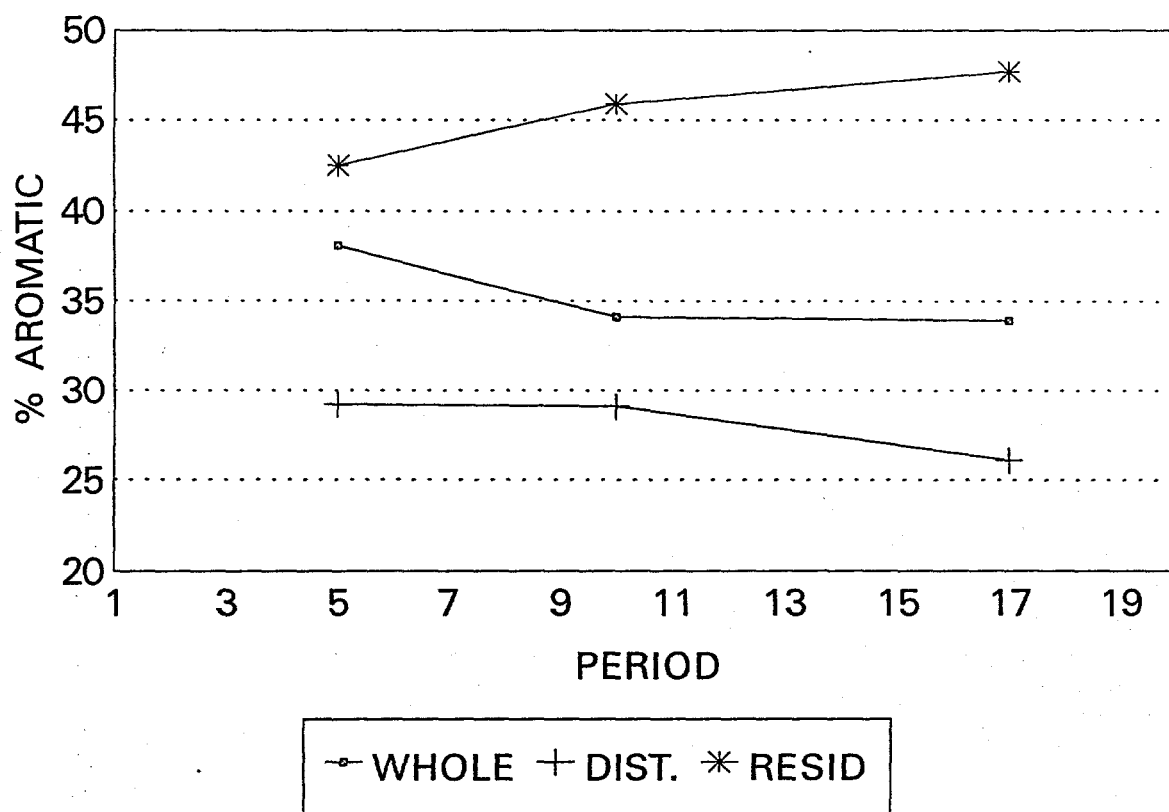


Figure 3. Proton Aromaticity of the Whole CAS Bottoms, CAS Bottoms Distillate, and CAS Bottoms Resid Samples During HTI Run CMSL-11.

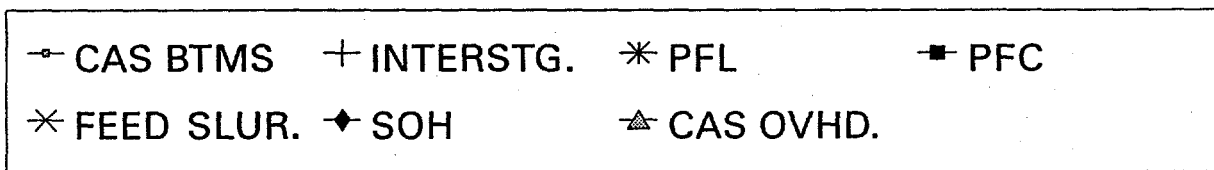
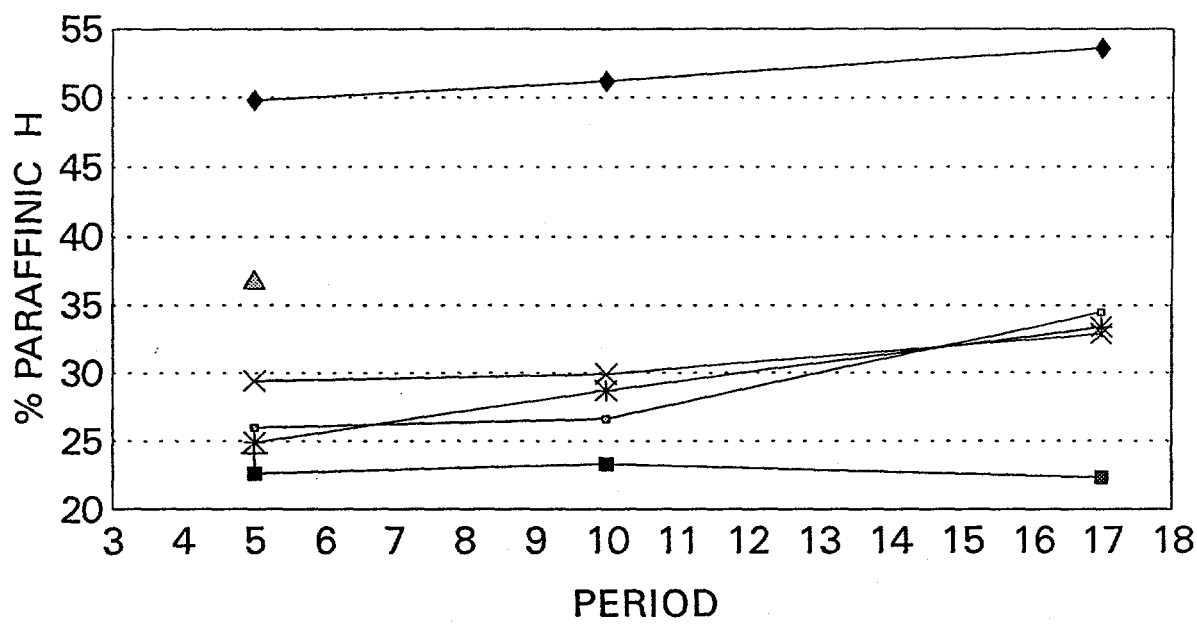


Figure 4. Proton Paraffinicity of Whole Process Stream Samples During HTI Run CMSL-11.

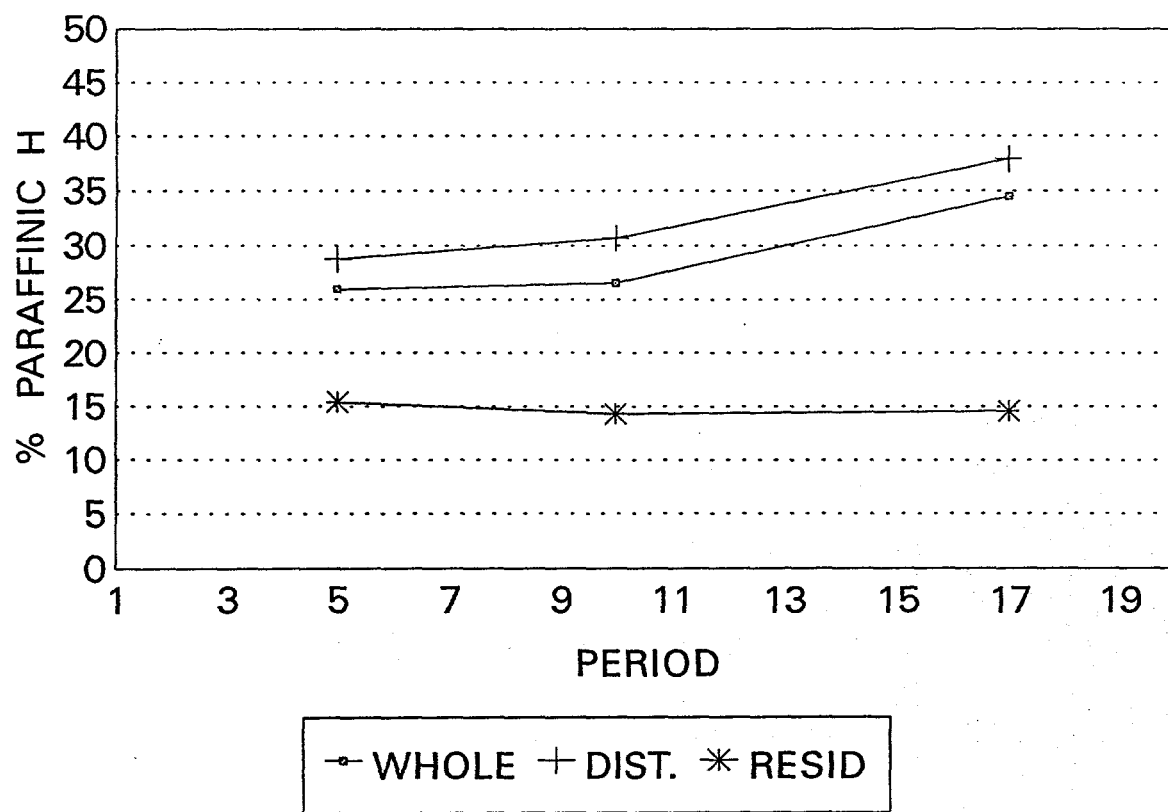


Figure 5. Proton Paraffinicity of the Whole CAS Bottoms, CAS Bottoms Distillate and CAS Bottoms Resid Samples During HTI Run CMSL-11.

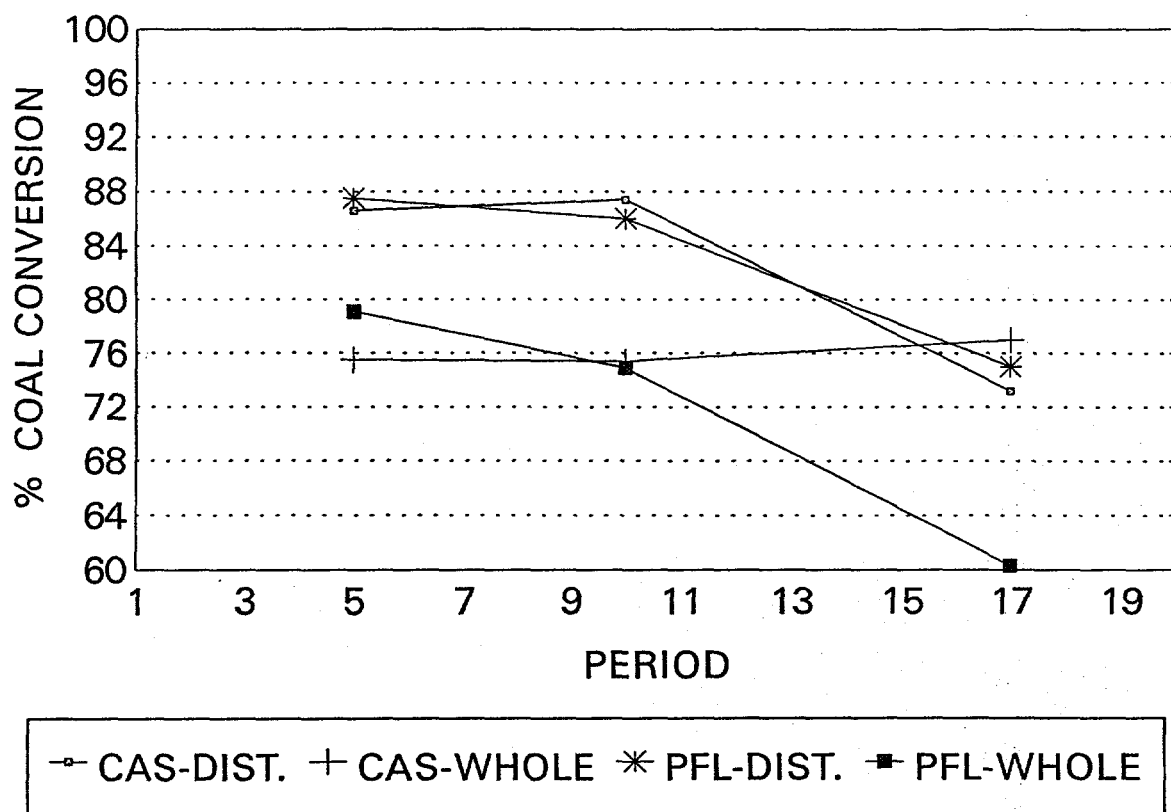


Figure 6. Donor Solvent Quality of Selected Whole and Distillate Samples During HTI Run CMSL-11.



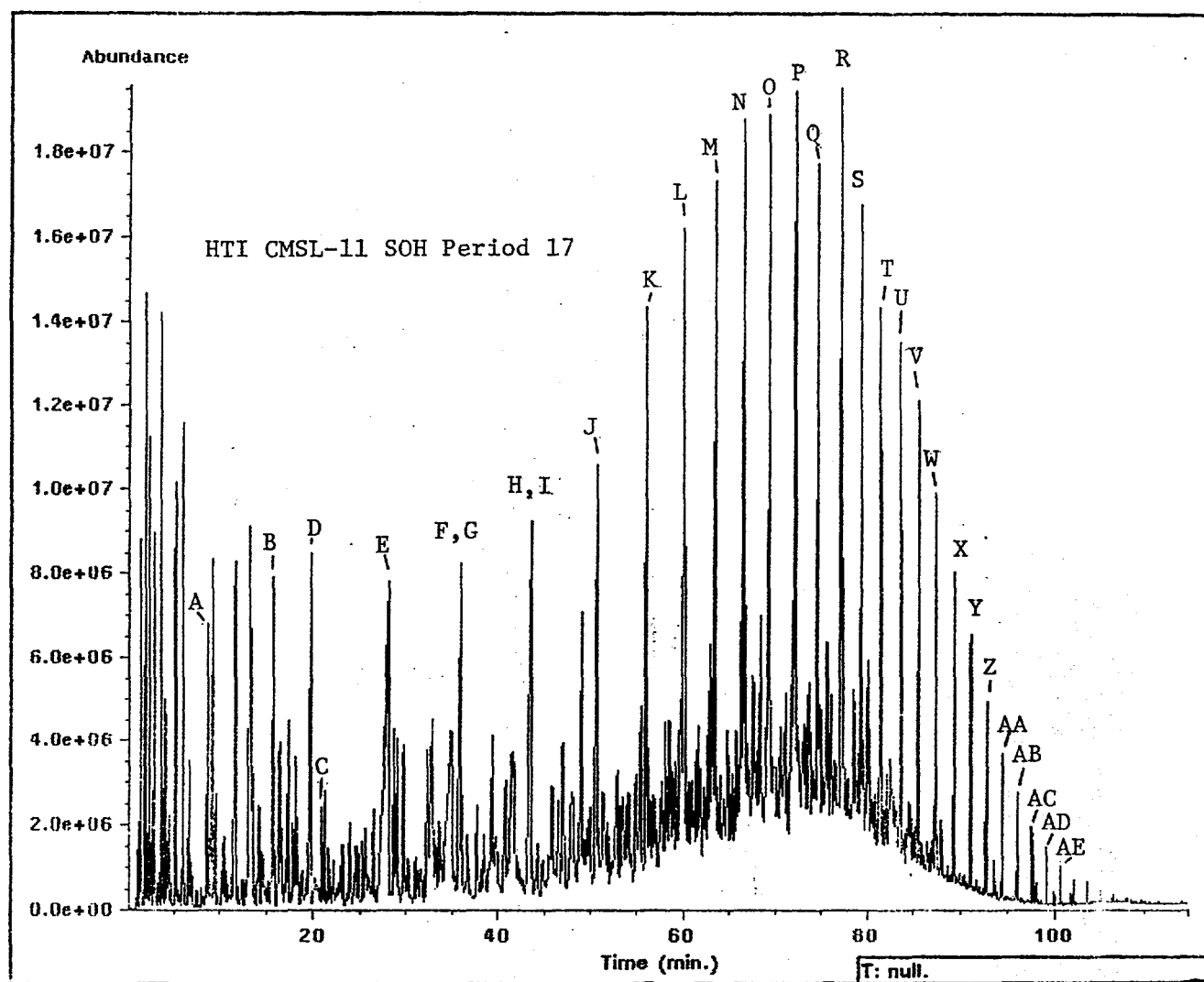


Figure 7. GC/MS Total Ion Chromatogram of SOH Product Oil from Coal/Plastics Condition 3B (Period 17).

## **APPENDIX 1**

### **SAMPLE REQUEST FOR HTI RUN PB-04**



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

June 7, 1996

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

Dear Vivek:

Our sample request for Run PB-04 is described below. We are requesting material in sufficient quantities to allow for sample distribution to other research groups, as needed. We understand that you cannot always provide the requested amounts, and we can work with smaller quantities.

We would like to receive from each run condition: 1) 250 g of separator overhead (SOH) oil; 2) 250 g of atmospheric still overhead (ASOH); 3) 350 g of 850 °F+ vacuum still bottoms (VSB); 5) 350 g of continuous atmospheric still (CAS) bottoms or its equivalent, such as O-6 bottoms; 6) 350 g of pressure-filter liquid (PFL); 7) 350 g of pressure-filter cake (PFC); 8) 350 g of feed slurry; and 9) 350 g of interstage sample (first-stage product). Please also include: 10) 250 g of the start-up/make-up oil from the beginning of the run; 11) 300 g sample of the feed coal; 12) 300 g sample of the feed resid; 13) 2 kg sample of the unprocessed feed auto-fluff; and 14) 250 g of SOH oil from any operating periods in which the in-line hydrotreater is bypassed.

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

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

Sincerely,

G. A. Robbins  
Sr. Research Chemist

/ls

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

## **APPENDIX 2**

### **UNIVERSITY OF DELAWARE QUARTERLY REPORT**

THE KINETICS OF COAL LIQUEFACTION DISTILLATION  
RESID CONVERSION

QUARTERLY REPORT  
4/16/96-7/15/96

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Date Published  
July 30, 1996

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

## QUARTERLY REPORT

### Resid Hydroprocessing

As per our agreement with CONSOL of May 17, 1996 we have been making hydroprocessing runs on the 13 resids provided. Processing conditions are for 30 minutes at 420°C at 3 to 1 tetralin to resid ratio and 1500 psig hydrogen. Runs are being made with 3% sulfided molybdenum naphthenate catalyst (3% Mo based on coal resid) and also without catalyst. In each resid, an ambient temperature run is made to provide the original ash value for calculating conversions. Thus far, all (13) ambient temperature runs and all runs without catalyst have been made. Two catalyzed runs have been completed.

The work-up of the runs however is an extensive process. The reaction mixture is filtered and the filter cake is washed with cold methylene chloride and dried in a vacuum oven. The methylene chloride is then distilled out of the filtrate at low temperature (below 45°C). The methylene chloride remaining in the resid filtrate and tetralin concentration in the methylene chloride distilled off are measured by gas chromatography. SymDistGA is performed on both the filtrate and the filter cake to allow the determination of the resid conversion product boiling below 850°F. Performance of each of these steps is being done at one time for all resid samples for efficiency and therefore no final values are yet available for any individual resid.

### Modeling

**Analytical** On the SARA fractions, to date, molecular weights have been determined for each of the aromatic fractions and several of the resin, asphaltene, saturate and preasphaltene fractions. Dichlorobenzene is used for the aromatics and toluene is used for the saturate fractions. THF is used in the determination of molecular weights for the resin, asphaltene and preasphaltene fractions. Initially, dichlorobenzene was used as VPO solvent for asphaltenes and resins; however the determined molecular weights for the asphaltenes (1500-1800) were significantly higher than values indicated by the literature (500-800). Results shown in Table 1 indicate that when THF is used as the solvent, molecular weight determinations are much closer to literature values.

THF has also been selected for the molecular weight determination of resins since dichlorobenzene results yield molecular weights in the asphaltene range. However, there is not enough remaining resin sample for runs 1-6 to determine molecular weight in THF. All of the resin samples 1-5 are dissolved in dichlorobenzene, and run six yielded unexplainably poor results. Either an additional SARA separation will need to be run at CONSOL or at Delaware to get another sample for these runs, or these molecular weights will need to be estimated in some other way.

All other analytical information has been supplied by CONSOL. Currently all of the necessary elemental analyses, <sup>1</sup>H NMR data, and SARA weight fractions have been determined, along with corresponding standard deviations.

**Modeling** Currently a molecular structure model for coal resid is being assembled. Each molecule is considered to be a juxtaposition of molecular attributes (e.g. number of aromatic rings, number of side chains, length of side chains). Neurock (1) et al, developed a Monte Carlo resid construction technique by random sampling of probability distribution functions (pdf's), one for each of the molecular attributes. The pdf is a function that provides the quantitative probability of finding the value or less of a given attribute. Monte Carlo sampling of the set (one set for each feed) of pdf's provides a large ensemble of "computer" molecules whose properties can be compared to experimentally measured values. An optimized set of pdf function parameter values can be obtained by minimizing a weighted objective function that compares the measured and predicted properties.

In the case of petroleum resid, the analytical properties considered were H/C ratio, sulfur content, alpha and aromatic protons, SARA fractions, and SimDis weight fractions. In the case of coal resids, SimDis is not yet being used because a quick and reliable method to measure SimDisTG on resid samples has not yet been established, and accurate boiling point correlations for large molecules typical of coal resids have not been determined. Since most of the coal resids boil above 1000°F, the omission will have little effect. Furthermore, CONSOL has provided a very detailed proton distribution analysis so that the fine detail of the representative molecules will be preserved. Elemental and SARA data have also been provided. The objective function used to optimize the pdf parameters will contain 14 terms (5 elemental, 7 proton types, 1 phenolic OH, 1 SARA).

Figure 1 shows the construction algorithm for a coal resid. In this case the aromatic and resin fractions are considered to be one fraction since a distinguishing characteristic between the two fractions could not be determined. The molecules of each fraction (except for the paraffin fraction) can consist of a number of unit sheets (ring cores) attached by 1 or 2 linkages. In the case of naphthenics, only phenyl and methylene type linkages are considered. For aromatics, asphaltenes, and preasphaltenes, linkages can also include sulfur and oxygen bridges. All of the heteroatoms are considered to be in the aromatics, asphaltenes, and preasphaltene fractions. The pdf's used to construct the representative molecules are listed in Table 2. This table also lists which fractions use which distributions during construction.

## References

- (1) Neurock, M. Libanati, C., Nigam, A, and Klein, M.T. Chem Eng. Sci 45, 2083, 1990

Table 1: VPO results

| Sample Number | Saturate MW | Aromatic MW | Resin MW | Asphaltene MW | Pre-Asphaltene MW |
|---------------|-------------|-------------|----------|---------------|-------------------|
| 1             | 288         | 320         | 676*     | 778           | 988               |
| 2             | 250         | 274         | 613*     | 926           | 1060              |
| 3             | 295         | 319         | 568*     | 680           | 919               |
| 4             | 305         | 362         | 718*     | 595           | 988               |
| 5             | 443         | 493         | 789*     | 864           | 1037              |
| 6             | 347         | 420         |          | 789           | 1201              |
| 7             |             | 348         | 426      | 708           |                   |
| 8             |             | 425         | 535      | 686           |                   |
| 9             |             | 323         |          |               |                   |
| 10            |             | 430         |          |               |                   |
| 11            |             | 386         |          |               |                   |
| 12            |             | 413         |          |               |                   |
| 13            |             | 336         |          |               |                   |
| 14            |             | 356         |          |               |                   |
| 15            |             | 345         |          |               |                   |

\* MWs determined using dichlorobenzene as solvent, results likely too high.



| Distribution                                                   | Name      | Used to construct fractions:                               |
|----------------------------------------------------------------|-----------|------------------------------------------------------------|
| Paraffin Length                                                | npdis     | Paraffins                                                  |
| # of Naphthenic Rings                                          | nrdis     | Naphthenics                                                |
| # of Sidechains                                                | nscdis    | Naphthenics, Aromatics/Resins, Asphaltenes, Preasphaltenes |
| Length of Naphthenic Sidechains                                | lscdis1   | Naphthenics                                                |
| Length of Aromatic Sidechains                                  | lscdis2   | Aromatics/Resins, Asphaltenes, Preasphaltenes              |
| Naphthenic # of Unit Sheets                                    | ndpdis    | Naphthenics                                                |
| Resin # of Unit Sheets                                         | rdpdis    | Aromatics/Resins                                           |
| Asphaltene # of Unit Sheets                                    | adpdis    | Asphaltenes                                                |
| Preasphaltene # of Unit Sheets                                 | pdpdis    | Preasphaltenes                                             |
| # of Aromatic Rings                                            | ardis     | Aromatics/ Resins, Asphaltenes, Preasphaltenes             |
| # of Naphthenic Rings on an Aromatic Core                      | nardis    | Aromatics/ Resins, Asphaltenes, Preasphaltenes             |
| # of Phenolic Oxygens                                          | frphh     | Aromatics/Resins, Asphaltenes, Preasphaltenes              |
| <b>Intersheet Connections</b>                                  |           |                                                            |
| Fraction of Oxygen Connections                                 | 0.25      | Resins, Asphaltenes, Preasphaltenes                        |
| Fraction of Sulfur Connections                                 | 0.25      | Resins, Asphaltenes, Preasphaltenes                        |
| Fraction of Methylene Connections                              | 0.05:0.25 | Naphthenics:Aromatics/ Resins, Asphaltenes, Preasphaltenes |
| Fraction of Biphenyl Connections                               | 0.05:0.25 | Naphthenics:Aromatics/ Resins, Asphaltenes, Preasphaltenes |
| <b>Heteroatomic Rings</b>                                      |           |                                                            |
| Fraction of Oxygen Rings                                       | frorings  | Resins, Asphaltenes, Preasphaltenes                        |
| Fraction of Sulfur Rings                                       | frsings   | Resins, Asphaltenes, Preasphaltenes                        |
| Fraction of Nitrogen Rings (5 and 6 members in a 2 to 1 ratio) | frnrings  | Resins, Asphaltenes, Preasphaltenes                        |
| Fraction of no Heteroatomic Rings                              | frhcrings | Resins, Asphaltenes, Preasphaltenes                        |

Table 2: Attribute distributions used to construct a molecular representation for coal resid.

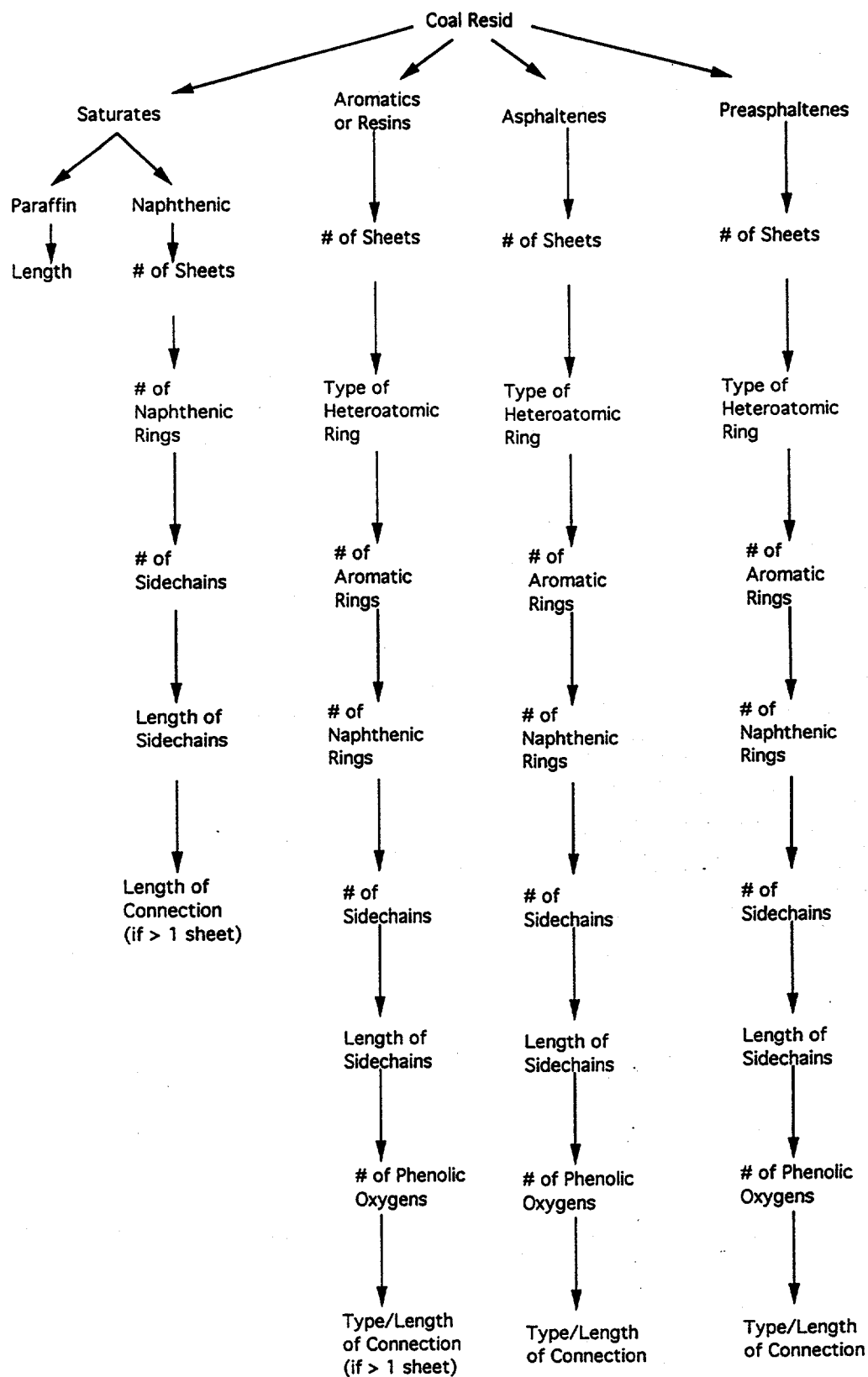


Figure 1: Coal Resid Construction Algorithm