BENCH-SCALE DEVELOPMENT OF COAL-OIL CO-PROCESSING TECHNOLOGY: EFFECT OF COAL CONCENTRATION ON REACTIVITY

JOHN E. DUDDY
and
SUDHIR V. PANVELKER

HYDROCARBON RESEARCH, INC.
100 OVERLOOK CENTER, SUITE 400
PRINCETON, NJ 08540

INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has been performing bench-scale development of coal-oil co-processing since 1985. The technology utilizes the ebullated bed reactor system invented by HRI. This reactor system is ideally suited for catalytic processes using feeds which contain solids or when the catalysts are prone to rapid deactivation or where reactions are highly exothermic. The ebullated bed reactor was first commercialized in the H-Oil® Process in 1968 and is currently employed in several refineries around the world for processing heavy crudes or residua. Several more units are under construction or being designed. The reactor system was also successfully demonstrated for coal slurry processing at the 200 TPD H-Coal pilot plant at Catlettsburg, Kentucky from 1980-82.

The HRI Coal-Oil Co-processing Process is shown schematically in Figure 1. Coal slurried with petroleum-derived residual oil (which include atmospheric or vacuum residua, heavy crudes, tar sands, shale oil, FCC clarified slurry oils, etc.), is pumped to reactor pressure, mixed with hydrogen, preheated and fed to the ebullated bed reactor system. The reactor system can consist of one or two stages depending upon the process requirements. Each stage contains supported hydroprocessing catalyst such as NiMo/Alumina, CoMo/Alumina and others. During operation, a fraction of the catalyst inventory is withdrawn and fresh catalyst added on a routine basis to maintain the average activity at an equilibrium level. The reactor effluent is separated into vapor and slurry streams. The vapor is separated to recover hydrogen which is recycled. The slurry is depressurized and fractionated to produce high quality distillate products and vacuum bottoms (which contain ash, unconverted coal and residual oil). Coal-oil feed is generally processed in an once-through mode, however, a small recycle can be employed to moderate the viscosity of feeds containing high coal concentrations.

PROGRAM DESCRIPTION

HRI is currently executing a bench-scale development program sponsored jointly by the U.S. Department of Energy and the following organizations:

- Alberta Research Council
- Electric Power Research Institute
- Mitsui SRC Development Company
- Ontario-Ohio Synthetic Fuels Corporation
- Ruhrkohle Oel und Gas
- HRI, Inc.

The program was initiated in October 1987 and will be completed in December 1991.

The technical program consists of the following three tasks:

- Laboratory Support
- Bench-scale Operations
- Engineering Assessment

Laboratory support work, done by Alberta Research Council, consists of feedstock characterization, batch autoclave reactivity studies, screening/testing of catalysts, and coal-oil agglomeration. Continuous bench-scale operations are being conducted to evaluate a number of feedstock combinations and to study different concepts with potential for process improvement. Engineering assessment covers process modelling based on the results from bench-scale operations, economic screening studies, and conceptual commercial plant design.

PROGRAM STATUS

Alberta Research Council, under a sub-contract from HRI, has completed the task of laboratory support. One of the accomplishments of this task was the demonstration of oil- agglomeration technique as applied to co-processing. High-ash coals can be cleaned through oil-agglomeration with the co-processing oil feed itself. Optimized agglomeration conditions were identified with Forestburg (Alberta) sub- bituminous coal and Cold Lake residuum and Athabasca bitumen. After tests with the agglomerates on a batch-autoclave scale, larger quantities were prepared for a bench-scale test. The bench test was successful and showed a potential for decreasing costs associated with the disposal of the bottoms product.

All bench-scale operations were conducted using two-stage reactor configuration using NiMo/Alumina catalyst. Tables 1 and 2 show the feedstock combinations used in the bench- scale operations. Six coals (lignite, sub- bituminous, and bituminous) and three oils were used in eight combinations. The tests to compare relative feedstock reactivity covered 133 operating days.

Texas lignite and Maya (vacuum) residuum was considered as the baseline feedstock for the program. All tests to test potential process improvement routes (with the exception of coal-oil agglomeration, which was done with Forestburg coal and Cold Lake residuum) were done using this feedstock combination. These operations covered 66 operating days. The following concepts were tested for process improvement:

- Low - High temperature staging
- Feedstock pretreatment (oil agglomeration)
- Catalyst cascading
- Dispersed catalyst
- Optimal coal concentration

For low-high temperature staging, the first-stage temperature was kept lower than the second-stage temperature in a manner similar to the HRI Catalytic Two-Stage Liquefaction Technology (CTSL). The overall conversions were lower than for equal temperature reactors as the overall severity was lower. However, the selectivity and the product quality was improved.

Forestburg coal, a high-ash sub-bituminous coal, was cleaned to lower its ash content through oil-agglomeration using Cold Lake residuum. The bench test comparing uncleaned and cleaned coals showed similar performance as far as the yield structure and the conversions were concerned. However, in a commercial facility, the cost of the product from clean coal is expected to be lower due to the decreased costs of disposing bottoms product.

In two-stage, equal-temperature processing, first-stage catalyst normally has a lower activity than second-stage catalyst of identical age. Catalyst cascading, where fresh catalyst is added to second stage and the recovered catalyst from this stage is added to first stage, was shown to have a potential for decreasing catalyst consumption or to give higher performance at the same catalyst consumption.

An iron oxide dispersed catalyst was used simultaneously with supported catalyst (in ebullated bed reactors). This did not show an appreciable improvement in performance. The test was conducted at temperatures suitable for using hydroprocessing catalysts. The iron catalyst was perhaps ineffective at this low temperature. The combined catalyst system might show some benefit if hydroprocessing catalysts with higher temperature tolerance are developed.

A bench test was conducted to evaluate the relationship between coal concentration and performance. The results are described in detail in the next section.

The data obtained from bench-scale operations was used for process modelling. A kinetic model for residuum conversion was developed which relates activity (rate constant) to temperature, catalyst age, and coal concentration. The model has been used to compare alternate feedstock combinations.

A conceptual commercial design of a 4800 TPD co-processing plant using Texas lignite and Maya residuum was prepared and economic sensitivity studies made. A topical report has been issued. (Report No. DE-79819-TOP-01).

EFFECT OF COAL CONCENTRATION ON REACTIVITY

This section describes the results from a bench-test performed to study the effect of coal concentration on co-processing performance using Texas lignite and Maya residuum.

Economic studies indicated that the cost of oil feedstock was the largest component of the direct operating costs. Obviously, coal concentration in the combined feed is an important variable in optimizing the process performance to get the lowest product cost.

Tables 3 and 4 show the analyses of Texas lignite and Maya vacuum-still-bottoms (VSB). Texas lignite used in this study was cleaned at the EPRI Coal Cleaning Test Facility in Homer City to reduce its ash content. Maya VSB is an extremely poor-quality residuum. It contains extremely high sulfur, metals (vanadium and nickel) and Conradson carbon residue (CCR) contents and is difficult to refine using conventional refining technologies. Coking would produce high yields of low-valued, poor-quality coke due to its high CCR content. Hydroconversion would have a high catalyst requirement due to its high metals content. As a result, refiners who can process sour crudes limit Maya to only a small fraction of their crude run. Both these feedstocks are available on the U.S. Gulf Coast where a large percentage of the U.S. refining capacity is located. Hence, Texas lignite and Maya residuum represent a logical feedstock combination for co-processing.

The bench test was conducted using the HRI bench unit No. 238 which is a two-stage ebullated-bed unit with a nominal capacity of 50 lb/day. It has been shown before that the results obtained on this scale can be readily scaled up. The only major difference between the operation of this unit and a typical commercial ebullated bed unit is that in commercial operation, a fraction of the catalyst inventory is withdrawn and fresh catalyst added on a routine basis to maintain the average activity at an equilibrium level. This is not possible with the small bench unit. The bench test was performed with a batch of catalyst which deactivated over the course of the test.

The bench test parameters are shown in Table 5. Both reactors were charged with fresh (commercially available) NiMo/Alumina catalyst. It was sulfided during the start-up by doping the start-up oil with a sulfiding agent. The reactor temperatures were constant at 810°F. The space velocity (based on total feed) was also maintained constant. In order to determine the maximum coal concentration in the coal-oil slurry which could be operable in bench-scale operations, viscosity of slurry was determined as a function of temperature and coal concentration. The slurry feed tank on the bench unit has a maximum operating temperature of about 350°F with steam heating. For proper handling, the maximum viscosity should be around 1500 cps. Based upon these considerations, the maximum coal concentration that could be tested on the bench unit is about 40 w%. The coal concentration was varied from 10-40 W% for the test.

As seen from Table 5, run conditions 2, 3 and 6 were identical. During condition 2, there were some operational problems. The unit was shut down after condition 2 where it was observed that the inlet to the second stage had been partially plugged. It was cleaned and reassembled (after adding a small quantity of fresh make-up catalyst to the second stage). The test was restarted and condition 2 repeated as condition 3. Condition 6 is used to estimate the effect of catalyst deactivation.

The test results are shown in Table 6. It is clearly seen that process performance improves with increasing coal concentration in feed. With 10 W% coal (dry) in the feed slurry, the 975°F+ conversion was 80.5 W% (MAF). At 40 W% coal loading, it varied from 86.7 to 90.0 W% (MAF) depending upon the catalyst age. Other levels of performance (coal conversion, HDN, and distillate yield) also showed improvements. C_1-C_3 gas yields were essentially constant (changes due to coal concentration were within the experimental scatter). Hydrogen consumption, of course, increased with increasing coal concentration.

The improved performance with increasing coal concentration can be due to (a) higher intrinsic reactivity of Texas lignite relative to Maya VSB and/or (b) positive interactions (synergism) which occur when processing these feedstocks. Figure 2 shows a plot of 975°F+ conversion against coal concentration. It is necessary to estimate the 975°F+ conversions at 0 W% coal and 100 W% coal to determine the cause for the observed behavior. The 975°F+ conversion at 10 W% coal was 80.5 W% (MAF). It is very unlikely, based on other data points, that it would be higher than 80.5 W% at 0 W% Coal (100 W% Maya). The maximum coal conversion obtained in the test was 90.9 W% (MAF). Assuming that coal conversion levels off with increasing coal concentration, one can consider 90.9 W% (MAF) as an estimate of the *maximum* 975°F+ conversion that would be obtained with 100 W% coal, i.e. all converted coal produces 975°F product. If a line joining this point to 10 W% coal is drawn, all data points are seen to lie above the line. This indicates possible synergy, the beneficial affect of processing coal and oil together rather than separately. It is understood that the estimate of the 975°F+ conversion at 100 W% coal could be in error. However, the conclusion that process synergy exists would be incorrect only if the real 975°F+ conversion is much higher (almost 100 W%) or if the conversion at 0 W% coal is higher than at 10 W% coal. This appears unlikely.

A simplified analysis of these results was performed to assess the relationship between the cost of feedstock and hydrogen consumption and the feed composition. Implicit is the assumption that other costs do not vary much. Texas lignite was assumed to be available at $20 per ton at the U.S. Gulf coast. The cost of hydrogen was assumed to be $1.50 per MSCF based on the steam reforming of natural gas. A base cost of $12 per barrel was assumed for Maya vacuum residuum. The calculated cost of feedstock and hydrogen is shown in Table 7. As shown, the cost for 33 w% coal is about the same as for 40 W% coal.

The sensitivity of the above cost was then calculated over a range of prices for Maya residuum, from $8-16 per barrel. At low resid prices, there is little sensitivity as shown in Figure 3. For higher resid price, there is a clear incentive to operate with high coal concentration.

FUTURE WORK

An additional bench run is planned. This run will use a high-sulfur bituminous coal and an extremely poor quality (very high-metals containing) residuum.

ACKNOWLEDGMENTS

TABLE 1

LIST OF FEEDSTOCKS

COALS	RANK
Westerholt	Bituminous
Forestburg	Sub-Bituminous
Black Thunder	Sub-Bituminous
New Mexico	Sub-Bituminous
Taiheiyo	Sub-Bituminous
Texas Lignite	Lignite

OILS
Maya atmospheric and vacuum residua.
Cold Lake vacuum residuum
Hondo vacuum residuum

TABLE 2

LIST OF BENCH RUNS

RUN NO.	COAL	OIL	OBJECTIVES
1	Texas Lignite	Maya	Feedstock Reactivity
2	Westerholt	Cold Lake	Feedstock Reactivity
3	Texas Lignite	Maya	Process Improvements
4	Taiheiyo	Maya	Feedstock Reactivity
5	Forestburg Black Thunder	Cold Lake	Feedstock Reactivity Process Improvements
6	New Mexico	Hondo	Feedstock Reactivity
7	Texas Lignite	Maya	Process Improvements
8	Texas Lignite Westerholt	Maya Hondo Cold Lake Cold Lake	Feedstock Reactivity
9	Texas Lignite	Maya	Process Improvements

TABLE 3

COAL ANALYSIS

Texas Lignite

Ultimate Analysis, W% Dry Coal

Carbon	64.7
Hydrogen	4.4
Nitrogen	1.3
Sulfur	1.3
Ash (SO_3 - free)	10.9
H/C Atomic Ratio	0.82
O/C Atomic Ratio	0.20

TABLE 4

OIL ANALYSIS

Maya Vacuum Residuum

API Gravity	3.1
Carbon, W%	85.4
Hydrogen, W%	9.9
Nitrogen, W%	0.7
Sulfur, W%	5.2
Ni + V, Wppm	667
CCR, W%	25.0
W% 975°F⁺	90

TABLE 5

Condition	1	2	3	4	5	6
Periods	1-6	7-9	10-14	15-17	18-20	21-24
Coal	——————————————Texas Lignite———————————					
Oil	——————————————Maya VSB———————————					
Relative Space Velocity	——————————————1.0———————————					

Temperature, °F

First Stage	——————————————810———————————					
Second Stage	——————————————810———————————					
Coal Concentration in Feed (W%, dry)	33	40	40	10	20	40

TABLE 6

BENCH-SCALE YIELDS AND PROCESS PERFORMANCE

Condition	1	2	3	4	5	6
Periods	4/5/6	8/9	13/14	17	20	23/24
Coal Concentration in Fresh Feed, W%	33	40	40	10	20	40

Yields, W% Fresh Feed

	1	2	3	4	5	6
C_1-C_3	5.69	6.80	6.90	6.33	6.19	6.73
C_4-350°F	14.31	16.71	15.89	12.71	13.28	14.37
350-650°F	35.66	33.49	33.45	31.38	32.39	32.92
650-975°F	23.32	20.48	23.23	26.06	26.20	22.33
975°F⁺	7.55	6.23	6.22	16.16	11.95	8.49
Unconverted Coal	3.21	3.33	3.23	1.40	2.41	3.53
Ash	3.61	4.45	4.46	1.21	2.29	4.47
H_2S, NH_3, H_2O, CO_x	11.74	13.62	11.99	8.01	9.31	11.86
TOTAL (100 + H_2 Consumption)	105.04	105.11	105.37	103.26	104.02	104.66

Process Performance, W%

	1	2	3	4	5	6
975°F⁺ Conversion (MAF)	87.9	89.4	90.0	80.5	84.1	86.7
Coal Conversion (MAF)	89.0	90.7	90.9	85.6	87.0	89.8
HDS	94.9	93.3	94.6	91.8	91.5	91.9
HDN	70.4	70.0	74.0	59.0	59.1	65.6
Net C_4-975°F Distillate (MAF)	74.2	72.3	74.4	68.2	71.3	71.1

TABLE 7

COST OF FEEDSTOCKS AND HYDROGEN

% Coal	10	20	33	40
Cost, $/Barrel				
Hydrogen @$1.50/MSCF	3.98	4.79	5.82	6.05
Coal @$20/T	0.43	0.84	1.33	1.68
Oil @$12/Bbl	12.60	10.92	8.76	8.16
TOTAL	17.01	16.55	15.91	15.89

FIGURE 1

HRI Coal-Oil Co-Processing Technology

Simplified Process Flow Diagram
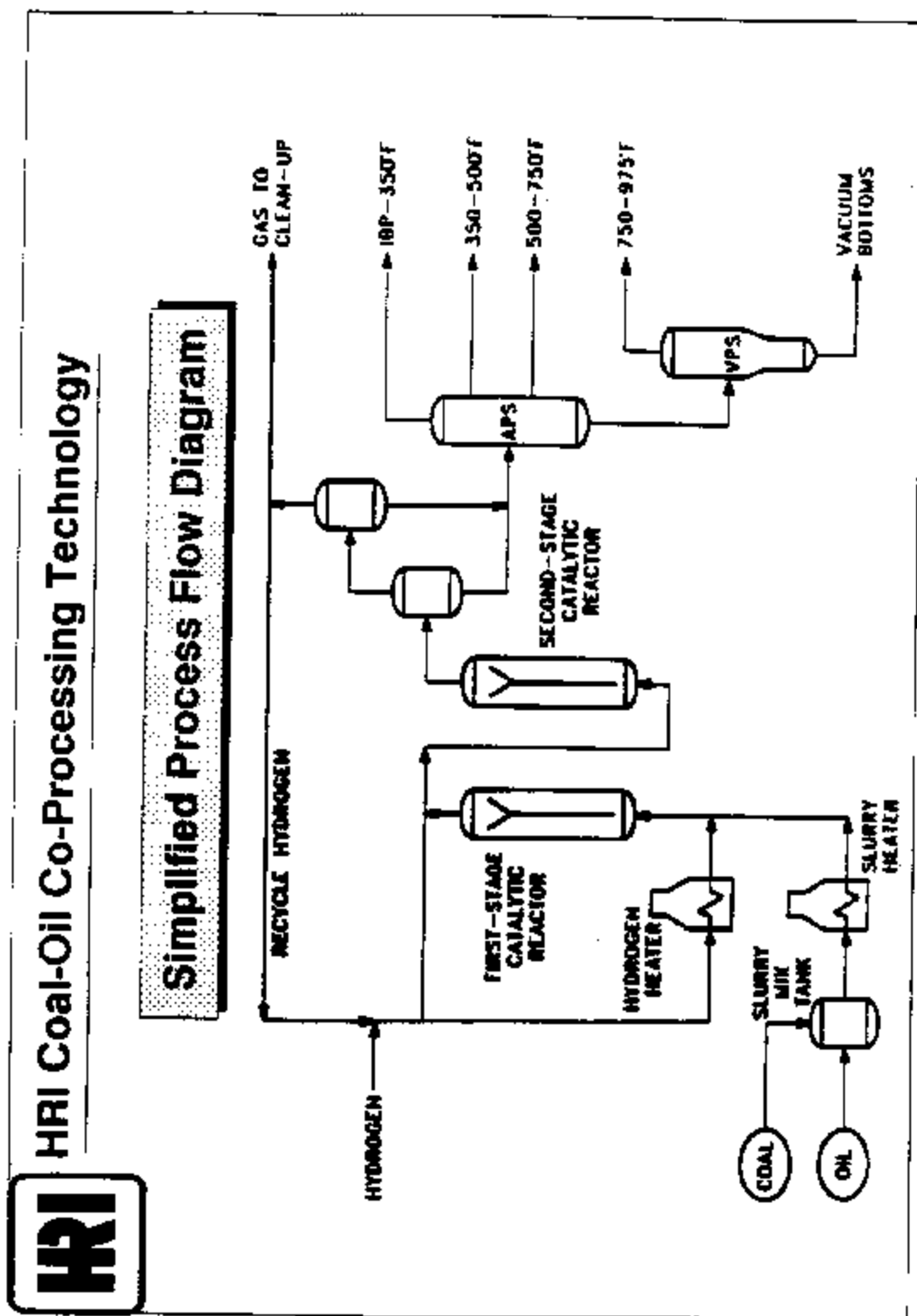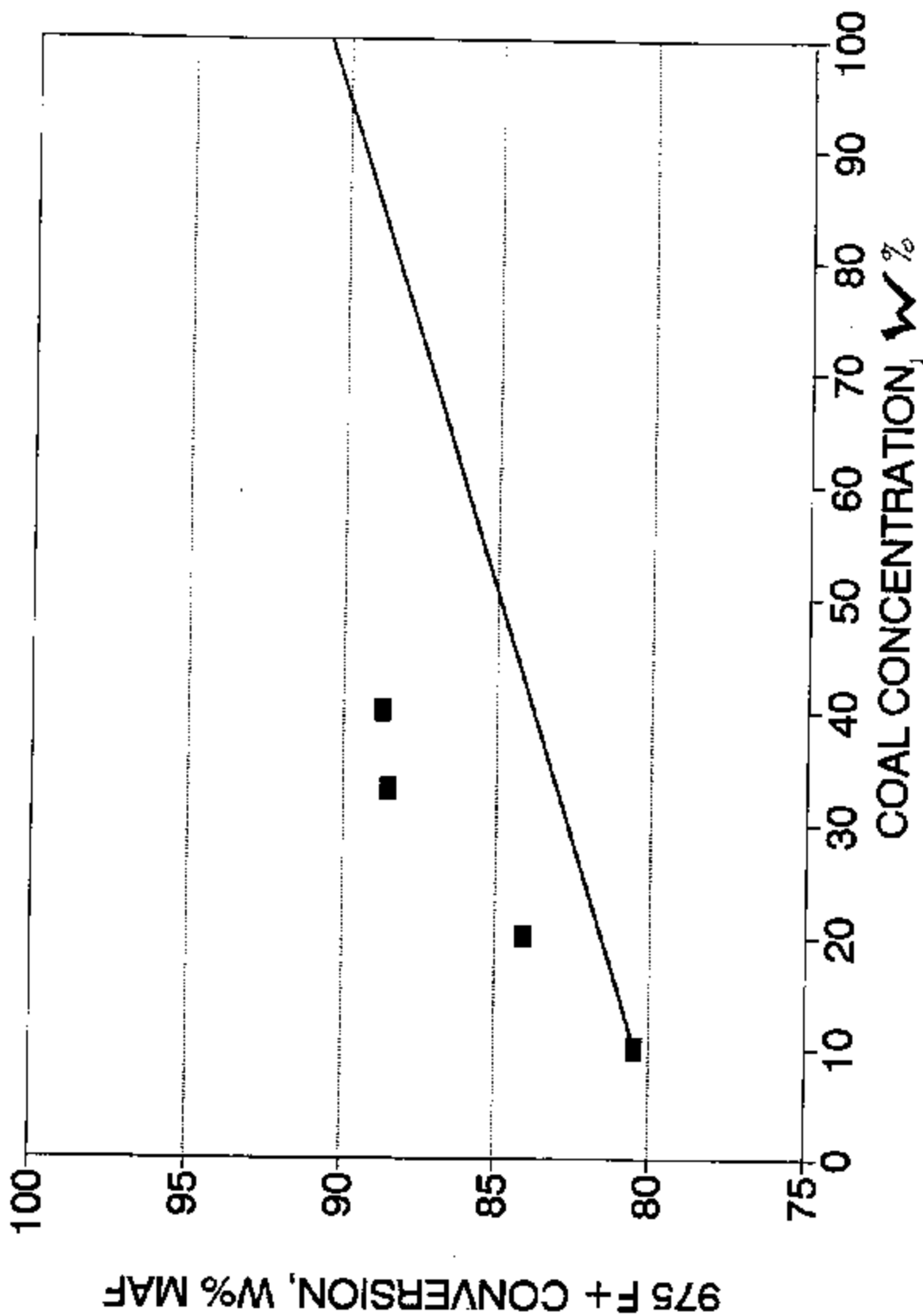
FIGURE 2

CO-PROCESSING OF TEXAS LIGNITE/MAYA
EFFECT OF COAL CONCENTRATION

FIGURE 3

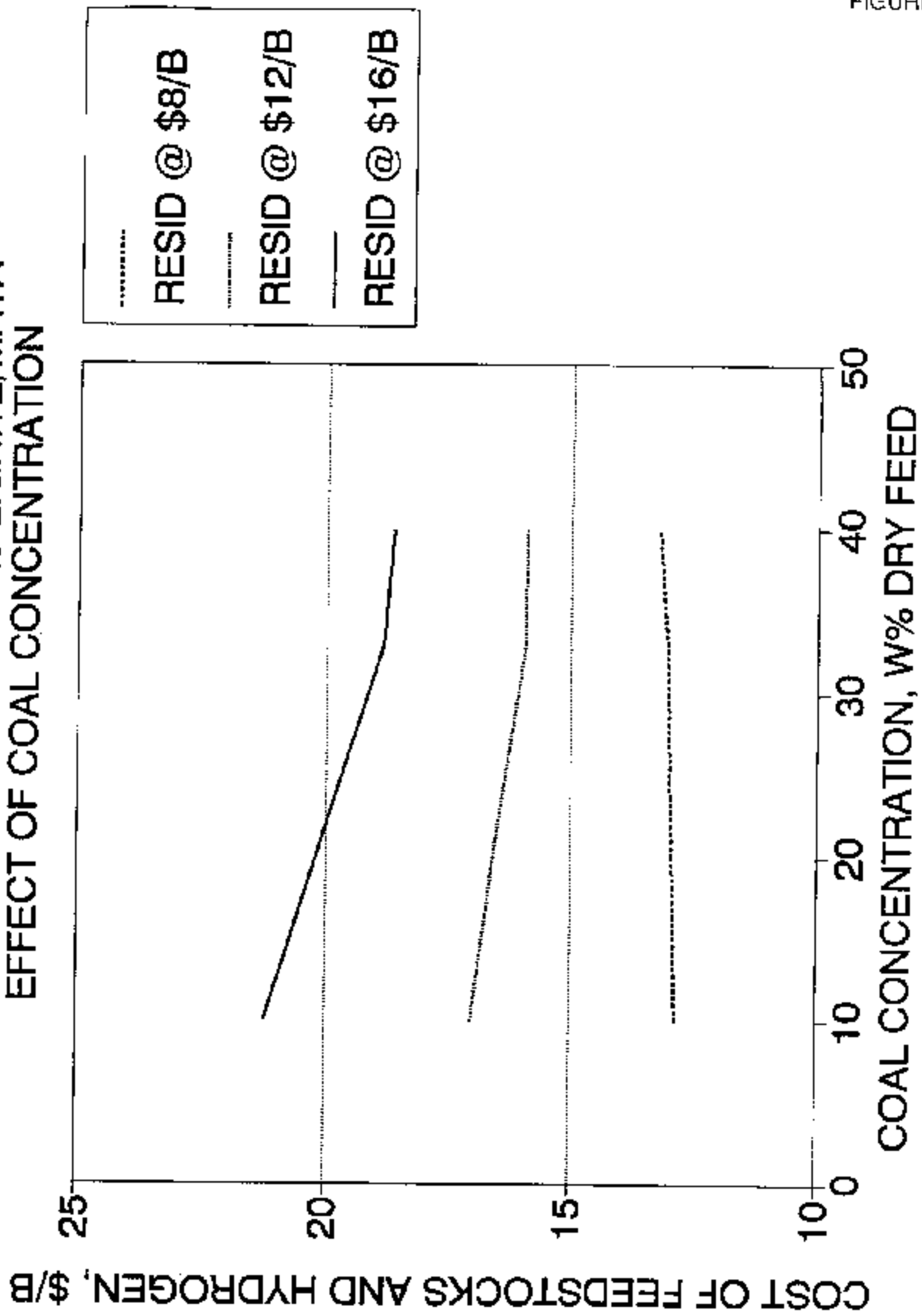CO-PROCESSING OF TEXAS LIGNITE/MAYA
EFFECT OF COAL CONCENTRATION

Legend:
- RESID @ $8/B
- RESID @ $12/B
- RESID @ $16/B

X-axis: COAL CONCENTRATION, W% DRY FEED (0, 10, 20, 30, 40, 50)

Y-axis: COST OF FEEDSTOCKS AND HYDROGEN, $/B (10, 15, 20, 25)

ANALYSIS OF COPROCESSING PRODUCTS

Raymond P. Anderson
James W. Vogh
John B. Green

IIT Research Institute
National Institute for Petroleum and Energy Research
P.O. Box 2128
Bartlesville, Oklahoma 74005
(918) 336-2400

ABSTRACT

One phase of improving understanding of the fundamental chemistry of coprocessing involves development of the ability to distinguish between products originating from coal versus those originating from petroleum resid. A primary objective of this project was to develop analytical techniques to determine the source (coal versus resid) of the various compound types found in coprocessing products. A corollary objective was to develop an expanded knowledge of the detailed composition of coprocessing products. This knowledge will aid in the development of improvements in coprocessing, guide development of refining methods for coprocessing liquids and provide information on the quality of coprocessing products. Two approaches were evaluated for distinguishing between products originating from coal and those originating from petroleum resid. One was based on the use of carbon isotope ratios and the other was based on variations in compound classes in response to changes in the ratio of coal to resid in the coprocessing feed. Other researchers using carbon isotope ratios to determine the origin of products have typically examined distillation fractions. This project involved determination of the origin of chemical classes (e.g., saturates, neutral aromatics, phenols, indoles, etc.) rather than distillate classes. Maya resid and Illinois No. 6 coal (with coal feed varying from 2 to 40 percent) were coprocessed in a batch autoclave to obtain products for detailed analysis.

Coprocessing products were separated into a number of fractions--first by distillation and then by a comprehensive chromatographic separation scheme developed at NIPER. The use of carbon isotope ratios to determine the source of particular compound classes was made more difficult by substantial isotope fractionation between compound classes. For example it was found that acid and base fractions are strongly enriched in the carbon-13 isotope -- even in a completely petroleum derived product. Relationships between concentrations of particular compound classes and the ratio of coal and resid in the feed were established. As an example, it was shown that coal was clearly the dominant source of both acids and bases. The acid fractions consisted primarily of phenols and, to a lesser extent, pyrrolic nitrogen compounds (indoles and carbazoles) while bases were primarily aromatic amines and pyridine types (quinolines, benzoquinolines, etc.).

Similar techniques were used for analysis of coprocessing products produced by another DOE contractor using a continuous product development unit. Emphasis was placed on determination of the composition of the coprocessing resid; composition of this material is of interest as it is the material which failed to be converted to the desired distillate range material.