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

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ABSTRACT

This is the Technical Progress Report for the fifteenth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period January 1 through March 31, 1998. Described in this report are the following activities:

- CONSOL characterized 41 process stream samples obtained from HTI Run PB-01 (227-90), in which Black Thunder Mine coal, Hordo VTB resid, municipal solid waste (MSW) plastics, and virgin plastics were co-liquefaction feedstocks with all-dispersed Fe and Mo catalysts.
- A request was made for samples from the Nippon Coal Oil NEDOL pilot plant in Kashima, Japan.
- Phenols were extracted from two samples of separator overhead oil from HTI Run PB-01 Periods 10A and 10B. The phenols were converted to ethylphenyl ethers, and the ethers were distilled to produce a sample within the diesel fuel boiling range. The ethers were mixed with diesel fuel to make 1%, 5%, 10%, and 20% solutions. The four mixtures and a control sample (0% ether) were tested for diesel fuel properties by Intertek Testing Services, Caleb Brett. .
- Computational studies related to the University of Delaware's resid conversion model were continued on the Hewlett Packard Apollo HP-735 RISC workstation at CONSOL R&D. The Structure Optimization Program and the Structure Once-Through Program were used to generate physicochemical properties and structure models for the 15 coal resid samples which have been under study.

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Section 1

EXECUTIVE SUMMARY

CHARACTERIZATION OF SAMPLES FROM HTI RUN PB-01

CONSOL characterized 41 process stream samples from HTI Run PB-01 (227-90), in which Black Thunder Mine coal, Hondo vacuum tower bottoms (VTB) resid, municipal solid waste (MSW) plastics, and virgin plastics were co-liquefaction feedstocks with all-dispersed Fe and Mo catalysts. The major conclusions from CONSOL's analyses of samples from HTI Run PB-01 follow.

- The use of Hondo resid (with or without plastic) and low coal concentrations with a low recycle ratio in Conditions 4-9 resulted in significantly diminished (by 10-35% absolute) donor solvent quality of the whole PFL and separator bottoms streams. The donor solvent quality in Conditions 1-3 during coal-only feed periods with recycle ratio equal to 1.0 was good to excellent (85-89%).
- The only clear change noted in CONSOL's analyses as a result of switching to ashy recycle in Condition 2 was an increase in coal conversion. This is an expected result, but it contrasts with HTI's lower conversion value.
- The increase in space velocity and reactor 1 temperature in Condition 3 relative to Condition 1 was accompanied by only minor differences in many properties.
- When Black Thunder Mine coal was replaced by Hondo vacuum tower bottom resid, with or without plastics, as the liquefaction feedstock, process stream properties changed generally as expected. Use of plastics feedstock was accompanied by the appearance of extractable plastic (unconverted polyolefins that report as IOM in standard liquefaction product analyses) in certain streams. However, during inconsistent feed operations in Condition 6, only a trivial amount of extractable plastic was found in the pressure-filter solid (PFS), indicating no rejection of plastic with the PFS.
- In Condition 8, the recycle mode was changed to ashy recycle (recycle of PFC), and the space velocity was about 10% higher than previous periods. There were changes in some process stream characteristics as a result, although the mechanism for the changes was

not always clear. An increase in the recycle of unconverted plastic with ashy recycle seems to account for increased IOM and extractable plastic contents of some streams.

ETHYLPHENYL ETHERS AS DIESEL FUEL ENHANCERS/EXTENDERS

Phenols were extracted from two samples of separator overhead oil from Hydrocarbon Technologies Inc. direct coal liquefaction Run PB-03 Periods 10A and 10B. Approximately 800 g of phenols were converted to ethylphenyl ethers and the ethers were distilled to produce approximately 650 g of ethers within the diesel fuel boiling range. The ether distillate was mixed with diesel fuel to make 1%, 5%, 10%, and 20% solutions (1750 g each). The four mixtures and a control sample (0% ether) were analyzed and tested by Intertek Testing Services, Caleb Brett. Caleb Brett's analyses of the five ethylphenyl ether-doped diesel fuel samples indicates that the cetane number of the samples decreases with increasing concentration of ethers. The baseline fuel has a cetane number of 42.7; ether loadings of 1, 5, 10, and 20 wt % resulted in cetane numbers of 42.2, 41.7, 39.1, and 33.9, respectively. Other properties of the diesel fuel change as the ether loading increases. However, no change (except in the cetane number) places the value outside of ASTM specifications for Grade 1-D diesel fuel. Although these data indicate that the ethylphenyl ethers are not cetane enhancers, the ethers could be considered diesel fuel extenders at the lower loadings.

NEDOL SAMPLE REQUEST

A request was made for samples from the Nippon Coal Oil NEDOL pilot plant in Kashima, Japan.

TECHNICAL TRANSFER

A paper, "The Reactivity of Direct Coal Liquefaction Resids", co-authored with researchers at the University of Delaware, was presented at the 23rd International Technical Conference on Coal Utilization and Fuel Systems in Clearwater, FL, March 9-13, 1998.

Section 2

INTRODUCTION

This is the Technical Progress Report for the fifteenth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period January 1 through March 31, 1998.

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 resid toward hydrocracking at liquefaction conditions (i.e., resid reactivity) was examined. From the literature and experimental data, a kinetic model of resid conversion was constructed and is being refined. Such a model will provide insights to improve process performance and the economics of direct coal liquefaction.

CONTRACT ACTIVITIES THIS PERIOD

- CONSOL characterized 41 process stream samples obtained from HTI Run PB-01 (227-90),¹ in which Black Thunder Mine coal, Hondo VTB resid, municipal solid waste (MSW) plastics, and virgin plastics were co-liquefaction feedstocks with all-dispersed Fe and Mo catalysts. Those results are described in the Results and Discussion section of this report.
- A request was made for samples from the Nippon Coal Oil NEDOL pilot plant in Kashima, Japan (Appendix 1).
- Phenols were extracted from two samples of separator overhead oil from HTI Run PB-03 Periods 10A and 10B. Approximately 800 g of phenols were converted to ethylphenyl ethers, and the ethers were distilled to produce a sample within the diesel fuel boiling

range. The ethers were mixed with diesel fuel to make 1%, 5%, 10%, and 20% solutions (1750 g each). The four mixtures and a control sample (0% ether) were tested for diesel fuel properties by Intertek Testing Services, Caleb Brett. Results are provided in the Results and Discussion section of the report; experimental details are provided in the Experimental section of the report.

- Computational studies related to the University of Delaware's resid conversion model were continued on the Hewlett Packard Apollo HP-735 RISC workstation at CONSOL R&D in Library, PA. The Structure Optimization Program and the Structure Once-Through Program were used to generate physicochemical properties and structure models for the 15 coal resid samples which have been under study. This work is described in the Results and Discussion section of the report; a portion of it is given in Appendix 2.
- A Topical Report describing the University of Delaware subcontract was revised and is in review. It will be released next quarter.
- A paper, "The Reactivity of Direct Coal Liquefaction Resids", co-authored with researchers at the University of Delaware, was presented at the 23rd International Technical Conference on Coal Utilization and Fuel Systems in Clearwater, FL, March 9-13, 1998. The paper was authored by S. D. Brandes and R. A. Winschel of CONSOL, and W. H. Calkins, M. T. Klein, H. Huang, D. Campbell, S. Wang, and K. Wang of the University of Delaware. Because it was previously reported² when presented at another conference, it is not reproduced here.

ACTIVITIES IN PROGRESS

- Characterization work is continuing on samples from HTI Run PB-08.
- Task 2.1 was started. It will include an updated (1994-present) literature review of analytical methods useful for resids and resid conversion kinetic models. This report will be issued next quarter.

Section 3

RESULTS AND DISCUSSION

CHARACTERIZATION OF PROCESS STREAM SAMPLES FROM HTI RUN PB-01

INTRODUCTION AND RUN BACKGROUND

CONSOL characterized 41 of 43 process stream samples received from HTI Run PB-01 (227-90), in which Black Thunder Mine coal, Hondo VTB resid, municipal solid waste (MSW) plastics, and virgin plastics were co-liquefaction feedstocks with all-dispersed Fe and Mo catalysts. Samples of the PFL and PFS streams were not provided from period 41 in Condition 9. Samples referred to here as separator bottoms were received from HTI labeled as CAS (continuous atmospheric still) bottoms. We chose to designate them as separator bottoms because the CAS was shut down after period 6, and separator bottoms is more consistent with the sample designation in later runs in the PB program.

Operating conditions and plant performance data for Run PB-06 are provided in Table 1¹. A diagram of the HTI unit 227 as configured for Run PB-01, is provided in Figure 1. Some of the equipment used for this run was located on HTI's unit 238, which is similar to unit 227.

Technical objectives of Run PB-01 included investigation of the feasibility of "once-through" (low recycle) operating modes, testing of concepts carried over from catalytic multi-stage liquefaction (CMSL) testing (described in more detail below), studying the co-processing of vacuum resid with plastics, both with and without coal, investigation of dispersed catalyst staging, and studying the effect of recycling the slurry catalyst (ashy recycle) and process severity with interstage separation on performance. Run PB-01 covered nine operating conditions with five feedstock combinations over 41 periods (days) of operation.

Throughout the run, interstage vapor/liquid separation, pressure filtration for solids separation, and in-line distillate product hydrotreating were used. The fresh feed was 100% coal and the recycle ratio was 1.0 in conditions 1-3. The recycle ratio was reduced to 0.17 for the rest of the run (Conditions 4-9). The fresh feed was 100% Hondo resid in Condition 4, and 50% coal and 50% Hondo resid in Condition 5. In Conditions 6, 7, and 8, the fresh feed consisted of 33% coal, 33% Hondo resid, and 33% plastics. In Condition 9, the fresh feed consisted of 50% Hondo resid and 50% plastics. The plastics fed were 100% municipal solid waste (MSW) for period 26 and about half of period 27 in Condition 6, and then they were changed to 76% MSW, 16% high

density polyethylene (HDPE) and 8% polystyrene (PS) for the rest of the plastics feed periods. Reactor temperatures were about 430/450 °C in Reactor K-1/K-2 in Conditions 1 and 2, about 440/450 °C in Reactor K-1/K-2 in Conditions 3 through 5, and about 450/460 °C in Reactor K-1/K-2 in Conditions 6 through 9. Recycle was non-ashy, except in Conditions 2 and 8 when ashy recycle was used. The catalyst staging, normally addition of Mo catalyst precursor to the first reactor and Fe catalyst precursor to the second reactor, was reversed for Condition 7.

In Run PB-01, HTI evaluated long-duration continuous processing (12 days) of wastes with coal and Hondo resid in Conditions 6 through 8, and demonstrated some of the process concepts that came out of the CMSL bench test program. CMSL concepts that were tested were the use of interstage separation, in-line hydrotreating of distillates, use of dispersed-only catalyst, use of low solvent-to-coal ratios, and coprocessing of Black Thunder Mine coal with petroleum vacuum resid and waste plastics.

During coal-only operations in Conditions 1-3, coal conversion was 92.8-94.7%, resid conversion was 82.6-88.0%, and C₄-524 °C MAF distillate yield was constant at 61-62%. Hydrogen consumption was about 6% MAF, and C₁-C₃ gas yield was 8.5-11.7%, dry feed basis.

HTI found no performance improvements and a slight decrease in coal conversion when ashy recycle was used in Condition 2. In Condition 3, when the space velocity was higher and the first-stage temperature was higher, the light gas yield was lowest of the coal-only conditions.

HTI found that the product oil properties were improved in Conditions 4-9 when vacuum resid and/or plastics were feedstocks with and without coal. There were improvements in API gravities, S and N content, and H/C ratio evident in Conditions 4-9. The weight percent of the light naphtha fraction increased to over 50% of the product oil from Condition 6 on.

HTI felt that overall performance was good with catalyst doses that were about one-half of those used in prior runs.

GENERAL TRENDS IN PROCESS STREAM CHARACTERISTICS

The estimated composition of the MSW feed material was previously determined by CONSOL as approximately 96% HDPE + PP, 2% PS, and 1.6% ash.^{2,3} The MSW plastics were described in detail previously.^{2,3} The analyses of the process streams are provided in Tables 4 through 8.

Provided in Table 9 are aromatic hydrogen content and paraffinic hydrogen content, obtained by combining proton categories in the distributions from Tables 3-5 as obtained by NMR spectrometry. The trends are evident in Figures 2-10. A distinct difference between Conditions 1-3 and Conditions 4-9 is generally shown in the figures. Conditions 4-9 had the common features of Hondo resid in the fresh feed, $\leq 50\%$ coal in the fresh feed, and a recycle ratio of 0.17. Conditions 1-3 all had 100% coal in the fresh feed and a recycle ratio of 1.0. In many cases in Figures 2-10, these differences made the major distinction between the characteristics of the process streams.

The use of Hondo resid (with or without plastic) and low coal concentrations with a low recycle ratio in Conditions 4-9 resulted in significantly diminished (by 10-35% absolute) donor solvent quality of the whole PFL and separator bottoms streams. The donor solvent quality in Conditions 1-3 during coal-only feed periods with 1.0 recycle ratio was good to excellent (85-89%), in contrast.

EFFECT OF ASHY RECYCLE DURING COAL-ONLY OPERATION

Non-ashy recycle was used in Condition 1 of Run PB-01. In Condition 2, the change was made to ashy recycle operation through recycle of separator bottoms plus PFC. Later in Condition 2, ashy recycle was performed by recycle of PFC only, when the CAS was shut down because it was not working. The effect of ashy recycle was observed by comparing the characteristics of process streams produced in these two run conditions. There was also a minor space velocity decrease in Condition 2, from 694 to 633 kg MF fresh feed/h/m³ reactor. The switch to ashy recycle had an effect primarily on the properties of the feed slurry stream and the separator bottoms stream. Increases in ash content occurred in the whole feed slurry and PFL streams (from 3.1-4.7% to 7.5-7.9%), and, to a greater degree, in the separator bottoms stream (from 5.1% to 10.5%). Normally, only a trace of ash is found in the PFL. The presence of ash indicates that there were problems with filtration, probably the result of a slow filtration rate, since HTB procedure is to puncture the filter paper and let unfiltered material through, rather than disrupt operations. The whole feed slurry was increased substantially in IOM content from 43% to 52%, and decreased in THF-soluble 454 °C⁺ resid content from 54% to 40%. The whole feed slurry contained substantially more decalin/THF insolubles and less decalin/THF solubles when ashy resid was recycled. The whole PFL increased somewhat in donor solvent quality, from 71% to 76%, as a result of ashy recycle use. However, the whole separator bottoms decreased substantially in donor solvent quality, from 74% to 65%. It appears that the decline in donor

solvent quality of the separator bottoms could result from the changes in aromatic and paraffinic hydrogen content in the 454 °C⁺ resid fraction. The 454 °C⁺ resid portion of the separator bottoms stream became less aromatic and more paraffinic with use of ashy recycle. The 454 °C⁺ resid portion of the separator bottoms stream also became less phenolic and its 454 °C⁻ distillate portion became more phenolic in Condition 2. It is possible that changes in the separator bottoms stream in Condition 2 reflect the shutdown of the CAS system.

The IOM/ash ratio obtained from CONSOL results was lower in Condition 2 than in Condition 1, indicating higher coal conversion in Condition 2. This is in contrast to HTI results, which show slightly lower coal conversion in Condition 2. HTI's results may have been influenced by a low (92%) material balance in Condition 1. Generally it is expected that the coal conversion should improve with the use of ashy recycle, through increased residence time by recycle of the unconverted coal and of dispersed catalysts. The ash content of all the streams tested by CONSOL were increased in ash content in Condition 2, as one would expect with ashy recycle.

EFFECT OF TEMPERATURE AND SPACE VELOCITY INCREASE

Relative to Condition 1, in Condition 3 the liquefaction unit was operated at an increased space velocity (from 694 to 876 kg MF fresh feed/h/m³ reactor), and with an increased temperature in the first reactor (from 433 to 441 °C). The whole feed slurry decreased in THF solubles content from 54% to 47%, and increased in IOM content from 43% to 49%, in Condition 3, relative to Condition 1. The whole PFL was higher in donor solvent quality in Condition 3 (increased from 71% to 80%), but the whole separator bottoms was lower in donor solvent quality (decreased from 74% to 67%). The 454 °C⁻ distillate and 454 °C⁺ resid portions of the whole PFL and the 454 °C⁻ distillate portion of the separator bottoms were about 0.2 meq/g higher in phenolic -OH in Condition 3 than in Condition 1. This is directionally consistent with increased space velocity, but the impact of increased temperature is unclear. There were only minor differences in other properties, such as aromatic hydrogen content.

EFFECT OF CO-LIQUEFACTION OF COAL AND HONDO RESID AT LOW RECYCLE RATIO

Condition 5 used the same space velocity, reactor 1 temperature, and recycle type (non-ashy) as Condition 3, but the feed was 50% coal and 50% Hondo resid (instead of 100% coal), and the recycle ratio was 0.17 MF fresh feed (instead of 1.0 MF fresh feed). A comparison of process stream characteristics from these two conditions provides an indication of the effect of these differences.

This change significantly decreased the aromatic hydrogen content and significantly increased the paraffinic hydrogen content of nearly every process stream. The aromatic hydrogen content of the second-stage SOH was not affected, because in-line product hydrotreating makes this material nearly devoid of aromatics (only 3-6% of the SOH₂ hydrogen was aromatic over the entire run). The 454 °C⁻ distillate content of the whole PFL and whole separator bottoms increased slightly from ca. 44% to ca. 48%. Donor solvent quality of distillate and whole PFL and separator bottoms streams decreased by about 8-25%. In Condition 5, the whole feed slurry was higher in THF solubles content, and the whole PFL was higher in THF-soluble 454 °C⁺ resid content. The whole PFS was higher in ash content and lower in IOM content in Condition 5 compared with Condition 3. Otherwise, in Condition 5, the whole feed slurry, PFL, and separator bottoms streams were lower in IOM and ash content. The phenolic -OH content of every sample type except SOH₂ was lower by 0.12-0.24 meq/g in Condition 5. The concentration of decalin/THF insolubles in the whole feed slurry, and in the 454 °C⁺ resid portion of the PFL, was lower in Condition 5. The opposite effect occurred with the decalin/THF solubles content. The concentration of Hondo resid in the fresh feed was 50%, and its concentration in the reactor feed was 42.7%. Had the recycle ratio in Condition 5 been set at 1.0, as it was in Condition 3, the Hondo resid concentration in the total feed would have been only 25%. The feed slurry should be especially sensitive to this kind of change, because it is a sample of the total feed. The phenolic -OH concentrations were also lower, because the Hondo resid is relatively low in phenolic -OH and oxygen concentrations. The specific relationship between the differences in process variables and the observed effects on other stream characteristics are less clear. Lower ash and lower IOM contents are consistent with the lower-ash Hondo feedstock.

EFFECT OF USING 100% HONDO FEED

Many of the differences noted when 50% of the fresh coal was replaced by Hondo resid were extended further on comparing stream characteristics in Condition 5 (50% coal, 50% Hondo resid) with those in Condition 4 (100% Hondo resid). This comparison shows a lower aromatic hydrogen content and higher paraffinic hydrogen content of nearly every process stream in Condition 4. There is a significantly higher THF solubles content in the whole feed slurry and a higher THF soluble 454 °C⁺ resid content in the whole separator bottoms in Condition 4. There is a significantly lower IOM content in the whole feed slurry, a lower IOM content in the whole separator bottoms in Condition 4, and a higher IOM content in the whole PFS in Condition 4. The ash content of the whole feed slurry and whole separator bottoms streams were also lower in Condition 4. Donor solvent quality of the distillate and whole PFL and separator bottoms streams

was lower in Condition 4 than in Condition 5 by about 6-17%. The phenolic -OH content of every sample type except SOH2 was lower by 0.08-0.48 meq/g in Condition 4. The concentration of decalin/THF insolubles in the wholefeed slurry was substantially lower, and the concentration of decalin/THF solubles was substantially higher, in Condition 4 than in Condition 5. These occurred for the same reasons that were given in comparing Conditions 3 and 5, with regard to the nature of the Hondo resid relative to coal. The Hondo resid is relatively aliphatic and paraffinic, and is lower in phenolic -OH and oxygen content. Evidently, the presence of aromatics (from the coal) is important for high donor solvent quality. However, it is unclear in dispersed catalyst liquefaction systems to what degree that donor solvent quality is important for good process performance. The role of donor solvent quality was important in thermal systems, but is uncertain in catalytic systems such as those with supported and dispersed catalysts.

EFFECT OF PLASTICS ADDITION TO COAL AND HONDO RESID AND REACTOR TEMPERATURE AND SPACE VELOCITY INCREASES

Several process variables were changed from Condition 5 to Condition 6. In Condition 5, the fresh feed was 50% coal and 50% Hondo resid, whereas, in Condition 6, the fresh feed was composed of 33% coal, 33% Hondo resid, and 33% plastics. In addition, the temperature was increased by about 10 °C in each reactor, to 449 °C in the first reactor, and 459 °C in the second reactor. This was done to improve cracking to facilitate high plastics conversion. In addition to these changes, the space velocity was increased from 870 kg MF fresh feed/h/m³ reactor in Condition 5 to 976 kg MF fresh feed/h/m³ reactor in Condition 6. Starting in Condition 6 period 27, the plastics portion of the fresh feed was changed from 100% MSW (L-854) to 76% MSW, 16% HDPE, and 8% PS. The soluble portion of the whole feed slurry and of the whole PFS, and, to a lesser degree, the PFL 454 °C⁺ resid, increased in aromatic hydrogen content as a result of the condition changes from Condition 5 to Condition 6. These were accompanied by decreases in the paraffinic hydrogen content of these streams. Substantial decreases in THF-solubles concentrations and increases in the IOM concentrations occurred in the whole feed slurry, PFL, separator bottoms, and PFS streams. Since unconverted polyolefins report as IOM (THF insolubles) by this method, this is an expected result. In the whole feed slurry and PFL 454 °C⁺ resid, a substantial concentration of extractable plastic was found in Condition 6 when plastics were a co-feed. The whole PFS in Condition 6 contained a trivial (i.e., baseline) amount of material reporting as plastic, as was also found in Condition 5 when no plastic was fed. It appears that no plastic was being rejected from the system during Condition 6; this suggests that the system was not at steady-state. Several feed disruptions occurred in Condition 6 that may

have contributed to such a situation. In later conditions that included plastic as a feed, the PFS stream only contained about 2% plastic, a typically low, but non-trivial value. The whole feed slurry, whole PFS, and PFL 454 °C⁺ resid decreased in decalin/THF solubles content in Condition 6. The concentration of decalin/THF insolubles decreased in the whole feed slurry, and increased in the whole PFS in Condition 6. The whole separator bottoms and its PFL 454 °C⁻ distillate fraction exhibited decreased donor solvent quality in Condition 6. Several streams decreased in phenolic -OH concentration by 0.14-0.31 meq/g in Condition 6. This occurred because the plastic does not contain or contribute phenolic -OH.

EFFECT OF CATALYST ADDITION MODE

The mode of dispersed catalyst addition was reversed from addition of Mo catalyst precursor to the first stage and addition of Fe catalyst precursor to the second stage in Condition 6 to addition of Fe catalyst precursor to the first stage and addition of Mo catalyst precursor to the second stage in Condition 7. There was a small space velocity increase from 976 kg MF fresh feed/h/m³ reactor in Condition 6 to 1033 kg MF fresh feed/h/m³ reactor in Condition 7. Few stream samples were provided by HTI from Condition 7; therefore, data for this condition are limited. There was an increase in the plastics fraction content of the whole PFS from a trivial value in Condition 6. This increase may have resulted from more-consistent operation with the plastics as a feed component during Condition 7.

EFFECT OF ASHY RECYCLE WITH COAL, PLASTICS, AND HONDO RESID FEEDSTOCKS

Non-ashy recycle was used in Condition 6 of Run PB-01. In Condition 8, the recycle mode was changed to ashy recycle through recycle of PFC. The space velocity was also somewhat higher, 1086 kg MF fresh feed/h/m³ reactor in Condition 8, up from 976 kg MF fresh feed/h/m³ reactor in Condition 6.

The soluble portion of the whole PFS and of the PFL 454 °C⁺ resid were decreased in aromatic hydrogen content in Condition 8, relative to Condition 6. These streams, the whole PFL, and the PFL 454 °C⁻ distillate were increased in paraffinic hydrogen content in Condition 8, relative to Condition 6. The whole PFL from Condition 8 was lower in 454 °C⁻ distillate content. The whole PFS was substantially lower in THF solubles content in Condition 8. The whole PFL and whole PFS were significantly higher in IOM content in Condition 8. Phenolic -OH concentration was unchanged in Condition 8, except in the PFL 454 °C⁺ resid, in which case it decreased from 0.77 meq/g to 0.50 meq/g. Comparing Condition 8 with Condition 6, the plastics fraction content of the

PFL 454 °C⁺ resid increased from 12% to 22%, and an increase from 0.5% to 2% was observed in the whole PFS stream. The decalin/THF solubles content of the same material decreased from Condition 6 to Condition 8. The whole separator bottoms and its 454°C⁻ distillate were increased in donor solvent quality by 16-22% from Condition 6 to Condition 8. It is unclear how these stream characteristics were directly related to the use of ashy recycle in Condition 8.

EFFECT OF ELIMINATING COAL FROM THE CO-LIQUEFACTION FEEDSTOCK MIX

In Condition 6, the fresh feed consisted of one-third each coal, Hondo resid, and plastics. In Condition 9, the fresh feed consisted of 50% Hondo resid and 50% plastics. Comparison of the characteristics of process streams between these two run conditions allows the effect of eliminating coal from the feedstock mix to be examined. There was a confounding factor of a higher space velocity in Condition 9 (1250 kg MF fresh feed/h/m³ reactor) than in Condition 6 (976 kg MF fresh feed/h/m³ reactor). However, the lack of a full set of samples from Condition 9 limited the scope of these comparisons. In Condition 9, the streams that were tested were lower in aromatic hydrogen content (except for the second-stage SOH, which was not significantly different), and all of these (including the SOH₂) were higher in paraffinic hydrogen content. This is an expected change, since coal is the main source of aromatics in the feeds. The whole feed slurry sample was higher in THF solubles content and lower in IOM content in Condition 9 than in Condition 6. The whole separator bottoms stream was higher in IOM content in Condition 9. The 454 °C⁻ distillate portion of the separator bottoms stream was lower in donor solvent quality by about 8% in Condition 9. This is most likely a result of the differences in aromatic and paraffinic hydrogen content. The 454 °C⁻ distillate portion and THF-soluble 454 °C⁺ resid portion of the separator bottoms stream were both about 0.2 meq/g lower in phenolic -OH in Condition 9 than in Condition 6. The whole feed slurry was higher in extractable plastic content and solubles content, and lower in insolubles content in Condition 9 than in Condition 6. These changes are not surprising, since coal was the main source of ash and organic insolubles.

ETHYLPHENYL ETHERS AS DIESEL FUEL ENHANCERS/EXTENDERS

INTRODUCTION

Phenols are produced during the direct liquefaction of coal. Crude (i.e., unhydrotreated) direct coal liquefaction products always contain phenols, although the concentration depends on the specific liquefaction process, feed coal, operating conditions, and boiling point of the products. Phenols must be removed in order to make transportation fuels. This is commonly done by hydrotreating. An alternative method is to extract the phenols. Extraction has the potential advantages of reducing the overall hydrogen consumption and producing a cresylic acid byproduct. The cresylic acids could be converted to methylphenyl ethers, which could serve as high-octane oxygenated gasoline extenders. It also may be possible to produce ethylphenyl ethers from the cresylics and grain alcohol and to use the ethers as oxygenated extenders for diesel fuel. This would eliminate the need to hydrotreat the phenolics (and the associated expense of hydrogen and hydrotreater capacity) and would provide a substantial yield of potential oxygenated diesel fuel component. Those products may be entitled to special tax considerations, because of their production from grain alcohol.

Previously, work done at CONSOL⁴ demonstrated that authentic coal-liquefaction phenolics readily produced ethylphenyl ethers when reacted with diethyl sulfate in a modification of the Williamson Synthesis. Thus, the potential for producing alkylphenyl ethers, and specifically ethylphenyl ethers, from coal liquefaction phenols is high. The work reported here addressed the feasibility of using the ethers as diesel fuel enhancers or extenders.

APPROACH

A large sample (4022 g) of net product from direct coal liquefaction was obtained from the Hydrocarbon Technologies Inc. (HTI) bench unit Run PB-03 (a.k.a 227-93). The sample was produced from Black Thunder Mine subbituminous coal and with an all-dispersed catalyst. The on-line hydrotreater was by-passed in collection of this sample. The phenolics were extracted using caustic. Ethylphenyl ethers were produced by reaction of the phenolics with diethyl sulfate. The resulting ethers were distilled to produce material in the diesel fuel boiling range. The ether distillate was blended with commercial low-sulfur diesel fuel (Table 10) in four ratios (1 wt %, 5 wt %, 10 wt %, and 20 wt %). Experimental details are provided in the Experimental Section of this report. The blends then were evaluated by an independent testing laboratory (Intertek Testing Services, Caleb Brett). Fuel-quality tests and authentic engine tests were done for the four blended samples and one sample of diesel fuel.

RESULTS

The combined SOH oil from periods 10A and 10B of HTI bench run PB-03 (4000 g) had a phenolic -OH content of 1.8 meq/g. Extraction of the oil and concentration of the phenolics (see Experimental Section) gave a product with 6.72 meq/g phenolic -OH. Phenolics recovered were 20.1 wt% of the SOH oil (810.2 g). The phenolics were etherified with diethyl sulfate; 799.4 g of ethers were recovered. About 12 g of ethers were reserved, and the remaining 788 g was distilled. 85.6 wt % of the ethers (674.5 g) boiled in the diesel fuel boiling range (160-337°C). Elemental analysis of the distilled ethers is given in Table 11. A comparison of the GC/MS chromatograms of the ethers before and after distillation is given in Figure 13.

Four blends of ether 160-337°C distillate and diesel fuel were made (Table 12) and sent for testing to Intertek Testing Services, Caleb Brett with a sample of the unadulterated diesel fuel. The samples were not identified for Caleb Brett. The results are given in Table 13. Given in Table 14 are some ASTM specifications for diesel fuel oils.⁵

As the concentration of ethers in the samples is increased, the fuel quality declines. Cetane numbers determined from engine tests decrease from the pure diesel fuel value of 42.7 to 42.2, 41.7, 39.1, and 33.9 for the 1, 5, 10, and 20 wt% additive blends, respectively. The cetane index (a calculated value based on the API gravity and mid boiling point) follows the cetane numbers. The cetane number ASTM specification for diesel fuel Grade 1-Dis 40 (minimum). Therefore, it may be possible to blend up to 10 wt % ethylphenyl ethers with the diesel fuel and meet ASTM cetane number specifications.

The ethers were distilled to be within the diesel fuel boiling range before blending. Therefore even the higher loadings do not affect the distillation end point significantly. Even in the 20 wt % blend, the lower temperature (337 °C) end point of the ethers reduces the final boiling point of the blend only 6 °C from that of the starting fuel. It is encouraging to note that addition of the ethers does not increase the residue or the volume recoverable. This indicates that the ethers are stable and non-reacting under ASTM D86 distillation conditions. The haze rating for the fuel is unchanged, as is the corrosion value, regardless of ether loading. The flash point is essentially unchanged and all blends meet the ASTM requirement of 38°C (100 °F) minimum.

The cloud point of the diesel fuel is specified regionally based on the tenth percentile minimum temperature.⁶ As an illustrative example, the lowest temperature month (January) for western

Pennsylvania was chosen. This temperature is 6 °C. The ASTM specification is 6 °C above this temperature, or 12 °C (53 °F). All fuel blends meet this specification.

The kinematic viscosities for all blends fall within the specifications for Grade 1-D diesel fuel (between 1.3 and 2.4), albeit they were measured at a higher temperature. The Caleb Bret kinematic viscosity tests were made at 50 °C, not 40 °C for which the ASTM specification is given (Table 14). The sulfur content of the ethers (Table 11) is 0.02 wt %. This value adds insignificantly to the sulfur content of the diesel fuel even when blended at 20 wt %.

CONCLUSIONS

The isolation of cresylics (phenols) by extraction from coal-derived oils is easily accomplished in the laboratory. The caustic extraction method is employed in commercial petroleum refineries. Gulf Research and Development in 1980 reported on the isolation of 2180 lb of mixed phenols from 7547 lb of coal-derived liquid.⁷ The synthesis of the alkylphenyl ethers, a variation on a Williamson Synthesis, is a small-scale commercial process. Therefore, production of alkylphenyl ethers from coal-derived liquids is technically feasible.

Ethylphenyl ethers are not useful as cetane enhancers because of their negative effect on the cetane number of the fuel. However, ethylphenyl ethers may be useful diesel fuel extenders. Their production from phenols native in coal liquids plus grain alcohol could reduce the overall hydrogen consumption in the coal-to-finished-fuels chain. Potentially, tax credits could be earned for the use of grain alcohol in the fuel production process.

STRUCTURE OPTIMIZATION STUDIES FOR COAL LIQUEFACTION RESIDS

INTRODUCTION

Computational studies on the resid conversion model developed at the University of Delaware were continued on the Hewlett Packard Apollo HP-735 RISC workstation at CONSOL R&D. Focus was on the Structure Optimization Program and the Structure Once-Through Program. These programs were used to generate physicochemical properties and structure models for the 15 coal resid samples which have been under study. Subsequent work will involve the application of the Reaction Optimization Program and the Reaction Once-Through Program to these same samples.

Revised analytical data were used with the Structure Optimization Program to compute best fit (chi-square) values for each of the 15 resid samples. These were compared with the values previously generated. Improvements were achieved for all the samples; and in most cases, the results show a marked improvement in goodness of fit (total chi-square value).

Efforts were made to ensure that global optimum, not local optimum, values were obtained for the predicted structure model parameters. This was done by using a common set of upper and lower bounds of the 33 structure parameters for all 15 coal resid samples, using a common starting point (initial vector) for these structure parameters, and testing the optimization results using other initial vectors.

RESULTS AND DISCUSSION

The Structure Optimization Program uses an algorithm to find sets of 33 structure parameter values until it minimizes the weighted squared differences between observed (analytical) and model-predicted physiochemical properties. This is dictated by the Simulated Annealing Optimization Algorithm (Appendix 1). The algorithm used for this optimization requires an initial guess (starting vector) and lower and upper bounds for each parameter. The University of Delaware set different bounds and starting vector (represented by an array of 33 values) for each resid. CONSOL R&D investigated the effect of using the same starting vector and bounds for every coal resid sample.

The Structure Optimization Program was run on an HP-735 RISC computer for each of the 15 coal resid samples. Each of these runs required approximately 50 hours of computer time. An optimal set of 33 parameters resulted from each of these runs. For each of these coal resid

samples, the 33 parameters were processed through the Structure Once-Through Program to generate structure model properties. A summary of optimization parameters is presented in Table 15. The Once-Through Structure Model properties for the 15 coal resid samples are presented in Table 16.

Table 15 shows the University of Delaware set of bounds and starting vector, and the current bounds and vector selected by CONSOL R&D. The starting vector, which represents the initial value of each of the 33 structure parameters, was chosen by CONSOL to be approximately midway between the upper and lower bounds.

Most of the structural elements are modeled with an exponential distribution. However, four structural elements are modeled with gamma distributions. These are naphthenic ring distribution, resin degree of polymerization, asphaltene degree of polymerization, and pre asphaltene degree of polymerization.

For these four structural elements, both the mean and the standard deviation are among the 33 structure parameters being optimized. For example, rdpmean and rdpstdev are, respectively the mean and standard deviation of the “resin degree of polymerization” element. For certain combinations of means and standard deviations, arithmetic overflows occurred. To prevent this, the lower bound on the above four standard deviation parameters was set, on each iteration, to 20% of the corresponding mean parameters. This prevented arithmetic overflow. This also had the effect of reducing the lower bound for these standard deviations.

Using the current bounds and starting vector, each of the 15 coal resid samples were run through the Structure Optimization Program. This resulted in 15 sets of 33 optimized structure parameters. For each of the 15 sets, the optimized structure parameters were incorporated into the analytical characterization file. The resulting 15 analytical characterization files were then used as input to the Structure Once-Through Program.

Table 15 also shows the minimum and maximum value of each structure parameter for the 15 resid samples. It can be seen that most parameters fall well within the current bounds specified. The exceptions to this are for the four standard deviation parameters (nrstdev, rdpstdev, adpstdev, pdpstdev), the lower bounds of which were adjusted because of the arithmetic overflows, as described above.

STRUCTURE ONCE-THROUGH RESULTS

The structure optimization results for the 15 coal resid samples were processed with the structure once-through program to generate the coal resid model properties shown in Table 16. The table gives the experimentally determined resid characteristics (obtained for the soluble portion of the 15 resids), the predicted model values, and the computed goodness of fit parameters (chi-square values) for each resid.

Generally, the structure optimization program was able to achieve very good predictions for the model properties. In most cases, the greatest chi-square values were for the elemental hydrogen prediction, as seen in Table 16. The total chi-square value, that is the sum over all the properties of these tables, is listed on each of these tables. These sums also are shown in Table 17.

In Table 17, the chi-square values resulting from the structure once-through program runs for each of the 15 coal resid samples are shown. For comparison, the values obtained at the University of Delaware using physical property data, which included analyses of both soluble and whole resids, are shown along with the results recently computed at CONSOL R&D using soluble resid physical property data and the revised structure optimization strategy.

The coal resid samples F, K, and O show chi-square values noticeably higher than the other samples. The chi-square value for the elemental hydrogen for each of these was 14.14, 14.16, and 8.25, representing the largest contributor in each case. The total chi-square for each was 35.66, 37.32, and 36.51. Thus, the hydrogen contribution represented 37.6%, 37.9%, and 14.2%, respectively, of the totals. For resid I, for which the lowest chi-square was obtained, the hydrogen contribution was of the order of 13% of the total.

The Structure Optimization and Once-Through Programs were re-run for coal resids D and F, using substantially different initial vectors, to verify that the results were not substantially dependent upon the starting point for the search algorithm. The total chi-square values obtained for each were 2.10 versus the 2.18 shown for resid D and 32.09 versus the 35.66 shown for resid F in Table 16. Thus, very good agreement was achieved, indicating independence from the specific value chosen for the initial vector.

Section 4

EXPERIMENTAL

ETHYLPHENYL ETHERS AS DIESEL FUEL ENHANCERS/EXTENDERS

SAMPLE AND REAGENT PREPARATION

Two samples of separator overhead oil (SOH) from Hydrocarbon Technologies Inc. Run PB-03 (a.k.a. 227-93) periods 10A and 10B were combined to provide a 4022 g sample from which phenols were extracted. Run PB-03 fed Black Thunder Mine subbituminous coal. The phenolic -OH content of the oil was determined by Fourier transform infrared (FTIR) spectroscopy to be 1.8 meq/g. NaOH solutions (6%, 10%, and 25%) were prepared with deionized water and NaOH pellets (Fisher Scientific). NaCl solution (10%) was prepared from crystalline NaCl (Fisher Scientific). Concentrated HCl (Fisher Scientific), methylene chloride (Fisher Scientific), and diethyl sulfate (99%, Acros Organics N.V.) were used as received. Low-sulfur diesel fuel was obtained from the Refinery Control Laboratory of Conoco Inc. in Ponca City, OK.

PHENOL EXTRACTION

The SOH oil was extracted in 400 g aliquots. Each aliquot of oil was extracted in a 2 L separatory funnel four times with 120 mL of 6% NaOH solution. After each extraction, the oil/water layer was allowed to separate. The water layer was transferred to a 2 L Erlenmeyer flask (or 2 L beaker). The oil layer was washed three times with 100 mL deionized water. After each washing, the oil/water layers were allowed to separate. The water was added to the same 2 L Erlenmeyer flask. The oil layer was reserved. Concentrated HCl was added to the water to neutralize the solution; pH paper was used to test for neutrality. The neutralized water/phenol solution was returned to a clean 2 L separatory funnel. It was extracted four times with 120 mL methylene chloride. After each extraction, the water/CH₂Cl₂ layers were allowed to separate. The CH₂Cl₂ layer was removed to a tared 1000 mL round bottom flask. The CH₂Cl₂ was removed from the phenols by rotary evaporation. Phenols collected from each aliquot of oil were combined.

The combined phenol sample contained significant amounts of non-phenolic oil components (Figure 11). The sample was concentrated further by repeating all extraction steps on the combined sample. This resulted in 810.2 g of product containing 6.72 meq/g phenolic -OH (Figure 12).

ETHERIFICATION

This step was performed in a fume hood. 100 g of phenols were weighed into a 1000 mL round bottom flask with a stirring bar. 500 mL of 10% NaOH solution were added. 120 mL diethyl sulfate was slowly added to the flask, with stirring. A condenser was placed on top of the flask. The solution was heated to boiling. Reflux occurred in the condenser without cooling-water flow. The solution was allowed to reflux for 3 h with stirring and then was allowed to cool. 25 mL of 25% NaOH solution was added. The contents of the flask were transferred to a 2 L separatory funnel; the layers were allowed to separate. The water layer was removed and discarded. The organic layer was washed twice with 125 mL 10% NaOH/10% NaCl solution. The washed ethers were transferred from the separatory funnel to a 500 mL flask. An equal volume of deionized water was added.

The contents of flask were warmed to ca. 90°C for 2 h (to destroy any unreacted diethyl sulfate). The flask contents were returned to a separatory funnel. The water layer was removed and discarded. The organic (ether) layer was reserved and combined with ethers extracted from the other aliquots.

DISTILLATION

Distillation of the ethers was required to produce material in the diesel fuel boiling range. GC/MS chromatograms of the ethers before and after distillation are given in Figure 13.

Equipment

All glass equipment has 24/40 joints

• 2 1000 mL round-bottom distillation flasks	• 4 500 mL receivers (round bottom flasks)
• 2 straight condensers (about 18" long)	• stirring bar
• Claisen distillation head with thermocouple well	• stirring plate
• Receiver adapter with vacuum joint	• heating mantle

Procedure

Half (about 400 g) of the ethers was placed in each of the 1000 mL distillation flasks. The ethers were distilled at 5 torr to 32 °C (atmospheric equivalent temperature of 160 °C). The receiver was removed and replaced. Distillation was continued at 5 torr to 170°C (atmospheric equivalent temperature of 337 °C). The distillate and pot bottoms were weighed and reserved. No

IBP-160 °C distillate was recovered. The 160-337 °C fractions were combined to give 674.5 g of ethers in the diesel fuel boiling range. The pot bottoms were combined and reserved.

DIESEL FUEL BLENDS

A 5 gal sample of low-sulfur diesel fuel was obtained from Conoco Inc. Ponca City, OK, Refinery Control Laboratory. Analyses provided with the sample are given in Table 10. Blends were made of the ethylphenyl ether 160-337 °C fraction and diesel fuel to produce 1, 5, 10, and 20 wt% solutions. Blending ratios are given in Table 12.

Section 5

CONCLUSIONS

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

Section 6

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Section 7

LIST OF ABBREVIATIONS AND ACRONYMS

CMSL	Run designation used by HTI for catalytic multi-stage liquefaction
DOE	Department of Energy
FTIR	Fourier-transform infrared
GC-MS	Gas chromatography-mass spectrometry
HDPE	High density polyethylene
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
LDPE	Low-density polyethylene
MAF	Moisture and ash free
MF	Moisture free
NMR	Nuclear magnetic resonance
PB	POC bench option, HTI run designation
PFC	Pressure filter cake
PFL	Pressure filter liquid
POC	Proof of concept
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SOH	Separator overhead
SOH1	First-stage SOH; a component of the HTU feed
SOH2	Second-stage SOH; the hydrotreated net product
THF	Tetrahydrofuran
TNPS	Di-tertiary-nonyl polysulfide
VSF	Vacuum still bottoms
VSO	Vacuum still overhead
VTB	Vacuum tower bottoms

TABLE 1

OPERATING CONDITIONS AND PROCESS PERFORMANCE SUMMARY FOR HTI RUN PB-01 (227-90)

Condition Period No. Work-Up Period	1 1-5 5	2 6-10 10	3 11-15 15	4 16-20 20	5 21-25 25	6 26-30 30	7 (a) 31-34 34	8 35-37 37	9 38-41 41
<u>Feed Composition, wt %</u>									
Coal	100	100	100	0	50	33.33	33.33	33.33	0
Waste Plastics	0	0	0	0	0	33.33	33.33	33.33	50
Hondo Resid	0	0	0	100	50	33.33	33.33	33.33	50
Space Velocity, kg/hr/m ³ Reactor Stage	694	633	876	1059	870	976	033	1086	1250
Recycle Type (b)	N-ashy	Ashy	N-ashy	N-ashy	N-ashy	N-ashy	N-ashy	Ashy	N-ashy
Recycle Ratio	1.0	1.0	1.0	0.17	0.17	0.17	0.17	0.17	0.17
<u>Temperatures, °C</u>									
First Stage	433	433	441	441	442	449	450	450	451
Second Stage	449	448	450	451	450	459	461	460	460
In-Line HTU	379	379	379	379	379	379	379	379	379
Material Balance, % (gross)	98.97	92.26	96.23	100.06	97.87	98.78	96.46	92.99	94.15
Recycle Solvent Balance, wt % Dry Feed	22.60	19.99	24.84	51.52	34.14	40.34	35.98	36.91	49.79
<u>Estimated Normalized Yields, wt %</u>									
<u>Dry Fresh Feed</u>									
C ₁ -C ₃ in Gases	11.72	10.37	8.49	4.99	7.15	5.18	7.43	5.64	4.27
C ₄ -C ₇ in Gases	4.75	4.14	3.19	2.95	2.94	2.82	4.30	3.50	3.26
IBP-177 °C in Liquids	15.20	15.83	18.67	13.23	16.28	21.28	21.20	20.07	17.98
177-260 °C in Liquids	11.57	10.62	10.87	13.80	13.65	11.32	12.99	12.15	12.85
260-343 °C in Liquids	14.81	11.98	11.01	13.83	12.69	11.50	11.04	10.65	11.23
343-454 °C in Liquids	9.52	12.31	11.66	21.06	15.87	18.04	15.99	17.39	20.35
454-524 °C in Liquids	2.45	3.02	3.04	11.05	6.27	7.08	5.46	6.92	9.90
524 °C ⁺ in Liquids	6.18	9.05	9.46	16.50	13.07	12.71	10.65	13.57	15.61
Unconverted Feed	4.99	6.58	6.80	0.12	3.76	3.17	3.58	2.96	0.26
Ash	5.75	5.75	5.75	0.15	2.95	2.47	2.47	2.47	0.84
H ₂ O	12.25	11.00	12.68	0.06	4.99	5.19	5.77	5.71	2.70
CO	1.10	1.45	0.72	0.08	0.62	0.43	0.43	0.51	0.07
CO ₂	4.71	3.98	2.52	0.04	1.73	0.70	0.84	0.55	0.04
NH ₃	0.95	0.85	0.72	0.23	0.48	0.33	0.28	0.23	0.06
N ₂ S	-0.04	-0.24	-0.16	3.64	1.65	0.87	0.91	0.78	1.94
Hydrogen Consumption	5.91	4.90	5.44	1.72	4.09	3.09	3.34	3.09	1.34
<u>Process Performance, wt % MAF Feed</u>									
Feed Conversion	94.7	93.0	92.8	99.9	96.1	96.7	96.3	97.0	99.7
C ₄ -524 °C Distillate Yield	61.8	61.4	62.0	76.0	69.7	73.9	72.8	72.5	76.2
524 °C ⁺ Conversion	88.0	85.2	82.6	83.3	82.7	83.7	85.4	83.1	84.0

(a) During Condition 7, the dispersed catalyst addition mode was switched so that iron was added to reactor K-1 and molybdenum to K-2.

(b) During the ashy recycle mode of operations, the catalyst concentration multiplier of about 1.5 was obtained by recycling the filter cake.

TABLE 2

HTI ANALYSES OF BLACK THUNDER MINE FEED COAL, MUNICIPAL SOLID WASTE PLASTICS, AND HONDO VTB RESID

Feed	Black Thunder Mine Coal (a)	MSW Plastics^{2,3}	Hondo VTB Resid
Moisture Content, wt %	10.01	N/A	N/A
<u>Proximate Analysis, wt % Dry</u>			
Volatile Matter	43.48	N/A	N/A
Fixed Carbon	50.52	N/A	N/A
Mineral Matter	6.00	N/A	N/A
<u>Ultimate Analysis, wt % Dry</u>			
Carbon	70.12	80.51	83.84
Hydrogen	5.11	11.42	10.13
Nitrogen	0.99	0.00	0.90
Sulfur	0.35	0.21	4.39
Ash	6.19	1.64	0.15
Oxygen (Diff.)	17.24	6.06	0.59
Chlorine	N/A	0.16	N/A

(a) HTI Designation: HTI-6213

N/A = Not available

Source: Reference 1

TABLE 3

COMPONENT DISTRIBUTION OF WHOLE SAMPLES, HTI RUN PB-01 (227-90)

Sample	Condition	Period	wt % of Sample			
			454 °C ⁻ Distillate	454 °C ⁺ Resid THF Solubles	IOM	Ash
PFL	1	5B	43.0	44.7	5.5	4.7
PFL	2	10B	40.4	42.8	6.9	7.9
PFL	3	15A-B	44.4	45.2	5.6	3.6
PFL	4	20B	47.9	50.4	<0.1	<0.1
PFL	5	25B	47.6	50.2	0.5	<0.1
PFL	6	30B	50.6	38.0	10.4	<0.1
PFL	7	34B	49.9	37.4	10.7	0.1
PFL	8	37B	41.7	38.1	18.7	<0.1
Sep. Btms.	1	5B	44.8	43.2	5.6	5.2
Sep. Btms.	2	10B	42.9	38.2	8.2	10.5
Sep. Btms.	3	15A-B	43.5	43.7	6.6	5.5
Sep. Btms.	4	20B	49.5	48.4	0.6	0.5
Sep. Btms.	5	25B	47.7	43.4	3.6	3.6
Sep. Btms.	6	30B	49.5	36.3	11.9	1.1
Sep. Btms.	8	37B	49.9	36.9	12.2	0.9
Sep. Btms.	9	41B	46.7	33.7	19.2	<0.1
THF Extraction of Whole Samples						
P. F. Solids	1	5B	ND	50.3 (a)	22.3	27.4
P. F. Solids	2	10B	ND	50.9 (a)	20.3	28.8
P. F. Solids	3	15A-B	ND	49.4 (a)	26.0	24.6
P. F. Solids	4	20B	ND	46.0 (a)	28.8	29.3
P. F. Solids	5	25B	ND	48.0 (a)	22.3	29.7
P. F. Solids	6	30B	ND	39.5 (a)	28.8	31.7
P. F. Solids	7	34B	ND	34.8 (a)	31.9	33.3
P. F. Solids	8	37B	ND	27.8 (a)	38.2	34.0
Feed Slurry	1	5B	ND	53.9 (a)	43.0	3.1
Feed Slurry	2	10B	ND	40.4 (a)	52.1	7.5
Feed Slurry	3	15A-B	ND	46.9 (a)	48.8	4.3
Feed Slurry	4	20B	ND	98.1 (a)	1.8	0.1
Feed Slurry	5	25B	ND	63.7 (a)	34.1	2.2
Feed Slurry	6	30B	ND	57.1 (a)	41.2	1.7
Feed Slurry	8	37B	ND	53.2 (a)	43.5	3.3
Feed Slurry	9	41B	ND	68.7 (a)	30.5	0.8

ND=Not determined

(a) THF solubles determined on the whole sample by difference from IOM and ash.

TABLE 4

PROTON DISTRIBUTION OF WHOLE SAMPLES, HTI RUN PB-01 (227-90)

	Condition	Period	% of Protons						
			Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Whole Sample									
SOH (2nd Stg) Oil	1	5B	1.6	4.5	7.5	6.8	12.3	35.9	31.4
SOH Oil	2	10B	1.2	5.0	6.9	6.9	20.8	31.8	27.4
SOH Oil	3	15A-B	0.7	2.8	4.7	5.0	20.5	34.5	31.8
SOH Oil	4	20B	0.6	2.5	3.3	4.1	13.7	39.3	36.5
SOH Oil	5	25B	0.3	2.7	3.1	4.3	15.1	39.7	34.8
SOH Oil	6	30B	0.7	2.9	3.4	3.6	15.0	37.9	36.5
SOH Oil	8	37B	1.4	2.7	4.2	4.1	14.2	37.6	35.9
SOH Oil	9	41B	0.6	2.2	1.5	2.6	11.6	40.1	41.4
PFL	1	5B	22.1	12.6	14.8	12.2	11.2	17.2	9.9
PFL	2	10B	19.8	11.2	16.3	11.6	12.1	18.6	10.4
PFL	3	15A-B	19.8	11.9	14.9	11.9	11.4	19.8	10.2
PFL	4	20B	8.0	5.3	8.6	8.1	12.5	36.0	21.6
PFL	5	25B	11.2	7.1	12.6	9.5	12.8	31.1	15.8
PFL	6	30B	13.4	5.5	12.3	9.1	11.6	33.9	14.3
PFL	7	34B	15.3	4.8	12.2	8.9	11.1	34.0	13.7
PFL	8	37B	11.0	4.7	11.7	7.9	11.8	37.8	15.0
P. F. Solids (a)	1	5B	30.9	3.5	18.3	12.2	11.8	15.7	7.7
P. F. Solids (a)	2	10B	24.5	6.1	19.0	11.1	13.1	17.9	8.3
P. F. Solids (a)	3	15A-B	25.3	6.7	19.0	11.5	12.0	16.8	8.6
P. F. Solids (a)	4	20B	10.8	4.9	12.3	8.4	13.6	32.7	17.2
P. F. Solids (a)	5	25B	14.0	6.2	14.6	10.0	13.3	27.4	14.6
P. F. Solids (a)	6	30B	22.0	8.7	14.5	11.1	11.1	21.3	11.1
P. F. Solids (a)	7	34B	21.0	7.1	13.1	10.1	10.4	26.1	12.2
P. F. Solids (a)	8	37B	17.3	8.1	14.3	10.0	11.8	25.9	12.6
Feed Slurry	1	5B	22.4	8.5	14.3	11.8	10.6	21.0	11.4
Feed Slurry	2	10B	22.5	6.6	17.5	10.0	12.5	20.3	10.5
Feed Slurry	3	15A-B	21.6	6.2	18.5	10.4	12.6	20.7	9.9
Feed Slurry	4	20B	5.3	3.3	11.2	7.8	16.5	35.9	20.0
Feed Slurry	5	25B	4.7	3.0	12.7	7.7	16.4	35.1	20.5
Feed Slurry	6	30B	6.6	6.9	10.2	6.9	16.6	33.6	19.3
Feed Slurry	8	37B	6.3	7.8	9.3	6.9	16.1	34.8	18.7
Feed Slurry	9	41B	5.5	4.4	9.7	7.3	15.8	36.4	20.9
Sep. Btms.	1	5B	23.7	10.3	17.1	12.0	11.4	16.9	8.7
Sep. Btms.	2	10B	19.3	11.2	16.9	11.8	12.7	17.8	10.3
Sep. Btms.	3	15A-B	20.1	11.2	15.8	12.4	11.4	19.1	9.9
Sep. Btms.	4	20B	8.4	5.2	11.2	8.9	13.8	33.5	19.0
Sep. Btms.	5	25B	10.9	7.4	12.4	9.7	13.2	30.6	15.9
Sep. Btms.	6	30B	12.0	7.4	10.8	9.7	11.3	32.6	16.2
Sep. Btms.	8	37B	11.0	6.6	11.5	8.7	11.6	34.4	16.2
Sep. Btms.	9	41B	8.9	5.2	8.7	7.9	11.7	38.3	19.4

- (a) Dissolved in 99.96% d_5 -pyridine and filtered prior to running NMR spectrum. All other samples were dissolved in 99.8% $CDCl_3$ and filtered prior to running NMR spectrum, except that SOH oil samples were unfiltered.

TABLE 5

**PROTON DISTRIBUTION OF DISTILLATE SAMPLES AND RESID SAMPLES, HTI RUN
PB-01 (227-90)**

	Condition	Period	% of Protons						
			Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Distillates									
PFL	1	5B	20.5	5.9	16.5	12.2	12.2	22.0	10.7
PFL	2	10B	16.9	9.0	16.1	11.9	13.2	22.2	10.7
PFL	3	15A-B	17.2	8.9	15.3	12.0	12.3	23.2	11.2
PFL	4	20B	5.9	4.0	8.1	8.3	12.5	38.4	22.8
PFL	5	25B	7.7	5.3	11.0	9.3	12.9	35.7	18.0
PFL	6	30B	9.8	4.5	10.6	8.6	11.9	38.0	16.7
PFL	7	34B	10.2	6.1	10.6	8.9	12.1	37.5	14.6
PFL	8	37B	7.8	4.7	9.7	7.9	11.4	39.9	18.6
Sep. Btms.	1	5B	19.6	9.1	15.8	12.7	11.9	20.7	10.3
Sep. Btms.	2	10B	15.9	10.0	16.0	12.2	13.4	21.9	10.6
Sep. Btms.	3	15A-B	15.9	10.6	14.1	12.7	12.5	22.9	11.4
Sep. Btms.	4	20B	5.6	4.3	8.3	8.4	13.9	37.5	22.0
Sep. Btms.	5	25B	8.1	6.3	10.9	9.4	13.5	33.9	17.9
Sep. Btms.	6	30B	10.3	5.3	11.3	8.9	12.8	35.7	15.8
Sep. Btms.	8	37B	8.9	5.3	10.9	8.3	13.0	37.1	16.6
Sep. Btms.	9	41B	8.0	3.5	10.4	7.9	14.0	38.6	17.5
Resids									
PFL	1	5B	34.9	7.4	20.8	9.9	11.1	9.9	6.1
PFL	2	10B	32.6	6.7	19.8	10.3	12.2	11.6	6.8
PFL	3	15A-B	33.7	6.6	19.7	10.4	11.1	11.7	6.9
PFL	4	20B	13.8	4.5	11.7	8.8	14.5	30.0	16.7
PFL	5	25B	20.6	6.7	14.8	9.6	13.1	23.1	12.1
PFL	6	30B	26.9	3.7	18.0	9.8	12.6	20.2	8.8
PFL	7	34B	30.4	3.9	17.8	9.2	11.6	18.7	8.3
PFL	8	37B	22.9	3.4	16.4	8.7	13.2	24.0	11.2
Sep. Btms.	1	5B	35.0	7.5	19.8	10.8	10.7	10.1	6.1
Sep. Btms.	2	10B	27.1	6.0	17.3	9.9	7.6	21.3	10.9
Sep. Btms.	3	15A-B	33.7	6.6	20.5	10.1	11.0	11.6	6.4
Sep. Btms.	4	20B	14.5	4.6	12.0	8.8	13.4	30.9	15.7
Sep. Btms.	5	25B	21.9	5.9	16.4	9.9	13.7	21.2	11.1
Sep. Btms.	6	30B	25.6	5.0	16.6	10.0	11.7	20.8	10.3
Sep. Btms.	8	37B	25.4	4.7	16.3	8.8	12.1	22.6	10.1
Sep. Btms.	9	41B	17.8	3.6	12.4	8.0	13.2	30.6	14.4

Note: Resids were dissolved in 99.96% d₅-pyridine and filtered prior to running NMR spectrum. Distillates were dissolved in 99.8% CDCl₃ and not filtered.

TABLE 6

PHENOLIC -OH CONCENTRATION IN SAMPLES FROM HTI RUN PB-01 (227-90)

PHENOLIC OH	Condition	Period	Concentration, meq/g	Peak Pos., cm ⁻¹
Distillates				
PFL	1	5B	0.83	3300
PFL	2	10B	0.93	3300
PFL	3	15A-B	1.00	3294
PFL	4	20B	0.38	3307
PFL	5	25B	0.79	3304
PFL	6	30B	0.50	3302
PFL	7	34B	0.51	3305
PFL	8	37B	0.56	3307
Sep. Btms.	1	5B	0.86	3304
Sep. Btms.	2	10B	1.01	3307
Sep. Btms.	3	15A-B	1.07	3305
Sep. Btms.	4	20B	0.35	3309
Sep. Btms.	5	25B	0.83	3307
Sep. Btms.	6	30B	0.52	3307
Sep. Btms.	8	37B	0.59	3307
Sep. Btms.	9	41B	0.31	3311
THF sols				
PFL	1	5B	0.92	3291
PFL	2	10B	0.96	3293
PFL	3	15A-B	1.13	3292
PFL	4	20B	0.61	3299
PFL	5	25B	0.91	3296
PFL	6	30B	0.77	3294
PFL	7	34B	0.68	3293
PFL	8	37B	0.50	3298
Sep. Btms.	1	5B	0.95	3291
Sep. Btms.	2	10B	0.67	3292
Sep. Btms.	3	15A-B	1.02	3293
Sep. Btms.	4	20B	0.64	3298
Sep. Btms.	5	25B	0.90	3294
Sep. Btms.	6	30B	0.72	3294
Sep. Btms.	8	37B	0.80	3294
Sep. Btms.	9	41B	0.54	3298
P. F. Solids	1	5B	0.86	3294
P. F. Solids	2	10B	0.90	3298
P. F. Solids	3	15A-B	0.93	3294
P. F. Solids	4	20B	0.51	3298
P. F. Solids	5	25B	0.75	3298
P. F. Solids	6	30B	0.87	3290
P. F. Solids	7	34B	0.78	3293
P. F. Solids	8	37B	0.89	3294
Feed Slurry	1	5B	0.59	3294
Feed Slurry	2	10B	0.73	3295
Feed Slurry	3	15A-B	0.66	3297
Feed Slurry	4	20B	0.33	3309
Feed Slurry	5	25B	0.41	3305
Feed Slurry	6	30B	0.39	3304
Feed Slurry	8	37B	0.35	3306
Feed Slurry	9	41B	0.33	3308
Whole Sample				
SOH (2nd Stg) Oil	1	5B	ND	
SOH Oil	2	10B	0.13	3321
SOH Oil	3	15A-B	ND	
SOH Oil	4	20B	ND	
SOH Oil	5	25B	ND	
SOH Oil	6	30B	ND	
SOH Oil	8	37B	ND	
SOH Oil	9	41B	ND	

TABLE 7**MICROAUTOCLAVE SOLVENT QUALITY TESTS, HTI RUN PB-01 (227-90)**

Sample	Condition	Period	% Coal Conversion	
			Distillate	Whole
PFL	1	5B	85.5	70.8
PFL	2	10B	88.4	76.2
PFL	3	15A-B	84.7	79.8
PFL	4	20B	50.2	54.3
PFL	5	25B	59.6	71.8
PFL	6	30B	56.4	71.8
PFL	7	34B	54.4	ND
PFL	8	37B	52.6	67.6
Sep. Btms.	1	5B	87.3	73.6
Sep. Btms.	2	10B	89.0	65.1
Sep. Btms.	3	15A-B	87.9	67.4
Sep. Btms.	4	20B	53.7	51.5
Sep. Btms.	5	25B	63.6	57.8
Sep. Btms.	6	30B	57.5	46.5
Sep. Btms.	8	37B	73.3	68.6
Sep. Btms.	9	41B	50.0	48.8

Standard test conditions: 9 g solvent, 6 g Old Ben (Indiana 5) coal, 399 °C, 30 min, MAF conversion to THF solubles reported.

TABLE 8
RESULTS OF HOT DECALIN EXTRACTIONS OF SAMPLES
FROM HTI RUN PB-01 (227-90)

Hot Decalin Extractions	Condition	Period	% of Sample			Recovery, %
			Insolubles	Solubles	Plastics	
whole sample						
Feed Slurry	1	5B	39.4	60.1	0.45	95.1
Feed Slurry	2	10B	62.2	37.6	0.24	96.2
Feed Slurry	3	15A-B	54.0	45.5	0.48	96.6
Feed Slurry	4	20B	0.8	99.0	0.20	103.8
Feed Slurry	5	25B	31.5	68.4	0.15	99.8
Feed Slurry	6	30B	26.6	56.8	16.50	97.1
Feed Slurry	8	37B	26.1	55.2	18.70	104.0
Feed Slurry	9	41B	2.4	62.8	34.80	103.7
whole sample						
P. F. Solids	1	5B	54.3	45.6	0.04	99.6
P. F. Solids	2	10B	51.4	48.5	0.04	98.0
P. F. Solids	3	15A-B	52.1	47.6	0.23	98.5
P. F. Solids	4	20B	55.3	44.5	0.18	103.4
P. F. Solids	5	25B	55.6	44.0	0.43	97.0
P. F. Solids	6	30B	66.8	32.7	0.47	101.8
P. F. Solids	7	34B	68.5	29.6	1.9	96.5
P. F. Solids	8	37B	65.1	32.8	2.2	98.3
resid						
PFL	1	5B	18.3	81.6	0.15	104.7
PFL	2	10B	17.6	82.1	0.26	104.7
PFL	3	15A-B	15.5	84.3	0.18	104.3
PFL	4	20B	0.07	99.9	0.06	104.2
PFL	5	25B	0.30	99.6	0.09	103.5
PFL	6	30B	0.53	87.4	12.1	101.3
PFL	7	34B	0.66	86.1	13.2	98.2
PFL	8	37B	0.17	77.8	22.0	101.4

TABLE 9

**AROMATIC AND PARAFFINIC HYDROGEN CONTENT OF SAMPLES
FROM HTI RUN PB-01 (227-90)**

Condition	1	2	3	4	5	6	7	8	9
Period	1-5	6-10	11-15	16-20	21-25	26-30	31-34	35-37	38-41
Hydrogen Aromaticity (a), % of Protons									
SOH2	6.1	6.2	3.5	3.1	3.0	3.6		4.1	2.8
PFL 454 °C ⁻ Distillate	26.4	25.9	26.1	9.9	13.0	14.3	16.3	12.5	
Sep Btms 454 °C ⁻ Distillate	28.7	25.9	26.5	9.9	14.4	15.6		14.2	11.5
PFL Whole	34.7	31.0	31.7	13.3	18.3	18.9	20.1	15.7	
Feed Slurry Whole	30.9	29.1	27.8	8.6	7.7	13.5		14.1	9.9
Sep Btms Whole	34.0	30.5	31.3	13.6	18.3	19.4		17.6	14.1
PFS Whole	34.4	30.6	32.0	15.7	20.2	30.7	28.1	25.4	
PFL 454 °C ⁺ Resid	42.3	39.3	40.3	18.3	27.3	30.6	34.3	26.3	
Sep Btms 454 °C ⁺ Resid	42.5	33.1	40.3	19.1	27.8	30.6		30.1	21.4
Hydrogen Paraffinicity (b), % of Protons									
SOH2	67.3	59.2	66.3	75.8	74.5	74.4		73.5	81.5
PFL 454 °C ⁻ Distillate	32.7	32.9	34.4	61.2	53.7	54.7	52.1	58.5	
Sep Btms 454 °C ⁻ Distillate	31.0	32.5	34.3	59.5	51.8	51.5		53.7	56.1
PFL Whole	27.1	29.0	30.0	57.6	46.9	48.2	47.7	52.8	
Feed Slurry Whole	32.4	30.8	30.6	55.9	55.6	52.9		53.5	57.3
Sep Btms Whole	25.6	28.1	29.0	52.5	46.5	48.8		50.6	57.7
PFS Whole	23.4	26.2	25.4	49.9	42.0	32.4	38.3	38.5	
PFL 454 °C ⁺ Resid	16.0	18.4	18.6	46.7	35.2	29.0	27.0	35.2	
Sep Btms 454 °C ⁺ Resid	16.2	32.2	18.0	46.6	32.3	31.1		32.7	45.0

- (a) Aromatic hydrogen content defined as the sum of uncondensed and condensed aromatic proton categories, as reported in Tables 4-5.
 (b) Paraffinic hydrogen content defined as the sum of alkyl beta and gamma aliphatic proton categories, as reported in Tables 4-5.

TABLE 10
ANALYSIS OF LOW SULFUR DIESEL FUEL (a)

Test	Result
API Gravity @ 60 °F (16 °C), Composite	34.4
API Gravity @ 60 °F (16 °C), Top	34.4
API Gravity @ 60 °F (16 °C), Middle	34.4
API Gravity @ 60 °F (16 °C), Bottom	34.4
Distillation - ASTM D86, °F (°C)	
IBP	323 (162)
10% Recovered	404 (207)
20% Recovered	429 (221)
50% Recovered	503 (262)
90% Recovered	613 (323)
95% Recovered	639 (337)
End Point	676 (358)
Recovery, Vol %	98.7
Residual, Vol %	1.0
Colonial Haze	1
Viscosity @ 40°C	2.49
Pour Point, °F (°C)	-15 (-26)
Cloud Point, °F (°C)	12 (-11)
Flash PM Avg., °F (°C)	144 (62)
Reflectance Rating	93
Ash, wt %	<0.01
Cetane INDEX	45.1
Color	-2.0
CST 3 h @ 122°F (50 °C)	1A
Water & Sediment, Vol %	<0.05

(a) Supplied by Conoco Inc. Ponca City, OK, Refinery Control Laboratory; Test Date: 1/4/98

TABLE 11**ANALYSES OF DISTILLED ETHYLPHENYL ETHERS**

Ultimate Analyses (as determined), wt %	
C	78.81
H	9.24
N	0.08
S	0.02
O (by difference)	11.85

TABLE 12**DIESEL FUEL-ETHYLPHENYL ETHER BLENDS**

Sample	Diesel Fuel, g	Ethers, g	Ethers, wt %
A	1750.1	0	0
B	1732.5	17.5	1.0
C	1662.5	87.6	5.0
D	1575.0	175.0	10.0
E	1400.5	350.2	20.0

TABLE 13
ANALYTICAL RESULTS FOR DIESEL FUELS

Test	Method	Diesel Fuel with Ethylphenyl Ethers (a)				
		A	B	C	D	E
Cetane Number	D613	42.7	42.2	41.7	39.1	33.9
API Gravity @ 60 °F (16 °C)	2-API	34.1	34.0	33.3	32.4	30.7
Specific Gravity @ 60 °F (16 °C)		0.8543	0.8552	0.8587	0.8631	0.8723
Initial Boiling Point, °F (° C)	D86	353 (178)	348 (176)	346 (174)	343 (173)	342 (172)
% Recovery @ °F (° C)						
5		396 (202)	395 (202)	392 (200)	385 (196)	386 (197)
10		411 (211)	410 (210)	408 (209)	402 (206)	398 (203)
20		435 (224)	432 (222)	429 (221)	423 (217)	413 (212)
30		461 (238)	457 (236)	456 (236)	448 (231)	437 (225)
40		485 (252)	483 (251)	481 (249)	473 (245)	460 (238)
50		509 (265)	507 (264)	504 (262)	499 (259)	486 (252)
60		532 (278)	532 (278)	529 (276)	523 (273)	512 (267)
70		557 (292)	557 (292)	554 (290)	550 (288)	540 (282)
80		586 (308)	584 (307)	583 (306)	580 (304)	572 (300)
90		622 (328)	620 (327)	616 (324)	617 (325)	612 (322)
95		650 (343)	650 (343)	647 (342)	648 (342)	643 (339)
Final Boiling Point, °F (° C)		675 (357)	674 (357)	671 (355)	671 (355)	664 (351)
Recovery, vol %		98.6	98.7	98.6	98.2	98.1
Residue, vol %		1.4	1.3	1.4	1.4	1.4
Loss, vol %		0.0	0.0	0.0	0.4	0.5
Haze rating @ 70 °F (21 ° C)	CPL-HAZE	1	1	1	1	1
Pour Point, °F (° C)	D97	-6 (-21)	-6 (-21)	-11 (-24)	-11 (-24)	-17 (-27)
Cloud Pont, °F (° C)	D2500	12.0 (-11)	10.0 (-12)	10.0 (-12)	9.0 (-13)	9.0 (-13)
Flash Point (Method A), °F (° C)	D93	150 (66)	146 (63)	150 (66)	150 (66)	152 (67)
Cetane Index	D976	45.4	45.0	43.5	41.4	37.0
ASTM Color	D1500	1.5	1.5	<2.0	<2.0	<2.0
Viscosity @ 122 °F (50 ° C), cSt (b)	D445	2.093	2.083	2.033	1.928	1.804
Corrosion 3 h @ 122 °F (50 ° C)	D130	1a	1a	a	1a	1a

(a) A= 0%, B= 5%, C=10%, D=15%, E=20% ethylphenyl ether distillate.

(b) Note: ASTM specification is provided in Table 14 for viscosity at 40°C (104°F).

TABLE 14

**STANDARD SPECIFICATIONS FOR GRADE 1-D DIESEL FUEL OIL
FOR ENGINE SERVICE REQUIRING FREQUENT SPEED
AND LOAD CHANGES; D 975-81**

Test	Method	Requirement
Cetane Number	D 613	40 minimum
Distillation	D 86	
90 % Recovery @ °C [@ °F]		288 maximum [550]
Sulfur Content, wt %	D 129	0.50 maximum
Ash, wt %	D 482	0.01 maximum
Cloud Pont, °C [°F]	D 2500	maximum (a)
Flash Point (Method A), °C [°F]	D 93	38 minimum [100 °F]
Pour Point	D 975 (b)	-6 °C maximum [20 °F]
Viscosity @ 40 °C [104 °F], cSt	D 445	1.3 minimum 2.4 maximum
Corrosion 3 h @ 50°C [122 °F]	D 130	No. 3 maximum

(a) Must be specified as 6 °C above the tenth percentile minimum ambient temperature for the area in which the fuel will be used. For example, in the case of western Pennsylvania, this value for the coldest month (January) is 6°C; thus, the cloud point is 12 °C [53 °F]. The fuel specification for western PA is ≤ 12 °C (53 °F).

(b) Value obtained by ASTM D975 -1955.⁶

TABLE 15

STRUCTURE OPTIMIZATION CONSTRAINTS AND INITIAL VECTOR

Structure Parameter	University of Delaware (a)		CONSOL		Current Starting Vector	Structure Parameter Values	
	Original Lower Bound	Original Upper Bound	Current Lower Bound	Current Upper Bound		Minimum of 15 resid samples	Maximum of 15 resid samples
1 nrmean	3.050	6.000	3.050	6.000	4.500	3.664	4.570
2 nrstdev	0.500	4.000	0.750	4.000	2.000	0.743	0.930
3 nscmean	0.250	8.000	0.250	15.000	7.500	1.037	13.687
4 nslmean	1.050	7.000	1.050	8.000	4.500	1.168	7.996
5 rdpmean	1.050	5.200	1.050	8.000	4.500	1.163	6.670
6 rarmean	2.100	8.000	2.100	15.000	7.500	3.532	14.989
7 rnrmean	0.250	4.000	0.250	4.000	2.000	0.791	2.393
8 rscmean	0.250	5.000	0.250	6.000	3.000	0.539	2.181
9 rslmean	1.050	5.000	1.050	6.000	3.500	1.130	5.996
10 adpmean	2.050	8.000	2.100	15.000	7.500	2.650	14.633
11 aarmean	1.100	8.000	2.100	15.000	7.500	4.979	14.920
12 anrmean	0.240	5.000	0.100	4.000	2.000	0.150	1.096
13 ascmean	0.250	6.000	0.250	6.000	3.000	0.297	3.109
14 aslmean	1.050	5.000	1.050	8.000	4.500	1.354	7.992
15 pdpmean	2.050	9.000	2.100	15.000	7.500	4.982	13.696
16 parmean	1.250	10.000	2.100	15.000	7.500	2.921	14.954
17 pnrmean	0.250	6.000	0.100	6.000	3.000	0.211	1.497
18 pscmean	0.250	6.000	0.250	8.000	4.000	0.262	7.298
19 pslmean	1.050	5.000	1.050	8.000	4.500	1.082	7.932
20 fiso	0.000	1.000	0.001	0.990	0.500	0.001	0.878
21 fiss	0.000	1.000	0.001	0.990	0.500	0.001	0.421
22 fism	0.000	1.000	0.001	0.990	0.500	0.001	0.848
23 fisb	0.000	1.000	0.001	0.990	0.500	0.001	0.990
24 frorings	0.000	1.000	0.001	0.990	0.500	0.001	0.957
25 frsrings	0.000	1.000	0.001	0.990	0.500	0.003	0.064
26 frnrings	0.000	1.000	0.001	0.990	0.500	0.080	0.447
27 frhcrings	0.000	1.000	0.001	0.990	0.500	0.414	0.983
28 frinrings	0.000	1.000	0.001	0.990	0.500	0.408	0.990
29 frphh	0.000	1.000	0.001	0.990	0.500	0.074	0.311
30 f1rar	0.000	1.000	0.001	0.990	0.500	0.252	0.820
31 rdpstdev	0.500	4.000	0.750	8.000	4.000	0.263	7.763
32 adpstdev	0.500	4.000	0.750	6.000	3.000	0.882	5.714
33 pdpstdev	0.500	4.000	0.750	8.000	4.000	1.083	7.360

(a) One of 15 lower and upper bound sets used for one of 15 resid

TABLE 16

**EXPERIMENTALLY DETERMINED vs PREDICTED STRUCTURAL CHARACTERISTICS
AND GOODNESS OF FIT (χ^2)**

	Resid A			Resid B			Resid C			Resid D		
Characteristic	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2
Molecular Weight, Da	487.5	510.1	0.22	543.4	581.7	0.50	474.1	482.7	0.03	393.8	378.0	0.16
<u>Elemental, wt %</u>												
Hydrogen	6.10	6.47	5.33	6.49	6.81	4.00	6.74	7.02	3.01	7.98	7.92	0.13
Carbon	90.11	89.26	1.75	89.79	89.01	1.48	90.54	89.87	1.11	87.66	87.84	0.08
Sulfur	0.10	0.09	0.01	0.63	0.61	0.06	0.39	0.41	0.03	0.27	0.27	0.00
Nitrogen	1.21	1.24	0.06	1.06	1.06	0.00	0.91	0.92	0.01	0.96	0.94	0.04
Oxygen	2.48	2.94	0.09	2.03	2.52	0.11	1.42	1.79	0.06	3.13	3.03	0.00
<u>SARA, wt %</u>												
Saturates	2.2	3.7	0.16	2.3	3.0	0.07	2.7	2.8	0.24	6.3	7.2	0.04
Resins	49.6	47.8		49.1	48.6		59.5	57.2		56.0	56.0	
Asphaltenes	41.0	41.4		33.5	34.3		27.7	29.4		28.8	28.0	
Preasphaltenes	7.2	7.1		15.1	14.1		10.1	10.7		8.9	8.8	
<u>Proton NMR, %</u>												
Uncond Arom	7.6	8.6	0.24	2.6	2.8	0.01	5.4	7.0	0.63	3.8	3.3	0.07
Cond Arom	31.3	34.6	2.72	30.7	33.5	1.92	26.1	29.5	2.88	25.4	24.5	0.21
Alkyl Alpha	9.5	8.9	0.10	10.2	9.8	0.03	9.4	9.2	0.01	9.6	9.4	0.01
Cyclic Alpha	18.8	17.9	0.19	20.9	20.8	0.00	18.9	17.6	0.41	19.7	19.3	0.04
Alkyl Beta	11.9	10.3	0.61	13.4	12.0	0.52	14.6	12.9	0.72	16.8	16.9	0.01
Cyclic Beta	12.9	12.6	0.03	13.8	13.5	0.03	14.8	14.2	0.09	15.3	16.7	0.51
Gamma	8.1	7.1	0.23	8.4	7.7	0.13	10.8	9.6	0.34	9.3	9.9	0.09
Phenolic OH, meq/g	0.80	0.80	0.01	0.92	0.93	0.40	0.69	0.70	0.41	0.78	0.80	0.79
Total χ^2			11.75			9.26			9.99			2.18

TABLE 16 (Continued)

**EXPERIMENTALLY DETERMINED vs PREDICTED STRUCTURAL CHARACTERISTICS
AND GOODNESS OF FIT (χ^2)**

	Resid E			Resid F			Resid G			Resid H		
Characteristic	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2
Molecular Weight, Da	611.6	627.3	0.07	452.5	550.3	4.67	543.1	587.1	0.66	515.2	532.2	0.11
<u>Elemental, wt %</u>												
Hydrogen	7.37	7.53	1.04	6.68	7.28	14.14	7.22	7.45	2.12	6.85	6.98	0.63
Carbon	88.59	88.41	0.08	88.00	86.91	2.92	87.35	87.16	0.08	88.38	88.24	0.05
Sulfur	0.11	0.10	0.00	0.12	0.13	0.01	0.10	0.08	0.03	0.12	0.12	0.00
Nitrogen	0.89	0.89	0.00	1.00	0.97	0.07	1.04	1.07	0.08	1.04	1.02	0.05
Oxygen	3.04	3.06	0.00	4.20	4.71	0.12	4.29	4.23	0.00	3.61	3.64	0.00
<u>SARA, wt %</u>												
Saturates	6.9	7.6	0.03	10.9	13.7	0.32	9.0	11.7	0.28	6.3	6.7	0.08
Resins	49.4	48.7		49.1	48.3		47.8	46.5		51.7	50.3	
Asphaltenes	32.8	32.4		30.7	30.6		34.5	34.0		33.3	33.7	
Preasphaltenes	10.9	11.2		9.3	7.5		8.7	7.7		8.7	9.3	
<u>Proton NMR, %</u>												
Uncond Arom	3.7	4.1	0.04	3.9	4.8	0.22	3.7	3.3	0.04	3.8	4.2	0.04
Cond Arom	22.3	23.8	0.54	20.4	25.9	7.45	22.2	24.0	0.84	29.5	30.3	0.17
Alkyl Alpha	9.3	8.8	0.05	9.0	7.1	0.93	9.4	8.8	0.09	4.5	4.1	0.03
Cyclic Alpha	19.2	18.2	0.23	18.6	15.6	2.32	18.1	16.6	0.60	21.5	19.9	0.68
Alkyl Beta	20.9	20.5	0.04	21.9	20.3	0.60	21.3	21.0	0.03	17.0	16.2	0.16
Cyclic Beta	14.6	15.0	0.03	15.3	17.4	1.06	15.2	16.3	0.28	14.3	16.0	0.69
Gamma	10.0	9.6	0.04	10.8	9.0	0.82	10.1	10.1	0.00	9.3	9.3	0.00
Phenolic OH, meq/g	0.82	0.81	0.18	1.25	1.25	0.01	0.85	0.83	1.09	0.69	0.70	0.28
Total χ^2			2.39			35.66			6.22			2.98

TABLE 16 (Continued)

**EXPERIMENTALLY DETERMINED vs PREDICTED STRUCTURAL CHARACTERISTICS
AND GOODNESS OF FIT (χ^2)**

	Resid I			Resid J			Resid K			Resid L		
Characteristic	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2
Molecular Weight, Da	477.6	476.3	0.00	520.9	534.8	0.07	446.2	521.9	2.88	539.9	574.3	0.41
<u>Elemental, wt %</u>												
Hydrogen	7.32	7.37	0.08	6.80	7.10	3.44	6.61	7.21	14.16	6.46	6.81	4.91
Carbon	87.77	87.73	0.00	89.80	89.45	0.31	88.65	87.20	5.11	88.89	88.29	0.89
Sulfur	0.34	0.34	0.00	0.41	0.41	0.00	0.11	0.11	0.00	0.10	0.11	0.01
Nitrogen	1.02	1.00	0.04	1.00	1.00	0.00	1.06	1.06	0.00	1.10	1.13	0.05
Oxygen	3.55	3.56	0.00	1.99	2.05	0.00	3.57	4.42	0.32	3.45	3.67	0.02
<u>SARA, wt %</u>												
Saturates	3.6	4.4	0.03	7.8	8.2	0.31	9.1	10.4	0.09	4.2	4.7	0.01
Resins	57.9	57.5		42.8	40.0		50.9	51.2		58.4	58.1	
Asphaltenes	28.2	28.0		38.6	39.2		26.6	26.0		28.0	27.7	
Preasphaltenes	10.3	10.1		10.8	12.5		13.4	12.4		9.4	9.4	
<u>Proton NMR, %</u>												
Uncond Arom	4.5	4.5	0.00	3.8	4.4	0.08	4.3	6.0	0.74	6.8	8.0	0.39
Cond Arom	25.9	25.7	0.01	27.8	29.8	1.02	20.3	25.9	7.97	27.2	29.8	1.67
Alkyl Alpha	9.6	9.5	0.00	9.6	9.1	0.07	9.4	8.3	0.29	8.8	8.8	0.00
Cyclic Alpha	19.9	19.5	0.05	21.2	19.9	0.44	17.2	15.0	1.18	18.3	17.2	0.28
Alkyl Beta	16.0	16.3	0.02	13.4	12.7	0.13	21.2	18.2	2.31	16.6	15.2	0.49
Cyclic Beta	14.7	15.0	0.02	15.5	16.0	0.06	15.3	16.2	0.22	13.6	13.2	0.05
Gamma	9.3	9.5	0.01	8.7	8.2	0.06	12.3	10.3	1.02	8.7	7.8	0.21
Phenolic OH, meq/g	0.92	0.93	0.23	0.70	0.72	0.83	0.95	0.93	1.04	0.69	0.70	0.44
Total χ^2			0.51			6.81			37.32			9.83

TABLE 16 (Continued)

**EXPERIMENTALLY DETERMINED vs PREDICTED STRUCTURAL CHARACTERISTICS
AND GOODNESS OF FIT (χ^2)**

	Resid M			Resid N			Resid O		
Characteristic	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2	Experimental	Predicted	χ^2
Molecular Weight, Da	444.5	470.9	0.35	384.8	434.8	1.69	395.7	457.7	8.23
<u>Elemental, wt %</u>									
Hydrogen	7.31	7.43	0.59	8.58	8.80	1.81	8.36	8.82	8.25
Carbon	87.59	87.51	0.02	89.29	89.14	0.05	89.06	88.63	0.44
Sulfur	0.52	0.51	0.02	0.32	0.30	0.04	0.21	0.21	0.00
Nitrogen	1.10	1.09	0.02	0.47	0.47	0.00	0.31	0.31	0.00
Oxygen	3.48	3.46	0.00	1.34	1.29	0.00	2.05	2.03	0.00
<u>SARA, wt %</u>									
Saturates	10.9	12.6	0.16	16.8	20.9	0.72	27.6	32.7	1.23
Resins	45.4	44.1		77.7	75.0		67.4	63.1	
Asphaltenes	31.5	32.1		5.0	3.7		4.5	3.8	
Preasphaltenes	12.2	11.3		0.5	0.4		0.5	0.4	
<u>Proton NMR, %</u>									
Uncond Arom	4.9	5.4	0.06	5.9	5.5	0.05	4.3	2.2	1.08
Cond Arom	24.5	25.0	0.07	14.7	17.1	1.48	14.5	19.5	6.30
Alkyl Alpha	9.6	8.4	0.37	9.6	8.7	0.21	8.0	6.8	0.36
Cyclic Alpha	21.1	18.7	1.46	16.3	12.9	2.84	14.5	10.0	5.13
Alkyl Beta	15.6	15.3	0.03	24.2	24.3	0.00	30.0	28.6	0.51
Cyclic Beta	15.2	17.9	1.86	16.1	18.1	1.01	15.1	19.6	4.95
Gamma	9.2	9.3	0.00	13.1	13.3	0.01	13.6	13.4	0.01
Phenolic OH, meq/g	0.88	0.89	0.08	0.50	0.50	0.00	0.22	0.22	0.00
Total χ^2			5.08			9.92			36.51

TABLE 17

**SUMMARY OF GOODNESS OF FIT OF
STRUCTURE MODEL PREDICTIONS**

Coal Resid Sample	Univ. of Delaware Chi-Square	CONSOL R&D Chi-Square
A	35.76	11.75
B	26.08	9.26
C	28.48	9.99
D	22.20	2.18
E	12.92	2.39
F	31.82	35.66
G	12.20	6.22
H	15.67	2.98
I	17.59	0.51
J	26.01	6.81
K	70.92	37.32
L	13.48	10.01
M	29.44	5.08
N	13.51	9.92
O	35.20	36.51

Figure 1. Simplified Schematic of HTI's Bench Unit Configured for Run PB-01 (227-90). Source: Reference 1.

HTI Run PB-01

Feed Slurry Composition

Figure 2. Feed Slurry Composition During HTI Run PB-01.

HTI Run PB-O1

Feed Slurry Proton Distribution

Figure 3. Hydrogen Distribution of the Soluble Portion of the Feed Slurry During HTI Run PB-01.

HTI Run PB-01

Phenolic -OH Concentration

Figure 4. Phenolic -OH Concentration of PFL and Separator Bottoms 454°C Distillates and Feed Slurry THF-Solubles During HTI Run PB-01.

HTI Run PB-01

Distillate Aromatic Hydrogen Content

Figure 5. Aromatic Hydrogen Content of PFL and Separator Bottoms 454°C- Distillates During HTI Run PB-01.

HTI Run PB-01

Distillate Solvent Quality

Figure 6. Donor Solvent Quality of PFL and Separator Bottoms 454°C Distillates During HTI Run PB-01.

HTI Run PB-01

Sep. Btms. Composition

Figure 7. Separator Bottoms Composition During HTI Run PB-01.

HTI Run PB-01

Sep. Btms. Proton Distribution

Figure 8. Hydrogen Distribution of the Soluble Portion of the Whole Separator Bottoms During HTI Run PB-01.

HTI Run PB-01

PFS Composition

Figure 9. Pressure-Filter Solids (PFS) Composition During HTI Run PB-01.

HTI Run PB-01

PFS Proton Distribution

Figure 10. Hydrogen Distribution of the Soluble Portion of the Whole Pressure-Filter Solids During HTI Run PB-01.

Figure 11. Extracted Phenols Before Second Extraction.

Figure 12. Extracted Phenols After Second Extraction.

Figure 13. Comparison of Ethers Before (Top) and After (Bottom) Distillation.

APPENDIX 1

SAMPLE REQUEST FROM NEDOL PILOT PLANT, KASHIMA, JAPAN

CONSOL Inc.
Research & Development
4000 Brownsville Road
Liberty, PA 15129-9566
412-854-6600
FAX: 412-854-6613
412-854-6568

January 6, 1998

Michael Baird
U.S. Department of Energy
Federal Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236-0940

Dear Mike:

As part of CONSOL's DOE contract "A Characterization and Evaluation of Coal Liquefaction Process Streams", samples from liquefaction facilities, such as HTI and the now-shuttered Wilsonville pilot plant, are acquired and analyzed. In a continuing effort to evaluate the progress being made in direct coal liquefaction, we would like to acquire samples from the Nippon Coal Oil Co. NEDOL Process. Your help in acquiring samples would be appreciated.

An evaluation of the NEDOL pilot plant process flow diagram resulted in identification of 24 sampling locations from which suites of samples would be desirable. (See attached flow diagram and table.) It would be desirable to obtain samples from steady-state or "lined-out" periods of the liquefaction tests. We would like to obtain samples from several steady-state conditions that differ in operating parameters, such that the significance of altering operating parameters can be evaluated. We understand that a high-rank and a low-rank coal are to be tested in the NEDOL Pilot Plant in 1998. Samples obtained from periods with similar operating conditions, but with two different feed coals also would be of considerable interest. We appreciate that not all the requested samples may be available, or available in the requested amounts.

CONSOL's analyses are supported by a thorough understanding of the process conditions under which the analyzed samples are produced. Therefore, in addition to the samples, we also request process conditions, process performance data, and material balance data associated with the production of the samples. This will be especially important if samples can be supplied that were produced under different operating conditions. If available, reports or publications documenting process upsets and/or exceptions from planned operating conditions would be useful for interpretation of the analytical data.

Thank you in advance for your help in acquiring both the samples and the associated process data. If there are any questions concerning this request, please contact Gary Robbins (412-854-6748), Dick Winschel (412-854-6683), or me.

Sincerely,

A handwritten signature in dark ink, appearing to read "S. D. Brandes", is written over a horizontal line.

S. D. Brandes
Sr. Research Engineer
/s/

cc: F. P. Burke
R. M. Statnick
R. A. Winschel
G. A. Robbins

B. Tomer - U.S.DOE/FETC-Morgantown
J. C. Winslow -U.S.DOE/FETC-Pittsburgh
E. Schmetz - U.S. DOE/HQ

**U. S. Department of Energy
Federal Energy Technology Center**

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

826 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

January 20, 1998

Mr. Sadao Wasaka
Mitsui SRC Development Co., LTD.
Technical Division
12-13, Nihonbashi-Muromachi 1-Chome
Chuo-Ku, Tokyo 103, JAPAN

Dear Sadao:

Greetings and Happy New Year! I bet you are happy to be back at your commercial company. I am happy that you will still be involved with the "Coal Liquefaction Project".

At the subcommittee for Coal Liquefaction last October, the U.S. asked if it would be possible to obtain samples from the 150 ton/day pilot plant. The Japanese delegation said it should be possible and that I should contact you.

CONSOL, Inc., one of our contractors, is analyzing samples from different liquefaction facilities to access the process being made in direct liquefaction. Samples from the NEDOL plant would certainly represent the current state-of-the-art in liquefaction technology. Any results that DOE would obtain would be shared with NEDO.

Enclosed are (a) a list of samples that would be of interest, and (b) a flow diagram showing the locations of the samples ("in Japanese"). We (DOE), with the assistance of President Clinton, will arrange for payment.

CONSOL (if possible) would like samples under the following conditions:

1. Samples from several steady-state conditions that differ in operating parameters.
2. Samples at similar operating conditions, but with two different coal feeds; a high rank coal and a low-rank coal.

Data supporting the above conditions, such as operating conditions, material balances, and overall conditions, such as recent upsets, etc. would be appreciated.

REPLY TO: Pittsburgh Office
Voice (412)892-4472

FAX (412)892-5917

baird@fetc.doe.gov

<http://www.fetc.doe.gov>

I will be happy to supply any additional information that you may need. My e-mail address is Baird@FETC.DOE.GOV.

Sincerely,

Michael J. Baird
Project Manager
Fuels Division

Attachments:

cc w attachments:
S. D. Brandes, CONSOL, Inc.
J.C. Winslow, FETC-Pittsburgh
E. Schmetz, U.S. DOE/HQ
B. Tomer, FETC-Morgantown

**SAMPLE REQUEST
FROM THE NIPPON OIL CO. NEDOL PROCESS**

Sample Number (a)	Sample	Requested Quantity, g
1	Catalyst	500-1000
2	Feed Coal	500-1000
3	Recycle Solvent	500-1000
4	Feed Slurry (before preheater)	500-1000
5	Feed Slurry (after preheater)	500-1000
6	First reactor-stage product (interstage)	250-500
7	Second reactor-stage product (interstage)	250-500
8	Third reactor-stage product	250-500
9	High-temperature separator overhead	250-500
10	High-temperature separator bottoms	500-1000
11	Medium-temperature separator overhead	250-500
12	Medium-temperature separator bottoms	500-1000
13	Low-temperature separator bottoms	500-1000
14	Oil/water separator bottoms	250-500
15	Atmospheric distillation tower bottoms	500-1000
16	Solvent feed tank to hydrotreater	250-500
17	Hydrotreater bottoms	250-500
18	High-temperature separator overhead (post hydrotreater)	250-500
19	High-temperature separator bottoms (post hydrotreater)	250-500
20	Low-temperature separator bottoms (post hydrotreater)	250-500
21	Liquefied naphtha	500-1000
22	Atmospheric gas oil	500-1000
23	Hydrogenated naphtha	500-1000
24	Liquefaction residue	500-1000

(a) Refer to attached flow diagram for sample locations.

パイロットプラントのプロセスフロー PILOT PLANT PROCESS FLOW

The NEDOL process consists of five major units: coal slurry preparation, liquefaction, distillation, solvent hydrogenation, and hydrogen production.

S = requested sample

NEDOLプロセスの心臓部は5つの主要設備、すなわち石炭
粉処理設備、液化反応設備、溶剤水素化装置、溶剤水素化装
置、水素製造設備から成り立っています。

水素製造設備
Hydrogen production

水素製造設備
Hydrogen production

水素製造設備
Hydrogen production

水素製造設備
Hydrogen production

水素製造設備
Hydrogen production

APPENDIX 2

DESCRIPTION OF THE SIMULATED ANNEALING OPTIMIZATION ALGORITHM

The “simulated annealing” algorithm is used by the Structure Optimization and Reaction Optimization programs. For the Structure Optimization program, the optimization problem is to minimize the difference between the analytical and theoretical results by varying the values of the 33 structure parameters.

Several simulated annealing parameters affect how the optimization progresses. To discuss these parameters, the following quantities must be defined:

N	Number of structure parameters to be optimized
X(N)	Vector of structure parameters (current iteration)
XP(N)	Vector of structure parameters (next iteration)
XOPT(N)	Vector of structure parameters (optimized)
LB(N)	Lower bounds vector
UB(N)	Upper bounds vector
VM(N)	Step length vector
F	Result of the function to be minimized (current iteration)
FP	Result of the function to be minimized (next iteration)
FOPT	Result of the function to be minimized (optimized)
T	Temperature
NS	Number of cycles until VM is adjusted
NT	Number of iterations before temperature reduction
RT	Temperature reduction factor
EPS	Error tolerance for termination
NEPS	Number of temperatures to examine
MAXEVAL	Maximum number of times to evaluate function

The values used for the simulated annealing parameters were those received from the University of Delaware:

VM(N)	= 0.5 for each N (initially)
T	= 5.0 (initially)
NS	= 20
NT	= 5
RT	= 0.7
EPS	= 1E-6
NEPS	= 4
MAXEVAL	= 1E5

The simulated annealing algorithm takes the initial vector, X(N), and calculates F. It then uses a random number to choose another point within the range $X(N) \pm VM(N)$ called XP(N). If XP(N) is within LB(N) and UB(N), it recalculates F as FP. If FP is less than F, XP(N) is kept. If FP is greater or equal to F, XP(N) may still be kept, depending on how “high” T is. In either case, if FP is the least so far, the new XP(N) is stored as XOPT(N) and the new FP as FOPT.

After NS*N iterations (20*33), VM(N) is adjusted so that approximately half of the previous NS*N attempts would have been accepted. For example, if most of the previous X(N)’s were accepted (> 60%), VM(N) is reduced. If few of the previous X(N)’s were accepted (< 40 %), VM(N) is lengthened.

After $NT \cdot NS \cdot N$ iterations ($5 \cdot 20 \cdot 33$), T is reduced by a factor of RT (0.7). That is,

$$T = T \cdot RT$$

Note that T never reaches 0. The FOPT for that temperature is stored as FSTAR. If neither of the termination criteria described below are met, $X(N)$ is set to $XOPT(N)$ and the algorithm continues.

The simulated annealing algorithm terminates when either of the following happens:

- 1) F is evaluated MAXEVAL times.
- 2) BOTH of the following occur:
 - 2A) At the end of a temperature cycle, the absolute difference between the last calculated F and the optimal F for that temperature is less than EPS ($1E-6$). That is,
$$ABS[F - FOPT] < EPS$$
 - 2B) For the last NEPS (4) temperatures, the absolute difference between the last calculated F and the optimal F 's for each of those temperatures is less than EPS. In our case,
$$\begin{aligned} ABS[F - FSTAR(1)] &< EPS \\ ABS[F - FSTAR(2)] &< EPS \\ ABS[F - FSTAR(3)] &< EPS \\ ABS[F - FSTAR(4)] &< EPS \end{aligned}$$

Because of the rather strict criteria used by the University of Delaware ($EPS = 1E-6$ and $NEPS = 4$), event 2 never happened. (As a matter of fact, event 2A rarely happens.) The Structure Optimizations completed when MAXEVAL ($1E5$) iterations completed.

It is anticipated that relaxing EPS and NEPS will allow the Structure Optimization to complete in less time with comparable results. After 100,000 iterations, F 's on the order of 10 are achieved. Therefore, an EPS around $1E-3$ should be sufficient. NEPS could be reduced to 1. These changes would allow the Structure Optimization program to complete in less than 100,000 iterations with only a slightly larger F value.