PART 4

COAL OIL CO-PROCESSING

Section 15

COAL/OIL CO-PROCESSING PROGRAM UPDATE

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ABSTRACT

Hydrocarbon Research, Inc. (HRI) is developing an advanced catalytic two-stage process to liquefy coal while simultaneously upgrading heavy crudes or petroleum residua. The development of the HRI Coal/Oil Co-Processing Technology is being sponsored by the Electric Power Research Institute (EPRI), Ontario Ohio Synthetic Fuels Corporation, Ltd. (OOSFC), Alberta Research Council (ARC) and DynCorp. The State of Ohio's Coal Development Office has supported the program through OOSFC. This ongoing coal/oil co-processing program is separated into two phases. Phase 1, completed in 1986, evaluated the technical, economic and commercial feasibility of coal/oil co-processing. Phase 2, which is currently in progress, is focused on process demonstration, evaluation of alternative feedstocks and improving process understanding. In addition to this ongoing technology development program, the HRI Coal/Oil Co-Processing Technology has been selected for use in a Prototype Commercial Coal/Oil Co-Processing Plant. This project, which was one of nine selected by the U. S. Department of Energy (DOE) for support under their clean coal technology solicitation, is scheduled to start up in 1991 and will be located in Warren, Ohio. Agreements on this project are currently being negotiated with DOE. This paper presents an updated summary on the status of these activities.

INTRODUCTION

Hydrocarbon Research, Inc.'s (HRI) Coal/Oil Co-Processing Technology refers to the combined liquefaction of coal and upgrading of poor quality heavy crudes or petroleum residua. While coal/oil co-processing is not a new concept, it has recently gained renewed interest. This interest is based on the potential of coal/oil co-processing to significantly reduce the cost of liquid fuels from coal and thereby accelerate their introduction into the marketplace.

HRI is actively developing advanced two-stage, catalytic, coal/oil co-processing technology. The HRI Coal/Oil Co-Processing Technology is based on the commercial H-Oil® Process (for upgrading heavy crudes and/or petroleum residua), the fully developed H-Coal® Process (for direct liquefaction of coal) and advances made at HRI in the Catalytic Two-Stage Liquefaction (CTSL) Process. This coal/oil co-processing program is currently ongoing and is funded by EPRI, OOSFC, ARC and DynCorp.

In parallel with the ongoing technology development program, and based on the excellent results obtained in the program, a proposal was submitted to the Department of Energy (DOE) under their Clean Coal Technology solicitation, for support of the design, construction and operation of a Prototype Commercial Coal/Oil Co-Processing Plant. The proposal was submitted by Ohio Ontario Clean Fuels, Inc. (OOCF) in April 1986 and the project was one of nine clean coal technology projects selected to enter into the negotiations with DOE. The technology selected for this project is the HRI Coal/Oil Co-Processing Technology. The State of Ohio Coal Development Office is also providing financial support for this project.

HRI COAL/OIL CO-PROCESSING TECHNOLOGY

The HRI Coal/Oil Co-Processing Technology is a logical outgrowth of HRI's prior experience in the commercial H-Oil® Process, the fully developed H-Coal® Process and new developments in Catalytic Two-Stage Liquefaction (CTSL).

In HRI's Coal/Oil Co-Processing Technology (Figure 1) coal is slurried with petroleum-derived residual oil. Petroleum derived residual oils which can be used include atmospheric and vacuum residua, FCC clarified slurry oils, heavy crudes or tar sands bitumen and shale oil. The feed slurry is pumped to reaction pressure, mixed with hydrogen, preheated and fed to the ebullated-bed reactor. Both singleand two-stage process configurations have been demonstrated. The reactor effluent is separated into vapor and slurry streams. The vapor is treated to recover hydrogen and recycled back to the reactor. The slurry is depressurized and fractionated to produce high quality distillate products and a non-distillate vacuum bottoms product, which contains all unconverted residual oil, unconverted coal and ash. High concentrations of coal in the fresh feed are possible by providing a small amount of recycle as a portion of the coal slurry oil.

Coal/oil co-processing has two intrinsic advantages. The first relates to its ability to effectively remove both sulfur and nitrogen from coal. SO_x and NO_x emissions from coal combustion contribute to the growing acid rain problem. Coal liquefaction in general, and coal/oil co-processing in particular, removes sulfur and nitrogen from coal as useful and marketable by-products. Subsequent combustion of the coal derived fuel from coal/oil co-processing will result in reduced SO_x and NO_x emissions.

The other advantage of coal/oil co-processing is the process synergy derived from the combined processing of coal and petroleum derived oil. This process synergy occurs in at least two ways. Overall conversion to distillate liquid products is greater by coal/oil co-processing than by separate processing. The presence of coal-derived liquids, with excellent hydrogen donor characteristics, enhances the conversion of the petroleum derived residuum. While the overall solvent quality is reduced due to the presence of the petroleum derived liquids, conversion of the coal to distillate liquids is not significantly effected. This aspect of the process synergy allows for high conversion operation in coal/oil co-processing. The other aspect of the process synergy relates to the affinity of the coal solids for the organometallics present in petroleum residua. It has been determined that most of the organometallics (primarily nickel and vanadium) in the feed oil are deposited on the coal solids during co-processing. The important implication of this, for catalytic processing, is that these metals are not deposited on the catalyst, and the spent catalyst can be more easily reused with conventional regeneration techniques.

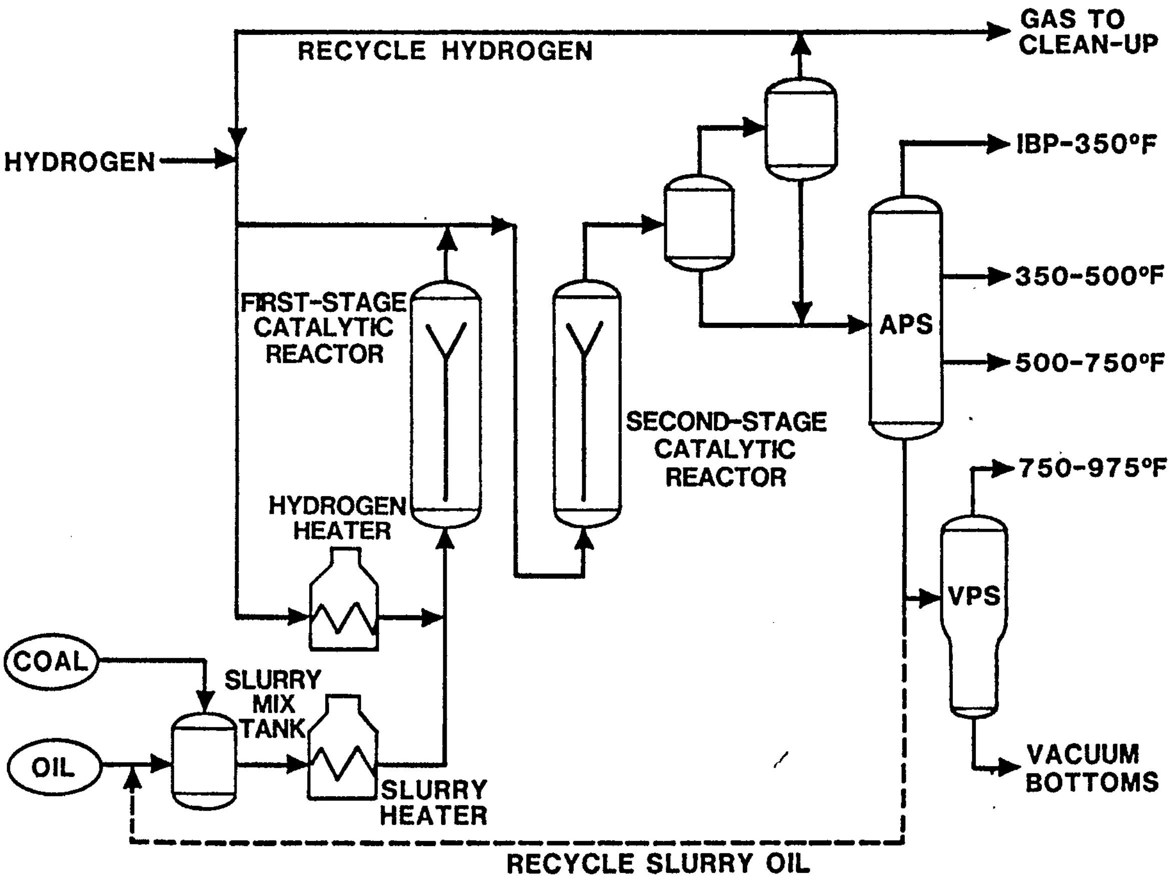

FIGURE 1. SIMPLIFIED FLOW PLAN

COAL/OIL CO-PROCESSING PROGRAM

In 1985, HRI initiated a private industry sponsored research and development program on coal/oil co-processing. Phase 1 of the program was sponsored by:

- Electric Power Research Institute (EPRI)
- Ontario-Ohio Synthetic Fuels Corporation Ltd. (OOSFC)
- Alberta Research Council (ARC)
- DynCorp

The State of Ohio's Coal Development Office has supported the program through OOSFC.

The objective of this program is to further develop, demonstrate and optimize coal/oil co-processing to produce high quality, environmentally acceptable products from poor quality feedstocks. The specific objectives are to:

- produce incremental liquid fuels from coal.
- upgrade (desulfurize, demetallize) poor quality residual fuels.

The Phase 1 Program was completed in 1986. The technical tasks (Table 1) included feedstock characterizations, batch reactivity screening, continuous bench unit operations, product characterizations, economic screening studies and commercial planning studies.

In September 1986 the coal/oil co-processing program continued into Phase 2 with the same sponsorship. In the Phase 2 program a bench-scale demonstration run was completed which will provide the design basis for the prototype commercial plant project. In addition, other studies have been directed towards upgrading the co-processing products and improved process understanding. A bench-scale operation evaluating other feedstock combinations is planned. The Phase 2 program will be completed in 1987.

TABLE 1

COAL/OIL CO-PROCESSING PROGRAM DESCRIPTION

TECHNICAL TASK	PHASE 1	PHASE 2
Feedstock Characterization	Complete on 4 coals and 4 oils.	Supplemental data and new feedstocks.
Reactivity Screening		
Microautoclave	Reactivity of base feedstocks and combinations	Reactivity of new feedstocks.
Autoclave	Preliminary yields and product quality	Improve fundamental understanding of process
Continuous Bench Unit Operations	Process Variables Runs 1. Single-Stage 2. Two-Stage	1. Demonstration Run 2. Alternative Feedstocks
Product Characterization and Upgrading	Characterization	Characterization and Upgrading
Economic Screening Studies	Single-Stage	Two-Stage
Commercial Planning Studies	Great Lakes Region	None

KEY RESULTS FROM PHASE 1

Overall, the Phase 1 program was successful in demonstrating the technical, economic and commercial feasibility of coal/oil co-processing and produced some very important results.

The technical feasibility of coal/oil co-processing was demonstrated in continuous bench-scale operations. Fifty-two days of continuous bench-scale operation were completed in both single- and two-stage process configurations. The feedstocks used were Ohio No. 5/6 coal and Cold Lake residuum. A wide range of process variables were evaluated including coal concentration from 33-67 W % of fresh feed, feedrates from 0.33-2.00 times the base feedrate and temperatures from 750-825°F. Over this range of process variables 975°F$^+$ conversion levels were from 60 W % M.A.F. to in excess of 90 W % M.A.F. Over this range of process severities no operability difficulties were encountered and product slates varied from all distillate (at high severity) to a high residuum containing product (at low severity).

Process synergy was demonstrated in both batch reactivity screening experiments and in continuous bench unit operations. This process synergy (as described earlier) occurs in at least two different ways. First, 975°F$^+$ conversion obtained in co-processing is greater than expected based on separate processing of the individual feedstocks. The other aspect of the process synergy relates to the observed affinity of the coal derived solids (unconverted coal plus ash) for organometallics (nickel and vanadium) contained in the oil feed. This was shown in continuous bench unit operations by analyzing the recovered coal solids from nickel and vanadium and is clearly shown by the analysis of the spent catalyst after the run.

Spent Catalyst Analysis

	Co-Processing	Typical Oil Only
Metals (Ni plus V) on Spent Catalyst, W %	2-3	20-40

Co-processing reduces the metals contaminants on the spent catalyst by an order of magnitude compared to oil-only processing (H-Oil® Process). This reduces the catalyst deactivation caused by metals deposition on the catalyst and allows the option of more efficient catalyst utilization through regeneration and/or cascading of catalyst in a two-stage system.

Excellent process performance was obtained in the continuous bench unit operations. In Bench Run No. 2 (two-stage), Condition 4 (at 50% coal in the fresh feed), the following process performance was obtained:

Process Performance	W % M.A.F.
Coal Conversion	96
975°F$^+$ Conversion	90
Hydrodesulfurization	86
Hydrodenitrogenation	80
Demetallization	99

Also at this condition excellent product quality was obtained. As a measure of product quality, the vacuum gas oil (650-975°F) quality was closely monitored. Target qualities were set at greater than 10 W % hydrogen, less than 0.5 W % sulfur and less than 0.35 W % nitrogen. These target qualities are nominal specifications for a utility turbine fuel. The vacuum gas oil qualities for Bench Run No. 2, Condition 4, are shown as follows:

Vacuum Gas Oil Quality -	Gravity, °API	13.3
	Hydrogen, W %	10.54
	Sulfur, W %	0.17
	Nitrogen, W %	0.35

These qualities meet or exceed the target qualities, thus the vacuum gas oil produced can be considered to be a potential utility turbine fuel, without any further upgrading.

Economic screening studies showed coal/oil co-processing significantly reduces the cost of liquids from coal compared to direct liquefaction. Economics were calculated for a single-stage co-processing add-on to an existing petroleum refinery and compared to grassroots direct liquefaction. In addition to reduced investment for the conversion facilities, coal/oil co-processing also makes efficient use of the existing refinery infrastructure (utilities, offsite, tankage, etc.) resulting in major savings on capital costs. The net result is to reduce the product cost for coal/oil co-processing to about half that for direct liquefaction. The coal/oil co-processing economic screening studies also showed that operation with 50% coal in the fresh feed, at high 975°F$^+$ conversion was directionally preferred.

Commercial planning studies identified a number of locations, in the Great Lakes region, where coal/oil co-processing is commercially feasible. Commercial feasibility for co-processing is generally defined as locations which have coal mines, crude oil pipelines, natural gas pipelines, existing refineries and product pipelines in close proximity. With the commercial feasibility established, proposals were submitted by Ohio Ontario Clean Fuels, Inc. (the U. S. subsidiary of OOSFC) to the U. S. Department of Energy and the State of Ohio Coal Development Office for support of a Prototype Commercial Coal/Oil Co-Processing Plant. The OOCF project was one of nine selected by DOE from over fifty proposals submitted.

DEMONSTRATION RUN RESULTS

The first bench run in the Phase 2 Program was a demonstration run. The demonstration run was designed to provide a long-term demonstration of the HRI Coal/Oil Co-Processing Technology at preferred commercial operating conditions. This run would then provide catalyst activity profiles with time onstream and products at a commercial catalyst age for characterization and preliminary upgrading evaluations.

The process objectives for the demonstration run were to obtain high 975°F$^+$ conversion and a high quality vacuum gas oil (650-975°F) product for potential use as a utility turbine fuel. High 975°F$^+$ conversion is generally in the range of 90 W % M.A.F., but the real limitation is a vacuum bottoms stream (975°F$^+$) containing less than 50 W % solids (unconverted coal plus ash). The basis for quality specifications for the vacuum gas oil was discussed earlier.

The coal and oil feedstocks used were Ohio No. 5/6 coal (Table 2) and Cold Lake atmospheric residuum (Table 3). The oil-to-coal feedstock ratio was 1:1 and a small amount of atmospheric bottoms was recycled. Overall the demonstration run was quite successful. No operating problems were experienced and the unit was extremely clean upon shutdown. Process performance objectives were met or exceeded for the entire thirty-day run. Day twenty-five performance is highlighted as follows:

Demonstration Run Results
(Day 25 Performance)

Process Performance	W % M.A.F.
Coal Conversion	95
975°F+ Conversion	88
Hydrodesulfurization	78
Hydrodenitrogenation	73
Demetallization	99
W % Solids in 975°F+ Vacuum Bottoms	48

Vacuum Gas Oil (650-975°F) Quality	W %
Hydrogen	10.7
Sulfur	0.37
Nitrogen	0.27

Process performance for the entire run is shown in Figures 2 (Coal and 975°F+ Conversion), 3 (Liquid Product Yield), 4 (HDS, HDN and Demetallization) and 5 (Sulfur and Nitrogen in VGO). These figures show no effect of time onstream (catalyst age) on coal conversion but a clear effect on 975°F+ conversion, hydrodesulfurization, hydrodenitrogenation and demetallization. Vacuum gas oil quality also decreases during the run to the target sulfur and nitrogen contents in day thirty of operation.

Product qualitites for liquid product fractions from day twenty-five are shown in Tables 4 and 5. The total liquid product (C_4-975°F) is 76.8 W % M.A.F. coal plus oil feed, 33.3 °API, with 0.25 W % sulfur and 0.14 W % nitrogen. The chemical composition of the product fractions shows that paraffins decrease with increasing boiling range, with a corresponding increase in aromaticity. The concentration of naphthenes hits a maximum in the 180-350°F boiling range, making this heavy naphtha an excellent feedstock for catalytic reforming.

The demonstration run operating conditions were selected based on performance obtained in the two-stage process variable run (Bench Run No. 2) in the Phase 1 Program. Target process performance was based on day fifteen performance in that process variable run. Demonstration run performance in day fifteen is compared with the earlier process variable run results in Table 6. Overall process performance is slightly improved in the demonstration run with higher 975°F+ conversion, hydrodenitrogenation and liquid product yield. These improvements are most likely due to slightly different operating conditions and use of a different catalyst in the demonstration run. The improvement made by the catalyst is more dramatic in the vacuum gas oil quality with considerably lower sulfur and nitrogen contents.

This run was highly successful in providing a demonstration of the HRI Coal/Oil Co-Processing Technology at constant operating conditions, over an extended period of time (thirty days). No operating problems were experienced. The unit was very clean upon inspection after shutdown and the catalyst was free-flowing on discharge. Process performance was improved compared to prior process variable run results and well within targets up to day twenty-five of operation. Day thirty process performance was at the target levels. Catalyst activity profiles were established with no observed effect of catalyst activity on coal conversion. Results of this demonstration run will be used to prepare a design basis for the Prototype Commercial Coal/Oil Co-Processing Plant project.

TABLE 2

DEMONSTRATION RUN RESULTS
COAL FEED ANALYSIS - OHIO NO. 5/6 BITUMINOUS COAL

Carbon, W %	73.05
Hydrogen, W %	4.82
Nitrogen, W %	1.49
Sulfur, W %	2.86
Ash, W %	8.53
Oxygen (By Difference), W %	9.25
	100.00

TABLE 3

OIL FEED ANALYSIS - COLD LAKE ATMOSPHERIC RESIDUUM (750°F$^+$)

Gravity, °API	6.6
Hydrogen, W %	10.22
Sulfur, W %	5.17
Nitrogen, W %	0.52
Nickel, Wppm	86
Vanadium, Wppm	242
CCR, W %	16.6
975°F$^+$, W %	69.8

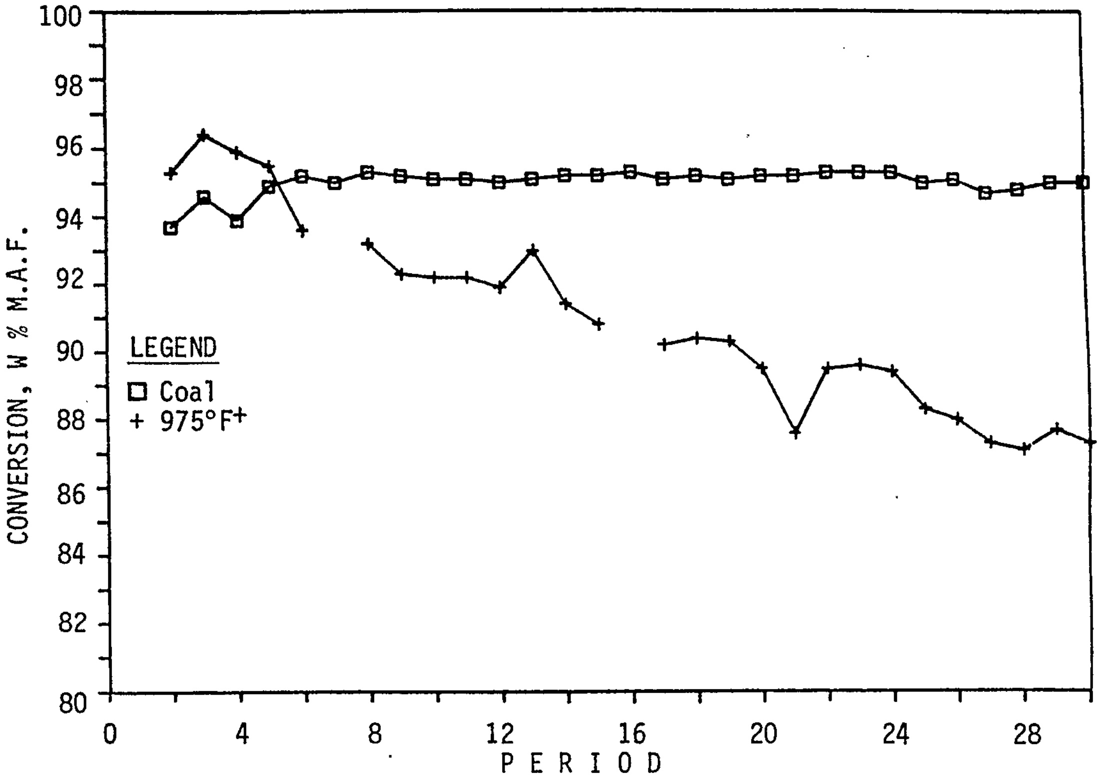

FIGURE 2. COAL AND 975°F$^+$ CONVERSION

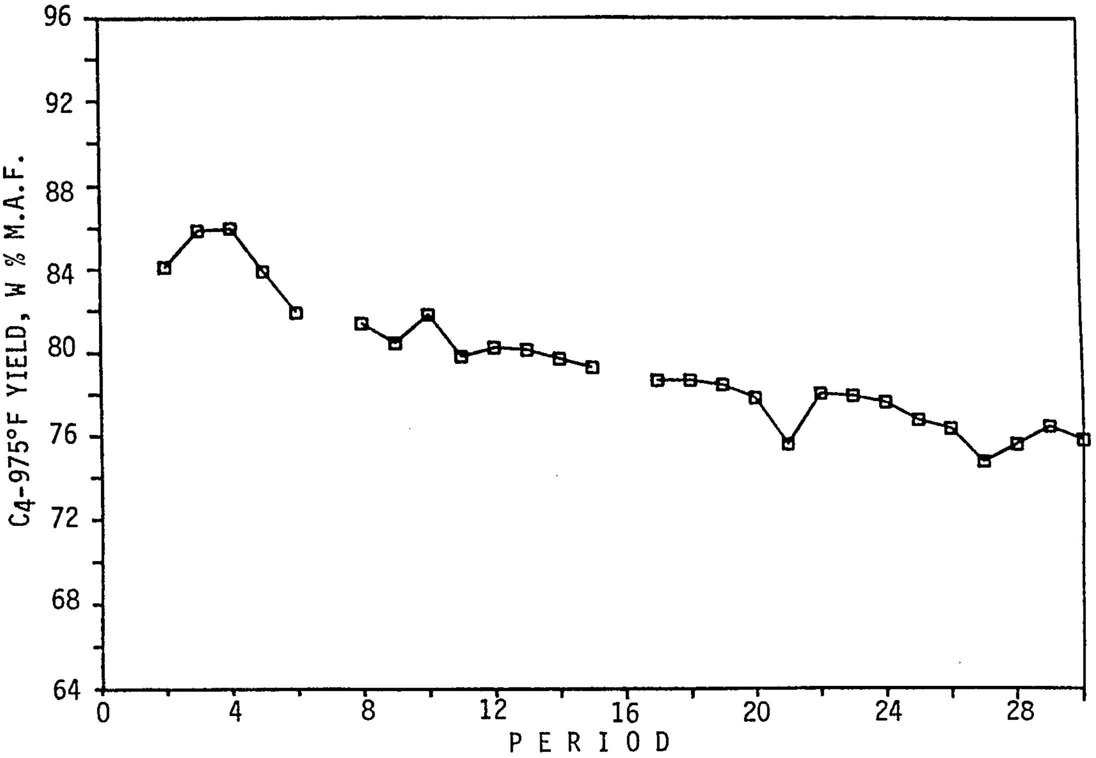

FIGURE 3. LIQUID PRODUCT YIELD

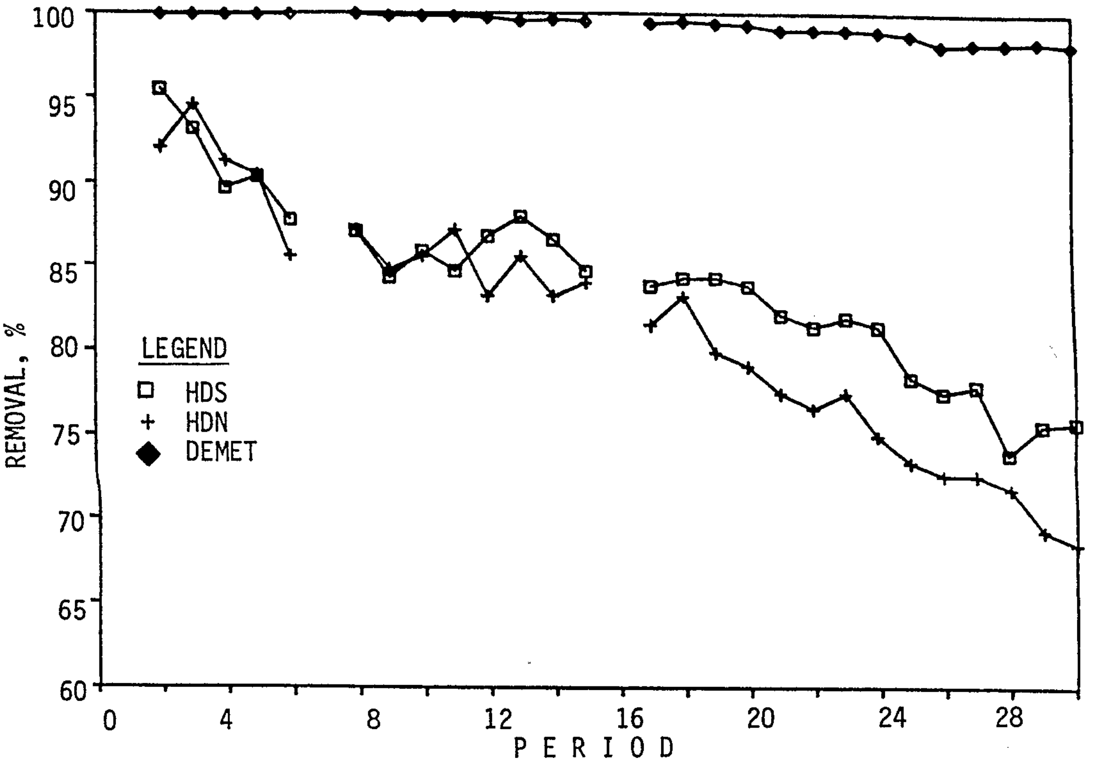

FIGURE 4. HYDRODESULFURIZATION, HYDRODENITROGENATION AND DEMETALLIZATION

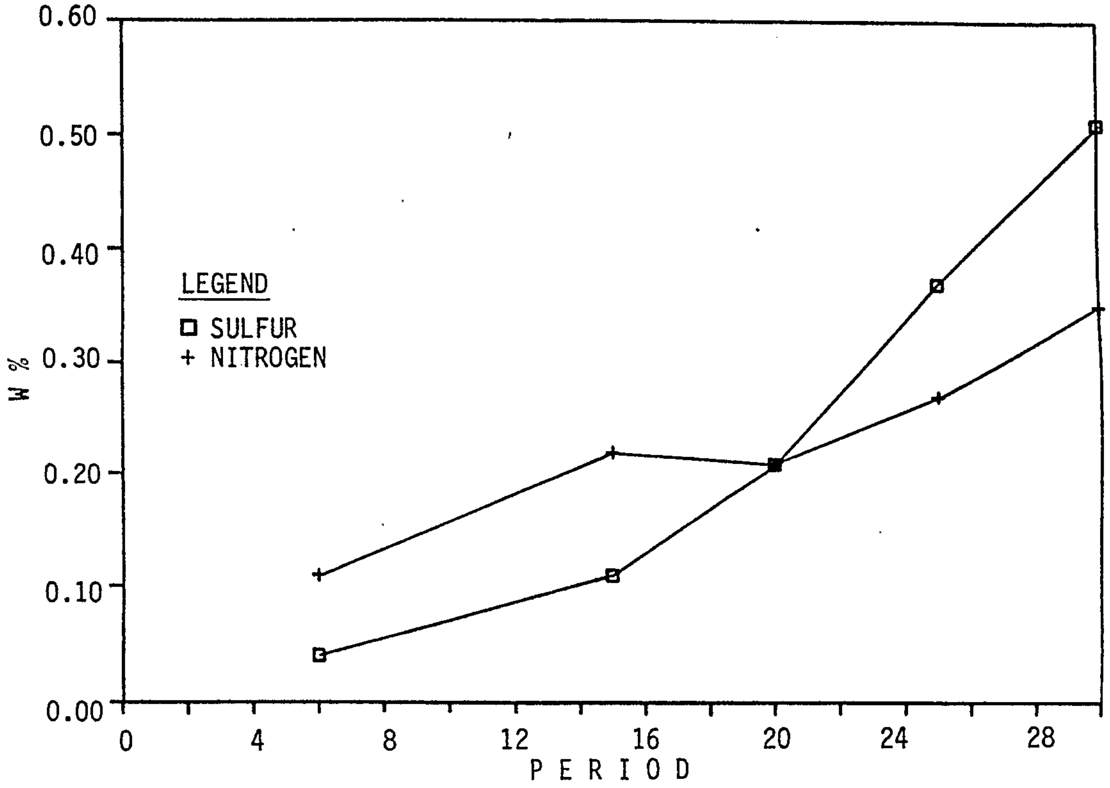

FIGURE 5. SULFUR AND NITROGEN IN VGO

TABLE 4

DEMONSTRATION RUN RESULTS - PRODUCT QUALITY(1)

BOILING RANGE, °F	YIELD, W %(2)	°API	ELEMENTAL, W %			
			C	H	S	N
C_4-C_7	5.2	94.4	83.5	16.5	-	-
IBP-180	1.2	73.1	84.4	15.6	0.02	0.01
180-350	10.9	50.9	85.7	14.0	0.15	0.01
350-500	17.1	34.0	86.5	12.5	0.21	0.11
500-650	23.7	24.5	87.5	11.8	0.31	0.14
650-850	15.1	16.6	88.9	11.0	0.30	0.20
850-975	3.6	4.1	89.6	9.3	0.65	0.57
Total C_4-975°F	76.8	33.3	87.1	12.4	0.25	0.14

(1) From Period 25 of Demonstration Run
(2) Based on M.A.F. coal plus oil feed

TABLE 5

DEMONSTRATION RUN RESULTS - PRODUCT QUALITY(1)

BOILING RANGE, °F	CHEMICAL COMPOSITION, V %			
	PARAFFIN	OLEFIN	NAPHTHENE	AROMATIC
C_4-C_7	87	-	13	-
IBP-180	62	7	28	3
180-350	39	7	41	13
350-500	39	13	20	28
500-650	35	9	10	47

(1) From Period 25 of Demonstration Run

TABLE 6

DEMONSTRATION RUN RESULTS - COMPARISON WITH PRIOR RESULTS

	TWO-STAGE PROCESS VARIABLE	DEMONSTRATION
PHASE	1	2
Run No.	2	1
Period No.	15	15
PROCESS PERFORMANCE, W % M.A.F.		
975°F+ Conversion	90	91
Coal Conversion	96	95
Hydrodesulfurization	86	85
Hydrodenitrogenation	80	84
Demetallization	99	99
C_4-975°F Yield	78	79
VGO (650-975°F) PRODUCT QUALITY		
Gravity, °API	13.3	14.3
Hydrogen, W %	10.54	10.74
Sulfur, W %	0.17	0.11
Nitrogen, W %	0.35	0.22

PROTOTYPE COMMERCIAL COAL/OIL CO-PROCESSING PLANT PROJECT

As described earlier in this paper, a Prototype Commercial Coal/Oil Co-Processing Plant project is currently being planned (Table 7). This plant will produce 11,750 BPSD of liquid products and will be located in Warren, Ohio. Feedstocks are Ohio No. 5/6 coal and Cold Lake heavy crude. The project is headed by Ohio Ontario Clean Fuels, Inc. (the U. S. subsidiary of OOSFC) who has teamed with Hydrocarbon Research, Inc. and the Stearns Catalytic Division of United Engineers. The total project cost is estimated to be $225MM, with $45MM funded by DOE, $10MM from the State of Ohio and $170MM privately funded.

The overall plant material balance is summarized in Table 8. As-received Ohio No. 5/6 coal (800 TPSD) will be processed. The Cold Lake residuum for co-processing is received via pipeline with condensate to reduce the viscosity of the crude. Prime products include 4,500 BPSD of naphtha and 7,250 BPSD of distillate. Product qualities are shown in Table 9. The naphtha will be hydrotreated to low levels of sulfur and nitrogen for sale to a local refiner for catalytic reforming and blending to gasoline. The distillate is planned to be used without furthur upgrading as a potential utility turbine fuel. Other by-products from the plant include C_3LPG, C_4's, sulfur and ammonia.

An overview of the project schedule is shown in Table 10. The project is split into three phases:

Phase 1 - Design and Permitting
Phase 2 - Construction and Start Up
Phase 3 - Operations

Phase 1 will start in 1987 and in addition to the engineering design and permitting activities, will include a PDU demonstration of the HRI Coal/Oil Co-Processing Technology. Start up of the plant is scheduled for 1991 with ongoing operations after successful start up.

TABLE 7

PROTOTYPE COMMERCIAL COAL/OIL CO-PROCESSING PLANT PROJECT

PROJECT SUMMARY

- PLANT PRODUCTION: 11,750 BPSD
- PLANT SITE: Warren, Ohio
- FEEDSTOCKS: Ohio No. 5/6 Coal
Cold Lake Residuum
- TECHNOLOGY: HRI Ebullated-Bed Coal/Oil Co-Processing
- PROJECT TEAM: Ohio Ontario Clean Fuels, Inc.
Hydrocarbon Research, Inc.
Stearns Catalytic Division of United Engineers
- PROJECT COST: $225MM
- PROJECT FINANCING: $ 45MM U. S. Department of Energy
$ 10MM Ohio
$170MM Private

TABLE 8

MATERIAL BALANCE SUMMARY

FEEDSTOCKS	
Ohio No. 5/6 Coal, TPSD As Received	800
Cold Lake Crude plus condensate, BPSD	8,675
Natural Gas, MMSCFD	10
PRODUCTS	
Naphtha, BPSD	4,500
Distillate, BPSD	7,250
	11,750
BY-PRODUCTS	
C_3-LPG, BPSD	340
C_4's, BPSD	190
Sulfur, TPSD	57
Ammonia, TPSD	14

TABLE 9

PROTOTYPE COMMERCIAL COAL/OIL CO-PROCESSING PLANT PROJECT

PRODUCT QUALITIES

NAPHTHA	
Boiling Range, °F	C_5-390
Gravity, °API	61
Sulfur, Wppm	< 1
Nitrogen, Wppm	< 1
DISTILLATE	
Boiling Range, °F	390-975
Gravity, °API	24
Sulfur, W %	0.2
Nitrogen, W %	0.2

TABLE 10

PROTOTYPE COMMERCIAL COAL/OIL CO-PROCESSING PLANT PROJECT

PROJECT SCHEDULE

PHASE 1 - DESIGN AND PERMITTING (1987 - 1989)

- Co-Processing PDU Demonstration/Design
- Detailed Engineering Design
- Environmental Permitting

PHASE 2 - CONSTRUCTION AND START-UP (1989 - 1991)

- Equipment Procurement
- Construction
- Inspection/Testing/Shakedown
- Start Up

PHASE 3 - OPERATIONS (1991 - ONGOING)

FUTURE WORK

Future work on the Phase 2 Coal/Oil Co-Processing Program includes a bench run on alternative feedstocks, product upgrading tests, batch reactivity screening tests and economic screening studies of two-stage processing options.

Concurrent with the Phase 2 Coal/Oil Co-Processing Program will be initial activities on the Prototype Commercial Coal/Oil Co-Processing Plant Project including preparation of the design basis for the co-processing unit, some bench-scale support work and PDU demonstration at HRI.

ACKNOWLEDGMENT

HRI would like to acknowledge the continued support and technical contributions of the Electric Power Research Institute, Ontario Ohio Synthetic Fuels Corporation, Ltd., Alberta Research Council (ARC) and DynCorp to the overall success of the program to date.

Section 16

UPDATE: LUMMUS CO-PROCESSING PROJECT AND RESULTS OF CATALYST ACTIVITY MAINTENANCE TESTING

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Lummus Crest, Inc.

ABSTRACT

Lummus Crest Inc. (LCI) has been performing an R&D program under joint funding with the DOE to determine the technical and economic feasibility of LCI's co-processing concept. The latter consists of a two-stage (thermal-catalytic), close-coupled reaction system in which the petroleum feedstock can be introduced into either of the two stages. In the standard mode, an externally hydrogenated petroleum feedstock, such as the unconverted vac bottoms from an expanded-bed hydrocracker (e.g., LC-Fining^{sm} process), serves as the slurry paste for the feed coal to the short contact time (SCT), thermal-stage reactor. In the alternative mode, a virgin (or externally hydrogenated) petroleum feedstock is injected into the close-coupled catalytic stage and unconverted, but hydrogenated vac bottoms from this catalytic stage are recycled to the thermal stage as a slurry paste for the feed coal.

Two extended catalyst activity maintenance tests were made in a continuous 50 pound/day bench-scale unit: one in the standard mode with commercial petroleum-derived hydrocracker vac bottoms from Amoco Oil's Texas City LC-Fining^{sm} unit; and one in the alternative mode with Arab Heavy vac resid. Both tests used Pittsburgh seam Ireland Mine coal.

Results of the standard mode activity maintenance test are presented in this paper along with the design basis and preliminary results of the conceptual plant design study.

BACKGROUND AND PROJECT STATUS

In October 1984, Lummus Crest Inc. (LCI) entered into a jointly funded R&D program with the Department of Energy (DOE) to determine the technical and economic feasibility of LCI's co-processing concept. The LCI concept was predicated on the use of low valued petroleum refinery streams that had been enriched in aromatics content as a consequence of partial conversion treatment in selected petroleum refining units. In particular, the unconverted residue from a resid hydrocracker, such as the LC-Fining^{sm} Process, was identified as a potentially attractive coal liquefaction co-processing feedstock. The particular co-processing scheme was based on LCI's Integrated Two-Stage Liquefaction (ITSL) process for coal which consists of a short contact time (SCT) thermal-stage close coupled to an expanded-bed catalytic (LC-Fining^{sm}) stage.

The final task, (see Table 1 below) currently in progress, is to translate the experimental results obtained from the operation of a continuous bench-scale unit to a conceptual commercial-scale application and to assess the techno-economic potential of the technology.

TABLE 1

PROJECT TASK BREAKDOWN STRUCTURE

		STATUS
TASK 1:	PROJECT MANAGEMENT PLAN	C
TASK 2:	FEEDSTOCK ANALYSIS	C
TASK 3:	CO-PROCESSING REACTIVITY SCREENING	C
TASK 4:	CONTINUOUS BENCH-SCALE UNIT OPERATION	C
TASK 5:	COST ESTIMATE OF CONCEPTUAL COMMERCIAL FACILITY	P
TASK 6:	FINAL REPORT	F

C Completed
P In Progress
F Future Task

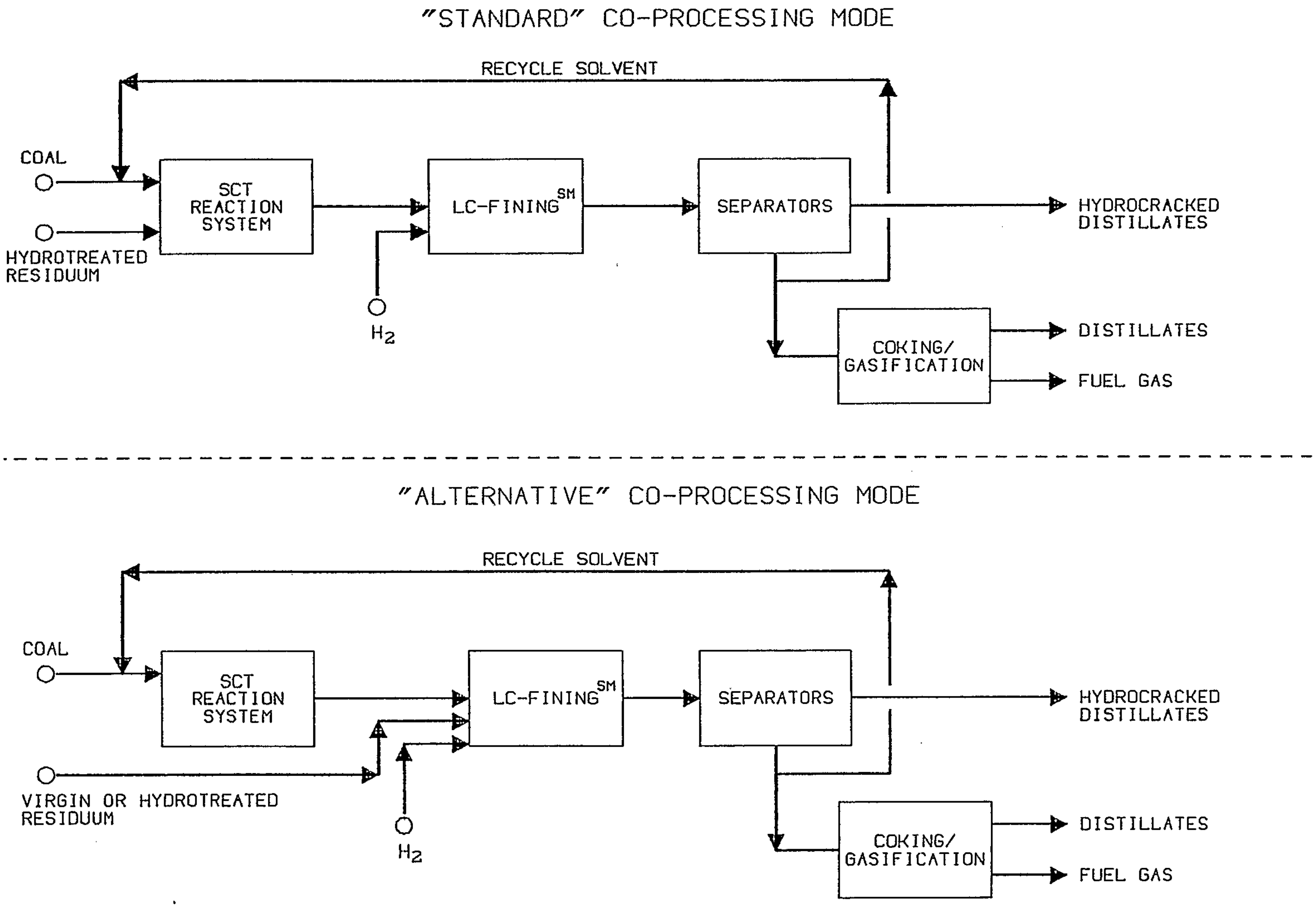
LCI CO-PROCESSING CONCEPT

Figure 1 is a schematic of two alternative processing schemes for the LCI co-processing concept. In the standard mode, coal is slurried with an externally hydrogenated petroleum feedstock, such as for example, the vac bottoms from an expanded-bed hydrocracker (LC-Fining^{sm}), and processed in a short contact time (SCT) thermal stage reaction system. The SCT reactor effluent is fed to an expanded-bed LC-Fining^{sm} reaction system in a close-coupled manner, i.e., no de-pressurization or deashing between stages. An ash-containing residual stream from the LC-Finate product separation system is recycled to the SCT reactor as necessary to supplement the solvency power of the petroleum component of the co-processing feedstock.

In the alternative mode, the petroleum feedstock, whether externally hydrogenated or virgin, is injected between the stages at the inlet to the close-coupled LC-Finer^{sm}. All of the SCT slurry vehicle for the coal feed is derived by recycling an ash-containing heavy oil stream from the close-coupled LC-Finer^{sm}. In both modes, bottoms processing is based on fluid coking of the co-processed vac bottoms with subsequent gasification of the resultant fluid coke.

CONTINUOUS BENCH-SCALE CO-PROCESSING UNIT

The continuous bench-scale unit consists of a slurry preparation/slurry feed system; a high pressure hydrogen feed system; a thermal stage reaction (SCT) system; a catalytic (LC-Finer^{sm}) stage reaction system; and a product recovery system. The thermal and the catalytic stages can be either operated independently or in the close-coupled mode. Figure 2 is a schematic of the bench-scale unit configured in the close-coupled mode.



"STANDARD" CO-PROCESSING MODE

"ALTERNATIVE" CO-PROCESSING MODE

Figure 1. Block Flow Diagram of LCI Co-processing Concepts

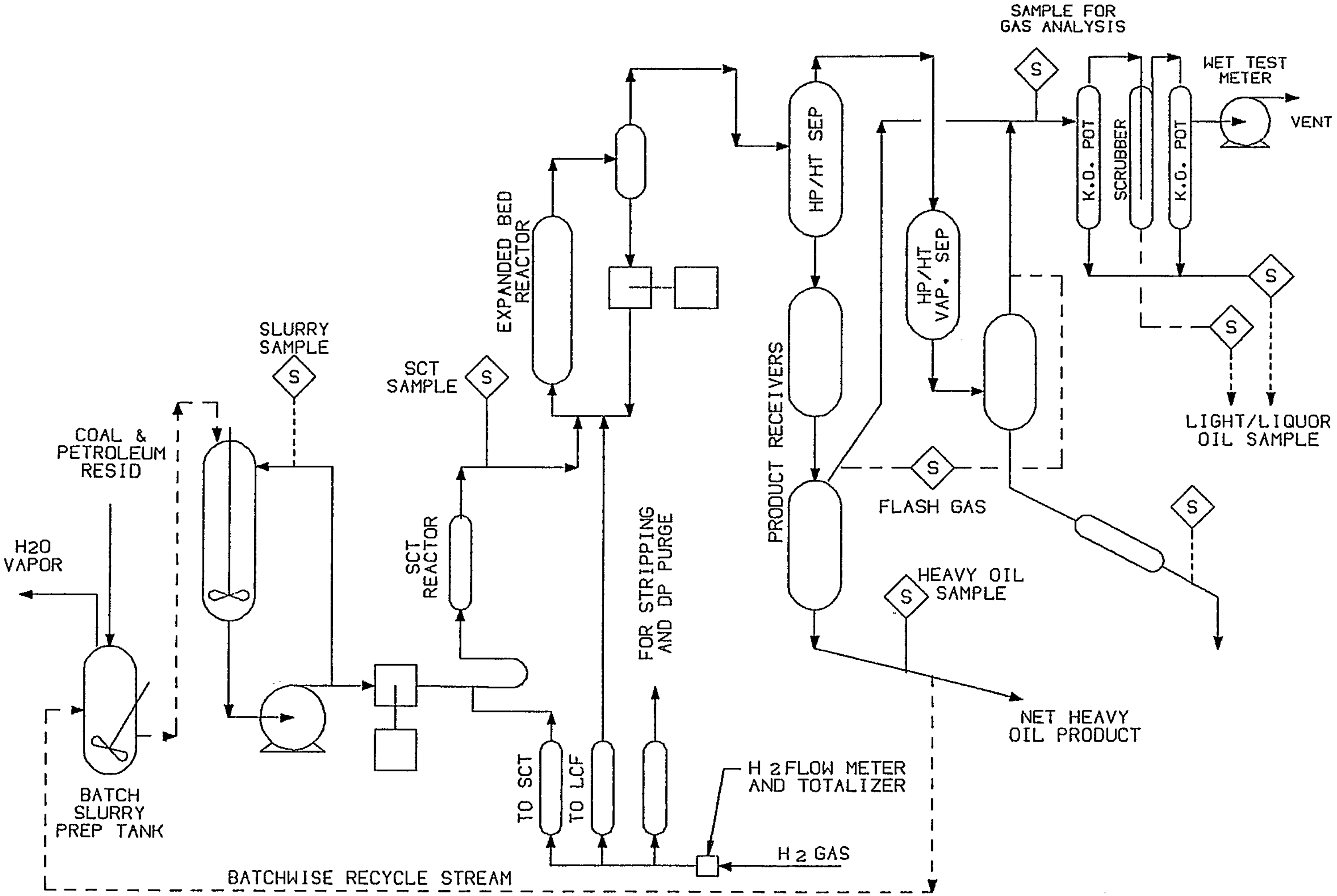


Figure 2. Schematic of Bench-Scale Two-Stage Co-processing Unit

- **Slurry Prep/Slurry Feed System**

The slurry of coal, petroleum resid and recycle solvent is prepared batchwise in stirred tanks external to the bench-scale unit. The thus prepared slurry is transferred to the slurry feed tank. The slurry in the feed tank is continuously stirred and circulated through a transfer line at about 5-10 psig back into the slurry feed tank using a Tuthill lobe pump. A high pressure piston-type slurry metering pump (Wallace-Tiernan) takes suction from the circulating slurry loop and pumps the slurry forward to the high pressure SCT reactor system. The slurry feed rate is monitored by the rate of weight loss of the slurry feed tank which is installed on a sensitive electronic weight scale. Changes in the slurry feed rate can be made by adjusting the plunger displacement on the Wallace-Tiernan pump.

- **Hydrogen Feed System**

A continuous supply of hydrogen is available from high pressure hydrogen trailers. The hydrogen is regulated to a low pressure (ca., 100 psig) and then recompressed to about 2500 psig with a diaphragm compressor. A high pressure piping manifold splits the compressed hydrogen and delivers it to the following process areas: the inlet of the SCT reactor; the inlet to the LC-Finer^{sm}; and the differential pressure sensors across the LC-Finer^{sm}.

Each hydrogen stream is metered with a calibrated high pressure Brooks rotameter. System pressure is monitored at several locations including the discharge of the Wallace-Tiernan slurry feed pump; inlet and outlet of the vertical SCT reactor; inlet and outlet of the LC-Finer^{sm}; heavy oil product separator and the light oil receiver. System pressure is controlled by a diaphragm-type backpressure regulator.

- **Reaction Systems**

The SCT preheater consists of a 0.245-in. inside diameter tube 120-in. in length and fabricated into a horizontal, "trombone-shaped" vessel. The preheater has been equipped with Calrod electric heaters providing for two separately controlled heating circuits. In this way, temperature profiles can be closely controlled. The vertical SCT reactor consists of a 1.0 in. i.d. by 9.5-in. long stainless steel pipe electrically heated via a Calrod heater. The SCT preheater and the vertical SCT reactor are directly connected and can be operated either in series with the catalytic stage reactor or as an independent thermal stage reactor.

In the close-coupled mode of operation, slurry from the SCT reaction system is fed to the LC-Fining^{sm} reactor feed loop which is fed directly to the inlet of the LC-Fining^{sm} reactor. This reactor loop consists of: (1) a 1.6 in. pipe reactor; (2) a vapor/liquid separator; and (3) a duplex, remote-head, high pressure recycle pump. A small amount of flush oil is periodically used to purge the internal recycle pump checks. All vessels, transfer lines and internal recycle pump heads are operated at essentially the same temperature in order to simulate an isothermal operation (within ± 3°F) for the catalytic stage.

- Product Collection System

  The recovery system consists of four high pressure separators, each one operated as sequentially lower temperatures. In the first vessel, solids-containing products are separated from the uncondensed hydrocarbons and heteroatoms. This separator is electric-traced and operated at system pressure and at a temperature of about 650°F. The resultant product slurry passes through a second separator (550°F) and is collected in a batch receiver vessel which is isolated from the high pressure reaction system, depressurized to ambient pressure, and then drained into an appropriate storage container.

  The overhead vapor stream is further separated in two consecutive high pressure separators, operated at about 250°F, and 175°F, respectively. The pressure of the uncondensed vapors from the last separator is reduced to atmospheric, and cooled further in two ambient water-cooled condensers. Light uncondensed gases and hydrogen are then metered by a wet test meter and then sampled for subsequent gas chromatographic analysis.

The operating approach taken for the present standard mode catalyst activity maintenance test was to start the unit with a slurry consisting of prehydrogenated petroleum vacuum resid, coal, and a coal-derived startup solvent. At the onset of the test, catalyst was loaded to the catalytic reactor to the required volume. Tables 2, 3 and 4 show the coal and petroleum feedstocks as well as the operating conditions. The unit was operated at essentially constant severity without any fresh catalyst addition. Every 3 hours, the net heavy oil was drained; a portion was blended with fresh coal and petroleum; and recycled in a batchwise manner to the SCT slurry feed tank. The heavy oil recycle consists of non-deashed material (nominally 600°F+ boiling range) from the LC-Finer^{sm}. The purge of light LC-Finate and net heavy LC-Finate was closely maintained to control a constant SCT slurry feed rate and feed composition.

CATALYST ACTIVITY MAINTENANCE TEST

Catalyst deactivation during hydroprocessing of either coal derived extracts or virgin petroleum feedstocks is a well recognized phenomenon. Catalyst stability and life over long periods of operation are extremely important in coal/petroleum co-processing. Catalyst deactivation particularly with respect to metals deposition, hydrogen uptake, net distillate yield and coal and resid conversions is important in predicting catalyst make up rates for commercial hydrocracking units.

Table 2

ANALYSIS OF PITTSBURGH SEAM IRELAND MINE COAL

<u>PROXIMATE, WT.%</u>	
MOISTURE	1.80
VOLATILE MATTER (DRY BASIS)	40.12
ASH CONTENT (DRY BASIS)	13.62
FIXED CARBON (DRY BASIS)	46.62
<u>ULTIMATE, WT.% MF BASIS</u>	
CARBON	70.61
HYDROGEN	4.72
OXYGEN (BY DIFF)	5.89
NITROGEN	1.30
SULFUR - TOTAL	4.24
PYRITIC	2.07
SULFATIC	0.05
ORGANIC	2.12
ASH	13.26
<u>RANK</u>	hvAb

Table 3

PROPERTIES OF HYDROCRACKED VACUUM PETROLEUM RESID PRODUCED IN AMOCO OIL'S TEXAS CITY LC-FINING^{sm} PLANT

<u>SPECIFIC GRAVITY</u>	
60/60°F	1.0481
°API	3.5
<u>ELEMENTALS, wt.%</u>	
CARBON	87.93
HYDROGEN	10.00
NITROGEN	0.80
SULFUR	1.27
<u>METALS, ppm</u>	
VANADIUM	38
NICKEL	33
<u>HEPTANE INSOLUBLES, wt.%</u>	13.5
<u>TOLUENE INSOLUBLES, wt.%</u>	1.3
<u>ASH, wt.%</u>	0.12
<u>CONRADSON CARBON RESIDUE, wt.%</u>	29.5
<u>PROTON NMR DISTRIBUTION, wt.%</u>	
AROMATICS	13.3
CYCLIC	24.0
ALKYL	47.5
GAMMA	15.2

Table 4

SUMMARY OF OPERATING CONDITIONS DURING CATALYST ACTIVITY MAINTENANCE TEST

COAL TYPE	PITTSBURGH SEAM (IRELAND MINE)
PETROLEUM RESID	AMOCO TEXAS CITY LC-FINATE VACUUM BOTTOMS
SCT REACTION CONDITIONS	
SLURRY COMPOSITION, WT.%	
COAL	35
PETROLEUM RESID	35
RECYCLE SOLVENT (CO-PROCESSED HEAVY OIL)	30
TEMPERATURE, ^{o}F	825
SPACE VELOCITY, lbs/hr/ft^3	420
H_2 FEED RATE, scf/bbl	2000
PRESSURE, psig	2100
LC-FINING^{sm} REACTION CONDITIONS	
TEMPERATURE, ^{o}F	790
H_2 FEED RATE, scf/bbl.	4000
RELATIVE LHSV	0.28
RELATIVE WHSV	0.43
CATALYST	SHELL 324M (Recovered from prior 75-hour co-processing recycle test)

An extended catalyst activity maintenance test was conducted in the bench scale unit in the standard co-processing mode of operation. The main objectives of this run were to:

- Obtain baseline data for establishing the batch catalyst deactivation trends for predicting catalyst addition rate under continuous commercial operations.
- To gain insight into the catalyst deactivation phenomenon when co-processing coal extract and petroleum based oils;
- To perform proof-of-the-concept type run for an extended period in order to demonstrate the long term operability of LCI's co-processing scheme.

The test conditions selected for this activity maintenance test were based on preliminary results from the process variable scans performed during the Task 3 experimental program. In this run, hydrocracked 975°F+ residuum obtained from vacuum distillation of LC-Finate from Amoco Oil's Texas City LC-Fining^{sm} unit was used. The aromatics hydrogen content of this petroluem resid is somewhat higher (13.3% of total) when compared to that of a typical virgin petroleum resid (5-8% of total). The vacuum resid derived from the LC-Finate heavy oil is fairly low in metals content (V + Ni equal 70 ppm). Vanadium and nickel content of the parent petroleum virgin vac resid are generally in the 300-700 ppm range.

The activity maintenance run was successfully completed in a 650-hour continuous operation with a total of 181 process-derived recycle solvent passes. This run successfully demonstrated the overall technical feasibility of LCI's two-stage close-coupled co-processing scheme. The bench-scale operation was fairly smooth throughout the run duration.

Coal conversions were measured by quinoline insolubles and ash concentrations. Periodic interstage samples (SCT effluent) were taken to monitor the performance of the thermal stage. Coal conversion in the thermal stage was the key parameter in evaluating the SCT reactor performance and the quality of the recycle solvent made in the subsequent second stage. Since there are essentially no quinoline insolubles (QI) in petroleum resid, all QI's were derived from the coal feed. Coal conversions were calculated on a moisture and ash-free basis.

Overall 975°F+ conversions were measured by vacuum distillation of the heavy liquid product from the LC-Fining^{sm} stage. All organic matter (moisture and ash-free) from coal as well as from the 975°F+ fraction from petroleum were included in the 975°F+ feed content.

Figure 3 shows the variations in overall two-stage coal conversions and 975°F+ conversions with catalyst age as measured by slurry on-stream time in hours. It is evident from Figure 3 that there is no appreciable drop in coal conversion and 975°F+ conversion performance parameters during the duration of the test. The coal conversions generally ranged from 91 to 94 wt% MAF which are well within the experimental accuracy. The 975°F+ conversions ranged from 61.5 to 64.5 wt%. Both these parameters were not very sensitive to catalyst age, i.e., the rate of deactivation was extremely low.

Other key co-processing performance parameters such as sulfur and nitrogen removal (Figure 4) and net distillate yield (Figure 5) also showed no appreciable signs of decline with catalyst age with the exception of denitrogenation which showed only a modest decline.

Hydrogen to carbon atomic ratios in the C_5-975°F syncrude, the 600°F+ LC-Finate heavy oil and the 975°F+ LC-Finate vac bottoms were found to be somewhat more sensitive indicators of catalyst activity decline. These parameters generally showed a small but positive decline with catalyst age (Figure 6). H/C atomic ratio may be dependent upon the hydrogen transfer ability of the catalyst. Thus, as the catalyst ages, its hydrogenation ability decreases. However, the calculated chemical hydrogen consumption, which is accurate to about ± 15%, appeared to stabilize after about 400 hours on-stream time (Figure 7).

Another sensitive performance parameter, which did show a definite deactivation trend, was the preasphaltene concentration in the LC-Finate heavy oil (Figure 8). Solids-free preasphaltene concentration was found to increase with catalyst age. However, the preasphaltenes concentration increase did follow two distinct profiles. Initially, the rate of increase was higher up to a catalyst age equivalent to about 400 hours of slurry on-stream time. This was followed by an essentially flat trend for the remainder of the activity maintenance test.

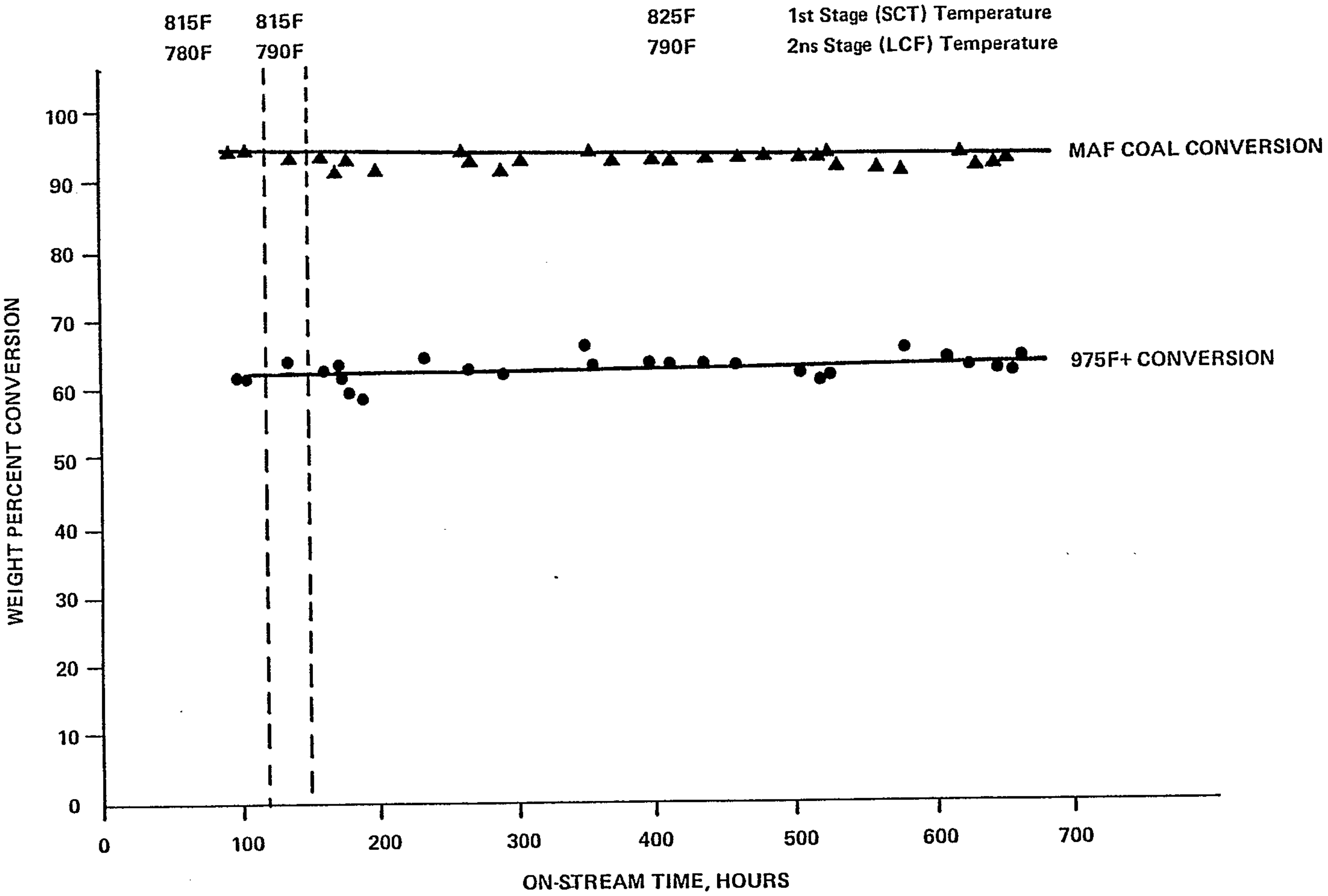


Figure 3. Two-Stage Co-Processing Performance During Catalyst Activity Maintenance Test

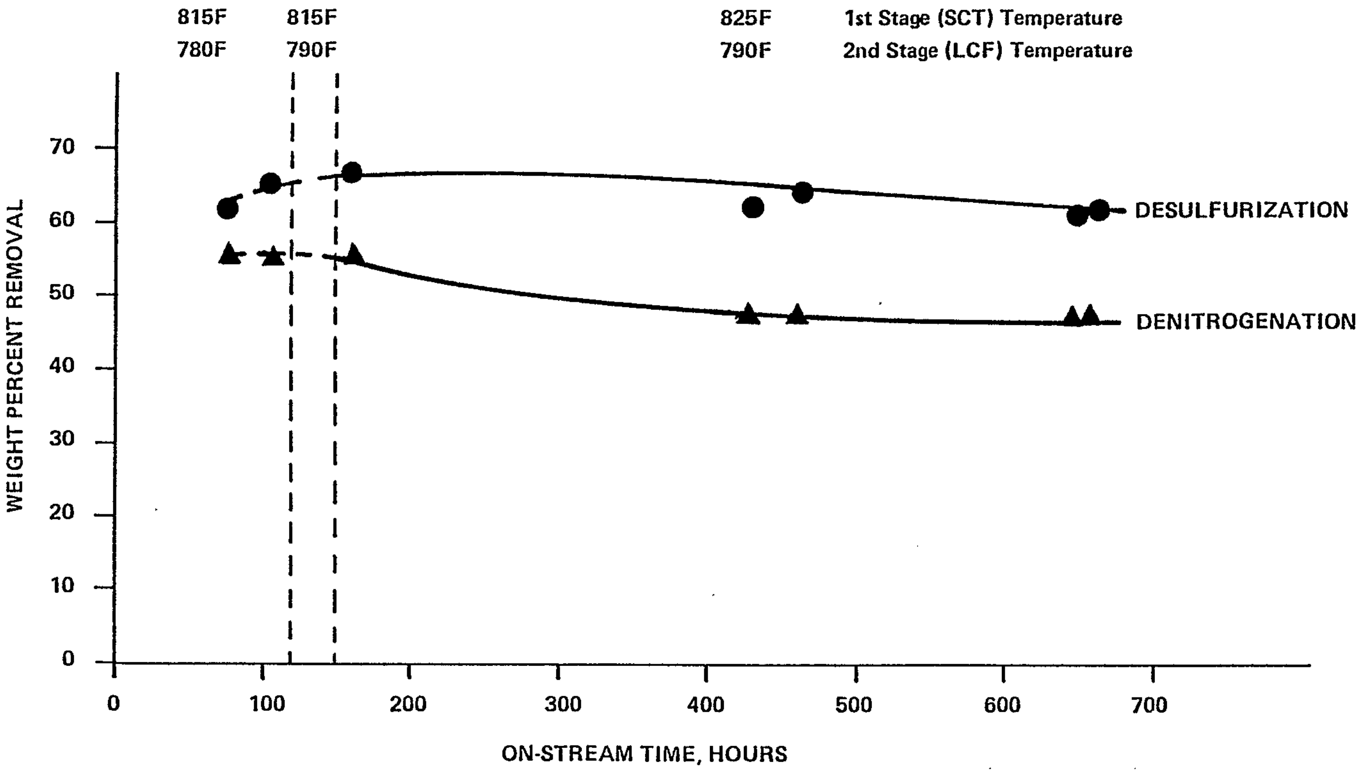


Figure 4. Desulfurization and Denitrogenation Performance During Catalyst Activity Maintenance Test .

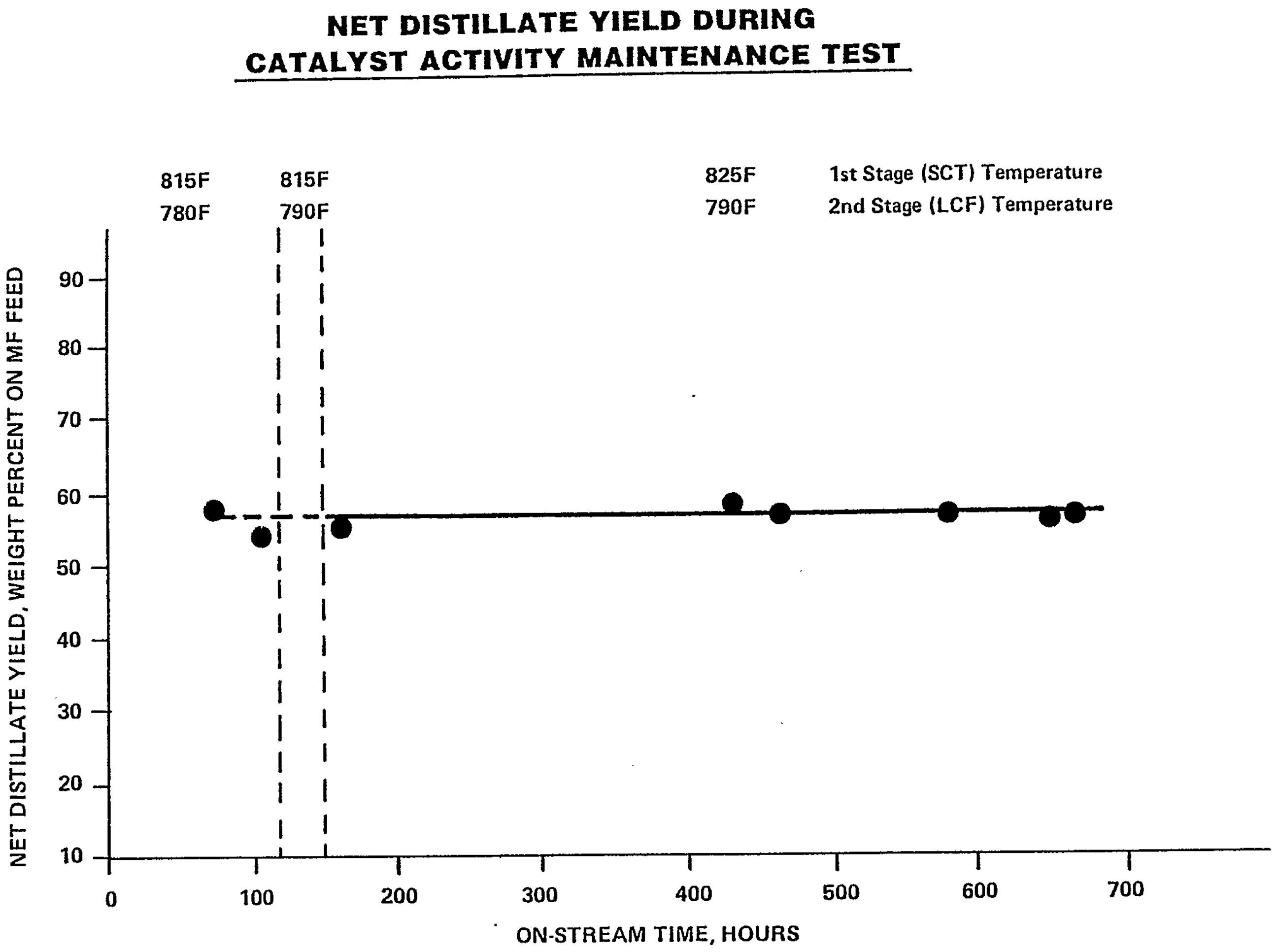


Figure 5. Net Distillate Yield During Catalyst Activity Maintenance Test

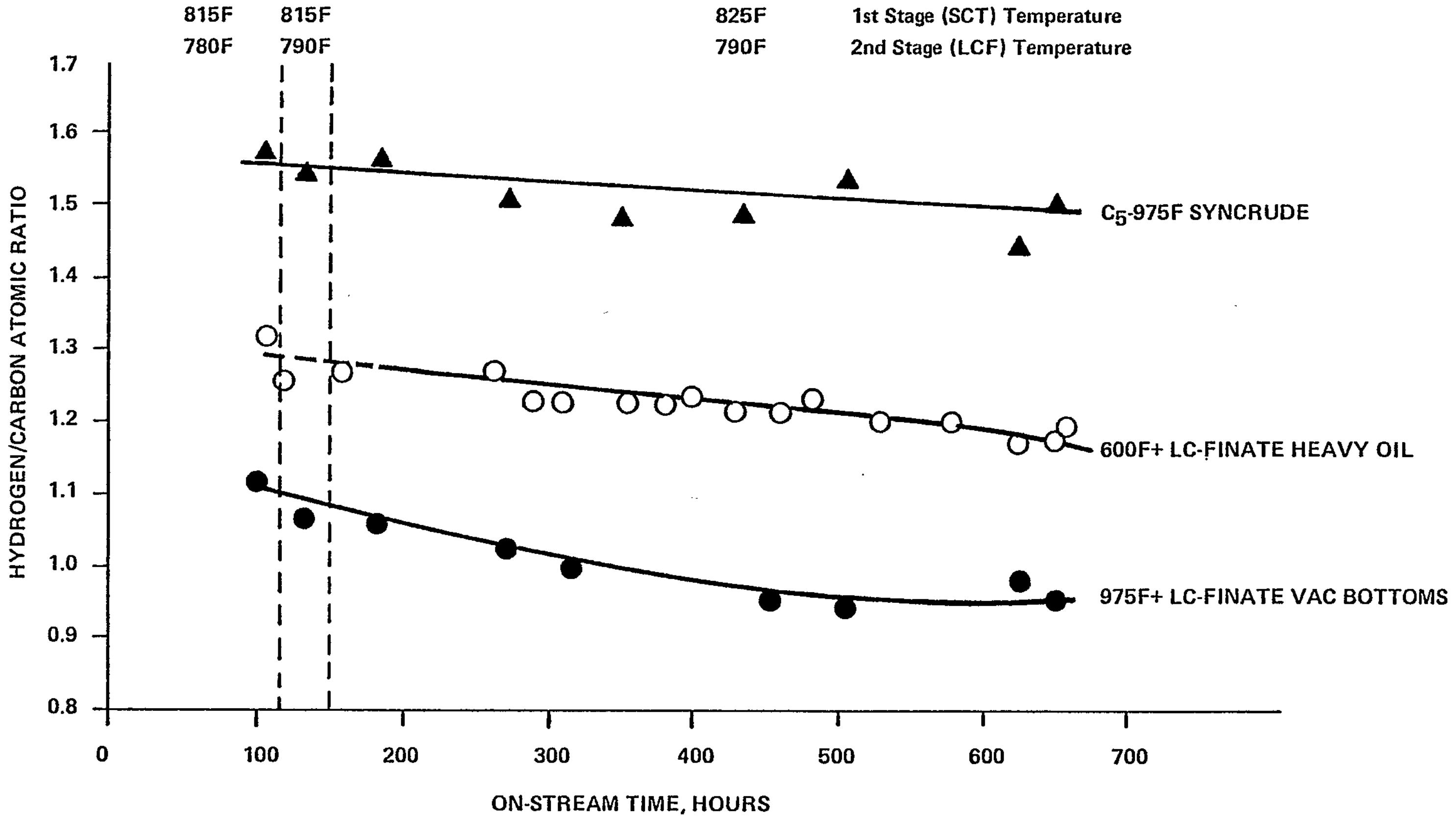


Figure 6. Hydrogen/Carbon Atomic Ratio of LC-Finates From Catalyst Activity Maintenance Test

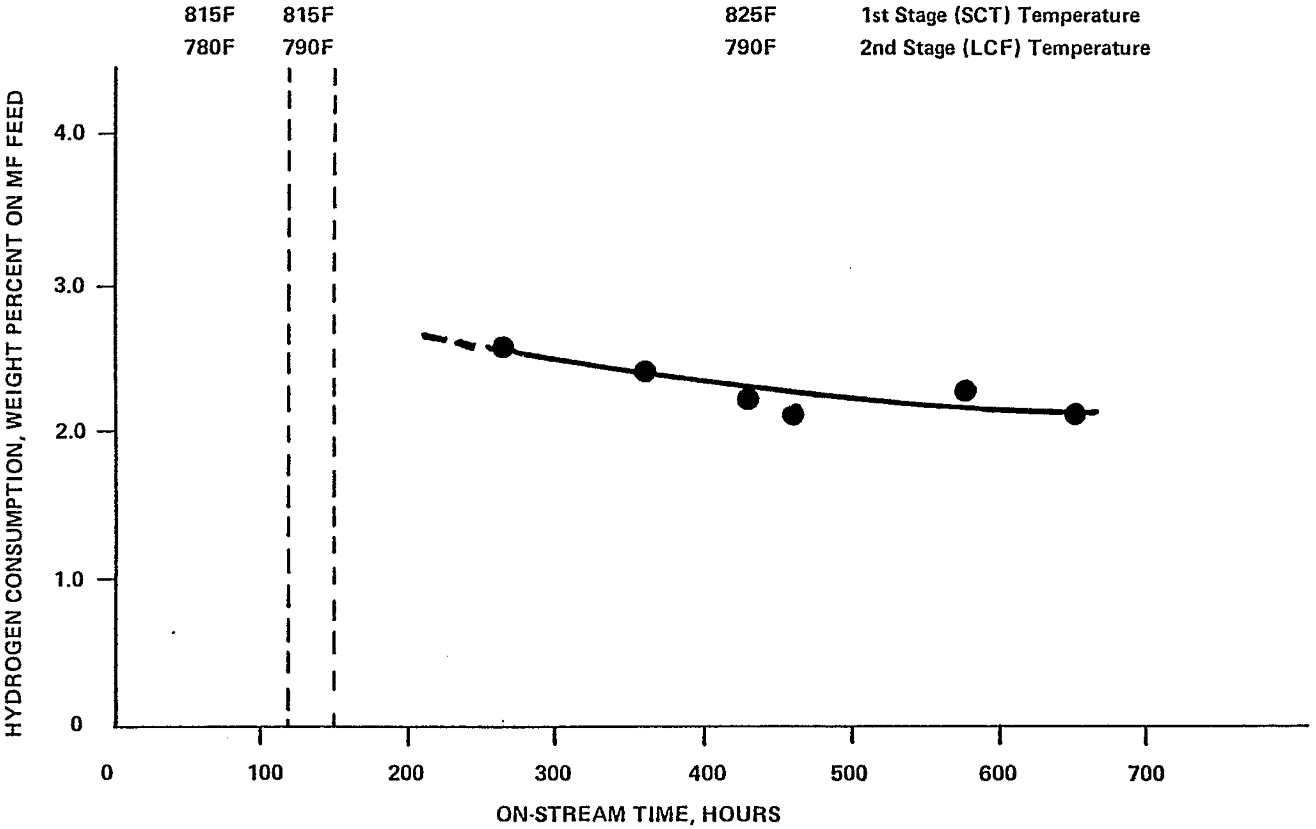


Figure 7. Calculated Hydrogen Consumption During Catalyst Activity Maintenance Test

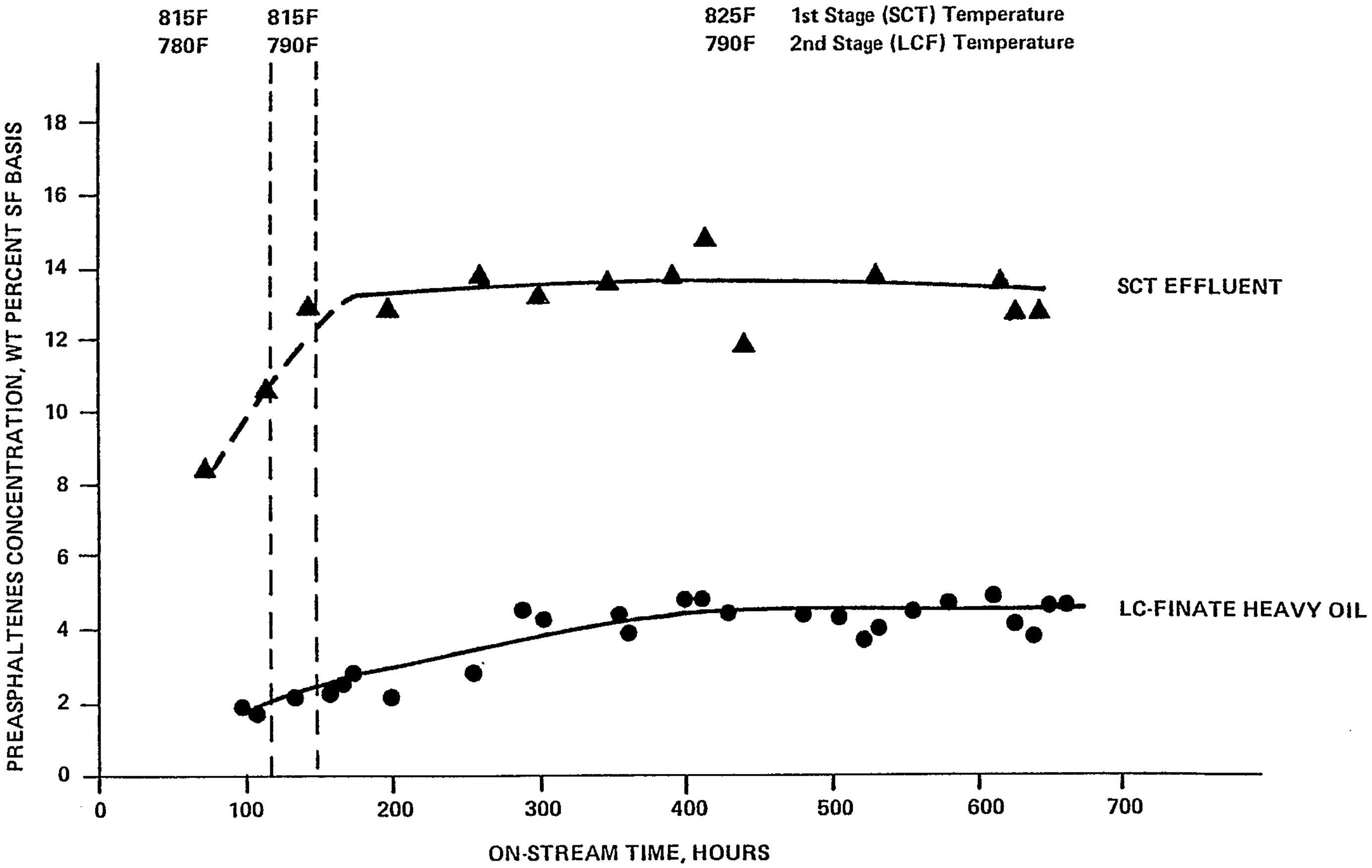


Figure 8. Preasphaltenes Concentrate During Catalyst Activity Maintenance Test

After completion of the catalyst activity maintenance test, a brief SCT scan in the Microautoclave Test (MAT) Unit was performed in order to assess the recycle solvent donor strength. Three recycle solvent fractions, one collected during early operation, a second from the middle of the run and the third from the end of of the run were tested in a standard batch MAT unit at SCT conditions comparable to those tests. Since there is no direct analytical method presently available which enables one to characterize the donor solvency of the co-processed recycle solvent, coal conversion obtained in the standard MAT unit represents the only analytical measure of the donor capacity of the recycle solvent.

Figure 9 shows the MAT characterization results of the recycle solvent samples as measured by SCT coal conversion and preasphaltene concentration in the SCT extract. Interestingly, MAT SCT coal conversions were essentially the same as those observed during the continuous bench-scale unit operation (as shown in Figure 10) indicating a close equivalence in the time-temperature reaction severity between the batch MAT and the continuous bench-scale unit. However, preasphaltene concentrations between the two units did not show such a direct correspondence. SCT coal conversions showed no significant decrease during the catalyst activity test indicating that this aspect of solvent quality was consistently maintained during the 650-hour test.

At the end of the activity maintenance test, the spent catalyst was removed, toluene washed, pyridine extracted and dried. Table 5 summarizes the analyses of the fresh and aged catalyst. Key catalyst properties were determined in order to assess the extent of catalyst deactivation. Upon inspection, the bulk density of the catalyst increased from 0.76 to 1.24 gms/cc and there was a four to five fold drop in BET surface area and mercury penetration pore volume. The carbon deposition on the catalyst amounted to about 19.5%, which is similar to carbon deposition during catalyst aging with hydroconversion of ITSL coal extracts.

The assessment of the trace metal concentrations in the spent catalyst revealed the following:

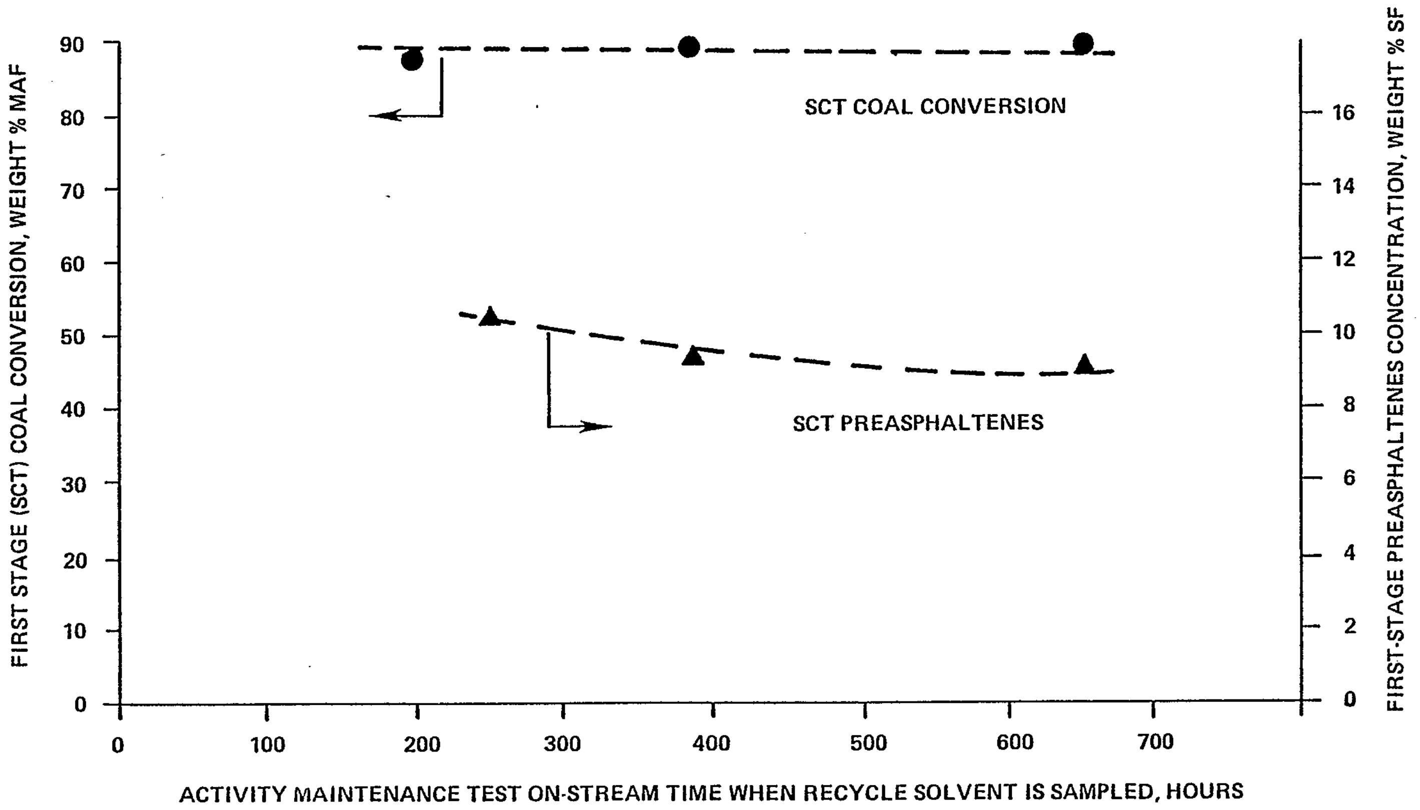


Figure 9. Microautoclave (MAT) Characterization of Recycle Solvent Samples From Catalyst Activity Maintenance Test At Standard Microautoclave Test Conditions

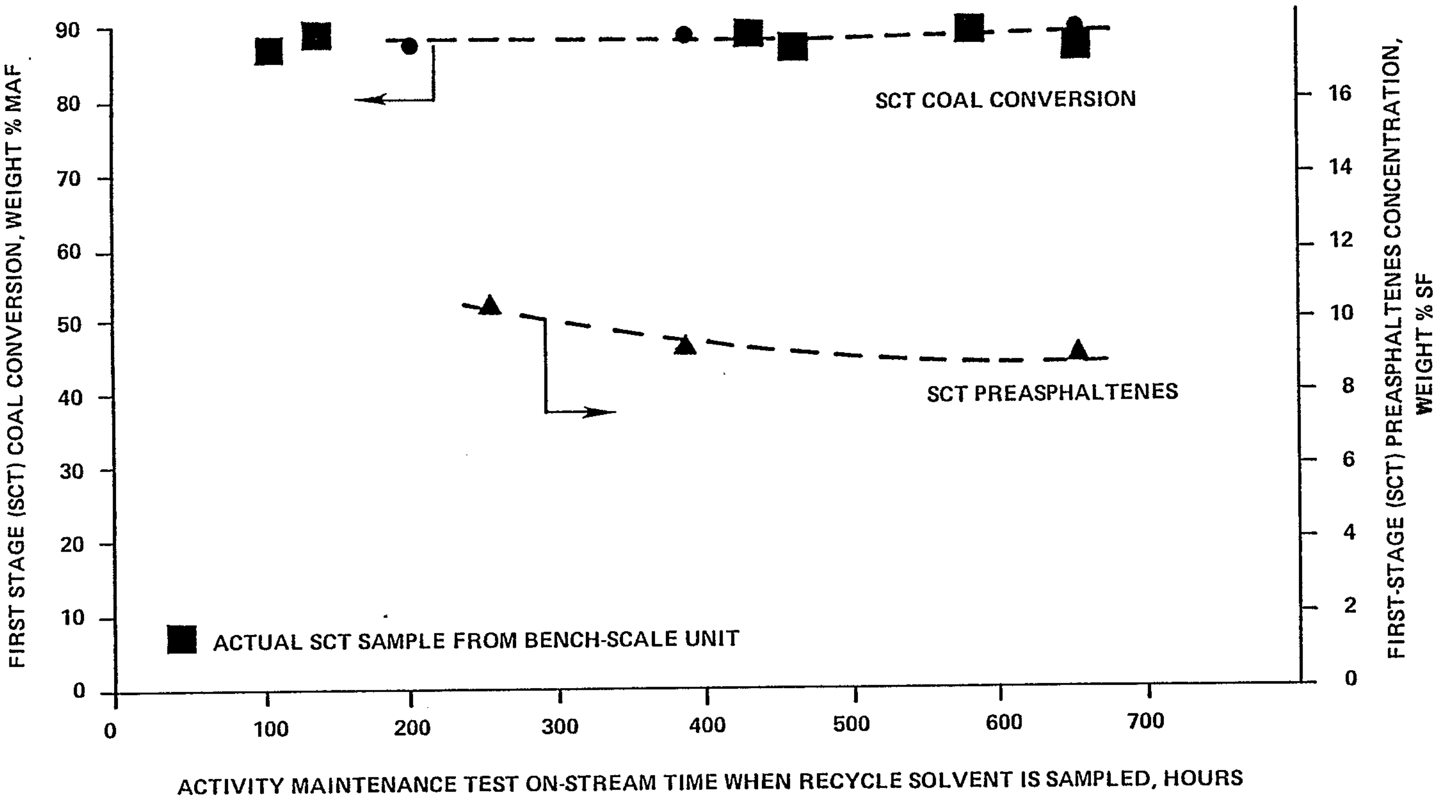


Figure 10. Microautoclave (MAT) Characterization of Recycle Solvent Samples From Catalyst Activity Maintenance Test at Standard Microautoclave Test Conditions

Table 5

SECOND STAGE CATALYST PROPERTIES*

	FRESH OXIDE	AGED AFTER 653 HOUR LIFE TEST
BULK DENSITY, g/cc	0.76	1.24
BET SURFACE AREA, m^2/gm	150	36.4
HG. PORE VOLUME, cc/gm	0.48	0.10
CARBON ON CATALYST, %	TRACE	19.4
TRACE METALS, ppm		
V	<5	122
Ca	75	436
Fe	125	533
Na	225	1800

* Shell 324M

- About 29% of the vanadium in the feed petroleum resid was picked up in the spent catalyst. The vanadium removal for a typical petroleum feedstock under similar LC-Fining^{sm} operating severity is in parity with 975°F+ conversion, i.e., about 60 wt. %. Therefore, the reduction in the devanadization rate by co-processing is estimated to be approximately 52%. There appears to be a positive synergistic effect indicating that coal ash and IOM tend to capture a significant portion of trace metals. This would therefore result in a considerable reduction in the catalyst deactivation rate that might otherwise result from the organometallic constituents present in the petroleum residua.
- Similarly, the coal-derived trace metals (i.e., Ca, Fe, Na, K and Ti) deposited on the catalyst has been observed to be very low.

Co-processing performance results from the activity maintenance test are summarized in Table 6 and 7. Over the test duration, the process performance ranged from:

- 87 to 89.5 wt.% MAF coal conversion in SCT;
- 11 to 16% concentration of preasphaltenes in SCT effluent;
- 93 to 95.5 wt.% MAF overall coal conversion across two stages;
- 62 to 65.5 wt.% 975°F+ conversion;
- 54.5 to 58.0 wt.% C_4-975°F net distillate product;
- 1.7 to 4% preasphaltenes concentration in the LC-Finate heavy oil;
- 61 to 72 wt.% overall desulfurization;
- 3.5 to 3.7 barrels of net distillate product per MF ton of fresh feed;
- 5.8 to 7.2 wt.% C_1 to C_4 gas yield.

A calculated (by the forced carbon balance method) product yield structure is presented in Table 8. In all of the material balance periods, the overall actual material and carbon balances ranged from 95 to 99 wt. %. This net product yield structure was used in the conceptual design.

In order to assess the nature of the co-processing products; downstream upgrading/hydroprocessing requirements and the disposition of the 975°F+ co-processed vac resid, the total liquid products from the last recycle pass were submitted for detailed analytical inspections. These results are summarized in

Table 6

PRELIMINARY CO-PROCESSING PERFORMANCE RESULTS FOR CATALYST ACTIVITY MAINTENANCE TEST

BASED ON FORCED CARBON BALANCES

	SCT REACTOR		TWO-STAGE PERFORMANCE				
On-Stream Time/Hrs	COAL CONVERSION WT% MAF	PREASPHALTENES CONCENTRATION WT% SF*	COAL CONVERSION, WT% MAF	%975°F+ MF CONVERSION	DISTILLATE YIELD ON 975F+ FEED, MF	% SF PREASPHALTENES CONCENTRATION	% MF DESULFURIZATION
103	88.1	10.6	94.3	64.2	54.6	1.7	72
160	89.6	12.9	93.4	65.0	55.5	2.0	67
433	88.5	11.8	93.3	65.6	58.0	3.9	64
433	87.0	16.6	92.7	63.9	57.1	3.9	61
575	88.7	13.5	93.0	63.5	57.0	4.0	65
650	87.0	16.0	94.3	62.0	55.9	3.2	62
653	----	----	95.5	64.0	57.3	3.2	62

* $\left(\frac{\text{TI-QI}}{\text{100-QI}}\right)$ X 100

Table 7

PRELIMINARY CO-PROCESSING PRODUCT YIELD STRUCTURES
BASED ON FORCED CARBON BALANCE CALCULATIONS

BASIS: Wt.% MF Coal + Petroleum Feed

Hours on Stream	103	160	433	458	575	650	653
CH_4	2.3	2.5	2.1	1.9	2.0	1.9	1.9
C_2H_6	1.9	2.1	1.6	1.6	1.6	1.6	1.6
C_3H_8	1.7	1.7	1.5	1.4	1.4	1.4	1.4
C_4H_{10}	1.0	0.9	0.9	1.0	0.9	0.9	0.9
C_1-C_4 Gas Yield	6.9	7.2	6.1	5.9	5.9	5.8	5.8
C_5-650°F	26.3	27.8	29.8	27.9	28.7	27.4	28.5
650-975°F	28.3	27.7	28.2	29.2	28.3	28.5	28.8
C_5-975°F	54.6	55.5	58.0	57.1	57.0	55.9	57.3
975F+ (SF)	22.5	23.7	22.9	22.6	24.0	26.0	24.2
IOM + Ash	9.3	9.5	9.5	10.8	9.7	9.1	9.1
$CO + CO_2$	0	0	0	0	0	0	0
H_2O	3.3	3.3	3.3	3.3	3.3	3.3	3.3
H_2S	1.9	2.0	1.8	1.8	1.8	1.8	1.8
NH_3	0.7	0.7	0.6	0.6	0.6	0.6	0.6
TOTAL	101.5	101.9	102.2	102.1	102.3	102.5	102.1

Table 8

NET YIELD STRUCTURE AND OTHER RELATED DATA FROM STANDARD MODE CATALYST ACTIVITY MAINTENANCE TEST

	COAL + PETROLEUM RESID, WT.% MF	
METHANE	1.9	
ETHANE	1.6	
PROPANE	1.4	
BUTANE	0.9	
C_1-C_4 GAS YIELD		5.8
C_5 - 650°F DISTILLATE	28.5	
650 - 975°F DISTILLATE	28.6	
C_5 - 975°F DISTILLATE		57.1
975°F+ (SOLIDS-FREE)	24.0	
IOM + ASH	9.6	
COx	TRACE	
H_2O	3.3	
H_2S	1.8	
NH_3	0.6	
HETEROATOMS		5.7
TOTAL	102.2	
HYDROGEN CONSUMPTION, SCF/TON FEED	8300	
TWO-STAGE COAL CONVERSION, %	93.2	
TWO-STAGE 975°F+ CONVERSION, %	63.7	

COAL: PITTSBURGH SEAM IRELAND MINE

PETROLEUM: LC-FINATE VAC BOTTOMS FROM AMOCO'S TEXAS CITY REFINERY.

Tables 9 through 12. C_5-400°F co-processed naphtha fraction is more paraffinic and hence more petroleum-like. The API gravity of this cut was 49.6° and the mid boiling point was 247°F. This fraction constitutes about 7.5% of the total liquid product. Middle distillate cut, 400-600°F (yield of 12.1%), had an API gravity of 27.9°. This fraction is rich in aromatics indicating that this cut had probably more coal-derived constituents (49% aromatics). The heavy gas oil fraction (600-975°F), with a yield of 33.8%, had a Watson "K" of 10.9 which indicates the presence of a high aromatics content that is characteristic of coal-derived liquids. The 975°F+ vacuum resid fraction, which contains unconverted organic matter and ash from coal, was produced at a yield of 46.6%. This stream is rich in Conradson Carbon Residue, asphaltenes and preasphaltenes.

The 975°F+ co-processed material was subjected to simulated fluid coking in a batch bench-scale unit to obtain yield data. This test was operated at high heating rates to simulate the type of performance that might be expected in a continuous fluid coker. The test was made at 1200°F and essentially at atmospheric pressure using nitrogen as a purge gas. The observed distillate yield was 7.9 wt. % based on fresh coal and petroleum feed to the co-processing unit. In a commercial conceptual design, the coke from the fluid coker could be gasified to make fuel gas.

CONCEPTUAL DESIGN STUDY BASIS

A project task was defined to translate the experimental results from the catalyst activity maintenance testing to a conceptual commercial application of LCI's co-processing concepts. Two design cases were formulated: 1) an over-the-fence co-processing facility based on the standard mode, and 2) a grass-roots facility based on the alternative mode.

The over-the-fence concept is predicated on a minimal capital investment scenario in which the petroleum feedstock would be derived from an adjacent large petroleum refinery and co-processed in the standard mode. In the study case, the co-processing plant was hypothetically sited adjacent to a Gulf Coast refinery, such as for example, Amoco Oil Company's Texas City refinery, which is equipped with an expanded-bed hydrocracker (LC-Fining^{sm}). The refiner would sell the

Table 9

COMPARISON OF PROPERTIES OF CO-PROCESSED C_5-400°F NAPHTHA FRACTIONS

	RUN CTS-26 (LIFE TEST)	RUN CTS-7
PETROLEUM SOURCE	COMMERCIAL LC-FINATE VAC. BOTTOMS	ARAB HEAVY
COAL/PETROLEUM RATIO	1.0	1.4
YIELD, WT.% TLP	7.5	7.5
DENSITY		
gms/cc	0.7813	0.7690
° API	49.6	52.5
WATSON "K"	11.4	11.6
ELEMENTALS, WT%		
C	86.2	86.4
H	13.8	13.6
N	<0.1	<0.1
S	<0.1	<0.1
H/C ATOMIC RATIO	1.92	1.90
BROMINE NUMBER	8.6	6.0
ANILINE POINT, °F	101	---
FIA SATURATES, VOL%	77.7	79.2
OLEFINS, VOL%	3.7	2.0
AROMATICS, VOL%	18.6	18.8

Table 10

COMPARISON OF PROPERTIES OF CO-PROCESSED 400-600°F MID DISTILLATE FRACTIONS

	RUN CTS-26 (LIFE TEST)	RUN CTS-7
PETROLEUM SOURCE	COMMERCIAL LC-FINATE VACUUM BOTTOMS	ARAB HEAVY
COAL/PETROLEUM RATIO	1.0	1.4
YIELD, WT% TLP	12.1	30.4
DENSITY		
gms/cc	0.8899	0.8933
° API	27.5	25.9
WATSON "K"	11.1	11.0
ELEMENTALS, WT%		
C	87.3	87.7
H	11.9	11.6
N	0.7	0.7
S	0.10	<0.1
H/C ATOMIC RATIO	1.64	1.59
BROMINE NUMBER	12.0	7.0
ANILINE POINT, °F	80	73
FIA: SATURATES, VOL%	47.8	44.2
OLEFINS, VOL%	2.9	1.8
AROMATICS, VOL%	49.3	54.0
DIESEL INDEX	22.0	18.9

Table 11

COMPARISON OF PROPERTIES OF CO-PROCESSED 600-975°F GAS OIL FRACTION

	RUN CTS-26 (LIFE TEST)	RUN CTS-7
PETROLEUM SOURCE	COMMERCIAL LC-FINATE VACUUM BOTTOMS	ARAB HEAVY
COAL/PETROLEUM RATIO	1.0	1.4
YIELD, WT% TLP	33.8	42.6
DENSITY		
gms/cc	0.984	0.9738
°API	12.3	13.8
WATSON "K"	10.9	11.1
ELEMENTALS, WT%		
C	89.1	89.6
H	10.1	9.9
N	0.6	0.3
S	0.2	0.2
H/C ATOMIC RATIO	1.36	1.32
ANILINE POINT, °F	124	95

Table 12

COMPARISON OF PROPERTIES OF CO-PROCESSED 975F+ VACUUM RESIDUUM

	RUN CTS-26 (LIFE TEST)	RUN CTS-7	CO-PROCESSING FEEDSTOCK
PETROLEUM SOURCE	LC-FINATE VACUUM BOTTOMS	ARAB HEAVY	COMMERCIAL LC-F VACUUM BOTTOMS
COAL/PETROLEUM RATIO	1.0	1.4	0
YIELD, WT.% TLP	46.6	19.5	100
DENSITY			
gm/cc	1.259	1.450	1.0481
o API	-19.1	-33.9	3.5
ELEMENTALS, WT.%			
C	76.3	70.1	87.93
H	6.5	4.8	10.00
N	1.0	0.6	0.80
S	2.1	3.4	1.27
H/C ATOMIC RATIO	1.02	0.82	1.37
% CONRADSON CARBON	59.2	76.1	29.5
TOLUENE INSOLUBLES,%	25.2	39.7	1.3
QUINOLINE INSOLUBLES,%	20.0	32.8	
ASH, %	14.1	26.6	0.12
VANADIUM, ppm	104	262	38
NICKEL, ppm	46	95	33

unconverted vacuum bottoms from the LC-Finer^{sm} over-the-fence to the co-processing plant operator who would also purchase certain utilities such as BFW, inert gas, cooling water, etc. from the refiner. Table 13 summarizes the design basis conditions for the over-the-fence, standard mode conceptual design.

A preliminary energy balance for the standard mode was computed as summarized in Table 14. The net usable thermal efficiency is estimated to be 84% which is marginally above that of the average efficiency that would be predicted for a coal only liquefaction process (ITSL) and a petroleum only hydrocracking process (LC-Fining^{sm}) operated at the respective fresh feed rates. The thermal efficiency is very sensitive to the method of bottoms processing and fuel utilization.

The grass-roots concept is predicated on the alternative mode utilizing a virgin petroleum resid which would be transported to the mine-mouth site of the co-processing plant. Table 15 summarizes the design basis conditions for the grass-roots concept. The co-processing facility is self-sufficient in fuel and utilities. Hydrogen is manufactured by partial oxidation of co-processed fluid coke and by the steam reforming of light hydrocarbons produced in the close-coupled LC-Finer^{sm} and in the co-processed vac bottoms fluid coker. The raw syncrude (LC-Finates and fluid coker distillates) are hydrotreated to produce clean distillate fuels for industrial or utility applications.

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Table 13

CONCEPTUAL PLANT DESIGN BASIS
Standard Mode: Over-the-Fence Concept

COAL:	2200 TPD PITTSBURGH SEAM COAL (MF)
PETROLEUM:	2200 TPD (12,000 BPD) LC-FINATE VAC BOTTOMS
SITE:	U.S.G.C.
YIELD STRUCTURE:	BASED ON ACTIVITY MAINTENANCE TEST CTS-26
PRODUCT SLATE:	C_5-650°F HYDROCRACKED DISTILLATES 650-975°F HYDROCRACKED DISTILLATES C_5-975°F COKER DISTILLATES SULFUR/AMMONIA FUEL GAS
BOTTOMS PROCESSING:	FLUID COKING OF CO-PROCESSED LC-FINATE VAC BOTTOMS; INTEGRATED AIR BLOWN GASIFICATION OF FLUID COKE
HYDROGEN MANUFACTURE:	STEAM REFORM LIGHT HYDROCARBON GASES FROM LC-FINING; FIRED FUEL FROM COKE GASIFIER
FUEL REQUIREMENTS:	NET EXPORTER OF FUEL GAS

Table 14

PRELIMINARY ENERGY BALANCE FOR STANDARD MODE CONCEPTUAL DESIGN

INPUT	MMM Btu/day	%
PETROLEUM	81.4	56.6
COAL	56.3	39.2
ELECTRICITY	6.0	4.2
	143.7	100.0
FUEL USERS		
SCT FURNACE	2.8	27.2
PRODUCT SEPARATION	1.5	14.6
STEAM REFORMER	5.1	49.5
OTHERS	0.9	8.7
	10.3	100.0
THERMAL EFFICIENCY CALCULATIONS		
USABLE PRODUCTS		
LC-FINATE DISTILLATES	95.4	78.9
FLUID COKER DISTILLATES	11.6	9.6
NET FUEL GAS	13.9	11.5
	120.9	100.0

% USABLE EFFICIENCY = $\frac{120.9}{143.7}$ or 84.1%

Table 15

CONCEPTUAL PLANT DESIGN BASIS
Alternative Mode: Grass-Roots Concept

COAL: (To Liquefaction):	10,000 TPD PITTSBURGH SEAM COAL (MF)
PETROLEUM:	10,000 TPD (54,700 BPD) VIRGIN ARAB HEAVY VAC RESID
SITE:	MORGANTOWN, WEST VIRGINIA REGION
YIELD STRUCTURE:	BASED ON ACTIVITY MAINTENANCE TEST CTS-32
PRODUCT SLATE:	HYDROTREATED NAPHTHA NO. 2 FUEL OIL NO. 4 FUEL OIL LPG SULFUR/AMMONIA
BOTTOMS PROCESSING:	FLUID COKING OF CO-PROCESSED LC-FINATE BOTTOMS
HYDROGEN MANUFACTURE:	PARTIAL OXIDATION OF CO-PROCESSED FLUID COKE AND STEAM REFORMING OF LIGHT HYDROCARBONS
FUEL GAS REQUIREMENTS:	LC-FINER GASES; FLUID COKER GASES

Section 17

EFFECT OF COAL CONCENTRATION ON PRODUCT DISTRIBUTION IN CANMET CO-PROCESSING

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ABSTRACT

The effect of feed coal concentration on the characteristics of distillate products was investigated using High Performance Liquid Chromatography(HPLC) and Field Ionization Mass Spectrometry(FIMS). The distillates were obtained by coprocessing Forestburg subbituminous coal and Cold Lake vacuum bottoms from Alberta in a nominal 1 kg/h bench scale unit. Distillates from three different coal concentration experiments at 3.7, 23.9 and 39.5 wt % on a maf slurry feed basis were chosen for this study. Gross distillate(205-525°C) characteristics were determined using elemental analysis and ^{1}H NMR. Results are consistent with the fact that as coal concentration is increased, more coal-derived liquids contribute to the distillate.

The distillates were separated into five different fractions using a Polar Amino Cyano (PAC) column. Analysis of the fractions indicated that increasing coal concentration from 3.7 wt% to 23.9 wt% results in an increase in the amount of polar materials and a subsequent decrease in the amount of saturated compounds. The weight percent of monoaromatics and polyaromatics were not effected by the amount of coal present in the slurry feed. The number and weight average molecular weights of the distillates boiling between 205-525°C and their hydrocarbon-type fractions decreased as the coal concentration increased. Each hydrocarbon-type fraction was analyzed by ^{1}H NMR and FIMS to determine the effect of coal concentration on compound-type distribution. The results show that increasing coal concentration has a significant effect on compound-type distribution and, in part, coal may enhance the upgrading of bitumen. Based on preliminary isotopic mass balance measurements which take advantage of the difference between the ^{13}C/^{12}C ratio of coal and bitumen, the amount of coal-derived carbon in the coprocessing distillate was estimated.

INTRODUCTION

In the coprocessing of coals and bitumens or petroleum resids both components of the feedstock are upgraded and contribute to the overall distillate product. In order to understand basic coal and oil interactions in coprocessing and to better evaluate different processing concepts, it is necessary to know what effect replacing part of the oil feed with coal has on the properties of the distillate product. This is especially relevant if coprocessing is to be critically compared with hydrocracking of the heavy oil only, since any advantage gained by coprocessing could be offset by negative changes in overall product quality.

The effect of feed coal concentration on process performance in coprocessing has been investigated by HRI, CANMET and PETC. A synergistic effect has been reported by HRI for pitch(+975°C) conversion at 50 wt % coal in the feed(1-2). For CANMET coprocessing, a synergistic effect in terms of distillate yield has been shown to exist for coal concentrations of less than 5 wt % in the feed(3). Miller(4) has also observed a rapid increase in distillate yield in the coprocessing of Wyodak subbituminous coal and heavy oil fractions with increasing coal concentrations to about 5 wt % coal. At PETC an increase in heptane solubles has been observed with specific coal and oil combinations containing up to 30 wt % coal in the charge to a microautoclave(5). A number of other investigators also refer to synergism during coprocessing(6-7). In the coprocessing of oil shales and coals a similar synergistic effect has also been reported i.e., the reactivity of the oil shale was enhanced in the presence of coal(8).

Coal conversion has also been shown to be effected by feed coal concentration in coprocessing. For instance, McLean et. al.(1) reported an increase in coal conversion as a function of coal concentration at lower process severities. It can also be expected that different levels of coal concentration in coprocessing feeds will affect distillate product quality. Detailed characterization of distillates is not only required for understanding of secondary upgrading but also for any economic evaluation or comparison of different processes.

This paper presents the results of work which was carried out to study the effect of feed coal concentration on the quality of distillates obtained in coprocessing Forestburg subbituminous coal and Cold Lake vacuum bottoms in the CANMET process.

EXPERIMENTAL

Coprocessing experiments were performed in a 1-L continuous-flow stirred tank reactor (CSTR) unit with a nominal capacity of 1 Kg/h of slurry feed. Product samples were collected over 1-h periods once steady state was reached. For all the experimental runs reported in this paper, material balance closures were within ± 5 wt %. Other details of the experimental unit are available elsewhere(3).

The analyses of the coal and solvent used in these experiments is given in Table 1. All experiments were carried out in the presence of $FeSO_4$ impregnated on part of the coal feed. Its concentration was kept constant for the three different coal concentrations of 3.7, 23.9 and 39.5 wt % on a maf slurry feed basis used in this study. Coprocessing experiments were performed at 450°C(723°K) with the total pressure maintained at 13.8 MPa, a nominal space velocity of 1 kg/h/l and a nominal hydrogen feed rate of 4 l/minute at 25 °C and 101 KPa.

Slurry products were fractionated using a spinning band still. Water and naphtha (IBP-205 °C) fractions were collected at atmospheric pressure. Distillation was continued under vacuum and a light gas oil (LGO) fraction was collected at an atmospheric equivalent 205-335 °C. Two heavy gas oil fractions were also collected, heavy gas oil 1 (HGO 1: 335-415°C) and heavy gas oil 2 (HGO 2: 415-525 °C).

To determine gross distillate properties the light and heavy gas oil fractions were mixed proportionally and then analyzed. Analyses were performed to determine elemental composition (carbon, hydrogen, nitrogen and oxygen by CHN 240 Perkin Elmer analyzer and sulphur by LECO analyzer) and aromaticity: f_a (by ^1H NMR applying the Brown Ladner treatment). The distillates(205-525°C) were deasphaltened(less than 1 wt % asphaltene) using 20 volumes excess pentane before being subjected to chromatographic analysis.

HPLC Separation of Distillates

The liquid chromatograph used was a Perkin Elmer LC series 4 equipped with an ASV-1 automatic switching valve, a LC-25 RI detector, LC-75 spectrophotometric detector and LC-100 computerized recorder. The distillate fractions (205-525 °C) of coprocessing runs containing 3.7 wt% and 23.9 wt % coal were separated by HPLC into saturates, monoaromatics, polyaromatics and polars using a semi prep., 25 cm x 1.3 cm, Polar Amino Cyano column (PAC). Saturates, monoaromatics and polyaromatics were eluted using pentane at a flow rate of 5.5 cc/min. The polars were eluted in two parts in a backflash mode using methyl-tert-butyl ether (MTB) designated as Polars 1, and tetrahyrofuran (THF) designated as polars 2. This procedure was repeated until a sufficient amount of material of each fraction was collected for analyses. The quantity of each fraction was measured gravimetrically after removing the solvent. Recovery of better than 95 % was obtained in each case.

Field Ionization Mass Spectrometry

FIMS was used to analyze distillate(205-525°C) fractions obtained in the coprocessing of 3.7 wt % , 23.9 wt % and 39.5 wt % coal with bitumen. Saturates, monoaromatics, polyaromatics and polars 1 fractions of coprocessing runs with 3.7 wt % and 23.9 wt % coal were also analyzed by FIMS. All FIMS analyses were performed at the facilities of SRI International, Menlo Park, CA. The detailed procedure of this technique has been published previously(9-10).

RESULTS AND DISCUSSION

CANMET coprocessing involves the simultaneous upgrading of coal and bitumen/heavy oils in a once through operation using $FeSO_4$ as a disposable catalyst. If coal-derived liquids contribute to the distillate products, the chemical composition of coprocessing distillates is expected to be different from that of hydrocracking distillates and may change with varying coal concentration. It is also possible that coal-derived liquids enhance the upgrading of bitumen, converting larger molecules to smaller molecules by providing hydrogen to bitumen-derived radicals. It was concluded that a detailed analysis of coprocessing distillates obtained at different levels of coal concentration would help in providing a better understanding of these solvent-coal interactions.

Effect of Coal Concentration on Product Characteristics

From material balance considerations it can be concluded that in CANMET coprocessing experiments up to 40-50 wt % of the converted coal ends-up in the distillate. This assumes that there is no positive interaction between coal and bitumen or that the excess distillate over what would be expected from the bitumen portion of the feed reacted separately, is assumed to be derived from coal. Since it is expected that coal-derived liquids would contribute more to the heavier fractions of coprocessing distillates, it was decided to perform detailed characterization of the 205-525°C fractions. The general characteristics of the distillates generated using the three different coal concentrations are shown in Table 2. Nitrogen and oxygen increased as coal concentration increased while the sulphur content decreased. There is a slight increase in aromaticity and a corresponding decrease in H/C atomic ratio as coal concentration increases. These results can be rationalized in terms of an increasing contribution of coal-derived liquids to coprocessing distillates as coal concentration is increased.

Chromatographic separation of the distillates obtained from two coprocessing experiments containing 3.7 and 23.9 wt % maf coal are shown in Figure 1. Saturated hydrocarbons account for about 44 wt % of the distillate at 3.7 wt % coal and about 35 wt % of the distillate at 23.9 wt % coal. The amount of monoaromatics and polyaromatics did not change significantly as coal concentration increased. However, relatively more polar compounds (polars 1) eluted in backflush mode with Methy-tert-butyl ether decreased slightly and THF-eluted hydrocarbons (polars 2) increased significantly. It appears that by adding more coal the quality of the products changes significantly. As will be discussed later, the characteristics of each fraction are also affected by increasing coal concentration.

These changes in product quality can be rationalized in terms of the contribution of more coal-derived liquids to the distillate as coal concentration is increased and/or enhancement in upgrading of the bitumen in the presence of coal. From the limited analysis shown in Table 3 it can be seen that there are no significant changes in the gross properties of the saturates and monoaromatics fractions at two levels of coal concentration. However, polyaromatics showed a decrease in aromaticity and consequently an increase in H/C atomic ratio. Aromaticity and nitrogen content of the polars 1 fraction increased significantly with increasing coal concentration. The limited amount of polars 2 fractions did not permit more detailed analyses. Table 4 lists the number and weight average molecular weights of the distillates and their hydrocarbon-type fractions. It is interesting to note that the molecular weights, both in distillates and the fractions decreased as coal concentration increased. The results indicate that the presence of coal enhances bond breakage in saturate and monoaromatic fractions. For polyaromatics, since molecular weight and aromaticity decreased, the presence of higher coal concentration appears to enhance both bond breakage and hydrogenation. The decrease in molecular weight and a large increase in aromaticity of the polars 1 fraction suggests that the contribution of coal-derived liquids to this fraction has increased with increasing coal concentration

^{1}H NMR analysis of the hydrocarbon-type fractions is shown in Table 5. Proton type distribution as defined by their chemical shifts(11) is illustrated in this table as a function of coal concentration. These analyses suggested slightly higher amounts of cyclic structures in the saturated fraction with 23.9 wt % coal. Little change in the proton distribution of monoaromatics was observed as coal concentration increased. The intensities of condensed aromatic protons in polyaromatics fractions decreased whereas alkyl beta and gamma protons increased as a result of increasing coal concentration. The results may be rationalized in terms of increasing the amounts of alkyl substituted polyaromatic compounds. For the polars 1 fractions the increase in coal concentration resulted in an increase in the condensed and uncondensed aromatic protons and a decrease in the alky beta and gamma protons. These results show that the amount of components with the higher number of aromatic rings and lower degree of alkyl substitution is increased with increasing coal concentration.

FIMS Analysis of Distillates and their Hydrocarbon-type Fractions

Field ionization mass spectrometry has been used extensively in the characterization of coal-derived liquids(12-16). Boduszynski et.al.(17-18) applied a combination HPLC (using a micro Bondapack NH_2 column) and FIMS to characterize distillates and residues isolated from the liquefaction of Wyodak coal. The micro Bondapak NH_2 column separated polycyclic aromatic hydrocarbons according to the number of aromatic rings (double bond) regardless of the type of alkyl substitution. FIMS separated these compounds according to nominal mass and Z values . The combination of HPLC/FIMS revealed detailed information on the composition of the hydrocarbons in heavy coal liquids. Recently FIMS has also been used in characterization of saturated hydrocarbons isolated from tar sand bitumens (19). In order to obtain fully quantitative data from FI mass spectra it is necessary to assume unit compound sensitivities. The intensities of the parent ion peaks are proportional to concentration and after correction for the natural abundance of ^{13}C isotope, these can be converted to wt %.

In the present study, coprocessing distillates and their hydrocarbon-type fractions mentioned earlier were analyzed by FIMS to determine changes in compound-types due to the presence of different levels of coal in the coprocessing feed. The amino-cyano column used in this work has a similar separating power compared to the micro Bondapak NH_2 column. However, due to the low concentration of each double bond series, polyaromatics were not separated according to their number of double bonds and were collected as one fraction. ^{1}H NMR analysis of the saturated fractions showed that these fractions were contaminated with small amounts of monoaromatics and olefins (area ratios of 96:2:2 respectively).

In the following analysis of the FIMS data, the methodology described by Boduszynski et.al.(18) was used as a basis for this study. The raw data from FIMS analysis was arranged into 14 columns each one unit apart. The peaks within each column were fourteen mass units (-CH_2) apart. The seven even-numbered and seven odd-numbered mass series (homologous series or Z series) were each two units apart. The concentration of each peak (compound-type) can be obtained directly from the FI spectrum in mole % if unit compound sensitivities are assumed. Since it is very unlikely that all the different components present in coprocessing distillates have the same sensitivity toward ionization, for quantitative comparison of individual compounds or homologous series the term " % intensity" or "apparent concentration" is used throughout this text. Because of the possibility of the overlap of different homologous series in FI spectra, prior chromatography separation is essential. Only limited information can be obtained from the FI spectra of unfractionated distillates. The % intensities of the apparent homologous series from Z=+2 to Z=-10 did not change significantly by varying coal concentration from 3.7 to 39.5 wt %. However, in all the apparent homologous series increasing coal concentration resulted in an increase in the intensities of relatively lower molecular weight compounds and a decrease in the intensities of relatively higher molecular weight compounds. These results are reflected in the lower molecular weights of the distillates shown in Table 4.

The Z-series type analyses for saturates and monoaromatics obtained from coprocessing distillates using 3.7 and 23.9 wt % coal are shown in Table 6. Since these two fractions were separated from the polyaromatics prior to FIMS analysis, it is not expected that there would be any interference between C_nH_{2n-12} homologous series represented by tricycloalkylbenzenes (3 double bonds) and naphthalenes (5 double bonds) and the acyclic C_nH_{2n+2} alkane series. As shown in Table 6, while the apparent concentration of homologous series Z=+2 to Z=-4 increased slightly, series Z=-6 did not change and series Z=-8 and Z=-10 decreased with increasing coal concentration. It should be mentioned that because of partial fragmentation of the saturate fractions the evaluation of part of the FI mass spectra below about 200 was difficult. Also, because of this fragmentation the total recovery (after correction for ^{13}C) of homologous series Z=+2 through Z=-10 was between 82-85 %. The saturate fractions consist of various homologous series ranging from acyclic alkanes (Z=+2) through hexacyclics (Z=-10). Acyclic alkanes in the saturate fraction obtained using 3.7 wt % coal range from about C_{13} to C_{39} with C_{22}(M/Z=310) being the most abundant. In the saturate fraction obtained using 23.9 wt % coal, acyclic alkanes range from about C_{13} to C_{35} with C_{19} (m/z=268) being the most abundant. This trend or the reduction in the range of the carbon skeleton and the change of maximum intensity to lower carbon number (molecular weight) as a function of increasing coal concentration was observed for all homologous Z series in the saturated fractions. This may imply that the addition of coal, in part, enhances the upgrading of bitumen. The formation of saturated hydrocarbons, even the acyclic homologous series Z=+2, from coal cannot be ruled out. Monocyclic alkanes (C_nH_{2n}, Z=0) consist of various alkyl cyclohexanes covering a broad mass range from C_{13} to C_{41} in the case of 3.7 wt % coal and C_{13} to C_{38} for the case of 23.9 wt % coal. The highest intensity in the later case can be assigned to alkyl substituted cyclohexanes having molecular weight of m/z=266. The intensity of this peak is increased more than twice upon increasing coal concentration from 3.7 wt % to 23.9 wt %. The next homologous series belong to dicyclic alkanes (C_nH_{2n-2}, Z=-2) which cover similar mass ranges as monocyclic alkanes. Possible structures which can be assigned to this series are alkyl-substituted saturated indanes, decalins and bicyclohexanes. The most abundant species in the dicyclic homologous series of saturated fractions obtained using 23.9 wt % coal belongs to m/z=278. A possible structure that can be assigned to this molecular weight is C_5 substituted decalin. The concentration of overall tricycloalkane homologous series did not change significantly as coal concentration was increased. The prominent peaks in this homologous series with 3.7 wt % coal are those at m/z=374, 346 and 318 whereas with 23.9 wt % coal the prominent peaks are at m/z= 262, 276, 248 and 234. The peak at m/z=262 in the liquefaction of Wyodak coal has been assigned to $C_{19}H_{34}$ tricyclic terpane. The intensity of this peak increased by a factor of two with increasing coal concentration from 3.7 to 23.9 wt %. The apparent concentration of the tetracyclic homologous series(C_nH_{2n-6}) in both saturated fractions is very similar. The increase in the intensities of individual peaks due to the presence of higher coal concentration is not as pronounced as in the previous series. The prominent peak at m/z=288 in the saturated fraction with 23.9 wt % coal can be assigned to a C_3 alkyl substituted tetracyclic compound. The peaks at m/z=372 and 400 in both saturated factions exhibited similar concentrations. These two peaks were also detected in liquids derived from Wyodak coal and were assigned to cholestane ($C_{27}H_{48}$) and stigmastane ($C_{29}H_{52}$) respectively. There may be some interference between pentacyclic alkanes(C_nH_{2n-8}) and monoaromatic hydrocarbons due to incomplete chromatographic separation. This source of interference has been reported earlier by Boduszynski et.al.(18). This overlap makes assignment of each peak to a particular compound more difficult. The overall intensity of pentacyclic alkanes was reduced in the saturated fraction as coal concentration increased. This may indicate that the major source of pentacyclic in coprocessing distillates is bitumen. In both saturated fractions, prominent peaks with the initial mass at m/z=370 can be assigned to pentacyclic triterpanes of hopanes and gammacerane which were also identified in liquids from Wyodak coal(18). The contribution of C_nH_{2n-10} homologous series to the saturated fractions is relatively small and decreases with increasing coal concentration.

The homologous series for monoaromatics are represented from C_nH_{2n-6} through C_nH_{2n-18}. C_nH_{2n-6} is represented by alkyl substituted benzenes and there may be an overlap between this series and tetracyclic alkanes. Although the apparent overall concentration of alkyl benzenes did not change significantly with increasing coal concentration, the intensities of the peaks from about m/z=190 ($C_{14}H_{22}$) to m/z=302 ($C_{22}H_{38}$) increased significantly. The largest increase in the concentration of homologous series of monoaromatics due to an increase in coal content appears to take place in the C_nH_{2n-8} and C_nH_{2n-10} series (Table 6). These series also dominated the monoaromatic fraction of coal-derived liquids obtained in the liquefaction of Wyodak coal(18). The most likely components of the C_nH_{2n-8} series are alkyl-substituted indanes, tetralins and cyclohexylbenzenes. There is a possibility that this series may overlap with pentacyclic alkanes. Possible structures that can be assigned to prominent peaks in the C_nH_{2n-10} series are alkyl-substituted tetrahydroacenaphthalenes, hexahydrofluorenes and octahydrophenanthrenes and/or-anthracenes. The intensities of the two peaks at m/z=186 and m/z=200 which may be assigned to the above compounds were increased almost five times as the coal concentration increased from 3.7 to 23.9 wt %. The prominent peaks in the C_nH_{2n-12} series are in the range of m/z=240 (C_{14}) to m/z=296 (C_{22}) and the monoaromatic fraction obtained in coprocessing with 23.9 wt % coal exhibited a higher concentration of these compounds. In the monoaromatic fraction obtained in the liquefaction of Wyodak coal the peaks in this mass range were assigned to alkyl-substituted octahydrocyclopentanophenanthrene, decahydropyrene and octahydrobenzofluorene.

The apparent concentration of polyaromatic fractions is shown in Table 7. Since no chromatographic separation according to the number of double bonds was carried out on this fraction, there is a possibility that each homologous series overlaps with the next(i.e. C_nH_{2n-12} with C_nH_{2n-26}). For this reason the Z-series for this fraction is referred to as an " apparent Z-series". However, it is clear from the apparent Z-series of the FI mass spectra that two and three rings components predominate. The C_nH_{2n-12} series is represented by alkyl-substituted naphthalenes and its apparent concentration increased with increasing coal content. The peak at m/z=170 is assigned to C_3 naphthalene and its intensity almost doubled as coal concentration increased from 3.7 to 23.9 wt %. Dibenzothiophene with an initial peak at m/z=184 should also appear in this column. However, because of chromatographic separation this compound most likely will be concentrated in the polar fractions. The homologous series C_nH_{2n-14} contributes significantly to the polyaromatic fractions in both distillates (22.4-26.7 %). The initial peak at m/z=154 can be assigned to either biphenyl (6 double bonds) or acenaphthalene (5 double bonds). The prominent peaks in both polyaromatic fractions are concentrated between m/z=154 and m/z=252. Other possible structures which can be assigned to this homologous series are alkyl-substituted binaphthyl and acenaphthalenes, cyclopentanonaphthalenes, tetrahydrophenanthrenes and/or anthracenes. Dibenzofurans with an initial peak at m/z=168 also appear in this column. The % intensity of this peak almost doubled with increasing coal concentration. The apparent concentration of the homologous series C_nH_{2n-16} did not change significantly when coal concentration was increased. The intensity of the peak at m/z=194 which can be assigned to phenylindane doubled with increasing coal concentration from 3.7 to 23.9 wt %. The intensities of the peaks between m/z=166 and m/z=264 remained relatively constant with increasing coal content. Possible components in this series are unsubstituted and alky-substituted fluorene, dihydrophenanthrene and/or anthracene. The overall concentration of the C_nH_{2n-18} homologous series did not change with increasing coal concentration, however, the distribution of components shifted toward lower molecular weights. In both polyaromatic fractions it is clear from the intensities of the individual components that more than one series is involved. Possible components in this series are unsubstituted and alkyl-substituted anthracenes and/or phenanthrenes. The concentration of these components in the polyaromatic fraction increased with increasing coal concentration. The homologous series of C_nH_{2n-20} accounts for approximately 19 % of the polyaromatic fraction and its overall intensity was not affected by changing the coal concentration. Possible components in this series include unsubstituted and alkyl-substituted dihydropyrenes and tetrahydrochrysenes. The presence of other compounds such as tetrahydronaphthol and phenoxycyclohexane in this homologous series cannot be ruled out. The contribution of the homologous series C_nH_{2n-22} and C_nH_{2n-24} to the polyaromatic fraction is relatively small and is decreased by increasing coal concentration. One of the prominent peaks in the C_nH_{2n-22} series is pyrene (m/z=202) the intensity of which increased slightly with increasing coal concentration.

The FI mass spectra of the polars 1 fractions are complicated and require further chromatography separation in order to obtain structural information. The total % intensities of even-numbered columns in the FI mass spectra after correction for ^{13}C in both polar fractions (3.7 and 23.9 wt % coal) was about 61 %. A substantial amount of nitrogen containing compounds belong to this fraction and their concentration in each homologous series increased with increasing coal concentration. For example, quinoline, tetrahydroquinoline, carbazole and their alkyl-substituted series are among a few nitrogenous compounds which can be named.

Isotopic Mass Balance Calculations

Isotopic mass balance measurements previously have been applied to determine the contribution of coal-derived liquids to coprocessing distillates(19). This method takes advantage of the difference in $^{13}C/^{12}C$ ratio between coals and bitumens/heavy oils which is in order of 3-5 parts per thousand. It has been demonstrated by using Athabasca bitumen and Vesta subbituminous coal from Alberta that increasing the coal concentration in coprocessing results in an increase in the coal-derived carbon in the coprocessing distillate. Preliminary results from applying this technique to the distillates used in this study indicated that they contain from 20 to 40 wt % coal-derived carbon and the amount of this carbon increased with increasing coal concentration.

CONCLUSIONS

The results of this work show that varying coal concentration in the coprocessing feed effects the characteristics of the distillate products. While the oxygen and nitrogen contents increased with increasing coal concentration, the sulphur content decreased. The molecular weight of the distillate(205-525°C) and its hydrocarbon-type fractions decreased with increasing coal content of the feed. This was rationalized both in terms of the contribution of more aromatic coal-derived liquids to the distillate and the enhancement in upgrading of the bitumen in the presence of coal.

The amount of coal in the feed has a direct effect on the hydrocarbon-type and compound-type distribution in the distillate. FIMS analysis of the hydrocarbon-type fractions indicated that the concentration of acyclic, monocyclic and dicyclic compounds increased with increasing coal concentration. The fraction of monoaromatics obtained with higher coal concentration contains higher concentrations of substituted indanes, tetralins and poly hydrogenated acenaphthalenes, fluorenes, phenanthrenes and anthracenes. The polyaromatic fractions mainly consist of two and three rings aromatic components the concentration of which are significantly increased with increasing coal concentration.

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FIGURES

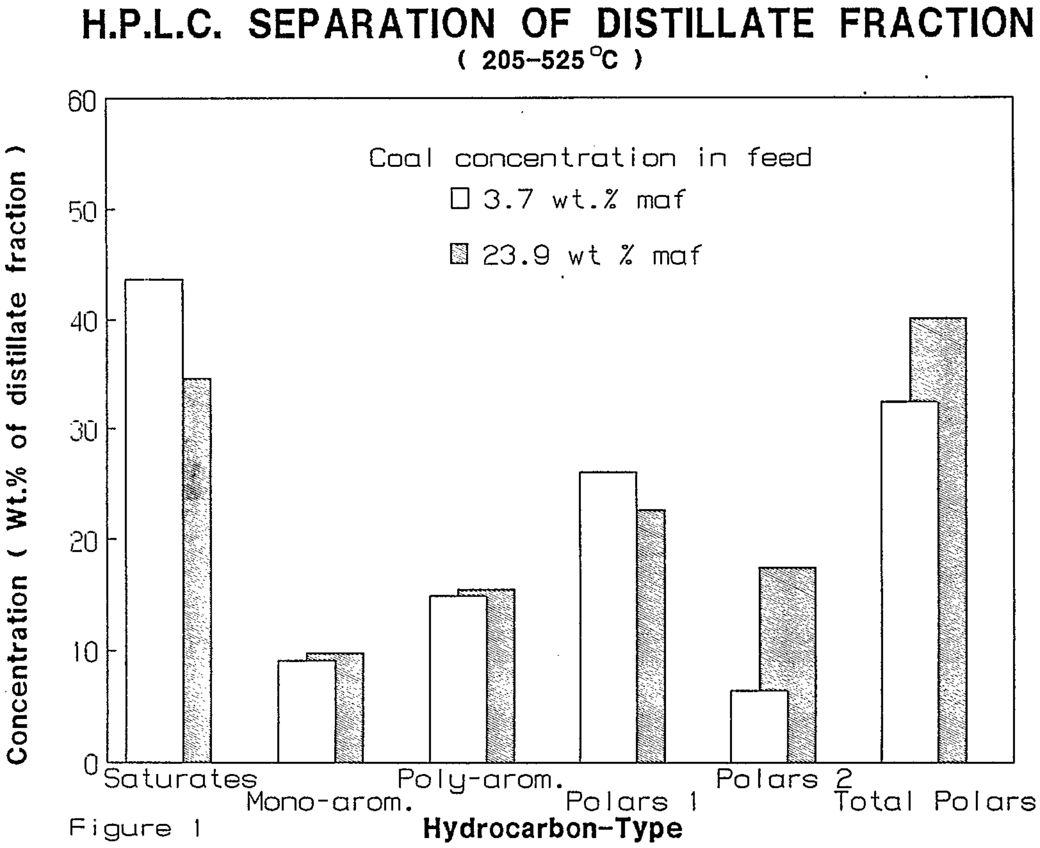

Figure 1

Table 1- Analysis of feedstocks

Forestburg Coal	
Proximate Analysis (as received, wt %)	
Moisture	19.2
Volatile	34.0
Fixed C	39.1
Ash	7.7
Ultimate Analysis (dry basis, wt %)	
Carbon	64.04
Hydrogen	3.87
Sulphur	0.53
Nitrogen	1.65
Oxygen[a]	20.41
Ash	9.5

Cold Lake vacuum bottoms	
Specific gravity, 15/15°C	1.038
Pentane insolubles, wt %	23.8
Distillate (-525°C), wt %	16.7
Residue (+525°C) , wt %	83.3
CCR , wt %	17.1
Elemental composition (wt %)	
Carbon	83.34
Hydrogen	9.69
Sulphur	5.84
Nitrogen	0.45
Oxygen[a]	0.68
Metal content	ppm
V	235
Ni	93
Fe	18

[a] by difference

Table 2- Elemental analysis(wt %) and aromaticities of distillate(205-525°C) fractions

Coal[a] Concentration	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	f_a	H/C
3.7	86.0	10.8	0.43	2.58	0.38	29.0	1.50
23.9	85.2	11.0	0.52	1.96	1.12	30.0	1.55
39.5	85.2	10.5	0.60	1.88	1.30	33.0	1.48

[a] wt %, based on maf slurry feed.

Table 3- Elemental analysis(wt %) and aromaticities of hydrocarbon-type fractions

Coal[a] Concentration		Saturates	Mono-aromatics	Poly-aromatics	Polars 1	Polars 2
3.7						
	C	85.7	86.0	83.7	83.9	80.6
	H	13.9	11.3	9.5	8.4	10.8
	N	< 0.1	< 0.1	< 0.1	0.69	< 0.1
	f_a	--	29.0	47.0	55.0	--
	H/C	1.95	1.57	1.36	1.20	1.60
23.9						
	C	85.5	86.5	86.3	82.9	82.0
	H	14.1	11.4	10.4	7.7	10.8
	N	< 0.1	< 0.1	< 0.1	2.0	< 0.1
	f_a	--	28.0	42.0	64.0	--
	H/C	1.98	1.58	1.44	1.11	1.58

[a] wt %, based on maf slurry feed.

Table 4- Molecular weight distribution of distillates(205-525°C) and their hydrocarbon-type fractions

Coal[a] Concentration	205-525°C fraction	Saturates	Mono-aromatics	Poly-aromatics	Polars 1
	Number(and weight) average molecular weight[b]				
3.7	308(340)	352(395)	346(388)	256(281)	344(381)
23.9	270(300)	321(352)	296(320)	225(242)	321(364)
39.1	244(270)	---	---	---	---

[a] wt %, based on maf slurry feed

[b] Determined using FIMS

Table 5- Proton distributions of hydrocarbon-type fractions

proton type	chemical shift	saturates		mono-aromatics		poly-aromatics		polars 1	
Coal Concentration (wt % , maf slurry feed)		3.7	23.9	3.7	23.9	3.7	23.9	3.7	23.9
		Proton Distribution, Area %							
condensed aromatics	10.5-7.15	---	---	---	---	17.0	12.2	16.3	25.8
uncond. aromatics	7.15-4.7	---	---	8.3	8.1	7.5	5.9	6.5	9.4
cyclic alpha	4.7-2.5	---	---	11.2	11.7	12.3	9.0	15.2	16.5
alkyl alpha	2.5-2.0	1.4	1.0	12.8	14.0	14.1	10.8	9.8	15.4
cyclic beta	2.0-1.4	6.5	9.7	13.5	14.7	11.8	12.6	12.0	10.4
alkyl beta	1.4-1.0	62.9	59.6	34.6	33.8	21.7	27.0	28.3	13.7
gamma	1.0-0.5	29.2	29.6	19.6	17.7	15.6	22.5	11.9	8.8

Table 6- Apparent concentration of saturates and monoaromatics homologous series

Hydrocarbon-type	Saturates		Mono-aromatics	
Coal Concentration (wt %, maf slurry feed)	3.7	23.9	3.7	23.9
Z series	Apparent Concentration (% Intensity)			
+2	9.5	11.3		
0	15.6	18.1		
-2	12.9	14.9		
-4	10.2	11.8		
-6	14.3	14.0	16.6	15.9
-8	11.8	9.6	17.4	21.7
-10	7.8	5.3	16.9	22.5
-12			14.8	14.6
-14			12.3	9.7
-16			8.3	6.4
-18			5.7	3.9

Table 7- % Intensities of polyaromatic homologous series

Coal Concentration (wt %, maf slurry feed)	3.7	23.9
Apparent Z series	% Intensity	
-12	17.3	20.3
-14	22.4	26.7
-16	15.0	13.2
-18	11.3	11.4
-20	19.1	18.6
-22	8.7	6.5
-24	4.1	2.5

Section 18

CONTINUOUS BENCH-SCALE TESTING OF CO-PROCESSING

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ABSTRACT

The UOP single-stage slurry catalyzed process was demonstrated in batch and continuous pilot plant operations. The results from the batch reactivity study are reviewed and include a process variable study, catalyst study and a feedstock sensitivity study. Six different petroleum resids, four different coals and two different catalyst systems were tested. Continuous bench scale tests were conducted using blends of Lloydminster vacuum resid with Illinois Coal No. 6 and Wyodak coal. The long term operability of the process was demonstrated with a 12-week test run using Illinois Coal No. 6 and Lloydminster vacuum resid. The run plots from this test run are presented.

INTRODUCTION

The UOP Co-Processing scheme is a single-stage, slurry catalyzed process that simultaneously upgrades the coal and petroleum resid feedstocks. The objective of this study is to determine if this scheme offers the potential for improved economics when compared to the alternative of upgrading the coal and resid separately.

A conceptual schematic flow diagram of the proposed process is shown in Figure 1. In this process, hydrogen, finely ground coal, petroleum resid and catalyst are mixed, heated and then directed to a single-stage reactor where the simultaneous conversion of the petroleum resid and coal occurs. The reactor effluent is directed to a series of separators where a hydrogen-rich gas is recovered and recycled back to the reactor inlet. The balance of the material is separated and the light gases, light oil and vacuum gas oil are recovered. The remaining material is sent to a catalyst recovery unit to recover additional oil product, unconverted coal, ash, residues and the catalyst. The catalyst is recycled back to the reactor.

This paper reviews the program objectives, the results from the reactivity study and the results from the recent continuous bench-scale operations. Six petroleum derived resids, three bituminous coals, one subbituminous coal and two different catalyst systems were tested during the reactivity study and a general co-processing data base was established. The continuous bench-scale operations evaluated the co-processing of Illinois Coal No. 6 with Lloydminster vacuum resid and the co-processing of Wyodak coal with Lloydminster vacuum resid. The long term operability of the continuous bench scale unit was also demonstrated with a continuous test run of ~2,000 hours.

PROGRAM OBJECTIVES

The first objective of this study was to demonstrate the technical feasibility of co-processing through batch and continuous bench scale testing. These test results were used to establish a process data base and will provide the foundation for the future engineering work that will establish the cost and economic incentives of a conceptual commercial facility.

The program has been divided into five major tasks: 1. Project Management Plan, 2. Feedstock Analysis, 3. Reactivity Screening, 4. Continuous Bench-Scale Operation and 5. Cost Estimate of a Commercial Facility. Work on Tasks 1 to 3 has been completed and we are in the final stages of Task 4. The following section briefly discusses the results of Tasks 2 and 3, and then presents the results from the continuous bench-scale operations.

FEEDSTOCK ANALYSIS AND REACTIVITY SCREENING

A process variable study, catalyst study and a feedstock sensitivity study were conducted as part of the reactivity testing. These tests were conducted in an 1800 cc rocking autoclave that was described in previous work (1). A resid/coal ratio of 2:1 and a pressure of 3000 psig were used as the base operating conditions.

The properties of the six vacuum resids tested are summarized in Table 1. These samples were fractionated at UOP in order to produce a vacuum resid with a 5 vol-% cut point of 510°C. This was done in order to eliminate any process variations that may be caused by different amounts of VGO in the fresh feed.

The properties of the four coal samples tested are summarized in Table 2. These samples were collected, dried and ground by the Kentucky Center for Energy Research Laboratory following accepted coal handling practices. It was necessary to dry the "as-received" Wyodak coal sample further because of its high water content (14.7 wt-%). Both of these Wyodak coal samples were analyzed and tested.

The results of these tests may best be characterized by the amount of coal conversion, non-distillable conversion and heptane insoluble conversion achieved. For this study, the coal conversion has been calculated as the disappearance of moisture and ash-free (MAF) coal, the non-distillable (or 510°C+) conversion has been based on the disappearance of MAF coal plus 510°C+ resid, and the heptane insoluble conversion has been based on the disappearance of MAF coal plus heptane insolubles in the resid. The MAF coal is defined as the ash-free portion of the toluene insoluble fraction. Also, a 371°C+ conversion has been reported. This conversion is defined in the same manner as the non-distillable conversion, but used 371°C instead of 510°C as the cut point. Since the feed to the Co-Processing unit contains a solid, these conversions are reported on a wt-% basis.

PROCESS VARIABLE STUDY

A reactor temperature survey was conducted using a 2:1 mixture of Lloydminster vacuum resid and Illinois Coal No. 6 with the UOP slurry catalyst at the base operating conditions. The non-distillable, 371°C+, heptane insoluble and coal conversions as a function of reactor temperature are shown in Figure 2. As the reaction severity was increased from 30°C below the base temperature to 30°C above the base temperature, both the non-distillable and 371°C+ conversion increased. The non-distillable conversion increased from 47.8 to 77.1 wt-%, while the 371°C+ conversion increased from 29.9 to 71.6 wt-%.

An important trend was observed for both the coal and heptane insoluble conversion as the reaction severity was increased. As illustrated in Figure 2, the coal and heptane insoluble conversion reached a maximum at the base reactor temperature and then decreased dramatically as the reactor temperature was increased by 30°C. The decreased coal and heptane insoluble conversion are theorized to be due to thermal degradation reactions that prevail at the higher temperature. As a result of this study, the remaining tests were conducted at the base temperature in order to minimize the thermal degradation reactions.

CATALYST STUDY

An active slurry catalyst is used to promote the upgrading reactions at reduced temperatures and thereby minimize any thermal degradation reactions. To establish the beneficial effects of the UOP catalyst, tests were conducted with this catalyst, a porous iron oxide (Fe_2O_3) catalyst and with no catalyst. Except for the catalyst type and concentration, these tests were all run at the base operating conditions using the Lloydminster and Illinois Coal No. 6 feedstocks. To compensate for the anticipated lower activity of the iron oxide, twice as much catalyst was used.

The results of the catalyst survey are summarized in Table 3. The addition of either catalyst had little effect on the degree of non-distillable conversion, but had a significant impact on the coal and heptane insoluble conversions. The coal conversion without catalyst addition was 66.6 wt-% and increased to 81.1 wt-% with the addition of the iron catalyst, and to 92.2 wt-% with the addition of the UOP catalyst. The heptane insoluble conversions followed a similar trend and were 21.3 wt-% without catalyst addition, 63.9 wt-% with iron catalyst addition, and 81.3 wt-% with the addition of the UOP catalyst.

The total liquid product properties for each of these tests are shown in Table 4. These results indicate that the UOP catalyst has the best hydrogenation capabilities of the three systems tested. This is also supported by the net hydrogen consumption ratio reported in Table 3. These hydrogen consumption rates are directly measured and are not based on the chemical analysis of the products. The hydrogen consumption rates are calculated as the difference between the makeup hydrogen rate (measured by a positive displacement meter) and the vented hydrogen (measured by the effluent wet test meter).

The better hydrogenation capabilities of the UOP catalyst results in a liquid product with a higher API gravity, higher hydrogen content, a lower sulfur content and a lower heptane insoluble content. The net result is a product that is less aromatic, has a lower tendency to foul conventional refinery upgrading catalysts and is more economically attractive to upgrade.

FEEDSTOCK SENSITIVITY STUDY

To determine the sensitivity of co-processing to changes in resid feedstock composition, screening studies were conducted with the UOP catalyst at the base conditions using blends of Illinois Coal No. 6 with each of the six resid feedstocks. The coal, heptane insoluble, non-distillable and 371°C+ conversions are shown in Figure 3 as a function of the resid API gravity. The non-distillable, 371°C+ and heptane insoluble conversions follow a general trend of decreasing conversion with increasing resid API gravity, while the coal conversions appear to be independent of the crude source.

A similar screening study was also conducted at the base conditions using blends of Lloydminster resid with each of the four different coal samples. The results of these tests are summarized in Figures 4 and 5. The observed conversions with the three bituminous coals and the dried subbituminous coal followed no particular trends, and the coal and heptane insoluble conversions were very similar. The high water content of the "as-received" Wyodak coal sample appears to have effected the catalyst activity as the coal and heptane insoluble conversions were significantly lower.

CONTINUOUS BENCH-SCALE OPERATIONS

The UOP Co-Processing concept was successfully demonstrated in the continuous bench-scale unit at the Allied-Signal Engineered Materials Research Center. A simplified flow diagram of the pilot plant is shown in Figure 6. Typical feed rates were 130 to 220 g/hr of MAF coal plus resid, and the unit contains many of the essential features of the anticipated commercial flow scheme. The reactor effluent is continuously fractionated into the four product streams shown, and a hydrogen-rich gas stream is continuously recycled. To minimize the laboratory analysis, the debutanizer bottoms and vacuum column overhead are recombined before they are analyzed.

In order to conduct the extended pilot plant test, it was necessary to collect additional feedstock samples. The coal samples were again collected by the Kentucky Center for Energy Research and are from the same site locations. A comparison of the continuous pilot plant coal samples and batch coal samples is shown in Table 5.

The Lloydminster resid feedstock was a commercially fractionated sample and was lighter than samples used during the autoclave work. A comparison of the two Lloydminster samples is shown in Table 6.

In order to establish a link between the new and old feedstocks, the new feedstocks were first tested in the autoclave at the base conditions. The results of this test are compared in Table 7 to the original autoclave test run. Use of the lighter, commercially produced Lloydminster vacuum resid had a minimal effect on the autoclave performance. The coal and heptane insoluble conversions with either feedstock were similar, while the non-distillable and product distribution were only slightly different.

PROCESS VARIABLE STUDY

Several test runs were completed during Task 4 and the results from Test Runs 5 and 11 are presented to illustrate the effects of changing process severity and coal types. The operating conditions used for these tests are shown below:

OPERATING CONDITIONS

Run	5		11
Resid	---------	Lloydminster	---------
Coal	IL No. 6		Wyodak
Resid/Coal Ratio, wt/wt	---------	2:1	---------
Temperature	---------	Varied	---------
WHSV	---------	Varied	---------
Catalyst	---------	UOP	---------

The effect of process severity is illustrated in Figures 7 and 8. As shown in Figure 7, increased conversion of the petroleum resid and coal to lighter products can be achieved by increasing the process severity. By increasing the reactor temperature, it was possible to increase the non-distillable conversion from 46.5 to 63.7 wt-% and the coal conversion from 82.2 to 90.8 wt-% when processing the Illinois Coal No. 6. A similar trend was observed during the Wyodak test run although the coal conversions were somewhat lower. The non-distillable conversion increased from 50.4 to 67.8 as the coal conversion increased from 78.6 to 87.0 wt-%.

There are, however, adverse effects to increasing the process severity. As shown in Figure 8, the optimum heptane insoluble conversion occurred at the moderate reaction conditions for both the Illinois Coal No. 6 and Wyodak coal test runs. This suggests that the higher process severity is too severe for heptane insoluble conversion due to an increase in thermal degradation reactions. A similar response was seen during the autoclave test runs.

As shown in Figure 9, optimizing the heptane insoluble conversion also results in a total liquid product with the highest quality. The API gravity of the total liquid product was seen to increase as the heptane insoluble conversion increased and was not dependent on the coal type. The sulfur content of the total liquid product, illustrated in Figure 10, was shown to decrease as the heptane insoluble conversion increased and did depend on the coal feedstock.

Although the Wyodak coal conversion was lower than the Illinois Coal No. 6 conversion, it was possible to obtain higher heptane insoluble and non-distillable conversion when processing the Wyodak coal. This implies that the Wyodak coal is more difficult to convert, but that the product is easier to upgrade. The total liquid product properties, product distribution and conversions at the optimum heptane insoluble conversion for both test runs are shown in Table 8. These results show that it is possible to obtain a high liquid yield and a high quality product when processing either Illinois Coal No. 6 or Wyodak coal with Lloydminster vacuum resid.

LONG TERM OPERABILITY

To demonstrate the long-term operability of the UOP Co-Processing scheme, a 12-week continuous pilot plant test run (Run No. 19) was conducted. Four different composite samples were collected during this test run in order to obtain detailed product characterizations and sufficient feedstock for the future Deasphalting (Task 4.5) and Catalyst Recovery (Task 4.6) studies.

The feedstock for Run 19 was a 2:1 mixture of Lloydminster vacuum resid and Illinois Coal No. 6 and the tests were conducted at the conditions established in

Run 5 for the optimum heptane insoluble conversion. Run 19 was on stream for ~2000 continuous hours and, as illustrated by the run plots of Figures 11 and 12, the operation was very stable and the results were very reproducible. Plant operations were extremely good and no major operation upsets were encountered. The observed coal, heptane insoluble and non-distillable conversions, shown in Figure 11, can be compared to the average value that is shown as a solid line. During this period, the average coal, heptane insoluble and non-distillable conversions were 89.3, 79.5 and 54.6 wt-%, respectively. Figure 12 summarizes the weight recoveries and liquid yields obtained during the run. The weight recoveries were very good, averaging 100.4 wt-%, with approximately 55 wt-% of the liquid product boiling below 510°C.

FUTURE PLANS

The final stage of Task 4.0 is nearing completion. The detailed composite sample analysis is almost complete and the Deasphalting Study (Task 4.5) and the Catalyst Recovery Study (Task 4.6) have been started. The long term operability test run will serve as the basis for the detailed design and economic evaluation of the conceptual Co-Processing unit during Task 5.0.

CONCLUSIONS

The technical feasibility of the co-processing concept was demonstrated during the batch and continuous bench-scale tests. Coal conversions greater than 89 wt-%, non-distillable conversions greater than 54 wt-% and heptane insoluble conversions greater than 79 wt-% were typical when processing Illinois Coal No. 6 with Lloydminster vacuum resid at a resid/coal ratio of 2:1. Coal conversions greater than 85 wt-%, non-distillable conversion of approximately 60 wt-% and heptane insoluble conversions of 83 wt-% were typical when processing Wyodak coal with Lloydminster vacuum resid at the same operating conditions. The long term operability of the unit was demonstrated during Run 19 and provides a firm experimental foundation for the design of the conceptual Co-Processing unit.

REFERENCE

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Table 1

CO-PROCESSING RESID FEEDSTOCKS

Resid Name	U.S. Mid-Continent	Kuwait	Alaskan North Slope	Lloydminster	Hondo	Maya
API Gravity @ 15.6°C	12.7	7.9	8.9	3.6	3.7	2.8
Specific Gravity	0.9813	1.0151	1.0078	1.0474	1.0466	1.0536
Distillation, D-1160, $^{\circ}$C						
IBP, vol-%	473	472	422	406	478	452
5	510	505	494	509	512	515
10	525	517	515	-	524	532
20	546	542	541	-	-	-
30	568	-	-	-	-	-
EP	568	556	550	509	524	532
% Over at EP	30	26	24	6	10	10
Analysis, wt-%						
Carbon	87.30	84.15	84.10	82.70	81.20	83.90
Hydrogen	10.25	10.55	10.85	10.15	10.10	9.15
Oxygen	0.30	0.35	0.27	0.29	0.36	0.48
Sulfur	1.0	4.9	2.3	5.6	6.6	4.9
Nitrogen	0.45	0.35	0.55	0.62	1.10	0.71
Carbon Residue	16.5	18.0	17.3	22.2	19.9	26.1
Petroleum Ash	0.030	0.020	0.020	0.090	0.110	0.126
Heptane Insolubles	8.29	5.95	4.80	18.10	17.80	22.40
S in Heptane Ins.	1.90	7.50	3.00	7.50	8.00	6.58
Nickel, ppm	35	28	38	122	157	116
Vanadium, ppm	113	100	79	278	435	595
Iron, ppm	62	4.5	2	82	42	29
Molecular Weight	839	1054	810	1444	1125	1015
Furol Visc., sec (121°C)	755	1016	1295	1921	1126	2217
Pour Point, $^{\circ}$C	38	38	32	91	79	91
Salt, lb/1000 bbls	2.9	3.5	1.2	3.3	4	20.7

Table 2

CO-PROCESSING COAL FEEDSTOCKS

Coal Name	Illinois No. 6	Kentucky No. 9	Indiana No. V	Wyodak (As-Received)	Wyodak (Dried)
Ultimate Analysis, wt-%					
Ash	9.65	8.68	8.12	10.30	12.00
Carbon	68.60	71.95	69.70	54.70	63.01
Hydrogen	4.51	4.78	5.40	3.83	4.50
Nitrogen	1.39	1.54	1.42	0.69	0.90
Sulfur	3.04	2.97	4.28	0.99	1.08
Oxygen (Diff.)*	9.66	8.53	9.37	14.79	16.73
Proximate Analysis, wt-%					
Moisture	3.15	1.55	1.71	14.70	1.78
Ash	9.65	8.68	8.12	10.30	12.00
Volatile Matter	39.95	42.35	48.25	37.00	42.60
Fixed Carbon (Diff.)	47.25	47.42	41.92	38.00	43.62

---

* Excludes moisture.

Table 3

CO-PROCESSING CATALYST COMPARISON STUDY
(Lloydminister Vacuum Resid and Illinois Coal No. 6)

Operating Conditions			
Catalyst Type	None	Fe_2O_3	UOP
Concentration	0	2 x Base	Base
Performance			
Conversions, wt-%			
Coal	66.6	81.1	92.2
Heptane Insoluble	21.3	63.9	81.3
Non-Distillable (510°C+)	69.3	73.6	72.1
Hydrogen Consumption, wt-%	1.8	1.7	2.7

Table 4

CO-PROCESSING CATALYST COMPARISON STUDY
TOTAL LIQUID PRODUCT PROPERTIES
(Lloydminister Vacuum Resid and Illinois Coal No. 6)

Catalyst Type	None	Fe_2O_3	UOP Reference
API Gravity at 15.6°C	9.3	8.5	13.3
Specific Gravity	1.0050	1.0107	0.9772
Carbon, wt-%	85.15	84.40	85.50
Hydrogen, wt-%	10.05	9.6*	10.30
Oxygen, wt-%	1.00	-	1.23
Sulfur, wt-%	2.75	2.30	2.10
Nitrogen, wt-%	0.60	0.90	0.73
Ash, wt-%	0.005	< 0.001	0.003
Heptane Insolubles, wt-%	37.03	14.52	7.37
Toluene Insolubles, wt-%	0.16	0.40	0.53
Carbon Residue, wt-%	14.6	16.5	15.1
Vanadium & Nickel, wt-ppm	19	9	23

---

* Estimated.

Table 5

COAL FEEDSTOCK COMPARISON

Coal Name	Illinois No. 6		Wyodak	
Designation	Batch Tests	Cont. Tests	Batch Tests	Cont. Tests
Ultimate Analysis, wt-%				
Ash	9.65	10.56	10.30	7.89
Carbon	68.60	68.77	54.70	58.60
Hydrogen	4.51	4.84	3.83	4.41
Sulfur	3.04	3.34	0.99	0.84
Nitrogen	1.39	1.37	0.69	0.80
Oxygen*	9.66	7.03	14.79	15.48
Proximate Analysis, wt-%				
Moisture	3.15	4.09	14.70	12.90
Ash	9.65	10.56	10.30	7.89
Volatile Matter	39.95	39.90	37.00	34.70
Fixed Carbon (Diff.)	47.25	45.45	38.00	44.51

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*Difference (excluding moisture)

Table 6

RESID FEEDSTOCK COMPARISON

Resid	Lloydminster Vacuum Resid	
Fractionation Equipment	Laboratory	Commercial
Designation	Batch Testing (R4)	Continuous Testing (R8)
API Gravity @ 15.6°C	3.60	6.50
Specific Gravity	1.0474	1.0254
Distillation, D-1160, °C		
IBP, vol-%	406.0	369.0
5	509.0	432.0
10	--	463.0
20	--	505.0
EP	509.0	523.0
Overhead, vol-%	6.0	26.5
Analysis, wt-%		
Carbon	82.70	83.70
Hydrogen	10.15	10.00
Oxygen	0.29	---
Sulfur	5.6	5.1
Nitrogen	0.62	0.48
Carbon Residue	22.20	17.30
Petroleum Ash	0.090	0.051
Heptane Insolubles	18.10	13.91
Nickel, ppm	122.0	83.0
Vanadium, ppm	278.0	165.0
Iron, ppm	82.0	3.6
Molecular Weight	1444.0	755.0
Furol Visc., sec (121°C	1921.0	266.1
Pour Point, °C	91.0	120.0
Salt, lbs/1000 bbls	3.30	5.2

Table 7

REACTIVITY TEST FEEDSTOCKS VERSUS CONTINUOUS BENCH-SCALE FEEDSTOCKS

	Reactivity Feedstocks	Continuous Bench-Scale Feedstocks
Feedstocks		
Lloydminster	R4	R8
Illinois Coal No. 6	C1	C1.2
Product Distribution, wt-%		
Hetero Gases + H_2O	6.9	2.7
Hcbn Gas C_4-	3.9	3.4
C_5 - 371°C	46.9	43.8
371 - 510°C	18.0	25.0
510°C+	24.4	24.9
MAF Coal	2.6	2.4
TOTAL	102.7	102.2
Conversion, wt-%		
Coal	92.2	92.5
Heptane Insoluble	81.3	80.0
Non-Distillable (510°C+)	72.1	68.1

Table 8

PRODUCT PROPERTIES, DISTRIBUTION AND CONVERSION AT OPTIMUM HEPTANE INSOLUBLE CONVERSION

	Run 5	Run 11
Liquid Product Properties		
API Gravity @ 15.6°C	16.0	16.6
Carbon, wt-%	86.4	86.1
Hydrogen, wt-%	10.9	11.0
Sulfur, wt-%	1.37	1.53
Heptane Insolubles, wt-%	7.13	2.63
Product Distribution, wt-%		
Hetero Gases + H_2O	8.9	11.0
HCBN Gas C_4-	2.5	3.1
C_5 - 371°C	31.3	30.1
371 - 510°C	25.9	24.4
510°C+	31.1	29.7
MAF Coal	3.0	4.8
TOTAL	102.7	103.1
Conversions wt-%		
MAF Coal	91.1	85.4
Heptane Insolubles	80.2	83.0
Non-Distillable (510°C)	60.8	59.9
Distillable (371°C)	40.1	40.4

FIGURE 1

PROPOSED RESID/COAL PROCESSING SCHEME

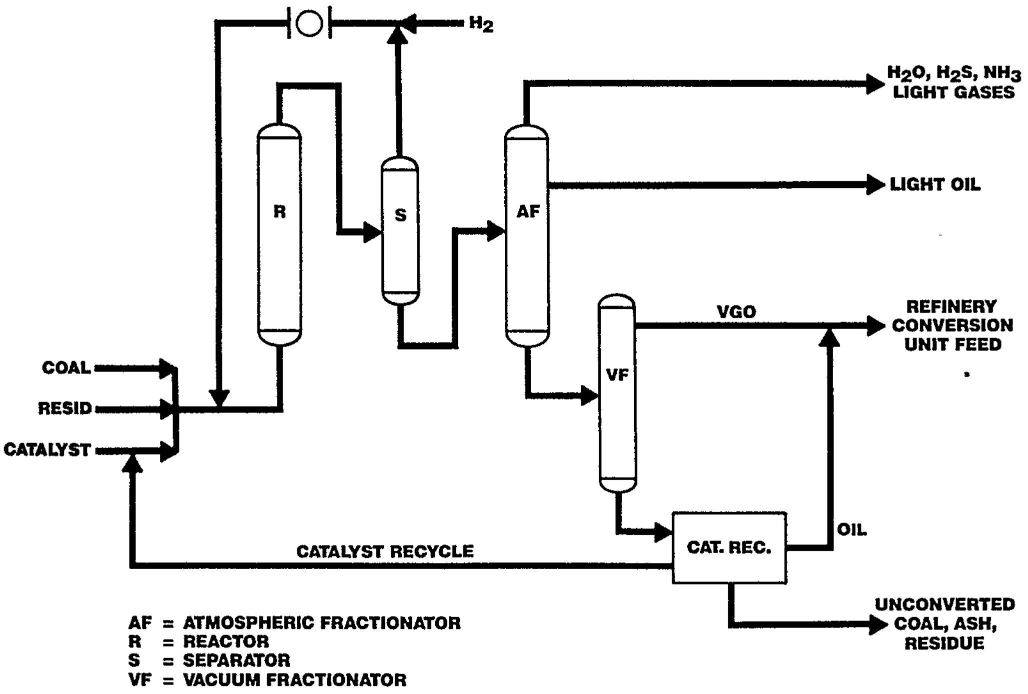
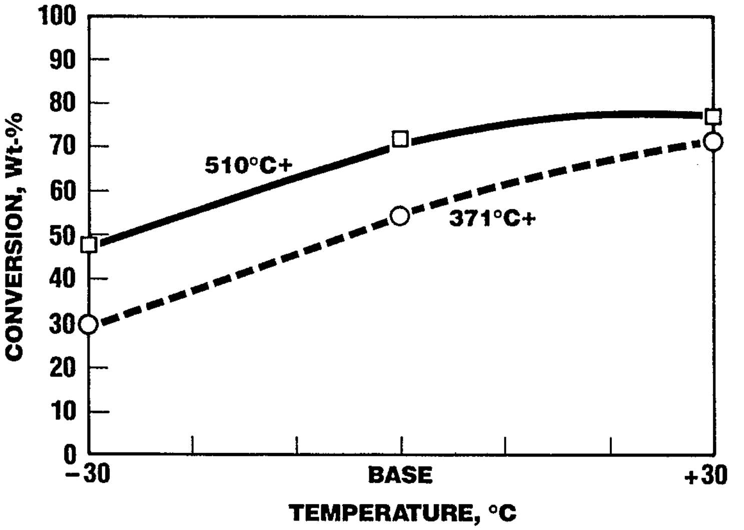


FIGURE 2

EFFECT OF TEMPERATURE



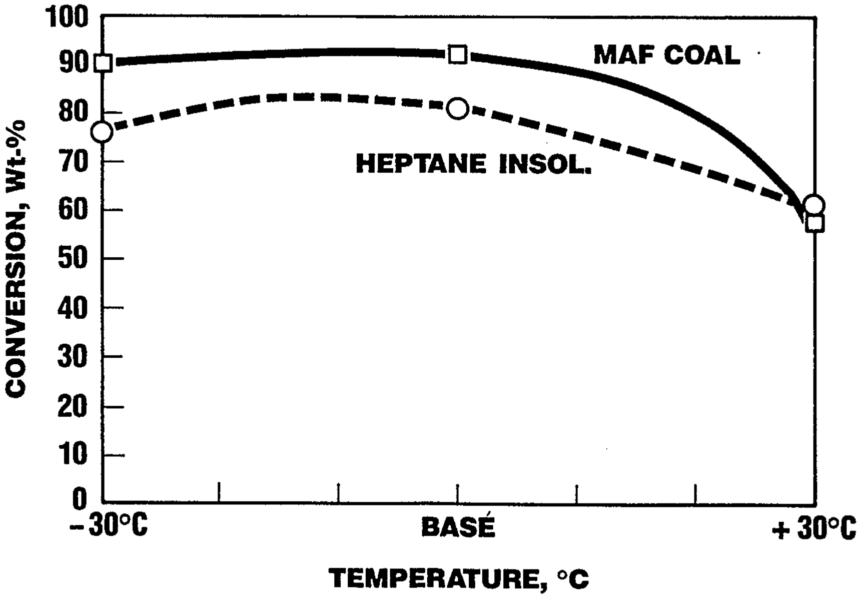


FIGURE 3

RESID REACTIVITY SCREENING

(ILLINOIS COAL NO. 6)

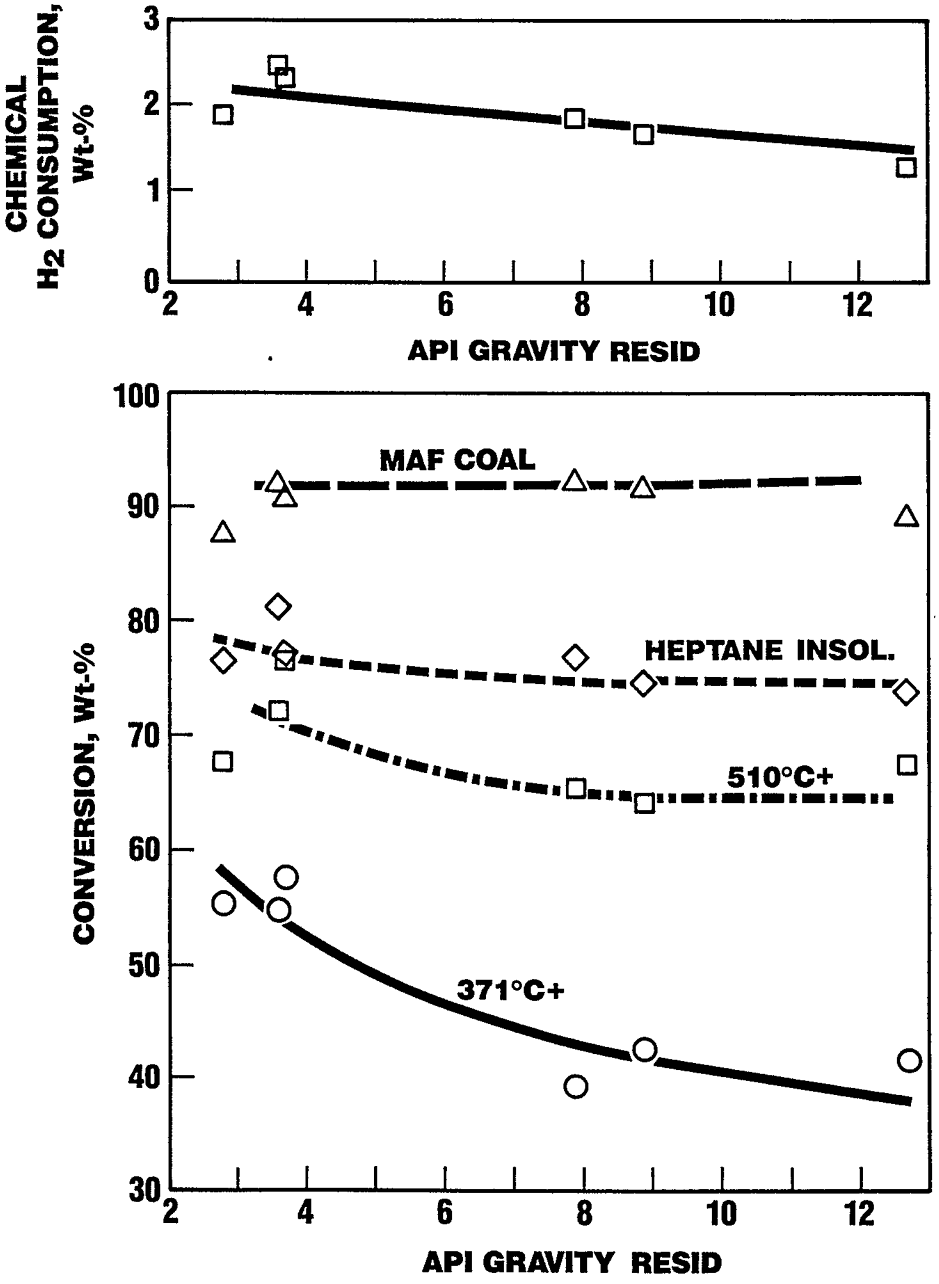


FIGURE 4

CO-PROCESSING COAL REACTIVITY SCREENING (LLOYDMINSTER RESID)

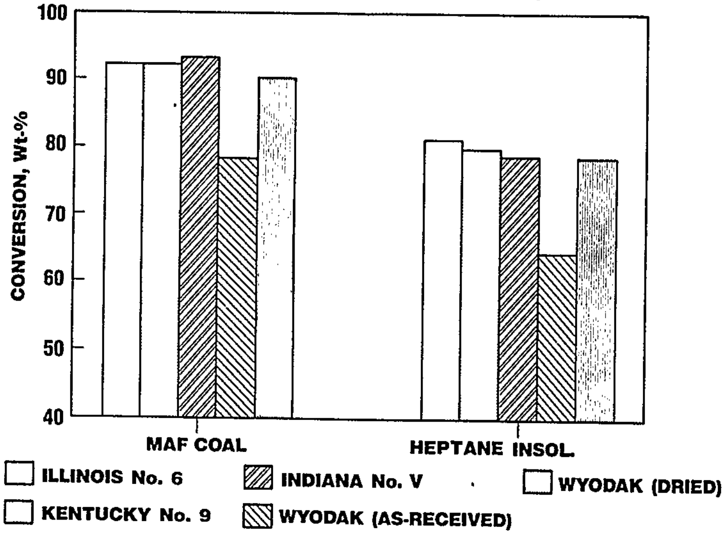


FIGURE 5

CO-PROCESSING COAL REACTIVITY SCREENING (LLOYDMINSTER RESID)

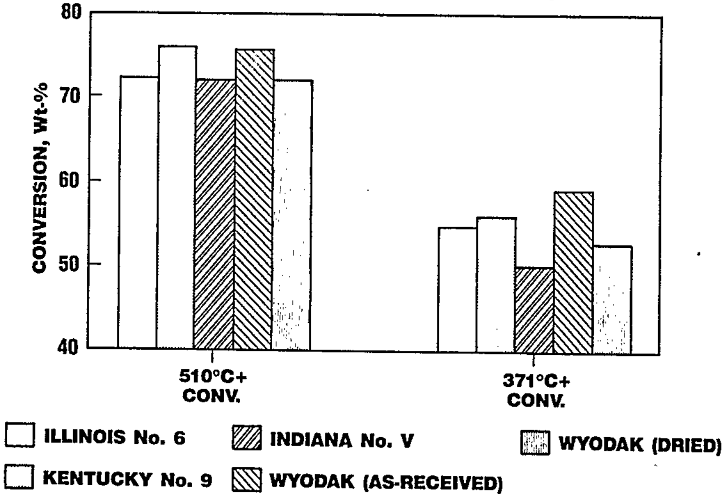


FIGURE 6

PILOT PLANT FLOW SCHEME

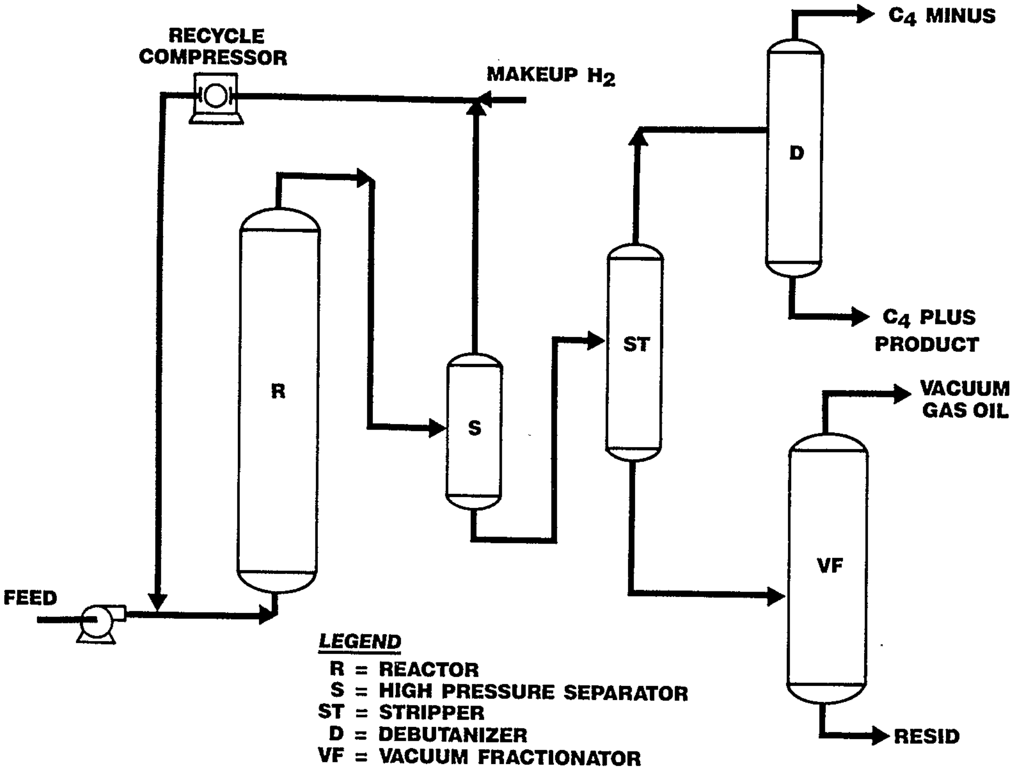


FIGURE 7

CONTINUOUS
CO-PROCESSING TESTS
COAL REACTIVITY SCREENING
(LLOYDMINSTER RESID)

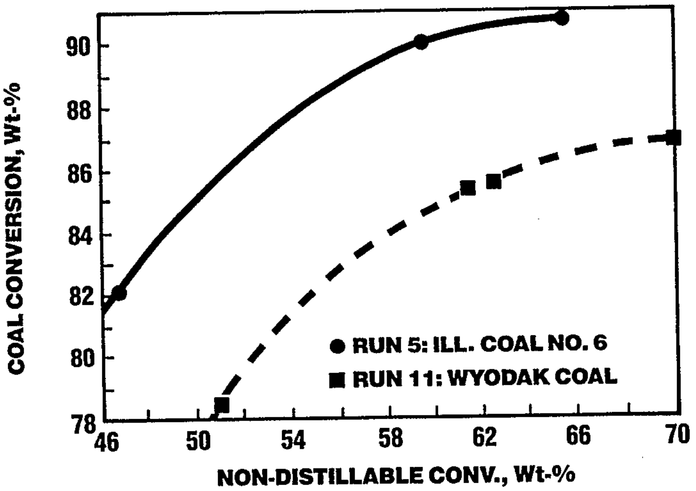


FIGURE 8

CONTINUOUS
CO-PROCESSING TESTS
COAL REACTIVITY SCREENING
(LLOYDMINSTER RESID)

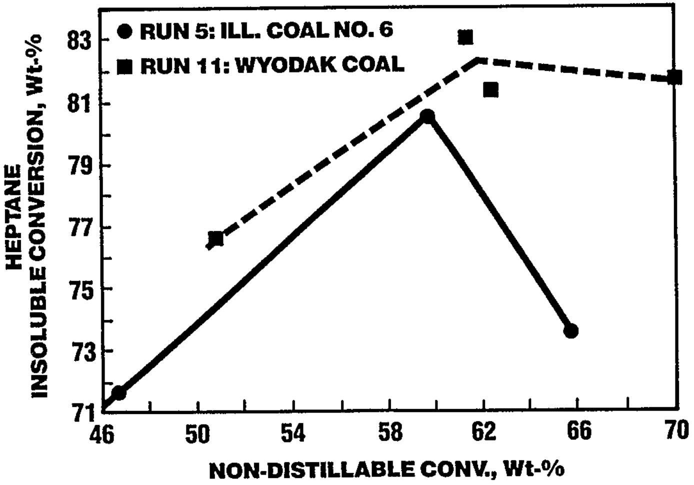


FIGURE 9

CONTINUOUS CO-PROCESSING TESTS COAL REACTIVITY STUDY

(LLOYDMINSTER RESID)

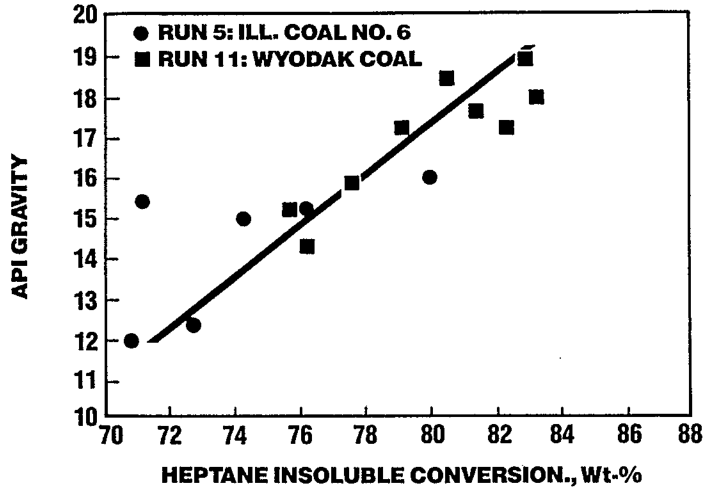


FIGURE 10

CONTINUOUS CO-PROCESSING TESTS COAL REACTIVITY STUDY

(LLOYDMINSTER RESID)

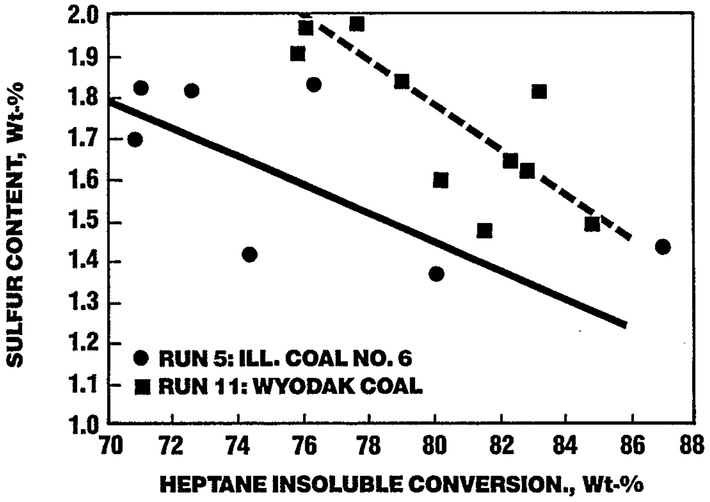


FIGURE 11

COAL LIQUEFACTION CO-PROCESSING: RUN 19

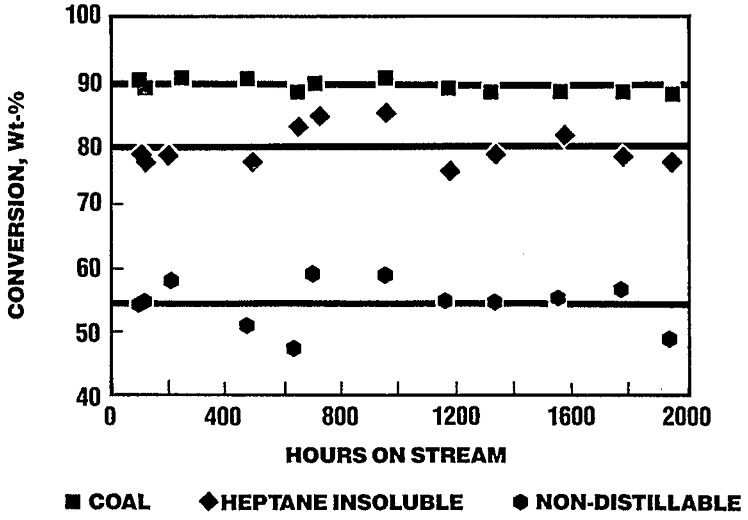
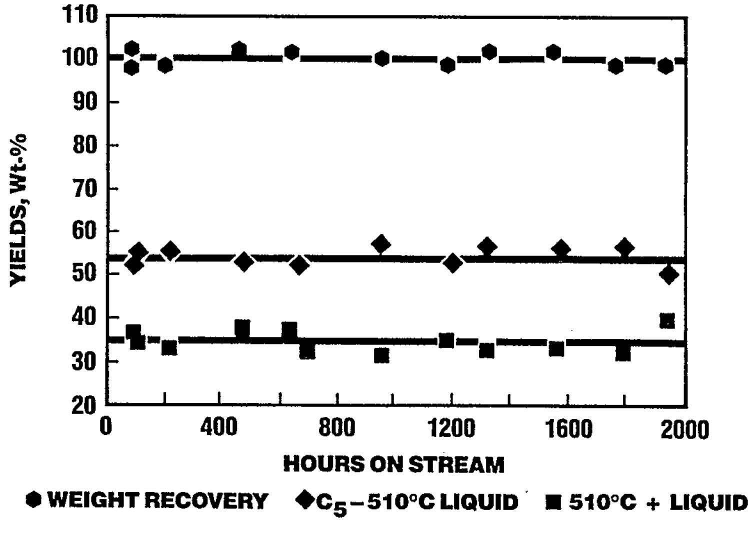


FIGURE 12

COAL LIQUEFACTION CO-PROCESSING: RUN 19



APPENDIX A

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