EXPLORATORY RESEARCH ON NOVEL COAI

Topical Progress Report

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ABSTRACT

The report presents the findings of work performed under DOE Contract No. DE-AC22 - 95PC95050, Task 3 - Flow Sheet Development. A novel direct coal liquefaction technology was investigated in a program being conducted by CONSOL Inc. with the University of Kentucky Center for Applied Energy Research and LDP Associates. The process concept explored consists of a first-stage coal dissolution step in which the coal is solubilized by hydride ion donation. In the second stage, the products are catalytically upgraded to refinery feedstocks. Integrated first-stage and solids-separation steps were used to prepare feedstocks for second-stage catalytic upgrading. An engineering and economic evaluation was conducted concurrently with experimental work throughout the program.

Parameters were established for a low-cost, low-severity first-stage reaction system. A hydride ion reagent system was used to effect high coal conversions of Black Thunder Mine Wyoming subbituminous coal. An integrated first-stage and filtration step was successfully demonstrated and used to produce product filtrates with extremely low solids contents. High filtration rates previously measured off-line in Task 2 studies were obtained in the integrated system. Residual conversions of first-stage products in the second stage were found to be consistently greater than for conventional two-stage liquefaction resid. In Task 5, elementally balanced material balance data were derived from experimental results and an integrated liquefaction system balance was completed. The economic analysis indicates that the production of refined product (gasoline) via this novel direct liquefaction technology is higher than the cost associated with conventional two-stage liquefaction technologies. However, several approaches to reduce costs for the conceptual commercial plant were recommended. These approaches will be investigated in the next task (Task 4) of the program.

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Section 1

EXECUTIVE SUMMARY

PROGRAM DESCRIPTION

A novel direct coal liquefaction technology is being investigated in a program being conducted by CONSOL Inc. under DOE Contract DE-AC22-95PC95050 in collaboration with the University of Kentucky Center for Applied Energy Research and LDP Associates. The novel concept consists of a new approach to coal liquefaction which avoids some of the inherent limitations of current high-temperature thermal liquefaction processes. The chemistry employed is based on hydride ion donation to solubilize coal at temperatures 350-400 °C significantly lower than those typically used in conventional coal liquefaction.

The work in this contract follows a Task structure. The first Task of the project was the production of a management plan.¹ Task 2 was an evaluation of reaction steps for the envisioned process. The process steps include low-temperature coal solubilization, filtration, and second-stage catalytic upgrading. Each reaction step was tested independently under Task 2. Task 2 findings were reported previously.² Under Task 3, partial integration of the process steps was experimentally tested. Also under Task 3, a second-stage catalytic reactor design was developed and tested. Task 5 is an engineering and economic study, which is being conducted concurrently with the other Tasks. Concurrent with Task 3, conceptual, fully integrated designs for the process were devised under Task 5 based on the findings of Tasks 2 and 3. Task 4 will consist of the experimental testing of the designs devised under Task 5 in a manner as fully integrated as possible. This report describes the findings of Task 3 and the corresponding engineering and economic evaluation carried out under Task 5.

There are three general objectives under Task 3. They are: 1) to use the findings of the experimental program conducted under Task 2 and the findings of the engineering and economic evaluation (Task 5) to refine and revise the original conceptual process design proposed at the onset of this program; 2) to experimentally integrate the low-temperature solubilization stage and the solids separation step and to investigate the combined system on a larger scale than was used in the screening studies under Task 2; and 3) to design and construct the catalytic upgrading stage in a scale to match that of the integrated first stage and solids separation units and to utilize the constructed equipment to provide data for the engineering and economic evaluation.

ACCOMPLISHMENTS

Accomplishments in Task 3 included the specification of a low-cost hydride ion reagent - promoted, high coal conversion, low-severity first-stage reaction system. The criteria used to screen parametric changes in the first stage was the maintenance of 90 wt % or higher coal conversion. Economic criteria then were applied to the conditions to determine the feasibility of further investigating the conditions in Task 4. The reaction system conditions specified were Black Thunder Mine subbituminous coal, Reilly Industries anthracene oil as solvent, hydride ion source "E", KOH catalyst, 375 °C, and 60 min. Another accomplishment is the execution of an integrated first-stage and filtration step. The product filtrates are extremely low in solids concentration and the filter cakes contain almost all the coal ash. Filtration rates are high and unwashed filter cakes contain about 50 wt % soluble material. Additionally, a large-scale second-stage catalytic upgrading reactor system was constructed and operated. The second-stage reactor system allows for continuous hydrogen gas addition and product gas recovery. Residue conversions for first-stage products were found to be consistently greater than for conventional two-stage liquefaction residues. In Task 5, elementally balanced material balances were derived from experimental results of first-stage and second-stage tests. An integrated liquefaction system (ILS) balance was completed. The balance that was derived is inclusive of support systems (such as off-line product upgrading). The economic analysis indicates that the production cost of refined product (gasoline) via this novel direct liquefaction technology is higher than the cost associated with conventional two-stage liquefaction technologies. However, reconfiguring of the conceptual commercial plant could result in a cost advantage over the conventional two-stage liquefaction process.

SUMMARY ASSESSMENT AND FORECAST

In Task 3, it was demonstrated that hydride ion reagent "E" (HI "E") could promote high coal conversions (>90 wt %) at relatively mild reaction conditions (60 min, 375 °C) in the presence of catalysts. A pre-filtration flash of first-stage products and in-line filtration of 300 °C⁺ products are routinely accomplished. Off-line distillation of the filtered material was used to produce a 566 °C⁺ material-rich feed to the second-stage. A second-stage reactor was designed, built, and employed to hydrotreat the distilled, filtered, first-stage materials. Single-pass residue conversions in the second-stage were demonstrated to be consistently higher for first-stage products than residue materials obtained from conventional two-stage liquefaction tests.

Concurrent with experimental testing, an economic and engineering evaluation of the individual stages and the overall process was performed. The process design was modified to reflect the use of HI "E".

Based on the economic evaluation of the HI "E" system, it is apparent that the costs associated with the first-stage reaction system must be significantly reduced. First-stage operating severity and cost can be reduced by:

- Reducing reactor residence time
- Minimizing the amount of excess CO shifted
- Reducing the steam to coal ratio
- Reducing the catalyst rate
- Lowering reactor pressure
- Lowering solvent to coal ratio
- Close-coupling the first- and second-stage reactor systems

The effect of reducing first-stage operating severity on coal deoxygenation via CO_2 removal is important and unknown. The advantage in efficiency of the process is the direct result of coal deoxygenation via CO_2 removal. Experimental work is needed to assess the impact of lower first-stage severity on coal deoxygenation via CO_2 removal.

Based on the results of the economic evaluation and the recommendations for reducing first-stage reaction system cost, an improved conceptual case was investigated. This conceptual paper study was intended to identify the potential improvements in the economics of the process and to serve as a guide for future experimental work. The economic evaluation of the improved case indicates that, versus the base case, a cost advantage can be achieved provided the performance assumptions are confirmed in future experimental work. Therefore, it is recommended that future experimental work investigate the effects of decreasing first-stage reaction-system severity on overall process performance and economics.

Task 4 testing will explore variables in both first and second stages that can lead to economic improvements in the process. The effects of solvent recycle, catalyst loading, solvent-to-coal ratio and first-stage system pressure will be investigated. The interstage filter will be altered to more closely approximate filtration conditions that would be encountered in a commercial

process. This would include the use of more robust filtration media, production of thicker filter cakes, and use of vacuum drying. As described above the first- and second-stage reactors may be close-coupled, removing the interstage filter to post second stage. In the second stage, process conditions will be altered to reduce gas yield while maintaining acceptable residual conversion levels. Lowered second-stage catalyst loading also will be tested.

Section 2

INTRODUCTION

FIRST-STAGE SOLUBILIZATION

The objective of the first-stage solubilization step is to explore a new, low-severity approach to direct coal liquefaction in which the primary coal dissolution step is effected by chemical rather than thermal cleavage of bonds in the coal. This novel coal liquefaction method is based on the discovery made by CONSOL R&D that certain reagents are capable of hydrolyzing to form hydride transfer agents that are very active for coal dissolution at temperatures in the range of 350-400 °C. These temperatures are significantly lower than typically used in coal liquefaction. Reaction at these low temperatures results in high conversion of the coal to a solubilized form, with little hydrocarbon gas make, and avoids the thermally induced retrograde reactions which are unavoidable in conventional thermal processes. In addition, for low-rank coals, a substantial portion of the oxygen in the coal is removed as CO₂ during the dissolution. It is believed that the higher selectivity to liquid products and rejection of oxygen as carbon dioxide will result in improved hydrogen utilization.

Although a detailed reaction mechanism has not been determined, the overall chemistry of the reaction is believed to involve hydrolysis reactions promoted by the hydride reagent. Hydrogen is supplied to the liquefying coal either from water introduced into the reaction as the inherent moisture in the coal or by water added to the reaction system. Therefore, there is no need for hydrogen to be introduced into the dissolution reactor. The species produced by hydrolysis of the hydride reagent then effects a hydride ion donation to the coal. The two reactions take place sequentially in the first-stage reactor. This necessitates operating in a temperature range where the rates of hydrolysis and hydride transfer are approximately the same. The range (350-400 °C) tested in Task 2 of this program is believed to be such a region.

The findings of Task 2 supported the concept of first-stage coal dissolution by hydride ion promoted reaction and prepared the way for Task 3. Low-severity reaction conditions (≤400 °C, ≤60 min) were determined for which high coal conversions (>90 wt %) to soluble products were obtained with five different coals of three different coal ranks. The effects on coal conversion of temperature, residence time, coal rank, hydride ion-to-coal ratio, solvent type, and total reactor charge size were determined. It was determined that some solvent in the first-stage reaction is necessary to achieve high coal conversion, although it does not have to be a hydrogen donating

solvent. The aromaticity of the solvent was found to be important for obtaining high coal conversions at the lowest severity reaction conditions.

Under Task 2, experiments were scaled up from 45 mL microautoclaves to a one-liter stirred autoclave. A hot transfer of first-stage products from the one-liter autoclave to a contiguous receiver vessel was completed. This allowed for the subsequent integration of a filtering unit with the first-stage reactor under Task 3 and for production of large quantities of product for subsequent second-stage catalytic upgrading in the 300 mL continuous stirred tank reactor (CSTR).

FILTRATION

The primary function of a solids separation stage in the coal liquefaction process is to ensure that solids are not present in the subsequent process streams where they may inhibit process performance or contaminate products. Economic considerations require that the rejected solids should not be diluted by liquid or pitch-like materials that can be upgraded to higher value products. Advantages of interstage filtration were discussed previously.² Briefly, they are that the overall size and cost of downstream processing equipment can be reduced, there can be significant reduction in erosion of reactor components, and an ash-free recycle around the second stage can be considered in which no second-stage catalyst would be rejected.

In Task 2, filtration of the first stage reactor products derived from a range of coals (bituminous, subbituminous, and lignite) and solvents (aliphatic and aromatic) and different hydride ion reagents, prepared under a range of conditions (temperature and residence time) were carried out at temperatures around 300 °C and at pressures of up to 350 kPa. Two principal criteria used for assessing the filter performance were met: 1) filtrates were produced which contained very low concentrations of mineral matter and insoluble organic matter (IOM) - the undissolved products from the dissolution stage, and 2) high filtration rates were invariably achieved regardless of the conditions used in the first stage. The high flow rates achieved under these conditions indicated that filtration of these materials would contribute only 40¢/bbl of crude oil equivalent in processing cost (i.e., capital and operating costs) when translated to a commercial-scale liquefaction plant. This cost is similar to solid/liquid separation costs in conventional direct liquefaction (e.g., ROSE-SR or filtration in an integrated two-stage liquefaction facility²). It was concluded at the conclusion of Task 2 that filtration is potentially a viable and economic means for removing undissolved solids from the first stage reaction products.

The majority of Task 2 work was carried out in small-scale equipment because first-stage products were limited in size having been produced in microautoclaves. Although microscale filtration gave adequate qualitative data, it was difficult to obtain quantitative data. At the end of Task 2 and in Task 3, larger solids separation equipment was employed and the filtration and reactor products from the first-stage one-liter autoclave were assessed.

FILTRATION THEORY

The relationship between filtration rate of a slurry and the parameters that influence it are described by Darcy's equation:²

$$\frac{1}{\text{Rate}(Q)} = \frac{dt}{dv} = \frac{\alpha \mu c v}{A^2 \Delta P} + \frac{\mu R}{A \Delta P} \quad (1)$$

where (dv/dt) is the volume flow rate at an applied pressure differential across the filter ΔP and α is the cake resistivity. This parameter, used to characterize the cake, will be dependent upon the nature and size distribution of the particles forming the cake and the way in which they pack together. The solids concentration (c) and the fluid viscosity (μ) are properties of the slurry, while the filter area (A) and the resistance of the filter membrane (R) are properties of the filter assembly. Following integration and insertion of boundary conditions:

$$\frac{t - t_o}{v - v_o} = \frac{\alpha \mu c (v + v_o)}{2 A^2 \Delta P} + \frac{\mu R}{A \Delta P} \quad (2)$$

Plotting $(t - t_o) / (v - v_o)$ against $(v + v_o)$ gives a straight line of slope, m , and intercept b . Thus:

$$\alpha = \frac{2 A^2 m \Delta P}{\mu c} \quad (3)$$

and:

$$R = \frac{b A \Delta P}{\mu} \quad (4)$$

Determination of the cake resistivity α and the fluid viscosity μ effectively define the filtration characteristics of the slurry. Filter cakes produced from coal digests have also been shown to be compressible, i.e., the cake resistivity increases with increasing pressure according to Equation 5.

$$\alpha = \alpha_0 \Delta P^n \quad (5)$$

where α_0 is a constant and n is the compressibility coefficient, normally falling in the range 0.3 to 0.7. Anthracite slurries show near ideal behavior with n close to zero, the particles packing in a consistent way regardless of the applied pressure³. A more detailed description of filtration theory and practice is given in the Task 2 topical report.²

CATALYTIC UPGRADING

The solids-free first-stage products were upgraded in the second-stage catalytic hydrotreater. The principal objectives are to maximize the conversion of the resid fraction in the feed (material boiling higher than 566 °C) to distillate, while limiting the yield of light hydrocarbon gas (C₁-C₃). The character of the feed to the hydroprocessor and the conditions used to upgrade it will principally govern the quality of the product. Some control over the quality of the products can be had by optimizing the amount of solvent that is stripped from the first-stage solids-free product prior to feeding the residue to the second stage.

During catalytic hydrotreating, hydrogen is transferred to the feed resulting in a reduction in its molecular weight and heteroatom removal. These reactions are promoted by catalysts, present either as a separate phase on a high surface area support, or dispersed throughout the reactants. Molybdenum is a preferred catalyst metal for upgrading coal derived products and can be conveniently added to the reactor in the form of an oil-soluble precursor. Two candidate precursors were identified from other studies: the catalyst precursor used in the Wilsonville pilot plant, Molyvan L, and molybdenum naphthenate, an effective catalyst precursor for petroleum resid upgrading.^{ref} A commercially available Ni/Mo supported catalyst (AKZO, A0-60) was used for comparison.

The primary objectives in Task 2 were to investigate the upgrading capability of the first-stage products, to determine the suitability of the dispersed catalysts, and to identify a set of reaction conditions that could be used in subsequent larger scale testing. All tests in Task 2 were carried

out in 50 mL microautoclaves. The performance of the catalysts was assessed by determining the conversion of a deashed resid (DAR) from the Wilsonville pilot plant. The variables investigated included catalyst type and concentration, pretreatment and run temperature, and residence time. It was shown that Molyvan L becomes active within the first few minutes of initiation of the reaction and that pretreatment to convert the Mo to the active sulfide form is not required. It also was shown that conversions of the DAR achieved with Molyvan L were comparable with those obtained with Mo naphthenate, and with a presulfided supported Ni/Mo catalyst with no pretreatment. However, a higher conversion was achieved when the supported Ni/Mo catalyst was used following a pretreatment.

It was shown that the first-stage product prepared from Glenharold Mine lignite was more reactive than the coal derived deashed resid from the Wilsonville pilot plant. Under severe reaction conditions (440 °C for 60 minutes), resid conversion averaged 72%. Under the same conditions, the DAR conversion averaged only 31% conversion. Reduced vehicle solvent concentration in the feed to the hydrotreater was found to give high resid conversion with good efficiency. Simulated recycle of the dispersed catalyst showed that recycled Mo (from Molyvan L), sulfided in the presence of a coal liquefaction resid, initially exhibited activity in recycle comparable to its activity in the first pass.

In Task 3, large scale tests were carried out in a 300 mL continuous stirred tank reactor (CSTR) with a continuous flow of hydrogen. This reactor system more closely resembles a commercial hydroprocessor than did the 50 mL microautoclaves. In Task 3, work continued using both dispersed and supported catalysts. Liquid and solid feedstocks and catalyst precursors were added batch-wise to the CSTR. H₂S was generated to sulfide the catalyst by decomposition of dimethyl disulfide (DMDS).

ENGINEERING AND ECONOMIC EVALUATION

Task 5 of this contract is the engineering and economic evaluation of the test results obtained in the program. A key element of this assessment is the comparison of this new process concept with state-of-the-art two-stage liquefaction (TSL) technology. The Wilsonville pilot plant operation with Black Thunder subbituminous coal was chosen as the basis for defining state-of-the-art TSL technology. During Wilsonville Runs 262 and 263, the pilot plant unit was operated in the so-called hybrid mode with dispersed iron and molybdenum catalysts used in the first reaction stage and a supported nickel-molybdenum catalyst used in the second stage ebullated bed

reactor. Material balance period 263J was chosen as the basis for developing a baseline conceptual commercial plant case against which the results of this program could be compared. The results of this comparison are provided in a confidential appendix (CA2) to this report.

Section 3

EXPERIMENTAL

REAGENTS

In Task 3, experimental testing initiated in Task 2 was continued and a set of reaction parameters was developed to meet the program goals of high coal conversion in a hydride ion promoted reaction under low-severity conditions. Evaluated in Task 3 were two feed coals, three solvents, and four first-stage catalysts. A single test made at conditions simulating the Wilsonville pilot plant preheaters utilized a Wilsonville distillate product from Run 263. Second-stage tests were all made with Molyvan L, a commercially available lubricant additive that contains ca. 6 wt % molybdenum. Dimethyl disulfide (DMDS) was used as an in-situ sulfiding agent for the Mo. Deashed resids obtained from Wilsonville Run 258A and Wilsonville Run 263J were used for baseline tests. Analyses of coals, resids, and solvents used in the program are given in Table 1.

COALS

Two coal were used in Task 3. They are a Glenharold Mine lignite from North Dakota and a Black Thunder Mine subbituminous coal from Wyoming (Table 1).

SOLVENTS

Four first-stage solvents were used in Task 3 (Table 1). Wilsonville pilot plant Run 263, end of run (EOR) distillate was used for one test (Run 13-LA). Lummus pilot plant pasting solvent from Run 3LCF7 was used in microautoclave tests and for one-liter autoclave tests. Two anthracene oils were used in Task 3. One of the anthracene oils was obtained from Kawasaki Steel Corporation; this oil is designated K-AO. The second anthracene oil was obtained from Reilly Industries; this oil is designated R-AO.

CATALYSTS

First stage

Four pure compounds (Na_2CO_3 , NaAlO_2 , NaOH , and KOH) were tested as first-stage catalysts in Task 3. All four chemicals were obtained from Fisher Scientific and used as supplied. NaOH , purchased as pellets, was crushed prior to use.

Second Stage

Molyvan L, a commercially available lubricating agent which has 6 wt % Mo content, was used as the second-stage catalyst throughout Task 3. Dimethyldisulfide (DMDS) was used as an in-situ sulfiding agent. Ultimate analyses for Molyvan L and DMDS are provided in Table 2.

SAMPLES FOR FILTRATION

In Task 3, experimental filtration tests were conducted on samples produced in the one-liter autoclave. Each sample was thoroughly mixed before subsamples of approximately 1 g were removed for determination of solubility in quinoline and tetrahydrofuran (THF). Another subsample was taken to determine boiling point distribution by simulated distillation (SimDist) using a dedicated gas chromatograph (gc). The remainder of the sample was either split into a number of parts for filtration studies on a common feedstock or, in some cases, the whole batch was filtered. With one or two exceptions, a 35 mm diameter filter unit was used in the filtration studies. However, it was necessary to employ a larger, 118 mm diameter filter unit in one test in which two batches of reactor product had been combined in order to expedite the production of feedstock for hydrotreating tests. Only in one test, where there was insufficient material for the larger filters, was it necessary to use the micro-filter used previously in Task 2.

EQUIPMENT

FIRST-STAGE REACTOR SYSTEM

The first-stage reactor system was described in the Task 2 Topical report for this contract.² The system is diagramed in Figure 2. The integration of an in-line filter with the reactor system is described below.

FILTRATION

35 mm Filter

The filter body consists of a 225 mm length of stainless steel tubing of 35 mm i.d. and capacity of 200 mL. Flanges at the lower end housed a 47 mm diameter filter screen and support grid. Filter elements consist of either a type GFA glass fiber paper supported on a perforated stainless steel plate (0.4 mm thick with 0.5 mm diameter holes, open area ~20%), or alternatively a Conidur element. Two grades of Conidur were tested, one with perforations of nominally 100 μm x 500 μm and with the feed side polished to provide a smooth surface to facilitate cake discharge. The other grade has perforations of nominally 60 μm x 400 μm diameter and, although rolled to

remove the major imperfections, it was not polished. These screens were made from 0.35 mm thick stainless steel sheet and had open areas of about 5%. A silicon rubber O-ring served both as main gasket and to seal the filter screen into the housing. The flanges were secured with three bolts and wing nuts, while the filtrate outlet was through a 4 mm bore ball valve containing a Teflon seal. The top of the unit was closed with a flanged lid containing a pressure port and a relief valve set to 0.7 MPa. This was held in place with a quick release clamp and sealed with a Teflon ring. The filter was heated in a 75 mm id x 127 mm o.d., 152 mm long cylindrical furnace. A variable transformer, manually adjusted, was used to control the temperature of the unit by monitoring the internal filter temperature measured with a sheathed thermocouple entering the vessel via the pressure port. The filter was pressurized and vented via a 6.3 mm o.d. tubing connection. Pressure was measured using a transducer with digital output.

118 mm Filter

The configuration of this filter was essentially the same as the 35 mm filter. The body of the filter is in the form of an open-ended domed cylinder, with three openings in the spherical surface. One contains a pressure relief valve, a second allows nitrogen pressure to be applied and a third, larger opening used as a fill port, is fitted with a screw cap and seal. The lower end is flanged to permit attachment with three capstan bolts to the base unit which contains the filter element, PTFE seal, and outlet valve. The body was heated by two close fitting 600 W band heaters and, the base was heated by a 800 W annular disk heater. The same type of filter elements were used as were installed in the 35 mm filter.

In-line Filter

Under Task 3, the first-stage solubilization and filtrations steps were integrated. A filter was designed to accept the entire one-liter autoclave contents in a single charge (Figure 1). All materials of construction are 316 stainless steel. The filter is cylindrical with a 92.1 mm internal diameter and 101.6 mm internal height. A Conidur screen is seated between the body and the lower removable flange. A glass fiber (Reeve Angel) filter is situated on top of the Conidur screen. In the lower flange, a single, centered outlet is finished with ½" NPT female thread to connect to a receiver vessel. The upper, fixed top contains four inlets: a pressure relief (rupture disk) assembly, a thermowell and pressure monitoring port, outlet to vacuum, and a fill port (finished with a ¼" NPT female thread to connect to the one-liter autoclave outlet). Maximum operating pressure is 4.5 MPa at 315 °C (650 psi at 600 °F). The filter was constructed by

Industrial Filter & Pump Mfg. Co., Cicero, IL. Integration of the filter in the first-stage reaction system is shown in Figure 2.

SECOND-STAGE CATALYTIC UPGRADING

Apparatus

Construction of the 300 mL continuously stirred tank reactor (CSTR) system was completed. The unit can operate with a high pressure, continuous flow of hydrogen and can accept charges up to 100 g. A process flow diagram of the experimental apparatus is shown in Figure 3a, 3b, and 3c. System maximum operating pressure was 17.2 MPa (2500 psig). The main pieces of equipment include:

- 300 mL CSTR (Pressure Products, Inc.) with thermal controller
- mass flow controller
 - Brooks mass flow controller (H_2 regulation at 1.7 sLpm maximum)
 - motor valve (model 5850TR)
 - flow computer (model 0151E)
- DMDS vaporizer (custom built)
- distillate accumulator (custom built)
- vent meter knock-out (Swagelok)
- back pressure regulation valves (Tescom Corporation and Nupro)
- vent meter (American Meter Co., model DTM-200A-3)
- rupture disk (2900 psig)

Line temperatures and pressure were monitored remotely with thermocouples and pressure transducers (Omega Engineering, Inc.) The reactor temperature was measured using the controller supplied with the CSTR.

The system capacity from the mass flow control valve to the back pressure regulator was determined by pressurizing the system with nitrogen to a predetermined value, and then venting through the dry gas meter. Calculations using the ideal gas law showed that the system volume was 1.113 L.

System Modifications

During shake-down tests, a number of problems were identified and remedial action was taken. The reactor heat-up rate was too slow. Operating temperature was not reached after 4½ hours. Fiberfrax insulation was used to encase the vessel, and two 400 W heat tapes were added. With full power output, a linear heating rate of 3.25 °C/min (20°C to 440 °C in 2 h, 9 min) was achieved. The stirrer shaft was lengthened to extend the stirrer blades to the bottom of the vessel for adequate agitation of the reactor contents. A faulty tachometer and a mass flow controller were replaced. The location of the gas sample point was changed to ensure representative samples were obtained.

PROCEDURES

FILTRATION

Off-Line Filtration

Samples were heated at atmospheric pressure to the required filtration temperature in glass flasks contained in a heating mantle. Distillate was collected in a receiver cooled with dry ice. Stirring during this procedure was effected using a PTFE coated magnetic stir bar and drive unit. Many of the samples contained some water and small quantities of other low boiling components. These occasionally caused problems with rapid foaming of the sample and consequent loss of material into the receiver. At the required filtration temperature, the sample was transferred manually to the pre-heated filter. The upper flange was closed, the filter was pressurized, and the outlet valve was opened. In some tests, a step-wise increase in nitrogen pressure was made during filtration in order to determine cake compressibility. Filtrate was collected in a flask on a top-loading pan balance. The weight of the filtrate was recorded as a function of time. After filtration was completed (flow of filtrate stopped and gas break through observed), the filter was depressurized, and the filter assembly was removed from the heater. When cool, the filter was disassembled, and the component parts were weighed. The filter cake thickness was measured, and its volume was estimated. In one test, which had to be terminated before completion due to the extremely low filtration rate, the filter was dismantled and the wet cake and supernatant liquor above it were sampled separately for characterization tests.

In-Line Filtration

The procedure for first-stage product collection with the filter installed is briefly described here. A detailed Standard Operating Procedure is on record at CONSOL R&D, Library, PA. After the

flash of low-boiling reactor contents into receiver S-1 at 250 °C, and product gas collection, the product remaining in the reactor is transferred by the pressure differential between the autoclave and the filter unit and gravity to the stainless steel, six-inch diameter filter (F-1) by opening the connecting valve (Figure 2). The filter is located directly under the one-liter stirred autoclave (A-1). Located directly under the filter is a 3.8 L (one-gallon) receiver (R-1). The connecting valve between the filter and R-1 is opened. The product contained in F-1 then is filtered through a glass fiber filter supported by a Conidur screen with 60 µm apertures into R-1. Drying of the filter cake is accomplished by blowing several times a charge of low pressure (0.2 - 0.3 MPa) nitrogen through the cake. A glass condenser is used to collect condensable products in the vented nitrogen stream. The recovered cakes are dry and approximately 0.5 cm thick.

SECOND-STAGE CATALYTIC UPGRADING

The procedure for hydrotreating in microautoclaves was provided previously.² The procedure for hydrotreating tests in the 300 mL CSTR is provided here. After charging the reactants to the CSTR, the autoclave is closed using 45 ft-lb torque on the hex-head nuts. The system is purged with nitrogen by pressurizing to 1.0 MPa (150 psig) and twice to 1.7 MPa (250 psig), venting after each pressurization. The reactor is purged with 1.7 MPa hydrogen, vented, and high-pressure leak tested with H₂ at 10.3 MPa (1500 psig). After system pressure integrity is verified, the mass flow controller (MFC) is calibrated in the "flow rate display" mode at 1.7 sLpm with a bubble flow meter (hydrogen pressure = 19.0 MPa (2750 psig)). Gas calculations are performed after correcting volumes to standard conditions at 0 °C and 14.7 psia. A meter calibration factor is calculated as shown in Equation 6.

$$\text{MeterFactor} = \frac{\text{Actual Measured Rate, sLpm}}{\text{MFC Display, sLpm}} \quad (6)$$

MFC meter factors have ranged from 1.08 to 1.14. Subsequently, the meter is calibrated using the mass flow controller in the "flow totalizer" mode by allowing the system to depressurize to 1.4 MPa (200 psig), then to repressurize to the start pressure and temperature with the MFC. The system temperature and pressure, as well as the meter temperature and pressure, are noted during this test. A meter factor is then calculated for the meter using the mass flow controller corrected total, as shown in Equation 7.

$$\text{MeterFactor} = \frac{\text{Corrected (with meter factor) Repressure Volume, sL}}{\text{Corrected (flowing T,P) Metered Volume, sL}} \quad (7)$$

Calculated factors ranged from 0.98 to 1.03.

Following the meter tests, the reactor is vented to atmospheric pressure. Repressurizing begins at a rate of 1.7 sLpm H₂ up to a pressure of 6.9 MPa (1000 psig), where the gas flow rate is reduced to 0.2 sLpm. At that time, the reactor temperature program is started, the system heat tapes are energized, and the H₂ flow is diverted through the DMDS vaporizer. Data are collected at ten-minute intervals. The stirrer is started when the feedstock in the autoclave is fluid. A strobe tachometer was used to measure the stirring rate of the air-motor driven stirrer. It was found to be 497 rpm unloaded at 0.41 MPa (60 psig) initial motor air pressure (0.36 MPa (52 psig) flowing), and estimated to be 365 rpm with a viscous load attached. The amount of H₂S present in the gas feed is controlled by varying the vaporizer temperature between 90 and 110 °C. The reactor heats to 440 °C in about 140 min. At that time, gas is allowed to begin exiting the system, and the designated run time is begun. Pressure in the reactor is controlled manually from 16.2 to 16.9 MPa (2350 to 2450 psig) using a needle valve on a vent line.

During tests, three gas samples are collected in 10 L acrylic gas sample pistons located upstream of the system pressure regulator. Initially, a 5L sample is collected from the sample points over the first ten minutes of reaction. The second gas sample is a composite of 1 L samples taken every ten minutes over the remainder of the run. The third sample is collected after the system is cool. This comprises 0.5 L of gas collected at 2 MPa (300 psig) intervals until the system is 10 psig. The total gas collected is 3.5 L. Two additional samples are collected in 45 mL stainless steel gas sample bombs as back-up.

To shutdown the reactor system, all heating power is disconnected, reactor insulation is removed, the vent line is closed, and the inlet H₂ line is closed. An internal water-cooled coil is used to cool the reactor to ambient conditions. The gas supply is switched to N₂, and 8 L N₂ are swept through the system before the reactor is opened.

PRODUCT WORK-UP

Filter cakes

The amount of material insoluble in quinoline and THF was determined for each filter cake. The filter cake is crushed and either a 1 g representative sample or the whole sample, if less than 1 g, is mixed with 20 mL of THF. The THF mixture is continuously stirred for about one hour at a temperature of about 30 °C. The slurry then is vacuum filtered through a pre-weighed glass fiber paper, washed with more THF, and dried in an oven at 70 °C. In some cases, the filter cake or THF insolubles from the filter cake were analyzed for ash and sulfur contents.

Filtrates

Selected filtrates were analyzed for THF solubility and ash content. If possible, the viscosity was measured using a Brookfield LVT viscometer with Thermosel unit over a temperature range of typically 100-300 °C. Measurement of viscosity at values of less than about 30 mPa·s are liable to error with this instrument, this being the lower limit of its range. However, at high temperatures many filtrates have viscosities lower than this value and in these cases the determination was made by extrapolation using known relationships between viscosity and temperature. These can only be used with any confidence over small temperature ranges. Likewise, where samples are inhomogeneous, measurements can be made with accuracy only at a temperature where all the extract is in solution and before evaporation of light components in the solvent becomes a factor. This only allows a narrow temperature band where viscosity measurements can be made.

The softening points of distillation residues were determined using either a Mettler FP5 instrument or by estimation from visual observation using a hot plate. This technique, in which a thermocouple was used to agitate the sample on a heated surface has proven reliable. The softening point of a fluid is the temperature at which its viscosity is approximately 10^6 mPa·s. The viscosity at other temperatures can be estimated from this value and used with caution. There is no substitute for the measurement of viscosity at the filter operating temperature. Any error in the prediction of the viscosity from measurements made under non-ideal conditions will have a proportionate and opposite effect upon the determination of the cake resistivity, α , particularly for thick filter cakes when the resistance of the medium becomes relatively insignificant. Hence, calculation of filtration rates for scaling purposes will not be invalidated since from equation 1:

$$rate = \frac{constant}{\alpha \mu} \quad (8)$$

The boiling point distribution of selected samples was determined by simulated distillation (this technique was described previously²).

In-line filter

The contents of S-1, R-1, and the filter cake are removed from the respective vessels. A wash solvent (typically THF) is used to clean the vessels and recover all remaining material. The washings are dried of THF and checked by ¹H-NMR for residual THF before combining with the bulk of the respective product. The filter cakes and filtrates are analyzed for soluble content and ash content (see above). The flashed material, usually a water/oil emulsion, is allowed to stand in a separatory funnel until the emulsion breaks (usually after several hours); the layers are separated and the weight of each fraction is determined. The oil layer is analyzed by GC/MS. Elemental analyses are obtained for all product fractions.

Second-Stage Feedstock Preparation

In order to prepare feedstock for second-stage tests, first-stage filtrate samples were vacuum distilled to concentrate the 566 °C⁺ coal extract content. Conditions of the filtrate distillations are given in Table 3. Filtrates were distilled under vacuum to produce predominately >566 °C residues for microautoclave and CSTR tests. The filtrates from Runs 23-LA, 23a-LA and 23c-LA were first composited and the combined filtrate was distilled. The distillation of the composited sample was carried out under vacuum and was cut to an atmospheric equivalent of 454 °C (850 °F). The cut temperature had previously been found to give a high yield of >566 °C without submitting the residue to unnecessary severe conditions in the still. The products collected were in the proportions, 74.7% <566 °C distillate and 25.3% >566 °C residue. Analysis of the distillate by simulated distillation gave 100% <566 °C, and, of the residue gave 6% <566 °C. The softening point of the residue was measured at 290 °C, which would make it difficult to handle in a continuous process. Runs 23d-LA, 23f-LA and 23g-LA were distilled to produce 70% distillate and 30% residue to provide residues with softening points of <200 °C. Each first-stage product was distilled separately. Lower softening points were achieved in 23d-LA and 23f-LA (both had a softening point of 165 °C). Mechanical problems controlling the vacuum resulted in 23g-LA

having a softening point of 255 °C. The resids of 23d-LA, 23f-LA, and 23g-LA were composited for a 300 mL CSTR second-stage test.

Second-Stage Reaction Products

Reaction products were recovered as four samples: a sample taken from the reactor without solvent (reactor dry scrape), a tetrahydrofuran wash of the reactor walls (reactor THF scrape), recovered material from the condenser (distillate accumulator dry scrape), and the THF washings from the condenser (distillate accumulator THF scrape). THF scrape material was distilled to 70 °C at 380 mm Hg vacuum to remove THF. Each product fraction was weighed. Except for the small distillate accumulator THF scrape sample, each product fraction and the feedstock were analyzed by proximate and ultimate analyses, and SimDist.

Gases were analyzed using a Carle gas chromatograph. The amount of DMDS remaining in the vaporizer was measured volumetrically. This volume was subtracted from the volume charged, and the difference converted to weight using a density of 1.06 g/mL.

Second-Stage Sample Nomenclature

A sample nomenclature system was enacted for second-stage feeds and products. Samples prepared in the 1-L autoclave first stage reactor are numbered consecutively and suffixed with 'LA'. If multiple tests are made at the same conditions, an alphanumeric system of labeling is used as follows: Run ##x - LA, where x = alphabetic. No series of tests made under Task 3 has more than ten tests. Consequently, 'o' is used as a place holder for the first test in a series. These samples then are distilled and, in some cases, combined to produce sufficient sample for second-stage upgrading. These combined samples were designated ##xyz. A suffix, indicating the consecutive run number for the test in which this feedstock was used followed by the type of the second-stage equipment used, is appended (ex., ##xyz-#, 300 CSTR for continuous stirred tank reactor or 50 MA for microautoclave). A designation of ##oxy indicates that the first test in the composite had no suffix.

Section 4

RESULTS AND DISCUSSION

SOLUBILIZATION

MICROAUTOCLAVE TESTS

Summary

In Task 2, hydride ion source "A" (HI "A") was determined to be effective for high coal conversions (>90 wt %) at low severity conditions (temperature = 350 °C, time = 60 min, pressure <25 MPa). However, at the conclusion of Task 2 it was determined that the cost of the hydride ion source "A" would be prohibitively high in commercial application. Several approaches to reducing costs were tested in Task 3. Lowered reagent to coal ratio and substitution of HI "A" with other hydride ion sources were investigated with different coals and several solvents. A substitute hydride ion reagent (HI "E") was identified as successfully maintaining high coal conversion and being economically attractive. Promotion of hydride ion from hydride ion source "E" requires the use of a catalyst. Several catalysts and catalyst loadings were tested in Task 3. One of the least costly of several effective catalysts (KOH) was chosen for continued use in first-stage testing and for the economic evaluation of the process. There is an economic advantage to the process if low-rank coal can be used. Because high coal conversions can be obtained with Black Thunder Mine subbituminous coal at low severity conditions (60 min, 375 °C), it was chosen to be the feedstock for the balance of the program. In Task 2, it was determined that coal conversion is dependent on solvent type at low severity conditions. Coal conversion increases at low severity conditions as the aromaticity of the solvent increases. First-stage microautoclave tests were made with lignite and subbituminous coal and several different solvents. An anthracene oil was found to be the most effective solvent with subbituminous coal. The commercially available oil was chosen for use for the balance of the program.

The culmination of Task 3 first-stage tests resulted in the selection of a reaction system on which to base the economic analysis. This system includes Black Thunder Mine subbituminous coal, hydride ion source HI "E", first-stage catalyst KOH, reaction time 60 min, reaction temperature 375 °C.

Results

Hydride ion sources

In Task 2, hydride ion source "A" was determined to be effective for high coal conversions (>90 wt %) at low severity conditions (temperature = 350 °C, time = 60 min, pressure <25 MPa). However, at the conclusion of Task 2 it was determined that the cost of the hydride ion source "A" would be prohibitively high for commercial application. A hydride ion reagent to dry coal ratio of 0.2 or lower was indicated for economically favorable use of this reagent. Tests were made at hydride ion source to coal ratio of 0.2 to determine if high coal conversions could be obtained. Tests used Black Thunder Mine subbituminous coal and an anthracene oil obtained from Kawasaki Steel Corporation (K-AO) (Table 4) and Glenharold Mine lignite, water, and K-AO (Table 5). Coal conversions for tests made at 350 °C (60 min), 400 °C (60 min), and 400 °C (120 min) at the reduced HI "A" loading were lower by at least 24 wt % (abs.) for both coals than when HI "A"/dry coal of 1 was used. Also, it was observed that long residence times at low HI "A" concentrations are detrimental, probably because retrogressive reactions occur due to lack of sufficient hydrogen in the system. It is apparent that coal conversions at ratios of 0.2 or lower are not effective in producing 90 wt % or better coal conversions. This line of investigation was discontinued.

A more economically favorable hydride ion source was sought. A series of tests was made to substitute some of the HI "A" reagent with other hydride ion sources. Methanol was chosen because it is a relatively inexpensive commodity chemical. The addition of methanol to the low- or high-concentration HI "A", Glenharold Mine lignite, K-AO systems did not improve coal conversion (Table 6).

The addition of another hydride ion source was further pursued with HI "D". Microautoclave tests were made with Glenharold Mine lignite, low HI "A" concentrations and HI "D" (Table 7). Tests were made in K-AO and Lummus pasting solvent. Coal conversions in the Lummus solvent (Run 180) were 21 wt % better than that obtained in the Kawasaki Steel Corporation anthracene oil (Run 181); however, coal conversion is substantially less than 90 wt %. Increasing the HI "D" concentrations in the low HI "A" system (Run 182) did not improve coal conversion. It is apparent that 90 wt % or better coal conversions are not maintained when just HI "D" is added to a low-concentration HI "A" reaction system.

The addition of first-stage catalysts to promote hydride ion formation was initiated in Run 183 (Table 8). Using conditions of Run 178, tests were made with Glenharold Mine lignite and NaAlO_2 as a catalyst. The NaAlO_2 was charged as a dry powder. In K-AO, coal conversion was lower with the addition of catalyst. Substitution of the K-AO with an anthracene oil obtained from Reilly Industries (R-AO) resulted in a large improvement in coal conversion. However, removal of the catalyst from the system (Run 203) showed that improvement in coal conversion was not a result of the catalyst, but of the change in solvent (see Solvent Type, below).

Microautoclave tests were made with Black Thunder Mine subbituminous coal at 350 °C, 60 min using HI "D"/ NaAlO_2 and HI "D"/ NaAlO_2 /HI "A" (Table 9). Dry (Run 187) and wet (Run 188) addition of NaAlO_2 to the HI "D" system resulted in the same coal conversion (ca. 80 wt %). The addition of more catalyst (Run 189a) did not improve coal conversion. The addition of HI "A" to the HI "D"/ NaAlO_2 reaction system in a HI "A"/dry coal ratio of 0.2 (Run 190) did not improve coal conversion over that obtained with the HI "D"/ NaAlO_2 system. Higher HI "D" to dry coal ratios were tested in Runs 192 and 193. Coal conversion was not further improved. Increasing the reaction temperature from 350 °C to 375 °C resulted in ca. 5 wt % (abs.) improvement in coal conversion (Table 10). Based on the improved coal conversion obtained when R-AO was used as the solvent with Glenharold Mine lignite (see above), a test was made with Black Thunder Mine subbituminous coal in R-AO with HI "D" (Run 194b). Coal conversion of 90 wt % was achieved. Four first-stage catalysts were tested to promote coal conversion in the HI "D" system (see First-Stage Catalysts, below). At 375 °C, 60 min with R-AO and Na_2CO_3 or K_2CO_3 , conversion of Black Thunder Mine subbituminous coal did not equal or exceed 90.2 wt %. When NaAlO_2 or KOH were used in the HI "D" system, coal conversions of 90 wt % could be achieved (Table 11). However, cost estimates for the use of HI "D" approached those of HI "A". Thus, another hydride ion source was investigated.

Microautoclave tests made with HI "E" and several different catalysts gave coal conversions higher or equivalent to those obtained with HI "D" at 375 °C (Table 12). The hydride ion source HI "E" is less costly than source HI "D". It was decided to continue Task 3 investigations with HI "E" and continue tests at 375 °C.

First-stage Catalyst

Microautoclave tests were performed using several different candidate catalysts (Table 11). The catalysts are NaOH, KOH, K_2CO_3 , and Na_2CO_3 . Test conditions used were: 375 °C, 60 min,

HI "D" or HI "E", and 500 mmol/kg dry coal catalyst. All tests were made with Black Thunder Mine coal and R-AO. Coal conversions obtained are 90 wt % $\pm$ 2 wt % with KOH and Na₂CO₃. With NaOH, coal conversion was about 75 wt %; with K₂CO₃, conversion was about 84%.

Microautoclave tests were made to determine the least amount of first-stage catalyst Na₂CO₃ necessary to maintain good coal conversions (Table 12). A baseline test (no catalyst, Run 233) also was made which confirmed earlier results (Run 226a). Coal conversion with no catalyst is ca. 83 wt %. Coal conversions with 850, 250, and 165 mmol/kg dry coal are all about 90 wt %. Of the catalysts tested, Na₂CO₃ was less costly than KOH. However, less KOH (500 mmol/kg dry coal) promoted higher coal conversions of Black Thunder Mine coal in the first-stage reaction system than Na₂CO₃ (800 mmol/kg dry coal). In addition, the use of Na₂CO₃ in large-scale (1-L autoclave) tests resulted in filtration difficulties (see below). The least amount of KOH required as a first-stage catalyst was investigated (Table 12). Catalyst loadings of 500 to 45 mmol/kg dry coal were used. Coal conversions are all within 2 wt % (abs.) of 90 wt %. Use of the reduced KOH loading substantially affects cost (see Economic Analysis, below). The 90 wt % or better coal conversions obtained with KOH at low catalyst loading (and because it is one of the least costly catalysts investigated) led to its choice as the first-stage catalyst on which to base an economic evaluation of the process.

Solvent Type

In tests performed under Task 2, an influence of solvent composition on coal conversion was observed.² It was concluded that the solvents with a higher aromatic content were better solvents for the first-stage coal conversion process. A supposition was made and presented that the more aromatic the solvent, the better would be its ability to solubilize the coal dissolution products. Thus, it would influence the reaction path of the first-stage reactions. Under Task 3, microautoclave tests were continued using aromatic anthracene oils as solvents. The anthracene oils used were distilled to have boiling point distributions lower than 454 °C, which is the cut point used to produce resid from the filtered first-stage products for second-stage catalytic upgrading. High coal conversions were obtained with Kawasaki Steel Corporation anthracene oil (K-AO) and Reilly Industries anthracene oil (R-AO). However, in a series of microautoclave tests made with Black Thunder Mine subbituminous coal, conversions are always higher with the R-AO (Table 13). It also was observed that in tests made with Glenharold lignite, an improvement of greater than 20 wt % (abs.) is obtained in some tests (Table 8). The Reilly Industries anthracene oil, which is commercially obtainable, was selected for first-stage testing for Task 3 tests.

Material Balance Tests

Several microautoclave tests were made during Task 3 for which mass balances were obtained. The tests were made with Black Thunder Mine subbituminous coal under a number of different conditions (Table 14). Test data were used in preliminary economic evaluations of the process (see Task 5, below).

ONE-LITER AUTOCLAVE TESTS

During Task 3, 23 successful one-liter autoclave tests were made to demonstrate the integration of a filter with the first-stage reaction, to produce sufficient sample for second-stage upgrading tests, and to produce data for the economic evaluation of the process. Each test requires one day to set up, one day to run and recover products, and a number of days for product analyses. Consequently, most one-liter autoclave tests were carried out only after conditions had been tested in the microautoclave scale and shown to have potential for economic improvement of the process. Several tests (Runs 11-LA, 12-LA, and 13-LA) were needed to produce data for economic evaluation and have no microautoclave test counter-parts. Runs 23-LA through 23h-LA were made at a single set of conditions, which formed the basis for the process economic and engineering evaluation. Multiple tests were made to provide sufficient product to composite for two second-stage catalytic upgrading tests (see below). Operating conditions for the tests are given in Table 15. A brief description of each test is presented here. Product analyses, including solubility data and distillation data, are presented in the following section of this report.

Test Descriptions

Run 10-LA

One-liter autoclave test Run 10-LA was the first test made in the program to include a flash of products from the reactor to a condensing vessel while the reactor was at elevated temperature and pressure. This test was made in preparation for integration of the filter with the one-liter autoclave. Filtration tests require a pressure let-down of the autoclave contents because of the pressure limitations of the small-scale filter. The test was made with Glenharold Mine lignite, Lummus pasting solvent and HI "A". At the conclusion of the one hour residence time, the reactor contents were allowed to cool to 300 °C and then flashed into Vessel S-1 (Figure 2). System pressure at the time of the flash was 9.6 MPa. The integrity of the test was questionable because operating pressure was low (approximately half of 20 MPa expected). The mass balance for the test was only ca. 85%. The flashed aqueous fraction was found to contain about 20 wt % of the feed HI "A". This is much less than was anticipated. It is presumed that there was

a system leak at the start of the run in which some of the HI "A" reagent was lost. This is confirmed by the low coal conversion.

Run 11-LA

One-liter autoclave test Run 11-LA tested anthracene oil as solvent and incorporated a flash of products at 300 °C. Glenharold Mine lignite and HI "A" were used. Solvent/dry coal = 1.5. Reaction temperature was 350 °C and reaction time was 60 min. System pressure was 21.9 MPa at temperature. The bulk of the product was used for off-line filtration and catalytic upgrading tests. The mass balance was 93.0% and coal conversion based on THF insolubles was ca. 91 wt %.

Run 12-LA

One-liter autoclave test Run 12-LA was made to simulate the SRC-type process. Glenharold Mine lignite and Lummus pasting solvent were fed with no hydride ion source or hydrogen. The test was made at 410 °C for 60 min. Solvent/dry coal ratio = 2. A flash of low boiling material was accomplished at 300 °C. Mass balance was 98.2%. Coal conversion based on THF insolubles was ca. 90 wt %.

Run 13-LA

Run 13-LA simulated the conditions of the Wilsonville pilot plant preheater. Glenharold Mine lignite, Wilsonville Run 263 EOR, V1074 488 °C⁻ distillate, H₂ (1050 psig cold) were fed. Solvent/dry coal ratio=1.5. The test was made at 410 °C for 15 min. The mass balance was 95.5% and coal conversion based on THF insolubles was ca. 75 wt %.

Run 14-LA

Results from microautoclave tests indicated that the Black Thunder Mine subbituminous coal/HI "A" system produced high coal conversions at mild conditions (375 °C, 60 min). Additionally, it was found that higher coal conversions could be obtained in aromatic solvents, such as Reilly Industries anthracene oil. It was decided to use the conditions of microautoclave test Run 195 to execute several one-liter autoclave tests to produce sufficient sample for subsequent second-stage upgrading tests. Run 14-LA used Black Thunder Mine subbituminous coal, Reilly Industries anthracene oil and HI "A". The solvent/dry coal ratio = 2.1. The test was made at 375 °C for 60 min. The product was flashed at 300 °C. The 300 °C⁺ product was filtered and distilled and used for second-stage upgrading tests.

Run 14b-LA

This successfully executed run was a replicate of Run 14-LA. The feed was Black Thunder Mine coal, Reilly Industries anthracene oil, and HI "A". Coal conversion determined from THF filtration of a grab sample and an ash balance was 88.4 wt %. The 300 °C⁺ sample was combined with Run 14-LA product and used for filtration and upgrading work.

Run 15-LA

At the time of one-liter autoclave tests Run 14-LA and 14b-LA, economic evaluation of the HI "A" system proved it to be too costly for commercial application. Microautoclave tests performed with HI "D" had shown that coal conversions could be maintained at low-severity conditions as long as catalyst was present in the reactor. Consequently, using the conditions of microautoclave test Run 194, the first one-liter autoclave test using HI "D" was made. Run 15-LA used Black Thunder Mine coal, Reilly Industries anthracene oil, NaAlO₂ catalyst (528 mmole/kg dry coal), and HI "D". Solvent/dry coal ratio = 2.6. The test included a post-run flash of products. Coal conversion was determined to be 83 wt % (approximately 6 wt % lower than the corresponding microautoclave test).

Run 15a-LA

Run 15a-LA was a replicate of Run 15-LA. Coal conversion for Run 15a-LA was determined from a five gram grab sample. Conversion was 83.6 wt %, the same as was obtained for Run 15-LA. The 300 °C⁺ sample was filtered and used for second-stage upgrading tests.

Run 16-LA

One-liter autoclave test Run 16-LA was the first test made in the one-liter reactor to use HI "E" as the hydride ion source. NaAlO₂ was used as the first-stage catalyst. The test was made at 375 °C for 60 min. Black Thunder Mine coal and Reilly Industries anthracene oil were used in a solvent/dry coal ratio = 2.6. In this test, the flash at 300 °C was followed by a second flash at 200 °C. The second flash brought the pressure in the 1-L autoclave to atmospheric. Upon opening the reactor, the cooling coil was found to be coated with a blonde crystalline material. This coating was combined with the remainder of the product in the autoclave. The THF washings were stripped of THF and combined with the product prior to taking a 5 g grab sample for pressure filtration to determine coal conversion (ca. 86 wt %). Difficulties were encountered when the 300 °C⁺ product sample was filtered (see below)

Run 17-LA

Run 17-LA was made with the same conditions as mass and elemental balance microautoclave test Run 227a (Table 11). The feed was HI "E" with Black Thunder Mine coal, Reilly Industries anthracene oil and NaAlO_2 . The HI "E"/dry coal ratio was more than double the ratio used in Runs 15-LA through 17-LA. Filtration of the 300 °C+ product sample, also filtered poorly (see below).

Run 18-LA

Run 18-LA also fed Black Thunder Mine coal and HI "E". The test was made at 350 °C for 60 min. Solvent/dry coal ratio = 1.8. Na_2CO_3 was chosen as the catalyst because it gave equivalent coal conversions in microautoclave tests to those obtained with NaAlO_2 (Table 11). It was hoped this would alleviate the filtration problems encountered in Runs 16-LA and 17-LA. This did not prove to be the case, and the products of Run 18-LA were virtually impossible to filter (see below).

Run 18a-LA

Run 18a-LA was a replicate of Run 18-LA. It was made to produce additional sample for filtration tests and analyses to determine the cause of the poor filtration properties found with Run 18-LA product. An 8 g aliquot of the product of Run 18a-LA was water-washed to attempt to remove the Na_2CO_3 catalyst. The water washings were analyzed for Na and found to contain about one-fifth the anticipated amount. The recovered product was distilled to remove water and subjected to filtration tests; this washed sample also had poor filterability.

Run 19-LA

This one-liter autoclave tests was executed to determine if the reason for the poor filtering performance encountered in Runs 16-LA through 18a-LA was a result of the Black Thunder coal solubilized in the HI "E"-promoted reaction. Run 19-LA was made with Black Thunder coal, Reilly Industries anthracene oil, and HI "E". No catalyst was used. The reactor loading was reduced by half from all previous tests, because products were intended for use only in filtration tests. The reactor contents, after flashing, were recovered and filtered off line. Filtration properties were better than those obtained in Runs 16-LA through 18-LA; however, coal conversion was poor. It was speculated that the half loading in the autoclave may be responsible for the poor conversion. The partial pressure of HI "E" reagent and steam pressure was lower than in

previous runs. Also, small charges may result in poor mixing and reduced catalyst-reactant contact in the one-liter vessel.

Run 20-LA

Another approach to determining why filtration properties were so poor in Runs 16-LA, 17-LA, and 18-LA was to reduce the catalyst (Na_2CO_3) loading. Based on microautoclave tests, which indicated that the catalyst loading could be reduced without reducing coal conversion (Table 12), the feed for Run 20-LA was Black Thunder Mine coal, Reilly Industries anthracene oil, HI "E", and 60 mmole/kg dry coal Na_2CO_3 . A reduced reactor loading was used as in Run 19-LA. The 300 °C+ products were filtered off line and had poor filtration properties. Coal conversion, as in Run 19-LA, was poor. The same speculation for the poor performance of Run 19-LA applies.

Run 21-LA

Run 21-LA also fed Black Thunder Mine coal, Reilly Industries anthracene oil and HI "E", but the first-stage catalyst was changed to determine whether the Na_2CO_3 used in Runs 15-LA through 18a-LA was the cause of the poor filtration properties. KOH was chosen for use in Run 21-LA. Microautoclave tests (Runs 228, 237, and 238) which span the range of catalyst loading from 500 to 111 mmole catalyst/kg dry coal indicated that coal conversion of 90 wt % could be obtained. Catalyst loading for Run 21-LA was chosen as 200 mmole/kg dry coal. Filtration rates for the products were good (see below). However, coal conversion was poor. The smaller-than-normal charge to the first-stage reactor may be the reason for the low conversion, as described above for Runs 19-LA and 20-LA.

Run 22-LA

The first attempt at using the filter in-line (Run 22-LA) was made. The run was aborted ca. 30 min after heat-up began (reactor temperature 251 °F) because of pressure loss in the reactor. It was found that the sample had blown through the closed valve between the reactor and the filter. The contents of the filter were filtered into the receiver. The valve was removed, cleaned, inspected, and pressure tested at reaction temperature (ca. 420 °F) before reassembly. It could not be determined why it failed; however, it is possible that the packing may have reseated on heating for the first time or the valve was not fully closed.

Run 23-LA

Run 23-LA fed Black Thunder Mine coal, Reilly Indus tries anthracene oil, 200 mmole KOH/kg dry coal, and HI "E". A reactor charge equivalent to those used prior to Run 19-LA was used. The products of reaction were filtered through the filter apparatus situated in line. The contents of the 1-gal receiver were analyzed and found to contain essentially all of the ash and catalyst fed to the reactor. No evidence was found that the sample by-passed the filter medium (glass fiber backed by Whatman 42 filter paper). It is, however, possible that the filter papers, which rested on a 1/16th inch stainless steel screen, punctured imperceptibly and allowed the ash to pass through into the filtrate. The entire product was filtered off line and reserved for second-stage testing. Coal conversion was determined to be ca. 83 wt %, lower by 9 wt % (abs.) than anticipated based on corresponding microautoclave tests. The valves between the 1-L autoclave and the filter (Valve 1) and the filter and the 1-gal receiver (Valve 2) functioned properly during the run.

Run 23a-LA

Run 23a-LA a replicate of Run 23-LA was successfully executed. Products were filtered in-line through a glass fiber filter supported by a 60 μ m Conidur plate. The filter cake was approximately 1/8 in thick. The material balance for the run was poor (ca. 88 wt %).

Run 23b-LA

Run 23b-LA was executed unsuccessfully. At run temperature, system pressure was only 3300 psi (about 800 psi below calculated). It is speculated that there was a small leak in the reactor system. There was no transfer of material into the filter. The collected gas quantity was unreasonably high (12 cu ft) and contained predominantly N₂. The reactor was cleaned and the products retained. No further work was done with them.

Run 23c-LA

Run 23c-LA was a successful test. System pressure was ca. 4100 psi. A dry 1/8" thick filter cake was recovered from the filter. The flash vessel contained ca. 35 g of oil and water. Total gas collected was ca. 3.5 cu ft. A mass balance of 101.8% was obtained. The hydrogen gas analysis obtained by difference was checked by direct measurement on a different apparatus. By difference the value was ca. 5.5 vol %; direct measurement gave a hydrogen content of ca. 1.5 vol %. Elemental analyses were obtained for all recovered material. A THF pressure filtration of the filtrate gave 7.26 wt % THF insolubles (THFI) and 1.52 wt % ash. A pressure filtration of

the filter cake was carried out. Attempts to close an ash balance were unsuccessful. Assuming the KOH reports to the ash, only 56% of the ash can be accounted for. Potassium analyses, however, show only ca. 0.0036 moles total K (or 0.20 g of KOH) recovered in the filter cake and the washings of the reactor system. The feed coal contained only 0.0001 moles K. If it is assumed that the KOH is not present in the ash, the ash balance is ca. 67%. An additional 0.183 g K (or 0.26 g KOH) was found in the filtrate, resulting in a 50% KOH balance. The amount of K present in the flashed oil/water layer was not determined. This could be a repository for the remaining 50% (which is only 0.46 g) of KOH.

Products of Run 23c-LA were further analyzed. The filtrate gave 0.3% quinoline insoluble (QI), and 2.2% THFI *by a hot THF extraction method*. The filter cake was found to contain 44.8% QI and 45.9% THFI. Coal conversion is calculated to be ca. 95% (THFI basis).

RUNS 23-LA, 23a-LA, 23c-LA

Ash balances for Runs 23-LA, 23a-LA and 23c-LA were inconsistent. Ash recoveries of 88%, 59% and 55%, respectively, were obtained. Run 23-LA, which had the highest ash recovery (3.9 g or 75% of the 88% recovered), also had the largest yield of filter cake. 2.6 g of ash (or 50% of the 59% ash recovery) was recovered from the filter cake of Run 23a-LA, and 2.0 g of ash (43% out of 55% recovered) was found in the filter cake of Run 23c-LA. This indicates that not all the ash is being detected in the filtrate or possibly flashed products in the form of potassium salts.

The filtrates from runs 23-LA, 23a-LA, and 23c-LA were composited to give 426.4 g of filtrate. This composite was distilled and the residue was used in second-stage testing (Run 23oac-1, 300 CSTR, see below).

Run 23d-LA

Run 23d-LA was successfully executed. Overall material balance was 99.8%. In-line filtration was monitored. It took 35 seconds at 103 kPa and 250 °C to filter the entire product. This corresponds to a rate of 276 kg/m²/h and can be compared to the 208 kg/m²/h achieved with Run 23-LA products in the 35 mm off-line filter. Yields were 167.25 g of filtrate and 23.35 g of filter cake. Analyses of all product fractions were obtained. It is believed that the larger quantity of filter cake obtained from Run 23d-LA vs. Run 23c-LA was a consequence of reduced nitrogen blowing, with the resultant filter cake containing more filtrate. This was confirmed by extraction

of the filter cake. Quinoline insolubles (QI) and tetrahydrofuran insolubles (THFI) were measured in the filtrate and filter cake. The filtrate QI = <0.1 wt % and the THFI = 2.2 wt %. The filter cake QI = 37.2 wt % and the THFI = 40.3 wt %. Coal conversion calculated from these values is ca. 94 wt % (QI basis) and 88 wt % (THFI basis).

Run 23e-LA

Run 23e-LA was aborted at 46 min because of a leak at the stirring shaft seal. The run products were collected, analyzed, and held in reserve. The products were not composited with other Run 23-LA series samples.

Run 23f-LA

Run 23f-LA proceeded as planned. Run 23f-LA was filtered in situ and yielded 165.08 g of filtrate (quinoline insolubles (QI) were 0.3%, tetrahydrofuran insolubles (THFI) were 3.5%) and 20.39 g of filter cake (QI were 40.4%, THFI were 44.9%). To provide a larger quantity of feed for second-stage tests and to reduce the possibility of cracking the first-stage product, a lower distillation cut point was chosen than 454 °C, which had previously been used. The filtrate was distilled under vacuum to an atmospheric equivalent temperature of 426 °C. The products collected were in the proportions 27.9% residue and 72.1% distillate. The residue had a softening point of 165 °C. Analysis by simulated distillation of the residue gave 19.9% of the product boiling <566 °C, compared with the 24.6% of the product of Run 23d-LA.

Run 23g-LA

Run 23g-LA developed a leak at the stirrer shaft seal 23 min into the run. Run 23g-LA (repeat) was made; however, this run did not filter on line. It is suspected that some residual material from Run 23g-LA lodged in the valve between the autoclave and filter, preventing the repeat test from filtering. The autoclave was cooled with the internal cooling coil and an external air flow. The gas and flashed material, along with the autoclave contents, were recovered. The products were filtered off line. Yield of filtrate was 143.37 g (QI were 0.2%, THFI were 2.0%). The filter cake yield was 15.61 g (QI were 40.8%, THFI were 42.1 %). Correcting these results for the product removed for analyses, the yields are 165.13 g of filtrate and 17.98 g of filter cake; overall material balance for the run was 104 %. The filtration rate was calculated to be 225 kg/m²/h with a cake resistivity of 34 x 10¹⁰ m/kg. These data compare well with the 208 kg/m²/h and 33 x 10¹⁰ m/kg achieved in Run 23-LA. The filtrate was distilled under vacuum to an atmospheric equivalent temperature of 440 °C. The resulting products were in the proportions 25.5% residue and 74.5%

distillate. The residue had a softening point of 255 °C. Analysis by simulated distillation of the residue gave 12.3% of the material boiling <566 °C.

Runs 23d-LA, 23g-LA, 23f-LA

The filtered products of Runs 23d-LA, 23f-LA, and 23g-LA were distilled independently and then combined to make sufficient feedstock for a single second-stage test (Run 23dfg-1, 300 CSTR).

Run 23h-LA

Run 23h-LA was filtered in situ and yielded 165.15 g of filtrate and 19.64 g of filter cake. Overall material balance was 98.4%. The filtrate from Run 23h-LA will be held in reserve for second-stage tests under Task 4.

FILTRATION

YIELDS AND COAL CONVERSION

Summary

Mass balance data, including product yields and coal conversions, are given in Table 16 for the first-stage tests Runs 10-LA through 23g-LA. Tables 17a and 17b provide a summary of the filtration performance of the first-stage products. The quality of solids removal from the filter feed was determined from the ash content of the filtrates and by examination of samples for the presence of coal minerals. EDAX analysis was used to make these determinations (Table 18). Ultimate analyses of filter cake THF insolubles, solvents, and coal extracts recovered from filtrates by distillation are given in Table 19. The distillation conditions and component yields are shown in Table 3.

At the end of the first stage dissolution step the reactor temperature is reduced to ca. 300 °C before the autoclave is vented into a sealed receiver (Vessel S-1, Figure 2). One purpose of this high temperature flash is to remove low boiling components from the reactor products prior to transfer to the filter. However, most products analyzed still contained small amounts of material boiling below 300 °C (Table 16). Analysis of the 300 °C⁻ distillate showed that it was principally composed of water with small amounts of light oil and/or hydride ion reagent. The yield of this light fraction was significantly reduced when multiple flashes were employed and the reactor was brought to atmospheric pressure prior to on-line filtration, a procedure initiated with Run 16-LA.

Filter cake yields (Table 16) are higher than expected in a commercial process. However, these cakes were only blown with nitrogen for a short period of time to recover some of the liquid wetting the solids in the cake. In Task 2, it was shown that vacuum drying could be used to recover all of the distillate liquid in a cake, but that the introduction of a cake washing step to recover the residual high boiling material of the liquid fraction was unlikely to be cost effective.

The amount of undissolved solids in the filter cake can be approximately equated to the yield of quinoline insolubles (QI). Values around 50% are indicative of cakes which contain only IOM and mineral matter wetted by residual coal solution, i.e., containing little or no precipitated solubilized coal material. These cakes are amenable to further liquid recovery. Filter cakes with significantly lower QI's can result from precipitation of solubilized coal products. The precipitate may be deposited on the mineral matter and IOM particles or dispersed in the solids of the cake. Alternatively, wet filter cakes (low QI's) can be produced when the fluid phase exhibits a high viscosity. This may occur when the fluid is a high molecular weight material such as a pitch or when the filtration temperature is too low.

The differential between the THF- and quinoline-insolubles in the filter cake (the fraction that is quinoline soluble and THF insoluble, QS/THFI) indicates how much high molecular weight material is retained in the cake. However, the filtrate also contains some material that is THF insoluble. The value of this differential (QS/THFI) was measured on the feed to the filter (first-stage product) (Table 16). Small values indicate that there is little soluble high molecular weight material present. This suggests that the first stage thoroughly depolymerized the coal. A high value suggests the contrary, with a higher concentration of material that is precipitated by the addition of THF. However, since the QS/THFI material is usually soluble in the process solvent and reports mostly to the filtrate following solid-liquid separation, it will be transferred to the hydrotreatment second stage and not be rejected with the undissolved solids. Although the conversion to THF solubles gives useful information on the proportion of the coal that is reduced to a certain molecular size, it is the conversion to quinoline solubles that more clearly shows how much of the coal has been extracted and is available for conversion to useful liquid products.

The coal conversions given in Table 16 are calculated on a dry, SO_3 -free ash-free basis. They are based on the determination of solids in the reactor product. The values have been determined from four separate measurements and the assumption that all the solids are

recovered from the first stage reactor. Conversions to both THF and quinoline solubles were calculated via single determinations of the solvent solubility of representative samples of the filter cake and reactor product. Measurement of coal conversion from the THF solubility of the cake does not account for the THF insolubles in the filtrate. Therefore, the value determined from this parameter will generally be higher than that determined from the reactor product. The conversion to quinoline solubles is independent of the procedure, since the filtrate contains little or no quinoline insolubles. These values are consistently higher than the equivalent measurement of conversion to THF solubles. Table 16 also includes conversions based upon the extent to which the ash content is enriched as the coal is solubilized; in this method no assumption has to be made about the overall mass balance.

Test Descriptions

Run 10-LA

Run 10-LA is not representative of one-liter tests made previously with Glenharold Mine lignite. The high cake yield of ca. 30% (expressed as a percentage of the feed to the filter) and low conversions can be attributed to the loss of solvent and hydride ion reagent that occurred as a result of the leak that developed during the run (see above).

Run 11-LA

In Run 11-LA, a filter cake yield of 12.5% was obtained with high coal conversions (90 to 94 wt %) for all three methods used (Table 16). There was only a small amount of high molecular weight QS/THFI material. This test was more representative of the first-stage conversion of Glenharold Mine lignite, as seen in tests made in Task 2. The use of anthracene oil as first-stage solvent may have contributed to the high coal conversions.

Run 12-LA

In Run 12-LA, high conversions were obtained (93 to 95 wt %), but with a larger amount of QS/THFI material than obtained in Run 11-LA. This resulted in a lower conversion to THF solubles (86 wt %). The cake yield was <10% as a consequence of the significantly drier cake (50% QI vs. 42%, est.). The increase in the solvent to dry coal ratio from 1.5 to 2.0 may have contributed to the low yield of filter cake.

Run 13-LA

The coal conversion to THF solubles in Run 13-LA was significantly lower than all other one-liter autoclave tests made in Task 3. Conversion was 74 to 76%, with lower yields and larger range of quinoline solubles (86 to 91 wt %). The cake yield in this test was substantially higher on a feed coal basis due to the lower conversion and relatively large amount of THFI/QS material.

Runs 14-LA and 14b-LA

Virtually identical results were obtained for the duplicate tests Runs 14-LA and 14b-LA. High coal conversions of 93 to 94 wt % and 93 to 95 wt %, respectively, and slightly lower conversions to THF solubles (87 wt % and 86 wt %) were obtained. Cake yields were about 7% and the cakes were dry (QI of 50-53%).

Runs 15-LA and 15a-LA

First-stage products of Runs 15-LA and 15a-LA were combined. The combined product is identified as 15-LA in Table 16. Coal conversion of ca. 85-87 wt % was obtained. The filter cake yield was double that found in Run 14-LA, reflecting the lower coal conversion.

Run 16-LA

In tests from Run 16-LA onward, HI "E" was used as the hydride ion source. In Run 16-LA, NaAlO_2 was the first-stage catalyst used to promote the production of hydride ion in the first stage. In Run 16-LA, conversion to quinoline solubles was high (93 to 94 wt %); however, there were inconsistent results in the determination of conversion to THF-solubles by the two methods used (Table 16). This product sample had unusual filtration performance (see below).

Run 17-LA

Coal conversion to QS in Run 17-LA (a replicate of Run 16-LA) was 95 wt % based on the QI content of the products.

Run 18-LA

In Run 18-LA, Na_2CO_3 was substituted for NaAlO_2 as the first-stage catalyst. The concentration of Na used in Run 18-LA was similar to that used in Runs 16-LA and 17-LA (600 mmole / kg dry coal vs. 550 mmole/kg dry coal, respectively) with a similar conversion to QS (92 wt %). Solids separation by filtration was not possible for this sample (see below).

Run 19-LA

In this test, no first-stage catalyst was used. Coal conversion as measured by QS and THFS on the reactor product was 70% and 55%, respectively. Filtration, however, was successfully achieved (see below).

Run 20-LA

In Run 20-LA, the concentration of Na was reduced from that used in Run 18-LA to 120 mmole/kg dry coal. This resulted in a decrease in coal conversion (82% based on QI and 60% based on THFI). Filtration properties were poor, as they had been for Run 18-LA products.

Run 21-LA

Run 21-LA was made with KOH as the first-stage catalyst. The products filtered successfully, but coal conversions were only 71.5% (based on QI) and 52.4% (based on THFI). These values are considerably lower than what would have been predicted from earlier microautoclave work.

It was speculated that the small batch-size used (about half of the usual amount) may have contributed to the low conversion as a consequence of poor agitation and hence inadequate gas/liquid contact.

Runs 23-LA through 23g-LA

Seven runs were completed (23-LA, 23a-LA, 23c-LA, 23d-LA, 23f-LA, 23g-LA and 23h-LA) using the same conditions as for Run 21-LA but using full-size batches. In all 23-LA series tests, coal conversions of >90% to both QS and THFS were achieved.

FILTRATION PROPERTIES

Tables 17a and 17b give a summary of the filtration data obtained for first-stage products prepared from Glenharold Mine lignite and Black Thunder Mine subbituminous coal. Two grades of Conidur screen were tested, one with 100 x 500 μm (nominal) apertures and the other with 60 μm x 400 μm openings. Their performance was compared with tests using glass fiber membranes (GFA) which retain particles larger than approximately 1 μm . The filtration temperature was kept as high as practical (~300 °C) in order to minimize the fluid viscosity, μ , and obtain maximum flow rates. In some tests, the differential pressure was varied in order to determine the compressibility of filter cakes derived from these feedstocks. The cake resistivity and total flow of filtrate per unit area of filter after a given length of time were used to characterize filtration. It has been shown that the maximum overall filtration rate is achieved when filtration time and down

time are of equal length.⁴ In Tables 17a and 17b, the period selected was 30 minutes, equivalent to one hour over a full filtration cycle.

The filtration data from Run 10-LA (Table 17a) indicate that the material tested is an ideal feedstock for solids separation by filtration. It has a very low cake resistivity and very high flow rates (~550 kg/m²/h). In some cases, the flow rates were so high that there was insufficient time to divert the flow of filtrate to a second receiver once bridging of the apertures of the Conidur screen had been established. Hence, the collected filtrate contained the first runnings, which are inherently high in solids (before bridging of the apertures occurs). Consequently, the filtrate ash content was higher than would otherwise be expected (0.5%, Table 18a). In an industrial-scale operation, the initial filtrate containing solids would be recycled to the filter feed. These good filtration characteristics are associated with the low conversion and resultant size and nature of solids in the feedstock.

The product of Run 11-LA was split into two parts. One part was filtered at 200 °C and 138 kPa and the other at 275 °C and 352 kPa. Both filtered at acceptable rates, although the second test at the more severe conditions would be preferred as the rate is almost double that of the first test despite the high cake resistivity. A comparison of the ash content of the first runnings, 46F (first), with the bulk filtrate, 46F, shows how the solids content falls rapidly (from 0.6% to 0.03%) once bridging of the apertures is initiated (Table 18a). A similar trend is shown for 47F from Run 12-LA, from which the ash content of the feed, first runnings, and bulk filtrate were 3.1% , 2.3%, and 0.10%. The latter figure compares favorably with the comparable filtration through GFA. The filtration rates of these two tests from Run 12-LA were acceptable, despite the higher cake resistivities.

The two tests representing Run 13-LA, one made with Conidur and the other with GFA, gave acceptable filtration rates. These tests were carried out at ~300 °C and ~350 kPa, and followed the classic filtration pattern with flow rate progressively falling off as cake thickness builds (Figure 4).

The filtration characteristics of first-stage products prepared using Black Thunder coal are significantly different from those using Glenharold lignite. Each of the samples from Runs 14-LA and 14b-LA, prepared using anthracene oil and HI "A" at 375 °C and 60 min, were split into two parts for filtration tests. Cake resistivities were significantly higher than those determined for the

reactor products from previous tests using Glenharold lignite, but the measured flow rates of 40 to 100 kg/h/m² are considered to fall in an acceptable range (Table 17b). The first subsample of Run 14-LA was filtered through glass fiber paper. Midway through this test, the differential pressure (ΔP) across the filter was increased. The increase in the cake resistivity (α) indicates that the filter cake is compressible. The value of the compressibility parameter ($n = 0.6$) is typical of coal residue solids ($n = 0.3$ to 0.7). The second sample was filtered using a 100 x 500 μ m Conidur screen. Initially, a rapid filtration rate occurred, but a subsequent refiltration (NCF54) of this filtrate through glass fiber showed that only about a quarter of the solids had been retained by Conidur. During the next period, the rate slowed in accordance with the expected cake build up, and the cake resistance was comparable with the first subsample. When the pressure was increased by a factor of 2.5, the rate increased by a factor of 10. Subsequent analysis of this sample showed that solids had again been forced through the screen. This behavior and the relatively high cake resistivity are indicative of a small average size of the particles of ash and IOM. Bridging across 100 x 500 μ m orifices is marginal, but a reduction in the orifice size could make a significant improvement in bridging. This sample also was refiltered through GF A (NCF53); similar values of α and flow rate were obtained.

In the first test on the subsample from Run 14b-LA, with GFA glass fiber filter paper as the membrane, the differential pressure across the filter was periodically increased during the test. α increased as the differential pressure was increased. This is indicative of a compressible cake. However, the calculated value of the compressibility parameter, n , is greater than 1; ($n = 0$ for an incompressible cake). This suggests that α changes with time, but not solely as a function of ΔP . This may be the case, for example, when the characteristics of the solids being deposited are changing with time. This can occur when very fine particles are left suspended in the liquid phase after the coarser particles have settled to form the initial cake, and could be a consequence of the long period of time required to complete the test. A similar observation was made when the second part of the feed was filtered through a Conidur screen. In this test using Conidur with 60 μ m x 400 μ m apertures, bridging of the apertures appeared to occur satisfactorily despite the low solids content (~4%) and the small size of the particulate in the filter feed. However, at the end of the test, just prior to gas breakthrough, there was a significant increase in the filtration rate. This suggests that some solids were being carried through into the filtrate (Figure 5). This was confirmed from the measurement of the solids content of the filtrate.

The large batch of Run 15-LA and 15a-LA composite (both tests were made with HI "D" and NaAlO_2 catalyst) was filtered through GFA paper in the 118 mm diameter filter unit at 250 °C. The pressure was increased stepwise from 150 to 580 kPa during the test. Cake resistivities were very high and flow rates were low, ($<20 \text{ kg/m}^2/\text{h}$). The compressibility of the cake, like that from Run 14-LA, appeared to be greater than one. This suggests that a change in the character of the solids being deposited was occurring with time. To investigate the unusual filtration behavior of these materials, product from Run 16-LA (made with HI "E" and NaAlO_2 catalyst) was well mixed, then divided into four parts for filtration tests in the 35 mm diameter filter unit. The first batch filtered relatively easily through GFA at 265 °C and 570 kPa. The flow rate of $70 \text{ kg/m}^2/\text{h}$ was quite acceptable, although the cake resistivity (α) was relatively high. However, when the test was repeated using a stepwise increase in pressure from 135 to 560 kPa (Figure 6), cake resistivities were significantly higher and flow rates much lower ($20 \text{ to } 24 \text{ kg/m}^2/\text{h}$). Duplication of the first test at 300 °C and 570 kPa gave equally low rates of filtration ($\sim 16 \text{ kg/m}^2/\text{h}$). These inconsistent results may be associated with the feedstock character changing with time, possibly attributable to the formation of unstable gels which are affected by the "handling" they undergo. For example, the viscosity of non-Newtonian fluids is dependent upon the shear stress imposed and the exhibition of thixotropic behavior may underlie these observations. The last subsample of 16-LA was filtered using a Conidur screen with $60 \mu\text{m} \times 400 \mu\text{m}$ apertures. Bridging of the apertures was only marginal as evidenced by sporadic increases in the flow rate imposed on the normal progressively reducing rate as cake builds and flow resistance increases. Three consecutive samples of filtrate were collected and analyzed for their solids content. The values obtained, 4%, 2%, and 1%, confirm the above observations, indicating that the particulate bridges across the screen apertures periodically collapsed to allow solids to enter the filtrate stream. The cause(s) for the substantially reduced flow rates and somewhat erratic behavior of these materials (15-LA and 16-LA) during filtration are unclear, but could possibly be attributed to two competing factors. The first may be the influence of the finely divided catalyst being deposited with the cake. Alternatively, the mild extraction conditions employed, and the change to HI "E", may produce plastic, deformable residual particles that inhibit flow through the cake.

Filtration of product from Run 17-LA, which was prepared under very similar conditions to Run 16-LA products, confirmed the problems associated with these particular materials. Attempts were made to filter this sample at 190 °C and 560 kPa through GFA. The temperature was raised stepwise during the test to 250 °C and then to 300 °C; this reduced the viscosity from 4 mPa-s to 0.7 mPa-s. Each time the temperature was increased, the filtration rate initially increased by

a factor of about two (i.e., roughly corresponding with viscosity). Subsequently, as further cake was built-up, the rate reduced more rapidly. At 190 °C, the filtration rate was only 15 kg/m²/h, confirming the low rates experienced with Run 16-LA. Substituting Na₂CO₃ for NaAlO₂ as the catalyst in Run 18-LA did not improve the filtration characteristics. The filtration test was conducted at 290 °C and 560 kPa using GFA. It had to be aborted when very low filtration rates of (ca. 5 kg/m²/h) were encountered. An attempt to remove the water soluble catalyst from a subsample of the reactor product of Run 18a-LA by washing with boiling water reduced the catalyst concentration by only about 20%. Filtration of the washed product, attempted at 280 °C through GFA using the micro filter unit, did not result in an improvement in filtration characteristics of the washed sample. Analysis of the wash water indicated that about 20% of the catalyst had been removed by this technique.

Run 20-LA products were prepared using a low concentration of sodium carbonate as catalyst. Solids separation by filtration was not viable. In Run 19-LA, no catalyst was used; the products filtered successfully. However, low cake resistivity (58 x 10¹⁰ m/kg) was achieved at the expense of a low coal conversion. This meant that the sample contained a large amount of solids which depressed the filtration rate (64 kg/m²/h).

The samples prepared using KOH catalyst, Runs 21-LA and the Run 23- LA series of tests filtered at 300 °C and 140 kPa - 210 kPa through GFA at high flow rates (100 kg /m²/h to 200 kg/m²/h) and had low cake resistivities. Samples from Runs 23a-LA, 23c-LA, 23d-LA, 23f-LA and 23h-LA were filtered in situ in the integrated unit. Although the data are less detailed, calculated cake resistivities were low (8 x 10¹⁰ m/kg), and estimated filtration rates were very high (~270 kg/m²/h). Samples from Runs 23-LA and 23g- LA were filtered in the 35 mm filter unit and had filtration rates of over 200 kg/h/m². This confirmed the high filtration rates achieved using the in-line filter unit. Such high rates indicate filtration costs in a commercial facility may be less than 40 ¢/bbl crude oil equivalent (COE), and possibly as low as 30 ¢/bbl COE.

The filtration characteristics of the reactor products are shown schematically in Figure 7. This figure illustrates how filtration rate is affected by the severity of the conditions employed in the first stage. The assessment of 'severity' may be a combination of factors including reactor temperature, pressure, gas composition, residence time, catalyst type and concentration, and their effect upon the hydrogen transfer to the liquefying coal. Before any reaction occurs, the filtration rate is fast; $\alpha = 4 \times 10^{10}$ m/kg for a slurry of Black Thunder Mine subbituminous coal in anthracene oil.

This is lower than for any conditions presented in Table 17b. When very mild conditions are employed and before the coal softens, filtration rates will be high and conversion to both QS and THFS low. Conversely, when more severe conditions are used, conversions to both QS and THFS will be high and filtration rates will be relatively high, depending upon the size distribution of the residual undissolved solids. However, in the intermediate zone (when solubilization of the coal is incomplete and soft, plastic particles are present), filtration will be slow and may be impossible. This regime often is characterized by the presence of significant amounts of material that, although soluble in quinoline (and in solution in the process solvent at the reaction temperature), is insoluble in THF. (Note: gas yields will increase progressively as the severity of the conditions is increased, and, if taken beyond the limits shown in the schematic where the hydrogen source may be depleted, the conversion will start to fall as regressive reactions predominate, but with beneficial effects upon the filtration rate).

ANALYSIS OF FILTER CAKES

Inspection of the elemental analyses for filter cake THF's (Table 19a) shows that while representing only ~10% of the original coal (on a DAF basis), C and O are little changed from Black Thunder coal (Table 1), but H content is significantly reduced. In contrast, the coal extract (i.e., distillation residue) comprising 65% to 70% of the original DAF coal is far richer in C and H and depleted in O (Table 19b). It appears that S is preferentially retained in the cake. Boiling point distribution by simulated distillation (with aromatic correction) for the reactor products, recovered solvents, coal extracts and first-stage light distillate products are given in Tables 20a, 20b, 21a, 21b, 22a, 22b, and 23. The information produced in these tables will be of more value once recycling of the solvent is initiated in Task 4 of the program. They do, however, show the differences in boiling point distribution for the three solvent types used. Analytical data for the recovered solvents and filtrates can be found in Appendix 1.

EDAX analysis, a qualitative technique, was used to determine the fate of the first-stage catalysts (NaAlO_2 , Na_2CO_3 and KOH). In Runs 16-LA, 17-LA, and 18-LA, the sodium aluminate added represents about a fifty-fold increase in Na over that present in the coal ash; in Run 20-LA, the increase is about ten-fold; and, in Run 21-LA, the K content is increased by thirty-fold. A summary of the elements identified from EDAX analysis for five separate regions spread across the sample are shown in Table 18a. In the THF insolubles of the reactor products, only the most common elements found in coal minerals (Ca, Al, Si and S) are observed in the sample with no added catalyst (Run 19-LA), while Na appears as a prominent peak in Runs 16-LA and 18-LA.

(catalysts NaAlO_2 and Na_2CO_3 , respectively) as does K in Run 21-LA (KOH catalyst). Surprisingly, Na is not identified in Run 20-LA, although a low concentration of Na_2CO_3 was added. In the THF insolubles of filter cakes from Runs 16-LA and 17-LA (58FC-THFI and 61FC-THFI), the same peaks, including Na, are seen, while for the samples derived from filtrates (58F-THFI, 61FDR and 63FDR), only Ca appears as a major peak with indications of trace amounts of S. Similar observations concerning the fate of K can be made for samples from Run 21-LA: no K is found in the filtrate stream. It would thus appear that the catalysts in the filter feed report to the filter cake. Table 18 gives quantitative elemental analysis of the ash in the filter cake. A more detailed investigation, including an ash component balance with analysis by atomic absorption spectroscopy is recommended for Task 4.

SECOND-STAGE CATALYTIC UPGRADING

MICROAUTOCLAVE TESTS

In Tasks 2 and 3, microautoclave tests were made to assess how the solids-free first-stage products would perform under a range of conditions in a second-stage hydrotreater. Typically, 2 g of solids-free resid were hydrotreated at 440 °C for 60 min using 10,000 ppmw (1 wt %) Mo (total resid feed basis). The experimental results are summarized in Table 24 and Figure 8. Included in Table 24 and Figure 8 are tests made in Task 2 (reported previously²). They are presented here for comparison with data generated in Task 3.

Glenharold Mine lignite was used for first-stage Runs 9-LA to 13-LA and Black Thunder Mine subbituminous coal was used beginning with Run 14-LA. The Glenharold Mine lignite-derived first-stage products made at 350 °C using HI "A" as the hydride ion source had higher resid conversions in the second stage than the first-stage products derived from Black Thunder Mine coal at 375 °C with HI "D". This assessment provided additional impetus to change from HI "D" to HI "E" later in the program.

First-stage Runs 12-LA and 13-LA were made as reference tests to simulate conventional liquefaction processes (see One Liter Autoclave Tests, Test Descriptions, above). Run 12-LA represents typical conditions found in the LSE donor solvent process and Run 13-LA simulates the ITSL processes with hydrogen transfer from the gas phase. The resids generated in both cases were less reactive than resids from Run 8-LA through 11-LA. Lower conversions and higher amounts of hydrogen uptake per unit resid conversion in Runs 12-LA and 13-LA indicate less efficient use of hydrogen under the same reaction conditions as Runs 8-LA through 11-LA.

Elemental analyses of the feeds to the second stage and the distillate and resid product fractions are presented in Table 25. Because of the small amount of sample usually available from these runs, only C, H, and N analyses were obtained. The four feedstocks contain about 5-6% H. Hydrotreated product distillates uniformly contain 8-9% H, and the corresponding resids contain 4-5% H. The carbon contents of the distillates in the runs using the 15-LA feedstock appear to be erroneously low, resulting in higher calculated O + S + Ash levels for those samples.

To assess the reactivity of the first-stage resids, microautoclave experiments were performed at 440 °C with 1% Mo, using a distilled composited filtrate from Runs 15-LA and 15a-LA (15oa). Runs were made at 30, 60, 90, and 120 min (Table 26). A plot of resid remaining vs reaction time shows resid conversion asymptotically approaching 53-55% (Figure 9). For comparison, conversion data are given for tests made using Wilsonville Run 258 deashed resid (DAR) at 60 min with 0.1%, rather than 1% Mo. It is believed that the comparison is valid because resid conversions of the Wilsonville Run 258 DAR at 60 min with 0.1% and 1.0% Mo previously were found to be the same. Resid remaining at each reaction time is greater for the DAR than the distilled first-stage filtrate. Figure 10 is a plot of hydrogen consumed per unit resid conversion for the reaction times of 30, 60, 90, and 120 min with the 15oa feed. As time progresses, H₂ consumption increased. These data are consistent with data previously obtained for microautoclave tests with first stage products.²

The Run 23-LA series first-stage product upgrading properties were compared with those of a conventional two-stage liquefaction resid. Three microautoclave tests were made with Run 23d-LA distilled filtrate (Table 27). All three tests (Runs 23d-1, 50 MA, 23d-2, 50 MA, and 23d-3, 50 MA) were made at the same conditions (440 °C, 60 min, 1% Mo). Average resid conversion for the three microautoclave tests was ca. 45 wt % 566 °C+. This is 10-17 wt % higher than resid conversions obtained in microautoclave tests with Wilsonville Run 258 A deashed resid.² The precision of microautoclave tests was determined from these replicate tests. Resid conversion was found to have a standard deviation of ±3%, and hydrogen consumption to have a standard deviation of ±4 mg/g MAF feed.

Gas yields in 300 CSTR tests are significantly higher than expected from the microautoclave tests was unusually high (17 wt % MAF feed). To examine the possibility that temperatures in the 300 mL CSTR are higher than the indicated value of 440 °C, a microautoclave test was made with Run 23d-LA distilled filtrate resid at 450 °C, 60 min, and 1% Mo. Resid conversion in this

microautoclave test (Run 23d-4, 50 MA) was 62 wt % (ca. 17 wt % higher than the average of Runs 23d-1, -2, -3, 50 MA). Gas yield also was higher than in the lower temperature (440 °C) tests, but only by ca. 4 wt % (to 7.7 wt % MAF feed). Calculations made using the ideal gas law and conditions in the reactor compare favorably with those made using the collected volume of product gas, indicating that there are no obvious errors to explain the high gas make in Run 23aoc-1, 300 CSTR. It is possible that the microautoclave tests may accurately represent trends, but not the magnitude of differences seen in the 300 mL reactor. Reaction severity will be further examined in the 300 mL CSTR in Task 4.

To further address the issue of high gas yields from some of the 300 mL CSTR tests (see below), C₁-C₃ gas yields for microautoclave tests 23d-1, 2, and 3 were calculated using both the ideal gas law (the method typically used) and the volume of gas collected in the sample cylinder at the end of the run. Calculated values were within one standard deviation of each other (Table 27). C₁-C₃ gas yields were found to be 4.2 ±0.9 wt % MAF feed (using the ideal gas law), or 3.8 ±0.7 wt % (calculated from the amount of gas collected). This finding lends credibility to the microautoclave results, and reaffirms the difference in gas make found in the CSTR tests.

300 mL CSTR TESTS

Under Task 3, second-stage catalytic upgrading tests were initiated using the 300 mL continuous stirred tank reactor (CSTR). Shake-down tests were made with Wilsonville Run 258A deashed resid in order to conserve limited supplies of filtered first-stage products. Five tests were completed using the 300 mL CSTR (Table 28). Feedstocks were the composited distilled filtrate residues from first-stage tests Runs 15-LA and 15a-LA, Wilsonville Run 258A deashed resid, composited distilled filtrate residues of first-stage tests Runs 23-, 23a-, 23c-LA and 23d-, 23f-, and 23g-LA, and Wilsonville Run 263J ashy resid. Elemental analyses of the feed and product streams for these five runs are given in Table 29a-e. Material balance data for the five tests are given in Table 30.

In the first run of the five tests, a 50 g sample of distilled composite filtrate residue from runs 15-LA and 15a-LA (NCF 57 FDR) was hydro treated in the 300 mL CSTR at the standard conditions of 440 °C for 60 min, using 1% Mo (feed basis) from Molyvan L as the catalyst precursor. The material balance for Run 15oa-1, 300 CSTR is 102%, with 101% C and 99% H balances (Table 30). Resid conversion was 49 % and H₂ uptake (calculated from the H₂ gas balance) was 54 mg/g MAF feed (Table 28). Comparable numbers from the microautoclave tests were 44%

conversion and 43 mg/g MAF feed H_2 consumption (Table 26). C_1 - C_3 gas yield for Run 150a-1, 300 CSTR was 23 %. This value is much higher than the ca. 9% yield obtained in the microautoclave study. CO/CO_2 yields were similar to those obtained in the microautoclave tests. The high gas yield indicates that there may have been coking of the reactants and/or products. A 270% increase in the fixed carbon content of the product, relative to the feed, supports this conclusion.

Several changes were made to the reactor and test start-up procedure to reduce the possibility of coking. An inlet gas tube to conduct fresh hydrogen feed gas to the bottom of the reactor was installed and the H_2 gas flow was increased from 0.2 to 1.7 standard L/min and allowed to flow continuously during heat up. The stirrer shaft length was extended, and the stirrer was changed from a pitched blade to a turbine type blade to provide better agitation. The feed charge was increased from ca. 50 g to ca. 100 g.

Run DARo-1, 300 CSTR was made after the modifications to the reactor system were completed. The charge was 100 g of Wilsonville Run 258A deasphalted resid and 12.3 g as-received Molyvan L (1% Mo on feed). Run conditions were 440 °C for 60 min. 566 °C⁺ resid conversion was 63%. This is higher than was obtained in the microautoclave tests made at the same conditions. The overall material balance was 100% (Table 30). Because of the suspiciously good material balances obtained in Run 150a-1, 300 CSTR, and Run DARo-1, 300 CSTR, the sampling and measurement system for the product gas stream were reviewed. The gas sampling point was separated from the vent meter by a 500 mL knockout scrubber. The gas vented first during a run should be high in H_2 content, since the system is pressurized with pure hydrogen prior to heat up. However, in Run DARo-1, 300 CSTR, the gas sample was initially 73.4% H_2 . The gas sampling point was relocated to a position just upstream of the regulating valve. In Run 230ac-1, 300 CSTR, the first 10 min sample contained 99.0% H_2 as a result of this change. This change affects the overall material balance. The volume of gas vented remains the same, but the molecular weight assigned to that volume is much lower. The impact on total gas yield is small, because this correction is applied only to sample collected in the initial 10 min of the run and three-quarters of the product gases are released at the conclusion of the run when the cold reactor is vented. Subsequently, gas compositions for the first period of Runs 150a-1, 300 CSTR, and DARo-1, 300 CSTR, were recalculated with the data from Run 230ac-1, 300 CSTR. The overall material balance reported in Table 30 reflects the recalculated values.

Microautoclave tests made with Wilsonville deashed resid resulted in gas yields and resid conversion comparable with the Wilsonville pilot plant operations.² Thus, runs in the CSTR with the deashed resid feedstock are useful in establishing markers for comparison with the Wilsonville base case.² The significantly higher gas yields and conversions found in the CSTR in comparison with microautoclaves under nominally the same conditions suggest that the conditions in the 300 mL CSTR are more severe. This may be partially attributed to differences in the heat-up time of the two reactors. Additionally, high temperatures at the walls of the CSTR may be a contributing factor. Heating to the operating temperature in the microautoclave is essentially instantaneous, whereas for the CSTR, the residence time between 350 °C and reaction temperature is significant (on the order of 30 min) in comparison with the run time at temperature (typically 60 min). To reduce the severity of the CSTR experiments and to be able to directly correlate microautoclave test results with CSTR results, shorter run times will be explored in Task 4.

Run 23oac-1, 300 CSTR, was made with 94 g of composited first-stage distilled filtrate residue from Runs 23-LA, 23a-LA and 23c-LA, and 11.6 g Molyvan L. Resid conversion was 57%, with an overall material balance of 96%. Light hydrocarbon gas yields were again higher than those obtained in microautoclave tests.

Run 23dfg-1, 300 CSTR was the second test made with first-stage products of the Run 23-LA series. The feed for this run contained a higher distillate content (ca. 20 wt %) than the first test, Run 23oac-1, 300 CSTR (ca. 6 wt %), but in all other respects was a duplicate of the first run. However, resid conversion for Run 23dfg-1, 300 mL CSTR was 65 wt %, 8% (abs.) higher than that which was obtained for Run 23oac-1, 300 mL CSTR. The hydrogen uptake and the hydrogen-to-carbon ratio of the 566 °C+ fraction increased.

A baseline test was made with products of the Wilsonville pilot plant to compare with the first-stage products of the Run 23-LA series. Run 263J-1, 300 CSTR was made with the distillation resid of interstage products from Wilsonville Run 263J. This ashy resid contains undissolved coal, fresh resid, and recycled process solvent. Simdist analysis of the feed found it to be 28.7 % 566 °C⁻, with an IBP of about 425 °C. Resid conversion was 44%, ca. 20 wt % less than that obtained with the first-stage filtrate residues from Run 23-LA series tests. Light gas yield was over 18 wt % (MAF feed basis), comparable to that obtained with the first-stage filtrates. The extraction of Run 263J-1, 300 CSTR feed gave 21.9 wt % IOM. The dry reactor-scrape product

contained 64.9% IOM (a 2.25 times increase for the total product). This result and the high gas yields may indicate that regressive reactions may have occurred and that the reaction conditions may have been too severe. This will be confirmed in work under Task 4.

Boiling Range Distributions of 300 mL CSTR Products

The product distributions of the 566 °C⁻ materials produced in Runs 150a-1, 300 CSTR, DARo-1, 300 CSTR, 230ac-1, 300 CSTR, 23dfg-1, 300 CSTR, and 263J-1, 300 CSTR, were estimated from Simdis analyses (Figure 11). The boiling point distribution of the organic portion of the Molyvan L catalyst precursor was determined from a Simdis analysis of the Molyvan L. The contribution of the Molyvan L in each boiling point range was subtracted from the analysis of the product fraction. The resulting fraction weights are presented as a percentage of the MAF feed.

Simulated distillation data for each of the 300 mL CSTR tests are provided in Appendix 2. The data presented in the tables were not corrected for the contribution from Molyvan L.

Analysis of Distillate and Residual Fractions

In order to assess the quality of the material remaining in the 300 mL reactor at the end of the run, the reactor products recovered without THF ("dry reactor scrape") from four of the 300 mL CSTR tests (DARo-1, 300 CSTR; 230ac-1, 300 CSTR; 23dfg-1, 300 CSTR; and 263J-1, 300 CSTR) were distilled to a 566 °C cut point. The distillate and residual samples were submitted for proximate and ultimate analysis. The results are summarized in Tables 32-35. The relatively low H/C ratio for all 566 °C⁺ products raises a number of questions which will be investigated in Task 4. It is not known at this time what the H/C ratio of the 566 °C⁺ fraction of the feeds to these CSTR runs was. This will be determined. Additionally, the effects of test condition severity on this value are not known. It also is not known what the behavior of these materials will be on recycle and how these low values affect ultimate conversion to 566 °C⁻ product. Tests to answer these questions are being designed for execution under Task 4.

Section 5

CONCLUSIONS

OVERVIEW

In Task 3, it was successfully demonstrated at the one-liter reactor scale that hydride ion reagent "E" (HI "E") could promote high coal conversions (>90 wt %) at relatively mild reaction conditions (60 min, $375\text{ }^{\circ}\text{C}$) in the presence of catalysts. A pre-filtration flash of first-stage products and in-line filtration of $300\text{ }^{\circ}\text{C}^{+}$ products were routinely accomplished. Off-line distillation of the filtered material was used to produce a $566\text{ }^{\circ}\text{C}^{+}$ -rich feed to the second-stage. A second-stage reactor was designed, built, and employed to hydrotreat the distilled, filtered, first-stage materials. Single-pass resid conversions in the second-stage were demonstrated to be consistently higher for first-stage products than materials obtained from conventional two-stage liquefaction tests.

Concurrent with experimental testing, an economic and engineering evaluation of the individual stages and the overall process was performed. The process design was modified to incorporate the use of HI "E". The cost of products from the conceptual process were estimated to be higher than the conventional two-stage liquefaction process base case. Recommendations to reduce costs were made. A paper study was completed that indicates if the recommendations are followed and can be experimentally confirmed, product cost will be lower than in the base case.

FIRST STAGE SOLUBILIZATION

First-stage processing conditions were selected to provide not only high coal conversions (≥ 90 wt %), but better economics than those obtained at the conclusion of Task 2. An economically attractive hydride ion reagent (HI "E") was identified to successfully produce high coal conversion (≥ 90 wt %). One of the least costly of several effective catalysts (KOH) was chosen for use in first-stage testing. Low-cost Powder River Basin (Black Thunder Mine) subbituminous coal was chosen to be the feedstock for the balance of the program. Processing conditions of 60 min at $375\text{ }^{\circ}\text{C}$ were adopted for Task 3 work. A commercially available anthracene oil was chosen for use for the balance of the program.

FILTRATION

Hot pressure filtration was demonstrated in Task 2 as an effective method for the removal of solids from the first-stage products. Two filtration modes were employed in Task 3; these were hot on-line filtration, and cooled, reheated off-line filtration of first-stage products. The rates of filtration achieved at around 300 °C and 0.3 MPa off-line were closely replicated in (limited) on-line tests. There appears to be no effect of interstage cooling on the filtration properties of the first-stage product.

It was found that the filtration characteristics of the first stage reactor products are closely related to the conversion of the coal to quinoline- and THF-solubles. The rapid filtration occurs at low conversions because the integrity of the coal particles is essentially unchanged. At moderate conversions, a significant proportion of the coal is quinoline-soluble/THF-insoluble, and filtration is slow. Filtration is difficult and is anticipated to be costly due to the precipitation of some of the coal extract. At high conversions to both quinoline- and THF-solubles, filtration is rapid.

High conversions and high filtration rates were achieved in the first stage with Black Thunder Mine subbituminous coal, Reilly Industries anthracene oil, HI "E" with KOH catalyst, at 375 °C for 60 min. Under these conditions, the cost of filtration for a commercial process would be ca. 40¢/bbl COE.

SECOND-STAGE CATALYTIC UPGRADING

A large-scale second-stage catalytic upgrading reactor system was constructed and operated. The second-stage reactor system allows for continuous hydrogen gas addition and product gas recovery. Residue conversions for first-stage products were found to be consistently greater than for conventional two-stage liquefaction residues.

ENGINEERING AND ECONOMIC EVALUATION

Based on the economic evaluation of the HI "E" system it is apparent that the costs associated with the first-stage reaction system need to be significantly reduced.

First-stage operating severity and cost can be reduced by:

- Reducing reactor residence time.
- Minimizing the amount of excess CO shifted.
- Reducing the steam to coal ratio.

- Reducing the catalyst rate.
- Lowering reactor pressure.
- Lowering solvent to coal ratio.

A significant reduction in the severity of first-stage operation could result in a significantly lower coal conversion, which may be undesirable. The only way to overcome such a reduction in coal conversion is to close-couple the reaction systems so that the second-stage reaction system can provide an acceptable coal conversion level prior to solids separation. The second-stage reaction system is designed to operate at a severity appropriate for resid conversion and, therefore, should convert the feed IOM to an acceptable level (>90% coal conversion) without an increase in severity. Close coupling of the reactors also would eliminate the costly double distillation required in the original process concept.

One advantage in the efficiency of the process is the direct result of coal deoxygenation via CO₂ removal. The effect of reducing first-stage operating severity on coal deoxygenation via CO₂ removal is important and unknown. Experimental work is needed to assess the impact of lower first-stage severity on coal deoxygenation via CO₂ removal. Based on the results of the economic evaluation and the recommendations for reducing first-stage reaction system cost, an improved conceptual case was investigated. This conceptual paper study was intended to identify the potential improvements in the economics of the process and to serve as a guide for future experimental work. The economic evaluation of the improved case indicates that, versus the Wilsonville base case, a cost advantage can be achieved provided the performance assumptions are confirmed in future experimental work. Therefore, it is recommended that future experimental work investigate the effects of decreasing first-stage reaction system severity on overall process performance and economics.

Section 6

PLANS

The project will continue in Task 4 (Integrated Flow Sheet Testing). The goal of Task 4 is to test the combined first stage, interstage filtration, and second-stage catalytic upgrading steps of the novel concept process to refine the engineering and economic analysis developed under Task 3. To achieve this goal, sufficient performance data must be developed. Recommendations to improve the economics of the process were formulated from Task 3 studies reported herein. They are the basis for Task 4 tests. Results of Task 4 tests will form the basis for a final engineering and economic evaluation which will constitute the final report of the project. Included in this final report will be a recommendation concerning further development (e.g., continuous testing) of the process.

FIRST-STAGE TESTING

The effects of the following changes in first-stage test conditions from the baseline conditions of 375 °C, 60 min, 3900 psi, 200 mmole catalyst/kg dry coal, and 2/1 solvent to dry coal ratio on coal conversion, filtration, second-stage resid conversion, and net yields will be studied:

- Catalyst loading will be decreased.
- Solvent/dry coal ratio will be decreased.
- H₂O addition will be decreased or eliminated.
- Solvent quality on recycle will be examined
- Total system pressure will be decreased.
- Residence time will be decreased.

Preliminary tests will be made on a microautoclave scale. One-liter autoclave tests will be made at those conditions that indicate substantive economic improvement to provide sufficient sample for filtration and second-stage catalytic upgrading.

FILTRATION

- Overall filtration rates will be measured with the in-line filter.
- Scale-up of the in-line filtration unit will be simulated by decreasing the filter area to produce thicker filter cakes.
- The impact of solvent recycle will be examined.
- The filter medium will be changed to a Conidur filter (60 µm)

- Vacuum drying of the filter cake will be studied to determine distillate recovery.
- Methods to reduce the amount of ash reporting to the filtrate will be implemented.

SECOND-STAGE TESTING

The effect of changes in the following second-stage test conditions on resid conversion will be studied:

- Fresh catalyst loading will be decreased.
- Alternative dispersed molybdenum catalysts will be tested
- Recycle of unconverted resid around the second-stage reactor will be tested.
- Processing of ashy feed (revised process configuration).

Preliminary tests will be made on a microautoclave scale. Large-scale autoclave tests will be made at those conditions that indicate substantive economic improvement.

OVERALL PROCESS

It is not possible to achieve steady state at the scale of operation defined for Task 4 studies. Resid conversion and overall process performance will be measured for 2-3 recycle passes both for tests of recycle around the second-stage reactor and around the whole process.

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TABLE 1

**ANALYSES OF FEED COALS AND SOLVENTS
AND REFERENCE RESIDS USED IN TASK 3**

	COALS		SOLVENTS				RESIDS	
	Glenharold Mine Lignite	Black Thunder Mine Subbituminous	Wilsonville Run 263J, EOR (b) Distillate	Lummus 3LCF7 Pasting Solvent	Kawasaki Steel Corp. Anthracene Oil	Reilly Industries Anthracene Oil	W(a) 258A Deashed	W (a) 263J Ashy
Ultimate, wt% Dry								
C	63.06	70.32	88.16	89.84	90.04	91.36	90.8	73.8
H	4.44	4.68	10.17	8.65	6.21	5.74	6.9	5.3
N	0.94	1.04	0.54	0.30	0.81	0.97	1.1	1.1
S	1.33	0.50	0.01	0.24	0.87	0.55	0.1	1.1
O (by diff)	20.72	17.89	1.12	0.97	2.07	1.38	1.05	4.2
SO ₃ -free ash	9.48	5.54	0.00	0.00	0.00	0.00	0.1	14.4
Major Ash Elementals								
SiO ₂	31.80	31.48						
Al ₂ O ₃	12.42	15.76						
TiO ₂	0.49	1.14						
Fe ₂ O ₃	7.09	5.48						
CaO	14.07	21.34						
MgO	4.05	4.30						
Na ₂ O	6.02	0.48						
K ₂ O	1.14	0.49						
P ₂ O ₅	0.15	0.96						
SO ₃	21.16	17.26						
Und	1.61	1.31						
Moisture, %	10.82	22.40						

- (a) W = Wilsonville pilot plant
(b) EOR = end of run

TABLE 2**ULTIMATE ANALYSES OF MOLYVAN L AND DIMETHYLDISULFIDE (DMDS)**

Sample	Molyvan L	DMDS
Ultimate Analysis, wt %		
C	50.9	27.1
H	9.3	6.3
N	1.4	1.8
S	11.7	58.1
O (by diff)	1.2	6.8
ash	25.6	0.0

TABLE 3
DISTILLATION OF FILTRATES

Run No.	Sample No.	pot temp. (°C)	vapour temp. (°C)	vapour pressure (torr)	yields (%)		residue softening point (°C)	mass balance (%)	equivalent atmospheric cut point	
					distillate	residue			(°C)	(°F)
10-LA	NCF44F	310	240	1	76.7	23.5	280	100.2	459	860
11-LA	NCF45F	320	256	2.2	72.7	26.4	250	99.1	460	860
	NCF46F	341	260	2	73.4	25.7	280	99.1	465	870
12-LA	NCF47F	340	265	1.3	80.1	19.5	240	99.6	482	900
	NCF50F	352	275	1.4	80.8	18.8	250	99.6	492	918
13-LA	NCF48F	352	275	1.1	79.5	20.3	240	99.8	498	929
	NCF49F	358	270	1.4	79.4	20.4	245	99.8	486	907
14-LA	NCF51F	338	265	1.5	76.7	22.9	250	99.6	478	892
	NCF52F	353	272	2.5	76.3	23.1	245	99.5	473	883
14b-LA	NCF55/56F	345	280	2.7	76.3	23.1	270	99.4	480	896
15-LA	NCF57F	346	282	5.1	72.5	27.2	270	99.7	464	868
16-LA	NCF61F	320	265	3.2	75.4	24.0	n/m	99.4	458	856
23aoc	23aocF	355	275	5.4	73.3	25.3	290	98.6	454	849
23d-LA	23dLA	240	340	5.0	78.5	29.5	165	98.1	416	780
23f-LA	23fLA	292	243	4.0	72.0	27.9	165	99.9	426	799
23g-LA	23gLA	349	255	4.0	74.4	25.4	255	99.9	440	824

n/m: not measured

TABLE 4**MICROAUTOCLAVE TESTS OF LOW HI"A"/DRY COAL RATIOS**

Black Thunder Mine subbituminous coal
Kawasaki Steel Corporation anthracene oil

Run No.	Temp., °C	Time, min.	HI"A"/Dry Coal, g/g	Solvent/Dry Coal, g/g	Coal Conversion, wt %
163c(a)	350	60	1.0	2.0	79.5
191	350	60	0.2	2.0	52.5

(a) Solvent heated to ca. 100 °C prior to test

TABLE 5**MICROAUTOCLAVE TESTS OF LOW HI"A"/ DRY COAL RATIOS**

Glenharold Mine lignite
Kawasaki Steel Corporation Anthracene Oil

Run No.	Temp., °C	Time, min.	HI"A"/dry Coal, g/g	Solvent/dry Coal, g/g	Coal Conversion, wt %
159	350	60	1.0	1.5	91.0
171	350	60	0.2	1.5	48.8
172	400	60	0.2	1.5	69.0
173b	400	120	0.2	1.5	50.8

TABLE 6**MICROAUTOCLAVE TESTS OF THE ADDITION OF METHANOL
AT LOW HI "A"/DRY COAL RATIO**

Glenharold Mine Lignite
Kawasaki Steel Anthracene Oil

Run No.	Temp., °C	Time, min.	Methanol/dry Coal, g/g	HI "A"/dry Coal, g/g	Solvent/dry Coal, g/g	Coal Conversion, wt%
159	350	60	none	1.0	1.5	91.0
174	350	60	0.10	0.2	1.5	56.1
175	350	60	0.21	0.2	1.5	51.8
176	350	60	0.35	1.0	1.7	91.8

TABLE 7**MICROAUTOCLAVE TESTS OF THE ADDITION OF HI "D" TO HI "A"**

Glenharold Mine Lignite
Kawasaki Steel Corporation Anthracene Oil

Run No.	Temp., °C	Time, min.	HI "D", moles	HI "A"/dry Coal, g/g	Solvent/dry Coal, g/g	Coal Conversion, wt%
177	350	60	0.05	0.5	1.5	80.5
178	350	60	0.07	0.2	1.5	36.7
179	350	60	0.09	0.2	1.5	44.4
180	350	60	0.09	0.3	1.5 (a)	68.5
181	350	60	0.09	0.3	1.5	47.7
182	350	60	0.15	0.3	1.5	44.2

(a) Solvent for Run 180 was Lummus Pasting Solvent

TABLE 8
MICROAUTOCLAVE TESTS OF THE ADDITION OF HI "D"
AND CATALYST TO HI "A" SYSTEM

Glenharold Mine Lignite

Run No.	Temp., °C	Time, min.	Solvent	HI"D", moles	HI"A"/Dry Coal, g/g	NaAlO ₂ , mmole/kg Dry Coal	Solvent/Dry Coal, g/g	Coal Conversion, wt %
178	350	60	K-AO	0.07	0.2	none	1.5	36.7
183	350	60	K-AO	0.07	0.2	1000	1.5	27.6
184	350	60	K-AO	0.07	0.2	500	1.5	33.9
203	350	60	R-AO	0.07	0.2	none	1.5	78.8
183a	350	60	R-AO	0.07	0.2	1000	1.5	61.5
184a	350	60	R-AO	0.07	0.2	500	1.5	57.6

TABLE 9
MICROAUTOCLAVE TESTS OF BLACK THUNDER MINE COAL
WITH HI "D"

Black Thunder Mine subbituminous coal
Kawasaki Steel Corp. anthracene oil, T=350 °C, t=60 min

Run No.	moles		NaAlO ₂ , mmole/kg dry coal	MF/dry Coal, g/g	Solvent/dry Coal, g/g	Coal Conversion, wt%
	HI"D"	HI"A"				
163c(a)		0.07		1.0	2.0	79.5
191		0.01		0.2	2.0	52.5
186	0.09				2.0	71.9
187	0.09		500		2.0	79.5
188a	0.09		500(b)		2.0	79.0
189a	0.09		1000		2.0	74.3
190	0.09	0.01	1000	0.2	2.0	80.6
192 ^a	0.12		500		2.0	80.4
193 ^a	0.12		660		2.0	80.1

(a) solvent heated to ca. 100 °C prior to test
(b) addition as water solution

TABLE 10**MICROAUTOCLAVE TESTS OF BLACK THUNDER MINE COAL WITH HI "D"**

Black Thunder Mine subbituminous coal
 Kawasaki Steel Corp.anthracene oil, 375 °C, 60 min

Run No.	moles		Solvent	NaAlO ₂ , mmole/kg dry coal	HI "A"/dry Coal, g/g	Solvent/dry Coal, g/g	Coal Conversion, wt%
	HI "D"	HI "A"					
194(a)	0.09		K-AO	500		2.0	85.4
195(a)		0.07	K-AO		1.0	2.0	85.7
194b	0.09		R-AO	500		2.0	90.1

(a) solvent heated to ca. 100 °C prior to test

TABLE 11**MICROAUTOCLAVE TESTS OF COMPARISON OF FIRST-STAGE CATALYSTS**

Black Thunder Mine Subbituminous Coal, Reilly Industries anthracene oil
 375 °C, 60 min, Solvent/dry Coal = 1.7, 500 mmole catalyst/kg dry coal

Run No.	Catalyst	Catalyst, g	HI "D", moles	HI "E", moles	Coal Conversion, wt%
194b	NaAlO ₂	0.28	0.09		90.1
219	KOH	0.19	0.09		90.2
220	Na ₂ CO ₃	0.36	0.09		88.8
222a	K ₂ CO ₃	0.47	0.09		83.9
223	none	----	0.09		72.6
227	NaAlO ₂	0.28		0.10	88.8
228	KOH	0.19		0.11	92.0
229	Na ₂ CO ₃	0.36		0.11	88.4
221	NaOH	0.14		0.08	75.8 (replicate
226a	none	----		0.10	83.5

TABLE 12

**MICROAUTOCLAVE TESTS OF THE EFFECT OF CATALYST LOADING
ON COAL CONVERSION**

Black Thunder Mine Subbituminous Coal
HI "E", 375 °C, 60 min

Run No.	Catalyst	Catalyst, mmole/kg dry coal	Coal Conversion, wt%
233	none	0	82.7
226a	none	0	83.5
229	Na ₂ CO ₃	850	88.4
230a	Na ₂ CO ₃	500	87.2
231	Na ₂ CO ₃	250	87.2
232	Na ₂ CO ₃	165	91.0
235	Na ₂ CO ₃	82	89.5
236	Na ₂ CO ₃	38	88.1
228	KOH	500	92.0
237	KOH	222	89.5
238	KOH	111	89.4
241	KOH	83	90.4
239	KOH	55	87.7
240	KOH	45	88.2

TABLE 13

**MICROAUTOCLAVE TESTS OF COMPARISON OF KAWASAKI ANTHRACENE OIL AND
REILLY INDUSTRIES ANTHRACENE OIL,
BLACK THUNDER MINE COAL, 60 MIN**

Run No.	Temp, °C	Coal, g	Solvent, g	Hydride Ion Source*	NaAlO ₂ , g	Coal Conv., wt% K-AO	Coal Conv., wt% R-AO
233	350	5.00	8.00	HI"A"	none	79.2	84.1 (replicate 84.3)
226a	350	4.47	7.15	HI"A",	0.28	80.6	87.7
229	350	4.47	7.15	HI"D",	none	71.3	72.5
230a	350	4.47	7.15	HI"D",	0.28	79.5	88.2
231	350	4.47	7.15	HI"D",	0.56	70.5	84.5
232	350	4.47	7.15	HI"D",	0.28	80.4	88.8/90.2
235	350	4.47	7.15	HI"D",	0.37	80.1	89.6
236	375	4.47	7.15	HI"D",	0.28	85.4	90.1 (replicate 96.0)
228	350	4.47	7.15	HI"E"	none	54.9	59.5

* For multi component hydride ion sources, ratios varied in these tests.

TABLE 14

MASS AND ELEMENTAL BALANCE MICROAUTOCLAVE TESTS

Run No.	194b	217a	227a
Coal	BT	BT	BT
Solvent	R-AO	R-AO	R-AO
Hydride Ion Source	HI "D"	HI "D"	HI "E"
Catalyst	NaAlO ₂	NaAlO ₂	NaAlO ₂
Catalyst loading, mmole/kg dry coal	500	500	500
Temperature, °C	375	375	375
Time, min	60	60	60
Coal Conversion, wt%	90.1	96.1	86.16
Mass Recovery, %	99.8	97.3	95.3

BT = Black Thunder Mine subbituminous coal
R-AO = Reilly Industries anthracene oil

TABLE 15

**ONE-LITER AUTOCLAVE TEST CONDITIONS,
RUNS 10-LA THROUGH 23h-LA**

Run No.	Coal (a)	Solvent (b)	Hydride Ion Source	Hydride Ion Source, moles	Catalyst, mmole/kg dry coal	Temp. (°C)	Time (min.)	Solvent/dry coal, g/g
10-LA	GH	Lummus	HI "A"	1.5	none	350	60	1.5
11-LA	GH	R-AO	HI "A"	1.5	none	350	60	1.5
12-LA	GH	Lummus	none	N/A(c)	none	410	60	2.0
13-LA	GH	W263	H ₂	2.9	none	410	60	1.5
14-LA	BT	R-AO	HI "A"	1.5	none	375	60	2.1
14a-LA	BT	R-AO	HI "A"	1.5	none	375	60	2.1
14b-LA	BT	R-AO	HI "A"	1.5	none	375	60	2.1
15-LA	BT	R-AO	HI "D"	1.1	NaAlO ₂ , 528	375	60	2.6
15a-LA	BT	R-AO	HI "D"	1.1	NaAlO ₂ , 556	375	60	2.6
16-LA	BT	R-AO	HI "A"	1.1	NaAlO ₂ , 551	375	60	2.6
17-LA	BT	R-AO	HI "E"	2.4	NaAlO ₂ , 530	375	60	1.8
18-LA	BT	R-AO	HI "E"	2.5	Na ₂ CO ₃ , 308	375	60	1.8
18a-LA	BT	R-AO	HI "E"	2.5	Na ₂ CO ₃ , 312	375	60	1.8
19-LA	BT	R-AO	HI "E"	1.4	none	375	60	1.8
20-LA	BT	R-AO	HI "E"	1.4	Na ₂ CO ₃ , 60	375	60	1.8
21-LA	BT	R-AO	HI "E"	1.4	KOH, 205	375	60	1.8
23-LA through 23h-LA	BT	R-AO	HI "E"	2.6	KOH, 202	375	60	1.9

- (a) Coal: GH = Glenharold Mine lignite
BT = Black Thunder Mine subbituminous coal
- (b) Solvent: Lummus = Lummus Pilot Plant, Run 3LCF7 Pasting Solvent Distillate
W 263 = Wilsonville Pilot Plant Run 263, V1067, End of Run
R-AO = Reilly Industries Anthracene Oil
- (c) N/A = not applicable

TABLE 16

MASS BALANCE DATA, ONE-LITER AUTOCLAVE TESTS

Run No.	Yields				Cake Insolubles		Solids in Feed		Coal Conversion				Coal Conversion from Ash Enrich.		Ash Balance
	Dist. (%)	Filtrate (%)	Cake (%)	Total (%)	THFI (%)	QI (%)	THFI (%)	QI (%)	(1) (%daf)	(2) (%daf)	(3) (%daf)	(4) (%daf)	(2) (%daf)	(4) (%daf)	(%)
10- LA	6.6	62.4	28.6	97.6	44.1	39.9	10.3	n/m	81.4	75.3	n/m	78.7	76.7	79.9	108
11- LA	4.5	78.6	12.5	95.6	47	n/m	7.1	6.1	91	93.1	93.7	n/m	92.4	n/m	94
12- LA	0.7	87.1	9.6	97.3	55.4	50.5	8.1	5.4	85.5	93	93.9	94.7	92.1	93.6	80
13- LA	6.9	71.3	20.7	98.8	61.5	46.4	13.5	7.3	73.7	75.7	90.6	86.2	75.3	85.7	97
14- LA	1.6	88	7.6	97.2	53.5	49.2	6.1	4.0	86.7	92.7	93.3	94.0	89.5	90.7	78
14b- LA	5.1	85.4	6.4	96.9	58.8	53.3	5.8	4.0	86.8	93.4	92.7	94.7	87.0	88.8	77
15- LA	7.1	80	12.9	100*	59.1	55	7.7	5.6	85.6	85.9	92.3	87.7	90.0	91.1	86
16- LA	1.5	79	15.2	95.6	43.7	38.5	11.4	6.2	78.3	90.8	93.1	94.1	89.0	90.7	71
17- LA	filtration aborted						8.8	5.8	87.4	n/m	95.2	n/m	n/m	n/m	n/m
18- LA	filter blinded						9.2	6.8	85.1	n/m	91.6	n/m	n/m	n/m	n/m
19- LA	1.8	53.4	41.3	96.5	47.7	40.8	22.1	15.5	54.7	60.3	70.0	66.7	50.2	58.2	94
20- LA	filter blinded						21.1	11.0	59.7	n/m	82.1	n/m	n/m	n/m	n/m
21- LA	1.1	64.5	31.0	96.6	53.1	48.6	23.1	15.0	52.4	68.0	71.5	71.3	62.6	66.3	86
23o- LA	0.8	86.1	11.5	98.4	45.7	43.4	7.9	5.3	87.3	93.8	93.8	94.6	90.4	91.2	88
23a- LA [#]	0.0	92.3	7.7	100	46.3	43.6	n/m	n/m	n/m	98.3	n/m	98.8	89.9	90.8	59
23c- LA [#]	4.5	89.9	5.6	100	45.9	44.8	n/m	n/m	n/m	100.1	n/m	100.3	91.9	92.2	55
23d- LA [#]	4.7	83.6	11.7	100	40.3	37.2	n/m	n/m	n/m	93.2	n/m	94.3	90.6	91.8	92
23f- LA [#]	4.9	84.7	10.4	100	44.9	40.4	n/m	n/m	n/m	94.2	n/m	95.3	91.6	93.0	97
23g- LA	4.9	84.4	9.2	98.5	42.1	40.8	7.6	4.6	86.1	96.1	94.4	96.4	90.5	91.0	75

*Mass balance forced to accommodate losses in handling

- Yields from in-situ filtration (% of filtration recovery)

n/m - not measured

Coal conversions determined on an SO₃ free basis from:

- (1) - THF insolubles in reactor product
- (2) - THF insolubles in the filter cake
- (3) - Quinoline insolubles reactor product.
- (4) - Quinoline insolubles in the filter cake.

TABLE 17A**SUMMARY OF FILTRATION TESTS - GLENHAROLD LIGNITE**

Run No.	NCF No.	Filter Membrane	Aperture, Retention (µm)	Temp (°C)	Viscosity (mPa s)	Solids in Feed (%)	Pressure (kPa)	Cake Resistivity (m/kg x 10 ¹⁰)	Total Flow After 30min. (kg / m ²)
10-LA	44	Conidur	100 x 500	300	1	11.5	210	2	551
11-LA	45	Conidur	100 x 500	200	2.8	6.2	138	67	63
	46	Conidur	100 x 500	280	0.6	6.2	352	220	110
12-LA	47	Conidur	100 x 500	300	0.4	5.4	348	685	91
	50	GFA	1	300	0.4	5.4	348	415	116
13-LA	48	Conidur	100 x 500	275	0.8	8.0	346	65	167
	49	GFA	1	310	0.5	8.0	347	31	306

TABLE 17B

SUMMARY OF FILTRATION TESTS - BLACK THUNDER COAL

Run No.	NCF No.	Filter membrane	Aperture, retention (µm)	Temp (°C)	Viscosity (mPa s)	Solids in Feed (%)	Pressure (kPa)	Cake Resistivity (m/kg x 10 ¹⁰)	Total Flow After 30min. (kg / m ²)
14 LA	51	GFA	1	290	0.6	4	143	450	67
							366	760	83
	52	Conidur	100 x 500	280	0.7	4	141	233	116
	53	GFA	1	300	0.5	3.1	143	439	84
	54	GFA	1	300	0.5	1.7	143	586	97
14b LA	55	GFA	1	300	0.6	4	138	630	56
							283	1400	54
							436	3450	43
							576	4260	44
	56	Conidur	60 x 400	300	0.6	4	143	560	61
							288	1510	52
							438	2340	52
							586	4470	43
15 LA	57	GFA	1	250	1	5.7	148	2660	18
							295	4720	19
							579	16600	14
16 LA	58	GFA	1	265	1	5.7	572	890	70
	59	GFA	1	270	1	6.2	135	1920	20
							286	2680	24
							564	6360	22
	60	Conidur	60 x 400	265	1	6.2	568	870	68
	61	GFA	1	300	0.6	6.2	566	12500	16
17 LA	63	GFA	1	200	4	5.8	560	3440	15
18 LA	62	GFA	1	290	0.5	6.8	566	221000	5
18a LA	64	GFA	1	280	0.8	6.8	filter blinded		
19 LA	65	GFA	1	255	1	15.5	139	58	64
20 LA	66 & 67	GFA	1	260	1	11	filter blinded		
21 LA	68	GFA	1	296	0.4	15	142	73	97
23o LA	69	GFA	1	300	0.4	5.3	210	33	208
23a LA	CONSOL	GFA	1	250	n/m	n/m	210	n/m	n/m
23c LA	CONSOL	GFA	1	250	n/m	n/m	210	n/m	n/m
23d LA	CONSOL	GFA	1	250	0.8	n/m	105	8	276
23f LA	CONSOL	GFA	1	250	n/m	n/m	210	n/m	n/m
23g LA	71	GFA	1	250	0.8	4.6	210	34	225
Coal/Oil Slurry	70	GFA	1	100	1	15	210	4	320

*erratic bridging of apertures
n/m: not measured.

TABLE 18

ASH IN FILTER FEEDS AND PRODUCTS

Run No.	NCF No.	Filter Membrane	Aperture, Retention (µm)	Ash Content (%)	Elements Identified in Filter Cake								
					S	Ca	Si	Al	Mg	Na	K	Ti	Fe
10-LA	44F	Conidur	100 x 500	0.5	✓	✓	✓	✓					✓
11-LA	45F	Conidur	100 x 500	0.2									
	46F(1 st)	Conidur	100 x 500	0.6	✓	✓	✓	✓	✓	✓		✓	✓
	46F	Conidur	100 x 500	<0.1	✓	✓							
12-LA	Feed			3.1	✓	✓	✓	✓	✓	✓	✓		✓
	47F(1 st)	Conidur	100 x 500	2.3	✓	✓	✓	✓	✓	✓	✓	✓	✓
	47F	Conidur	100 x 500	0.1	✓	✓	✓	✓					
	50F	GFA	1	<0.1	✓	✓							
13-LA	Feed			4.2	✓	✓	✓	✓	✓	✓	✓		✓
	48F	Conidur	100 x 500	<0.1									
	49F	GFA	1	<0.1									
14-LA	51F	GFA	1	0.1									
	54F	GFA	1	0.2									
14b-LA	55F	GFA		0.3									
	56F	Conidur	60 x 400										
15-LA	57F	GFA	1	0.1									
16-LA	Feed				✓	✓	✓	✓		✓			
	58F	GFA	1		t	✓				t			
	58FC				✓	✓	✓	✓		✓			
	61FDR			1.6	t	✓							
	61FC			16.7	✓	✓	✓	✓		✓			
17-LA	63FDR	GFA	1	0.4	t	t							
18-LA	Feed				✓	✓	✓	✓		✓			
19-LA	Feed			2.9	✓	✓	✓	✓					
20-LA	Feed			2.7	✓	✓	✓	✓					
21-LA	Feed			3	✓	✓	✓	✓			✓		
	68FC			7.8	t	✓	✓	✓			✓		
	68F	GFA	1				t			t			

F = Filtrate
 F(1st) = First runnings
 FC = Filter cake
 FDR = Filtrate distillation residue

√ = identified peak
 t = trace

TABLE 18 (Continued)

ASH IN FILTER FEEDS AND PRODUCTS

Run No.	NCF No.	Filter Membrane	Aperture, Retention (μm)	Ash Content (%)	Elemental Analysis % of Ash in Filter Cake									
					SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃
23o-LA	Feed													
	69FC			19.2										
	69F	GFA	1	0.5										
23a - LA	FC			18.8										
	F	GFA	1	0.5										
23c - LA	FC			21.3	30.3	15.9	1.0	6.1	20.8	4.5	0.4	7.4	1.2	10.2
	F	GFA	1											
23oac - LA	FDR			1.1										
23d - LA	FC			17.1	27.6	16.3	1.0	5.9	23.7	4.9	0.4	7.8	1.3	9.9
	F	GFA	1											
	FDR			0.6										
23f - LA	FC			20.4	28.6	16.5	1.2	6.0	22.4	4.7	0.4	6.9	1.2	10.2
	F	GFA	1											
	FDR			1.0										
23g - LA	Feed													
	71FC			17.8										
	71F	GFA	1											
	71FDR			0.8										
23h - LA	FC			19.8	27.1	16.9	1.1	5.8	23.7	5.0	0.3	8.3	1.2	9.8

F = Filtrate
 FC = Filter cake
 FDR = Filtrate distillation residue

TABLE 19A

ANALYTICAL DATA: FILTER CAKE INSOLUBLES

Run No	NCF No	Filter medium	Aperture/ Retention (µm)	Ash (%)	SO ₃ in Ash (%)	QI (%)	THFI (%)	C (%daf)	H (%daf)	O (%daf)	N (%daf)	S (%daf)
10LA	44	Conidur	100 x 500	34.6	n/m	39.9	44.1	n/m	n/m	n/m	n/m	n/m
11LA	45	Conidur	100 x 500	65.0	6.4	36.5	38.0	n/m	n/m	n/m	n/m	n/m
	46	Conidur	100 x 500	59.3	6.5	45.3	47.1	66.7	4.1	22.4	2.8	4.0
12LA	47	Conidur	100 x 500	61.9	7.8	51.2	55.8	n/m	n/m	n/m	n/m	n/m
	50	GFA	1	61.1	6.8	50.5	54.9	77.3	3.5	13.8	3.5	2.0
13LA	48	Conidur	100 x 500	31.2	8.0	43.9	59.7	79.8	4.7	11.4	2.3	1.9
	49	GFA	1	34.3	9.5	46.4	63.3	n/m	n/m	n/m	n/m	n/m
14LA	51	GFA	1	37.9	8.1	50.9	54.5	73.5	3.2	19.7	1.6	1.9
	52	Conidur	100 x 500	39.7	8.3	53.0	57.8	73.6	3.3	19.6	1.6	1.9
14bLA	55	GFA	1	32.8	10.4	54.2	59.6	74.6	3.7	18.2	1.5	2.0
	56	Conidur	60 x 400	36.1	9.1	52.3	57.9	77.2	3.8	15.5	1.4	2.1
15LA	57	GFA	1	40.6	9.0	55.0	59.1	74.8	4.5	18.3	1.4	1.0
16LA	61	GFA	1	39.6	n/m	36.7	42.1	70.0	4.6	22.3	2.0	1.1
19LA	65	GFA	1	11.5	n/m	40.8	47.7	81.0	3.9	12.8	1.5	0.8
21LA	68	GFA	1	14.8	n/m	48.6	53.1	82.1	3.8	11.7	1.5	0.9
23oLA	69	GFA	1	41.9	8.9	43.4	45.7	69.4	4.2	21.7	2.0	2.7
23aLA	consol	GFA	1	40.5	8.6	43.6	46.3	69.1	4.5	22.0	2.0	2.4
23cLA	consol	GFA	1	n/m	n/m	44.8	45.9	n/m	n/m	n/m	n/m	n/m
23dLA	consol	GFA	1	n/m	n/m	37.2	40.3	n/m	n/m	n/m	n/m	n/m
23fLA	consol	GFA	1	41.7	n/m	40.4	44.9	68.7	4.3	22.6	1.5	2.9
23gLA	71	GFA	1	42.2	n/m	40.8	42.1	65.8	4.0	25.8	1.5	2.9

Notes : Oxygen by difference

n/m : not measured

TABLE 19B

ANALYTICAL DATA: DISTILLATION RESIDUE, ONE-LITER AUTOCLAVE TESTS

Run No	NCF No	Filter Medium	Aperture/ Retention (μm)	ash (%)	SO ₃ in ash (%)	C (%daf)	H (%daf)	O (%daf)	N (%daf)	S (%daf)
10LA	44	Conidur	100 x 500	1.92	6.5	84.9	5.7	7.3	1.4	0.7
11LA	45	Conidur	100 x 500	0.59	6.4	80.2	6.8	11.2	1.2	0.6
	46	Conidur	100 x 500	<.01	6.5	80.1	6.0	11.7	1.6	0.6
12LA	47	Conidur	100 x 500	0.50	7.8	87.9	5.3	4.8	1.4	0.5
	50	GFA	1	0.39	6.8	86.6	5.6	6.1	1.3	0.4
13LA	48	Conidur	100 x 500	0.39	8.0	86.8	5.9	5.3	1.5	0.5
	49	GFA	1	0.07	9.5	86.5	5.9	5.7	1.4	0.5
14LA	51	GFA	1	0.47	8.1	84.1	6.3	8	1.3	0.3
	52	Conidur	100 x 500	0.89	8.3	84.2	6.1	8.2	1.3	0.3
14bLA	55	GFA	1	1.40	10.4	84.4	6.0	8.0	1.4	0.3
	56	Conidur	60 x 400	n/m	n/m	n/m	n/m	n/m	n/m	n/m
15LA	57	GFA	1	0.48	9.0	85.7	5.8	6.8	1.4	0.3
16LA	61	GFA	1	1.64	n/m	88.0	5.8	4.5	1.6	0.3
19LA	65	GFA	1	n/m	n/m	n/m	n/m	n/m	n/m	n/m
21LA	68	GFA	1	n/m	n/m	n/m	n/m	n/m	n/m	n/m
23oacLA	69/CONSOL	GFA	1	<0.01	n/m	85.3	6.1	6.9	1.5	0.3
23dLA	CONSOL	GFA	1	0.62	n/m	86.9	5.9	5.6	1.4	0.3
23fLA	CONSOL	GFA	1	1.04	n/m	85.9	6.1	6.2	1.5	0.3
23gLA	71	GFA	1	0.80	n/m	84.6	6.0	7.6	1.5	0.3

Notes: Oxygen by difference

n/m: not measured

TABLE 20

SIMULATED DISTILLATION OF FIRST-STAGE REACTOR PRODUCTS, ONE-LITER AUTOCLAVE TESTS

Sample No.		10LA	11LA	12LA	13LA	14LA	14bLA	15aLA	15LA	16LA	17LA	18LA	19LA	20LA	21LA	23oLA	23aLA	23cLA	23dLA	23fLA	23gLA
Found Recovery (%)		64.4	69.3	87.4	69.3	80.7	83.0	82.0	81.2	77.9	77.9	81.3	69.9	73.4	70.8	76.4	80.7	88.6	85.7	84.9	83.5
b pt (°C)	b pt (°F)	amount bpt < T ° (%)																			
150	302	0.0	0.3	0.0	0.0	0.4	0.4	0.0	0.0	0.0	0.2	0.4	0.0	0.00	0.3	0.3	0.3	0.0	0.0	0.0	0.0
200	392	1.2	1.3	0.7	0.5	0.7	0.8	0.7	0.7	0.8	1.4	1.5	0.6	0.7	1.3	1.4	1.5	0.8	0.4	1.3	0.7
250	482	2.4	4.9	3.3	1.0	6.3	6.6	6.4	6.3	4.3	5.3	5.8	4.1	3.5	5.0	6.2	6.5	5.4	3.5	5.6	3.4
300	572	4.7	8.1	6.5	1.7	10.1	10.0	9.8	9.7	7.9	8.7	9.4	6.7	5.9	7.8	9.9	10.3	9.0	6.9	9.5	6.8
350	662	14.8	23.3	19.0	3.0	26.6	26.1	25.9	25.7	26.1	25.4	26.8	21.3	25.1	23.6	28.3	28.4	29.6	25.2	28.7	26.1
400	752	34.1	40.4	42.4	7.4	49.2	48.6	48.4	47.9	51.8	49.1	50.8	42.6	50.3	46.0	52.7	54.1	56.1	52.5	56.3	54.3
450	842	54.1	56.8	67.6	30.5	66.2	64.9	65.2	67.7	66.7	63.5	65.7	56.6	64.9	59.9	67.5	69.1	73.0	69.3	72.1	70.3
500	932	60.3	62.7	77.0	57.5	73.5	72.0	72.2	71.3	73.2	70.0	72.4	62.7	70.6	65.8	73.8	75.7	80.1	77.0	79.2	77.8
550	1022	61.8	64.9	79.8	62.4	76.4	75.0	75.0	74.1	75.3	72.5	74.9	65.3	72.5	67.9	75.9	78.1	82.6	80.1	81.6	80.2
600	1112	63.1	66.5	82.5	64.2	78.5	77.5	77.7	76.5	76.6	74.3	76.9	67.1	73.3	69.5	76.4	79.6	84.5	82.2	83.3	82.0
650	1202	64.0	67.7	84.9	66.4	80.3	79.7	79.2	78.3	77.5	75.7	78.8	68.6	73.4	70.8	76.4	80.7	86.0	83.8	84.6	83.5
700	1292	64.4	68.5	86.3	68.0	80.7	81.1	80.5	79.6	77.9	76.7	79.9	69.6	73.4	70.8	76.4	80.7	87.0	84.8	84.9	83.5
750	1382	64.4	68.9	87.0	68.7	80.7	82.0	81.2	80.4	77.9	77.4	80.7	69.9	73.4	70.8	76.4	80.7	87.7	85.5	84.9	83.5
800	1472	64.4	69.3	87.4	69.3	80.7	83.0	82.0	81.2	77.9	77.9	81.3	69.9	73.4	70.8	76.4	80.7	88.6	85.7	84.9	83.5
510	950	60.7	63.1	77.7	59.6	74.2	72.7	72.8	72.0	73.7	70.6	72.9	63.3	71.1	66.3	74.3	76.3	80.6	77.6	79.7	78.3
566	1050	62.2	65.4	80.6	63.0	77.2	75.8	75.8	74.9	75.8	73.1	75.6	65.9	72.9	68.4	76.4	78.5	83.2	80.8	82.1	80.8

TABLE 21

SIMULATED DISTILLATION OF RECOVERED SOLVENTS FROM ONE-LITER AUTOCLAVE TESTS

Sample No.	NCF 44	NCF 45	NCF 46	NCF 47	NCF 48	NCF 49	NCF 50	NCF 51	NCF 52	NCF 55	NCF 57	NCF 61	NCF 63	23oac LAF	23d LAF	23f LAF	23g LAF	RAO
Found Recovery (%)	102.1	98.3	105.7	103	102.6	103.1	103.1	103.3	102.4	104.6	104.7	105.9	106.2	109.0	107.1	105.9	105.7	106.7
b pt (°C)	b pt (°F)	amount bpt < T ° (%)																
150	302	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0
200	392	0.6	0.7	0.4	1.0	0.0	0.0	0.5	0.9	0.8	0.5	0.0	1.7	1.8	0.9	0.9	1.6	1.8
250	482	1.5	5.7	5.1	2.8	0.0	0.7	2.0	6.8	5.1	6.0	2.8	4.0	7.0	6.3	6.6	7.8	10.1
300	572	4.4	10.5	10.0	6.7	0.8	1.2	5.6	11.7	10.0	10.9	6.0	8.0	12.0	11.0	12.0	13.0	15.7
350	662	20.3	34.4	34.3	22.7	2.4	3.0	21.7	33.3	31.3	34.5	29.0	32.0	35.5	35.5	38.5	38.3	38.0
400	752	52.0	66.4	67.0	53.5	8.8	10.0	52.0	64.0	62.0	66.5	64.0	68.0	69.0	70.0	76.7	74.5	70.7
450	842	87.5	88.5	89.0	87.0	46.0	47.0	86.0	87.2	86.2	89.6	90.1	89.9	89.8	90.7	96.2	94.1	89.9
500	932	98.2	96.3	97.3	98.3	91.0	91.5	97.8	96.2	95.3	97.2	97.7	98.3	97.2	98.3	100.0	99.0	97.7
550	1022	100.0	100.0	99.2	100.0	98.3	98.5	100.0	98.8	98.6	99.3	99.8	100.0	99.0	100.0	100.0	100.0	100.0
600	1112	100.0	100.0	100.0	100.0	99.4	99.5	100.0	99.8	99.8	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
650	1202	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
700	1292	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
750	1382	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
800	1472	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
510	950	98.5	96.6	97.9	98.8	94.3	95.0	98.1	97.0	96.5	97.8	98.2	98.8	97.6	98.6	100.0	99.2	98.0
566	1050	100.0	100.0	99.5	100.0	98.8	99.0	100.0	99.2	99.1	99.6	100.0	100.0	99.2	100.0	100.0	100.0	100.0

RAO = Reilly anthracene oil

TABLE 22

SIMULATED DISTILLATION OF DISTILLATION RESIDUES FROM ONE-LITER AUTOCLAVE TESTS

Sample No.		NCF 44	NCF 45	NCF 46	NCF 47	NCF 48	NCF 49	NCF 50	NCF 51	NCF 52	NCF 55	NCF 57	NCF 61	NCF 63	23oac LAF	23d LAF	23f LAF	NCF71
Found Recovery (%)		12.6	14.5	11.6	30.7	31.4	32.4	22.3	23.8	15.6	18.1	19.9	18.0	26.3	15.8	36.4	32.4	24.1
b pt (°C)	b pt (°F)	amount bpt < T ° (%)																
150	302	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.1
200	392	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.4	0.0	0.3	0.3	0.2	0.2	0.2
250	482	0.1	0.0	0.0	0.2	0.0	0.2	0.0	0.0	0.4	0.0	0.6	0.0	0.3	0.5	0.3	0.3	0.3
300	572	0.1	0.0	0.0	0.2	0.0	0.2	0.0	0.0	0.5	0.0	0.8	0.1	0.3	0.6	0.4	0.3	0.5
350	662	0.1	0.0	0.0	0.2	0.0	0.2	0.0	0.0	0.5	0.0	1.0	0.1	0.4	1.1	0.6	0.3	0.6
400	752	0.3	0.1	0.0	0.3	0.0	0.3	0.0	0.1	0.6	0.1	1.1	0.3	0.7	1.6	0.7	0.6	0.7
450	842	0.4	0.1	0.0	0.4	0.0	0.3	0.5	0.2	0.6	0.1	1.3	0.7	1.2	1.9	5.0	2.8	1.0
500	932	1.1	1.4	0.7	1.1	0.5	1.0	0.8	1.2	1.1	0.5	5.3	2.9	5.6	3.0	17.2	13.0	6.5
550	1022	2.4	4.3	3.7	3.5	1.9	2.9	2.8	5.2	3.5	1.9	9.8	6.6	9.5	5.3	23.3	18.5	11.1
600	1112	5.5	7.7	7.9	11.0	6.1	7.5	7.7	11.7	7.6	5.7	13.2	10.0	13.8	8.1	27.5	22.9	15.0
650	1202	9.0	10.7	10.4	20.6	15.4	16.8	14.1	17.2	11.5	10.4	16.0	13.1	18.3	11.3	31.1	26.7	18.3
700	1292	11.1	12.8	11.5	26.1	24.5	26.7	18.5	20.9	14.1	13.0	17.9	15.0	21.8	13.7	33.8	29.5	20.7
750	1382	12.0	13.8	11.6	28.6	28.6	29.3	20.4	23.0	15.4	16.3	19.1	16.2	24.2	15.0	35.5	31.1	22.4
800	1472	12.6	14.5	11.6	30.7	31.4	32.4	22.3	23.8	15.6	18.1	19.9	18.0	26.3	15.8	36.4	32.4	24.1
510	950	1.3	2.0	1.3	1.4	0.9	1.3	0.9	1.8	1.4	0.6	6.2	3.4	6.0	3.5	18.4	14.1	7.4
566	1050	3.3	5.4	5.0	5.2	2.8	4.0	3.8	7.1	4.7	2.9	10.9	7.4	10.9	6.2	24.6	19.9	12.3

TABLE 23

**SIMULATED DISTILLATION OF FIRST-STAGE DISTILLATE OILS
FROM ONE-LITER AUTOCLAVE TESTS**

Sample No.		23c-LA	23d-LA	23f-LA	23g-LA	23h-LA
Found Recovery (%)		87.5	91.7	96.8	98.5	97.5
b pt (°C)	b pt (°F)	amount in fraction (%)				
<150	<302	3.8	2.5	2.6	2.7	2.6
150-200	302-392	8.0	8.5	9.1	9.0	8.8
200-250	392-482	30.9	33.3	32.1	32.9	31.7
250-300	482-572	10.9	11.9	14.2	14.4	13.5
300-350	572-662	20.4	20.7	21.8	22.0	22.6
350-400	662-752	10.5	11.7	12.4	12.9	12.9
400-450	752-842	2.4	2.7	3.2	3.0	3.5
450-500	842-932	0.6	0.4	0.9	1.2	1.0
500-550	932-1022	0.0	0.0	0.5	0.4	0.9
550-600	1022-1112	0.0	0.0	0.0	0.0	0.0

bpt (°C)	bpt (°F)	amount bpt <T° (%)				
<150	<302	3.8	2.5	2.6	2.7	2.6
<200	<392	11.8	11.0	11.7	11.7	11.4
<250	<482	42.7	44.3	43.8	44.6	43.1
<300	<572	53.6	56.2	58.0	59.0	56.6
<350	<662	74.0	76.9	79.8	81.0	79.2
<400	<752	84.5	88.6	92.2	93.9	92.1
<450	<842	86.9	91.3	95.4	96.9	95.6
<500	<932	87.5	91.7	96.3	98.1	96.6
<550	<1022	87.5	91.7	96.8	98.5	97.5
<600	<1112	87.5	91.7	96.8	98.5	97.5

TABLE 24

COMPARISON OF MICROAUTOCLAVE HYDROTREATING RESULTS

First-Stage Sample No.	Filtration and Hydrotreat Run No.	566 °C* to Hydrotreater, wt % MAF Feed	566 °C* Resid Conversion, wt % MAF Resid	C ₁ -C ₃ Gas Yield, wt % Feed	C ₁ -C ₃ Gas Yield per g Resid Converted	H ₂ Uptake, mg/g MAF Feed	H ₂ Uptake per g Resid Converted
8-LA (A&B) heavy extract (a)	NCF 37DR; R6-227-1	44.4	55.3	4.5	18.2	20	81
	NCF 37DR; R6-228-1	44.4	59.6	4.1	15.4	26	97
8C-LA DR lights (b)	R6-309-1	32.5	53.5	4.5	25.6	35	201
8C-LA heavies (c)	NCF 42F1; R6-309-2	36.0	58.2	4.5	21.7	46	219
	NCF 42F1; R7-013-1	36.0	55.4	6.4	32.0	50	252
	NCF 42F1; R7-043-1 [1.5g sample]	36.0	53.0	4.6	23.8	44	230
10-LA (b)	NCF 44FDR; R6-323-1	99.0	57.3	na	na	na	na
	NCF 44FDR; R6-009-3	99.0	58.0	8.2	14.4	51	89
11-LA (b)	NCF 46FDR; R6-346-1	98.0	65.1	na	na	na	na
	NCF 46FDR; R7-013-2	98.0	59.2	8.5	14.6	47	81
	NCF 46FDR; R7-041-1	98.0	57.3	8.6	15.4	49	87
9-LA (d)	NCF 43F2DR; R7-048-1	99.7	37.5	7.8	20.8	27	72
	NCF 43F2DR; R7-048-2	99.7	38.9	7.8	20.0	33	85
12-LA (b)	NCF 47FDR; R6-352-1	94.8	33.1	na	na	na	na
	NCF 50FDR; R7-055-1	96.9	37.1	7.2	19.9	42	116
13-LA (b)	NCF 49FDR; R6-352-2	95.1	43.5	na	na	na	na
	NCF 48FDR; R7-063-2	97.2	44.7	7.3	16.8	49	113
14-LA (b)	NCF 51,52, 55&56 FDR R7-056-1	95.9	50.9	na	na	na	na
	NCF 51,52, 55&56 FDR R7-063-1	95.9	53.3	11.2	21.9	58	114
15-LA (b)	NCF 57FDR; R7-064-1	93.5	44.1	8.7	21.2	43	105

- (a) Hydrotreated at 440 °C for 60 min with 1,000 ppm Mo in Molyvan L.
 (b) Hydrotreated at 440 °C for 60 min with 10,000 ppm Mo in Molyvan L.
 (c) Insoluble in Wilsonville solvent at 60 °C; redissolved in aromatic solvent and concentrated to give higher extract concentrations.
 (d) No catalyst added, 440 °C for 60 min with 2% H₂S in H₂.

TABLE 25

SECOND-STAGE MICROAUTOCLAVE CATALYTIC UPGRADING PRODUCT ANALYSES

Run No.	Sample ID	Nitrogen, %	Carbon, %	Hydrogen %	O+S+ Ash, % (diff)	H /C ratio
NCF 50 FDR (12-LA)	44890	1.6	88.8	5.4	4.2	0.06
R7-055-1D	44883	2.0	90.3	8.2	-0.5	0.09
R7-055-1R	44884	1.5	86.6	4.7	7.2	0.05
NCF 48 FDR (13-LA)	44889	1.3	85.6	5.6	7.5	0.07
R6-352-2D	44887	1.7	90.2	8.8	-0.7	0.10
R6-352-2R	44888	1.3	85.4	5.0	8.3	0.06
NCF 51,52,55, 56 FDR (14-LA)	44891	1.6	82.7	6.0	9.7	0.07
R7-056-1D	44885	1.8	90.0	9.1	-0.9	0.10
R7-056-1R	44886	1.3	78.5	4.4	15.8	0.06
NCF 57 FDR (15-LA)	avg (2)	1.4	86.5	5.8	6.2	0.07
R7-064-1D	44990	1.7	78.9	9.4	10.0	0.12
R7-064-1R	44991	1.5	85.1	4.9	8.5	0.06
R7-091-1D	45103	1.8	84.8	9.1	4.4	0.11
R7-091-1R	45104	1.5	84.6	4.4	9.5	0.05
R7-097-1D	45105	1.4	80.6	9.7	8.4	0.12
R7-097-1R	45106	1.4	84.1	5.1	9.4	0.06
R7-099-1D	45107	1.7	86.7	9.0	2.6	0.10
R7-099-1R	45108	1.4	83.0	4.4	11.2	0.05

TABLE 26

**SECOND-STAGE TASK 3 MICROAUTOCLAVE TEST RESULTS
RUN 15-LA AND 15a-LA COMPOSITED FEEDSTOCK (150a) (a,b)**

Filtration and Hydrotreat Run No.	Hydrotreat Time, min	566 °C⁺ Resid Conversion, wt % MAF Resid	C₁-C₃ Gas Yield, wt % Feed	C₁-C₃ Gas Yield per g Resid Converted	H₂ Uptake, mg/g MAF Feed	H₂ Uptake per g Resid Converted
<i>NCF 57FDR 150a-3, 50ma [R7-097-1]</i>	30	38.7	6.6	18.2	38	104
<i>NCF 57FDR 150a-1, 50ma [R7-064-1]</i>	60	44.1	8.7	21.2	43	105
<i>NCF 57FDR 150a-4, 50ma [R7-099-1]</i>	90	49.7	10.6	22.8	56	120
<i>NCF 57FDR 150a-2, 50ml [R7-091-1]</i>	120	51.0	12.1	25.3	67	140

- a. Hydrotreated at 440 °C with 10,000 ppm Mo in Molyvan L.
b. 93.5 wt % (MAF feed basis) 566 °C⁺ to the hydrotreater, each run.

TABLE 27

**SECOND-STAGE MICROAUTOCLAVE HYDROTREATING TESTS
OF FIRST-STAGE RUN 23d-LA FILTRATE(a)**

Run No.	23d-1, 50 MA [R7-202-1]	23d-2, 50 MA [R7-202-2]	23d-3, 50 MA [R7-210-1]	Average ± Standard Deviation
Catalyst precursor	Molyvan L	Molyvan L	Molyvan L	-
Reaction time, min	60	60	60	-
Reaction Temperature, °C	440	440	440	
Mo, ppmw feed	10,028	10,082	10,043	10,051 ±28
Products, wt % MAF feed				
C ₁ -C ₃ gas (b)	3.2	4.5	5.0	4.2 ±0.9
C ₄ + vapor	1.4	2.2	2.3	1.9 ±0.5
CO + CO ₂	0.5	0.4	0.5	0.5 ±0.1
566 °C ⁻	51.8	51.8	53.5	52.4 ±1.0
566 °C ⁺	43.1	41.1	38.7	41.0 ±2.3
Total	100	100	100	100
Derived values				
Resid conversion, wt % 566 °C ⁺	42.6	45.2	48.5	45.4 ±3.0
H ₂ consumed, mg/ g MAF feed	46	37	41	41 ±4
C ₁ -C ₃ gas, wt % MAF feed (c)	3.0	4.0	4.4	3.8 ±0.7
SIMDIS adjustments to distillation resid weight, g	-0.064	-	-	-

- (a) 2g samples of 23d-LA distilled filtrate used in each test. The filtrate contained 1.36 wt % ash.
 (b) Calculated from composition, pressure and temperature of the mounted reactor, using the ideal gas correlation with a compressibility factor of 1.0
 (c) Calculated from composition and volume of recovered reactor gas (some gas may be lost transferring the reactor and filling the sample piston)

TABLE 28

SUMMARY OF TASK 3 300 mL CSTR SECOND-STAGE TEST RESULTS (a)

Run No.	15oa-1, 300 CSTR [R7-111-1]	DARo-1, 300 CSTR [R7-167-1]	23oac-1, 300 CSTR [R7-181-1]	23dfg-1, 300 CSTR [R7-223-1]	263J-1, 300 CSTR [R7-239-1]
Feedstock	15-LA Filtrate Resid [NCF 57 FDR]	R-258A DAR	23-LA Filtrate Resid Blend	23-LA Filtrate Resid Blend	Wilsonville Run 263J Interstage Product
Feed, g	50	100	94	93	100
Moly-van L, g	6.2	12.3	11.6	11.6	12.3
DMDS feed, g	4.8	6.9	7.2	7.1	7.4
566°C+ in feedstock, wt % MAF feed	89.0	75.7	93.8	80.9	66.5
566°C+ resid conv., wt % MAF feed	49.2	63.3	57.3	65.0	43.9
C ₁ -C ₃ gas yield, wt % MAF feed	22.6	12.6	17.3	15.2	18.4
C ₁ -C ₃ gas yield per g resid converted	51.6	26.3	32.2	28.9	63.0
H ₂ uptake by diff., mg/g MAF feed (b)	54	18	29	33	27
H ₂ uptake per g resid converted	123	38	54	63	92
H ₂ balance, (uptake basis), % (c)	99	110	107	98	101
Fixed carbon ratio, out/in (d)	2.7	1.6	0.8	0.7	1.0

(a) All tests 440C, 60 min.

(a) Includes the hydrogen associated with the decomposition of DMDS.

(b) Excludes hydrogen gas calculated to be merely passing through the reactor.

(c) Fixed carbon in product recovered from the reactor (excludes distillate) divided by fixed carbon in the feed.

TABLE 29A**ELEMENTAL ANALYSES OF PRODUCTS - RUN 15oa-1, 300 CSTR**

	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % (Diff)	Ash, wt %	Total
NCF 57 FDR (feedstock)	86.5	5.8	1.4	0.3	5.3	0.6	100.0
Molyvan L	50.9	9.3	1.4	11.7	1.2	25.6	100.0
DMDS	27.1	6.3	1.8	58.1	6.8	0.0	100.0
Dry reactor scrape	83.2	5.4	1.4	1.6	-0.0	8.4	100.0
THF reactor wash	81.4	5.4	1.7	1.2	2.8	7.6	100.0
Dry scrubber scrape	54.7	11.2	2.5	8.0	23.2	0.4	100.0
THF scrubber wash	54.7	11.2	2.5	8.0	23.2	0.4	100.0

TABLE 29B**ELEMENTAL ANALYSES OF PRODUCTS - RUN DARo-1, 300 CSTR**

	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % (Diff.)	Ash, wt %	Total
R 258A DAR	90.8	6.9	1.1	0.1	1.1	0.1	100.0
Molyvan L	50.9	9.3	1.4	11.7	1.2	25.6	100.0
DMDS	27.1	6.3	1.8	58.1	6.8	0.0	100.0
Dry reactor scrape	85.3	7.0	1.4	1.1	3.1	2.1	100.0
THF reactor wash	84.2	6.7	1.4	1.0	3.0	3.7	100.0
Dry scrubber scrape	82.0	11.4	1.1	2.7	2.7	0.1	100.0
THF scrubber wash	82.0	11.4	1.1	2.7	2.7	0.1	100.0

TABLE 29C**ELEMENTAL ANALYSES OF PRODUCTS - RUN 23oac-1, 300 CSTR**

	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % (Diff.)	Ash, wt %	Total
23oac resid feedstock	84.22	5.94	1.48	0.28	6.94	1.14	100
Molyvan L	50.88	9.27	1.37	11.7	1.21	25.57	100
DMDS	27.08	6.28	1.76	58.08	6.8	0	100
Dry reactor scrape	84.52	6.27	1.51	1.15	0.03	6.52	100
THF reactor wash	80.78	6.1	1.39	0.91	5.5	5.32	100
Dry scrubber scrape, tops	80.28	11.59	1.41	0.57	6.1	0.05	100
Dry scrubber scrape, bottoms	1.34	10.48	4.88	7.01	76.24	0.05	100
THF scrubber wash	80.28	11.59	1.41	0.57	6.1	0.05	100

TABLE 29D**ELEMENTAL ANALYSES OF PRODUCTS - RUN 23dfg-1, 300 CSTR**

	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % (DIFF)	Ash, wt %	Total
23d resid feedstock	86.9	5.9	1.4	0.3	4.9	0.6	100.0
23f resid feedstock	85.0	6.0	1.4	0.3	6.2	1.0	100.0
23g resid feedstock	84.6	6.0	1.5	0.3	6.9	0.8	100.0
Molyvan L	50.9	9.3	1.4	11.7	1.2	25.6	100.0
DMDS	27.1	6.3	1.8	58.1	6.8	0.0	100.0
Dry reactor scrape	82.2	6.8	1.7	1.1	2.5	5.7	100.0
THF reactor and scrubber wash	82.8	5.9	1.4	1.6	1.6	6.8	100.0
Dry scrubber scrape, tops	84.6	10.0	1.5	1.0	3.0	0.0	100.0
Dry scrubber scrape, bottoms	1.2	10.8	4.4	5.3	78.4	0.0	100.0

TABLE 29E**ELEMENTAL ANALYSES OF PRODUCTS - RUN 23J-1, 300 CSTR**

	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % (Diff.)	Ash, wt %	Total
263J interstage feedstock	73.8	5.3	1.1	1.1	4.2	14.4	100.0
Molyvan L	50.9	9.3	1.4	11.7	1.2	25.6	100.0
DMDS	27.1	6.3	1.8	58.1	6.8	0.0	100.0
Dry reactor scrape	68.5	4.6	0.6	2.7	0.4	23.3	100.0
THF reactor and scrubber wash	69.9	5.2	0.6	2.4	3.4	18.5	100.0
Dry scrubber scrape, tops	87.3	9.8	0.5	0.7	1.7	0.0	100.0
Dry scrubber scrape, bottoms	1.2	11.2	5.0	5.1	77.5	0.0	100.0

TABLE 30**MATERIAL BALANCE DATA FOR 300 mL CSTR TESTS**

Run No.	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % diff	ash, wt %	Total, wt %
15oa-1, 300 CSTR [R7-111-1]	101	99	97	100 ^a	89	162	102
DARo-1, 300 CSTR [R7-167-1]	100	105	96	86	177	61	100
23oac-1, 300 CSTR [R7-181-1]	95	103	98	60	101	113	96
23dfg-1, 300 CSTR [R7-223-1]	88	99	97	45	105	101	90
263J-1, 300 CSTR [R7-239-1]	94	100	84	73	102	99	95

(a) Forced sulfur balance via addition of DMDS to the feed (for this run only). Subsequent DMDS rates were measured volumetrically.

TABLE 31
ELEMENTAL ANALYSES OF DARo-1, 300 CSTR "REACTOR DRY SCRAPE" PRODUCT

Sample	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % diff	ash, wt %	Total, wt %	H/C Ratio
whole reactor dry scrape	85.27	7.00	1.40	1.12	3.14	2.07	100.00	0.082
566 °C ⁻ distillate fraction	91.53	7.15	1.01	0.03	0.11	0.17	100.00	0.078
566 °C ⁻ distillate fraction, normalized to 100% recovery	82.51	8.81	1.57	0.43	6.65	0.03	100.00	0.107
566 °C ⁺ residual fraction	89.44	4.27	1.14	2.16	-2.17	5.16	100.00	0.048

TABLE 32
ELEMENTAL ANALYSES OF 23oac-1, 300 CSTR "REACTOR DRY SCRAPE" PRODUCT

Sample	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % diff	ash, wt %	Total, wt %	H/C Ratio
whole reactor dry scrape	84.52	6.27	1.51	1.15	0.03	6.52	100.00	0.074
566 °C ⁻ distillate fraction	82.96	8.34	1.46	0.04	7.20	0.00	100.00	0.101
566 °C ⁻ distillate fraction, normalized to 100% recovery	88.07	10.44	1.67	0.29	2.56	-3.03	100.00	0.119
566 °C ⁺ residual fraction	81.91	3.20	1.39	1.78	(1.83)	13.55	100.00	0.039

TABLE 33
ELEMENTAL ANALYSES OF 23dfg-1, 300 CSTR "REACTOR DRY SCRAPE" PRODUCT

Sample	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % diff	ash, wt %	Total, wt %	H/C Ratio
whole reactor dry scrape	82.18	6.84	1.665	1.075	2.52	5.72	100.00	0.083
566 °C ⁻ distillate fraction	88.98	7.08	1.35	0.04	2.51	0.04	100.00	0.080
566 °C ⁻ distillate fraction, normalized to 100% recovery	83.08	9.73	2.03	0.12	7.24	-2.19	100.00	0.117
566 °C ⁺ residual fraction	81.11	3.44	1.24	2.20	-3.02	15.03	100.00	0.042

TABLE 34
ELEMENTAL ANALYSES OF 263J-1, 300 CSTR "REACTOR DRY SCRAPE" PRODUCT

Sample	C, wt %	H, wt %	N, wt %	S, wt %	O, wt % diff	ash, wt %	Total, wt %	H/C Ratio
whole reactor dry scrape	68.47	4.56	0.60	2.72	0.36	23.30	100.00	0.067
566 °C ⁻ distillate fraction	86.10	8.28	1.03	0.03	4.56	0.00	100.00	0.096
566 °C ⁻ distillate fraction, normalized to 100% recovery	91.78	10.91	-0.02	1.52	0.17	-4.36	100.00	0.119
566 °C ⁺ residual fraction	59.76	2.19	0.83	3.16	0.43	33.63	100.00	0.037

Figure 2. Process Configuration for Operation with Integrated Filter.

HP Continuous Flow CSTR Modifications

Figure 3a. Gas Supply System

Figure 3b. DMDS Supply and Reactor.

Figure 3c. Distillate Collection and Gas Scrubbing

Figure 4. Filtration Test NCF48.

Figure 5. Filtration Test NCF56.

Figure 6. Filtration Test NCF59.

Figure 7. Relationship Between Filtration Rate and Coal Conversion as a Function of Reaction Conditions Severity.

Filtrate Hydrotreating Data

440 C for 60 min, 10,000 ppmw Mo

Figure 8. Results of Microautoclave Studies: Resid Conversion and Hydrogen Uptake.

Resid Conversion Kinetics

440 C, 2% H₂S, 10.1 MPa (1450 psig) total charge pressure

*3g DAR with 0.1% Mo in Molyvan L

**2g NCF 57 FDR (15oa La) resid with 1% Mo in Molyvan L

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Figure 9. Resid Conversion Kinetics.

Hydrogen Requirements

440 C, 2% H₂S, 10.1 MPa (1450 psig) total charge pressure
2g NCF 57 FDR (150a La) resid with 1% Mo in Molyvan L

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Figure 10. Hydrogen Requirements of the Extended Run Time Microautoclave Tests.

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	15oa-1, 300 CSTR	DARo-1, 300 CSTR	23oac-1, 300 CSTR	23dfg-1, 300 CSTR	263J-1, 300 CSTR
488-566 C	2.84	13.72	3.86	4.91	6.41
427-488 C	1.89	8.84	2.32	4.86	5.73
315-427 C	4.30	10.84	8.23	12.15	10.99
177-315 C	10.13	13.91	19.89	26.92	15.08
IBP-177 C	6.24	4.32	3.67	3.50	3.69
C4+ vapor	5.93	8.01	4.35	3.96	1.84
Total	31.33	59.64	42.32	56.30	43.74

Figure 11. Calculated Net Boiling Ranges for the 566 °C⁻ Product Fractions for the 300 mL CSTR Runs.

APPENDIX 1

ANALYTICAL DATA FOR RECOVERED SOLVENTS AND FILTRATES FOR ONE-LITER AUTOCLAVE TESTS, RUNS 10-LA THROUGH 23g-LA

TABLE A1-1. ANALYTICAL DATA: RECOVERED SOLVENT, ONE-LITER AUTOCLAVE TESTS

Run No	NCF No	Filter medium	Aperture/ Retention, (µm)	ash (%)	C (%daf)	H (%daf)	O (%daf)	N (%daf)	S (%daf)
10LA	44	Conidur	100 x 500	0.06	91.9	8.7	-1.8	1.1	0.2
11LA	45	Conidur	100 x 500	<0.01	88.8	6.7	3.0	0.9	0.6
	46	Conidur	100 x 500	0.04	89.9	6.6	1.8	1.2	0.5
12LA	47	Conidur	100 x 500	0.02	92.1	7.7	-1.4	1.4	0.2
	50	GFA	1	0.04	93.1	6.8	-0.3	0.2	0.2
13LA	48	Conidur	100 x 500	n/m	87.6	9.7	1.8	0.8	0.1
	49	GFA	1	0.04	89.5	9.5	-0.2	1.2	0.1
14LA	51	GFA	1	<0.01	92.1	6.3	0.1	1.2	0.5
	52	Conidur	100 x 500	<0.01	92.2	6.2	-0.3	1.4	0.5
14bLA	55	GFA	1	0.09	91.8	6.2	0.2	1.3	0.5
	56	Conidur	60 x 400	n/m	n/m	n/m	n/m	n/m	n/m
15LA	57	GFA	1	<0.01	91.3	6.1	0.7	1.4	0.5
16LA	61	GFA	1	<0.01	93.4	5.9	-1.2	1.3	0.5
19LA	65	GFA	1	n/m	n/m	n/m	n/m	n/m	n/m
21LA	68	GFA	1	n/m	n/m	n/m	n/m	n/m	n/m
23oacLA	69/CONSOL	GFA	1	<0.01	91.9	6.1	0.3	1.1	0.5
23dLA	CONSOL	GFA	1	0.02	91.1	6.0	1.2	1.1	0.5
23fLA	CONSOL	GFA	1	<0.01	91.7	6.0	0.0	1.1	0.6
23gLA	71	GFA	1	0.08	91.6	6.0	0.7	1.1	0.5

Notes: Oxygen by difference

n/m: not measured

TABLE A1-2. ANALYTICAL DATA: FILTRATES, ONE-LITER AUTOCLAVE TESTS

Run No	NCF No	Filter medium	Aperture/ Retention (µm)	ash (%)	SO ₃ in ash (%)	C (%daf)	H (%daf)	O (%daf)	N (%daf)	S (%daf)
10LA	44	Conidur	100 x 500	1.92	6.5	84.9	5.7	7.3	1.4	0.7
11LA	45	Conidur	100 x 500	0.59	6.4	80.2	6.8	11.2	1.2	0.6
	46	Conidur	100 x 500	<.01	6.5	80.1	6.0	11.7	1.6	0.6
12LA	47	Conidur	100 x 500	0.50	7.8	87.9	5.3	4.8	1.4	0.5
	50	GFA	1	0.39	6.8	86.6	5.6	6.1	1.3	0.4
13LA	48	Conidur	100 x 500	0.39	8.0	86.8	5.9	5.3	1.5	0.5
	49	GFA	1	0.07	9.5	86.5	5.9	5.7	1.4	0.5
14LA	51	GFA	1	0.47	8.1	84.1	6.3	8	1.3	0.3
	52	Conidur	100 x 500	0.89	8.3	84.2	6.1	8.2	1.3	0.3
14bLA	55	GFA	1	1.40	10.4	84.4	6.0	8.0	1.4	0.3
	56	Conidur	60 x 400	n/m	n/m	n/m	n/m	n/m	n/m	n/m
15LA	57	GFA	1	0.48	9.0	85.7	5.8	6.8	1.4	0.3
16LA	61	GFA	1	1.64	n/m	88.0	5.8	4.5	1.6	0.3
19LA	65	GFA	1	n/m	n/m	n/m	n/m	n/m	n/m	n/m
21LA	68	GFA	1	n/m	n/m	n/m	n/m	n/m	n/m	n/m
23oacLA	69/CONSOL	GFA	1	<0.01	n/m	85.3	6.1	6.9	1.5	0.3
23dLA	CONSOL	GFA	1	0.62	n/m	86.9	5.9	5.6	1.4	0.3
23fLA	CONSOL	GFA	1	1.04	n/m	85.9	6.1	6.2	1.5	0.3
23gLA	71	GFA	1	0.80	n/m	84.6	6.0	7.6	1.5	0.3

Notes: Oxygen by difference

n/m: not measured

APPENDIX 2
BOILING POINT DISTRIBUTION OF PRODUCTS
FROM 300 mL CSTR TESTS

TABLE A2-1

**BOILING RANGE DISTRIBUTION FOR RUN 150a-1, 300 CSTR,
wt % AS DETERMINED**

Boiling Point Range, °C	Feed	Distillate Accumulator Dry Scrape	Reactor Dry Scrape	Reactor THF Scrape
0-100	N/A	2.67	N/A	N/A
101-150	N/A	34.56	N/A	N/A
151-200	N/A	17.24	2.88	N/A
201-250	N/A	17.16	1.46	6.06
251-300	N/A	11.89	1.87	1.67
301-350	N/A	8.69	3.84	3.74
351-400	N/A	4.71	5.46	5.20
401-450	1.30	1.37	5.29	5.09
451-500	3.96	1.72	4.99	4.67
501-550	4.53	N/A	3.60	3.37
551-600	3.43	N/A	2.93	2.71
601-650	2.78	N/A	2.68	2.45
651-700	1.91	N/A	2.43	2.15
701-750	1.22	N/A	2.06	1.81
751-800	0.77	N/A	1.20	0.99
800+	80.10	N/A	59.30	60.10
Total	100.00	100.00	100.00	100.00

TABLE A2-2**BOILING RANGE DISTRIBUTION FOR RUN DARo-1, 300 CSTR,
wt % AS-DETERMINED**

Boiling Point Range, °C	Distillate Accumulator Dry Scrape	Reactor Dry Scrape	Reactor THF Scrape
0-100	7.06	N/A	N/A
101-150	29.48	N/A	N/A
151-200	17.98	N/A	N/A
201-250	16.61	9.49	6.25
251-300	9.96	3.31	2.95
301-350	9.87	5.53	5.63
351-400	5.81	8.41	8.62
401-450	2.32	10.65	10.54
451-500	0.92	12.67	12.52
501-550	N/A	12.09	11.91
551-600	N/A	10.12	9.92
601-650	N/A	7.97	7.70
651-700	N/A	6.12	5.85
701-750	N/A	3.97	3.84
751-800	N/A	2.16	2.46
800+	N/A	7.50	11.80
Total	100.00	100.00	100.00

TABLE A2-3

**BOILING RANGE DISTRIBUTION FOR RUN 23oac-1 300 CSTR,
wt % AS-DETERMINED**

Boiling Point Range, °C	Feed: 23LA Blend	Distillate Accumulator Dry Scrape, Supernatant Fraction	Reactor Dry Scrape	Reactor THF Scrape
0-100	N/A	6.38	N/A	N/A
101-150	N/A	30.23	N/A	N/A
151-200	N/A	22.52	7.79	N/A
201-250	0.44	24.25	3.95	8.76
251-300	0.15	9.94	3.66	3.76
301-350	0.42	3.39	6.63	7.61
351-400	0.56	2.02	6.70	7.62
401-450	0.33	1.27	4.48	5.28
451-500	1.11	N/A	4.11	4.66
501-550	2.14	N/A	3.15	3.50
551-600	2.97	N/A	2.90	3.13
601-650	3.18	N/A	2.67	2.77
651-700	2.38	N/A	2.33	2.42
701-750	1.30	N/A	1.64	1.65
751-800	0.88	N/A	0.59	0.74
800+	84.14	N/A	49.40	48.10
Total	100.00	100.00	100.00	100.00

TABLE A1-4

**BOILING RANGE DISTRIBUTION FOR RUN 23dfg-1, 300 CSTR,
wt % AS-DETERMINED**

Boiling Point Range, °C	Feed 23D-FDR	Feed 23F-FDR	Feed 23G-FDR	Distillate Accumulator Dry Scrape, Supernatant Fraction	Reactor Dry Scrape	Reactor THF Scrape
0-100	N/A	N/A	N/A	4.73	N/A	N/A
101-150	N/A	N/A	N/A	16.27	N/A	N/A
151-200	N/A	N/A	N/A	15.34	11.62	4.56
201-250	N/A	N/A	N/A	19.80	5.11	4.65
251-300	0.39	0.41	0.47	18.48	4.46	4.83
301-350	0.17	0.11	0.09	14.79	6.74	8.39
351-400	0.17	0.11	0.09	7.51	7.96	9.66
401-450	4.34	2.19	0.28	3.10	6.30	8.04
451-500	12.19	10.16	5.49	N/A	7.04	6.97
501-550	5.99	5.50	4.68	N/A	3.73	3.95
551-600	4.32	4.46	3.92	N/A	3.30	3.46
601-650	3.65	3.72	3.28	N/A	3.03	3.15
651-700	2.63	2.81	2.46	N/A	2.75	2.87
701-750	0.57	1.71	1.62	N/A	1.83	2.08
751-800	2.18	1.21	1.72	N/A	0.34	0.70
800+	63.40	67.60	75.90	N/A	35.80	36.70
Total	100.0	100.0	100.0	100.0	100.0	100.0

TABLE A1-5**BOILING POINT RANGE DISTRIBUTION FOR RUN 263J-1, 300 CSTR,
wt % AS-DETERMINED**

Boiling Point Range, °C	Feed 263J Interstage Product	Distillate Accumulator Dry Scrape, Supernatant Fraction	Reactor Dry Scrape	Reactor THF Scrape
0-100	N/A	7.62	N/A	N/A
101-150	N/A	14.22	N/A	N/A
151-200	N/A	10.59	4.73	N/A
201-250	N/A	12.23	1.94	7.58
251-300	N/A	13.88	1.90	3.25
301-350	0.67	15.64	3.77	6.50
351-400	0.24	14.62	5.79	9.23
401-450	2.10	7.89	6.16	9.70
451-500	10.08	2.42	5.71	7.98
501-550	12.13	0.90	4.59	5.20
551-600	9.82	N/A	3.21	3.31
601-650	7.19	N/A	2.44	2.43
651-700	4.90	N/A	1.75	1.71
701-750	2.63	N/A	0.60	0.53
751-800	1.55	N/A	0.20	0.20
800+	48.70	N/A	57.20	42.40
Total	100.0	100.0	100.0	100.0

Following are SIMDIS plots of the 300 mL CSTR Feedstocks and Products.

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Paraffin Calibrant

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

Note: found recovery increased by 6.23% for retained THF

High-Temp SIMDIS Analysis with Paraffin Calibrant

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Paraffin Calibrant

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Paraffin Calibrant

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Paraffin Calibrant

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction

High-Temp SIMDIS Analysis with Aromatic Correction