SECTION 4

COAL OIL CO-PROCESSING

SINGLE STAGE PROCESSING OF COAL/RESID MIXTURE

M. Humbach and C. P. Luebke
Universal Oil Products
and
J. G. Gatsis and B. J. Nelson
The Signal Research Center, Inc.

SINGLE-STAGE PROCESSING OF COAL/RESID MIXTURE

C. P. Luebke*, M. J. Humbach*,
J. G. Gatsis** and B. J. Nelson**

INTRODUCTION

UOP Inc. and the Signal Research Center Inc. are working together on a coal liquefaction project sponsored by the U.S. Department of Energy (DOE). The objective of this study is to determine if a coal upgrading scheme called Co-Processing offers the potential for improved economics by simultaneously upgrading the coal and petroleum feedstocks.

The UOP Co-Processing scheme is a single-stage slurry catalyzed process where the vacuum resid acts as a coal liquefaction solvent. This eliminates the need for a hydrogenated, coal-derived recycle solvent, and allows the coal and resid to be simultaneously upgraded. The addition of a well dispersed catalyst allows the unit to operate at relatively moderate temperatures while maintaining good coal and heptane insoluble conversions. An added benefit to the low temperature operation is that thermal degradation reactions and the cracking of the coal and resid feedstocks to light gases are minimized.

This paper will review the results from the autoclave reactivity screening study and will present results from the recent shakedown runs of the continuous pilot plant unit. The results of the pilot plant study will also be compared to reference autoclave tests that processed the same feed blends. This experimental work has been conducted by the Signal Research Center Inc.

---

* UOP Inc., Des Plaines, Illinois
** The Signal Research Center Inc., Des Plaines, Illinois

PROCESS DESCRIPTION

UOP Inc. and the Signal Research Center Inc. began development of the resid/coal Co-Processing concept in 1970 and were issued a key patent in this area in 1972 (1). The objective of Co-Processing is to simultaneously upgrade the coal and resid feedstocks, and to maximize the amount of material that can be more efficiently upgraded using conventional refinery equipment.

A schematic flow diagram of the pilot plant is shown in Figure 1. The feed to this unit is a mixture of finely ground coal, petroleum resid and catalyst. This stream is mixed with a hydrogen-rich recycle gas stream and directed to the reactor. The effluent from the reactor is then sent to a series of separators where the various products are collected. The make-up hydrogen necessary to maintain the reactor pressure is automatically added to the system through a positive displacement metering system so that the hydrogen consumption can be accurately determined. This pilot plant flow scheme is very similar to the conceptual flow diagram of the commercial unit, except that a catalyst recovery unit will be required. This catalyst recovery unit will recover additional oil product, unconverted coal, ash residues and the catalyst from the vacuum bottoms. The catalyst will be recycled back to the reactor.

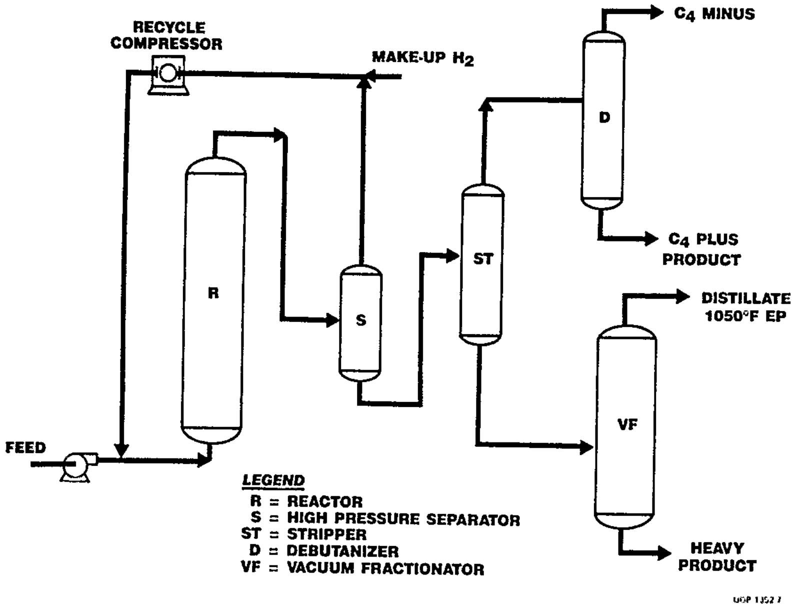

Figure 1. Pilot Plant Flow Scheme

REACTIVITY SCREENING STUDY

The primary objectives of the Reactivity Screening Study were to determine a range of operating conditions that could be used in the continuous pilot plant and to evaluate the effect of coal and resid changes. An 1800 mL rocking autoclave was used during this base testing condition development. This equipment and the procedure used have been described previously (2).

Six different vacuum resids, three bituminous coals and one sub-bituminous coal were evaluated during this screening study. The petroleum resids were selected based on their commercial importance and to provide a wide range of physical and chemical properties. The coal samples were selected primarily because of their use as reference feedstocks in other studies.

The chemical and physical properties of the resids and coals used in the reactivity screening study are summarized in Tables 1 and 2, respectively. The Lloydminster vacuum resid was selected as the reference petroleum feedstock as it represented an average of the resids to be tested. Illinois Coal No. 6 was used as the reference coal since it has been commonly used in other coal liquefaction studies.

TABLE 1

Autoclave Petroleum Resid Feedstocks

Resid Name	U.S. Mid-Continent	Kuwait	Alaskan North Slope	Lloyd-minster	Hondo	Maya
API Gravity	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, °C						
IBP, vol-%	473	472	422	406	478	452
5	510	505	494	509	512	515
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
Heptane Insolubles	8.29	5.95	4.80	18.10	17.80	22.40
Ni + V, ppm	148	128	117	400	592	711

TABLE 2

Autoclave 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.

Process variable studies were conducted, and it was confirmed that the reactor temperature, catalyst type and concentration have a pronounced effect on the process, while the process is not very sensitive to feedstock selection. The base operating conditions used during the reactivity testing were:

Resid/Coal Ratio, wt/wt	2:1
Pressure, psig	3000
Temperature, °C	Base
Residence Time, hr	2
Catalyst	UOP

For this study, the coal conversions have been calculated as the disappearance of moisture and ash-free (MAF) coal, the non-distillable conversions have been based on the disappearance of MAF coal plus 510°C+ resid, and the heptane insoluble conversions have been based on the disappearance of MAF coal plus heptane insolubles in the resid. Also, a 371°C+ conversion has been reported. This conversion is defined in the same manner as the non-distillable conversion, but uses 371°C instead of 510°C as the cut point. Since the feed to the Co-Processing unit contains a solid, it is reasonable to report each of these conversions on a wt-% basis.

The effect of temperature on conversions at these conditions is shown in Figure 2. As expected, the non-distillable conversion increased from 47.8 to 77.1 wt-% as the temperature was increased. Hydrogen consumption also increased as the temperature was increased, starting at 1.7 wt-% and increasing to 2.7 wt-%. Although not shown, the yield of C_4- gaseous products did increase substantially at the higher temperature.

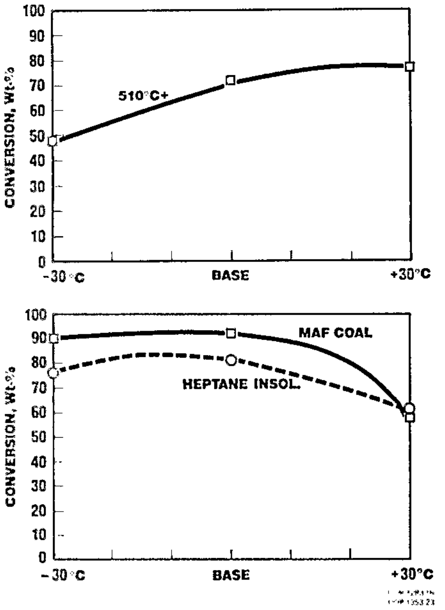

Figure 2. Effect of Temperature
(Lloydminster Vacuum Resid,
Illinois Coal No. 6)

The coal conversion and heptane insoluble conversion displayed an interesting trend as the temperature was increased. The coal conversion decreased slightly from 92.2 wt-% to 90.6 wt-% as the temperatures was decreased by 30°C from the Base temperature and also decreased markedly to 57.7 wt-% as the temperature was increased 30°C from the Base temperature. Heptane insoluble conversion behaved similarly, decreasing from 81.3 to 76.1 wt-% at 30°C below the Base temperature, and then decreasing sharply to 61.5 wt-% when the temperature was increased by 30°C. Both decreased coal conversion and heptane insoluble conversion at the higher temperature are theorized to be due to thermal degradation reactions that produce coke and light gases. As a result of this study, it will be important to maintain the reactor temperature at am optimum in order to maximize conversion while minimizing the thermal degradation reactions.

The addition of an active slurry catalyst is an integral part of the UOP Co-Processing scheme as this process uses the catalyst to promote the upgrading reactions at reduced temperatures. To establish the beneficial effects of the catalyst, test runs were conducted without catalyst, and with a disposable porous iron oxide (Fe_2O_3) catalyst and the UOP reference catalyst. It was anticipated that the activity of the iron catalyst would be lower than the reference catalyst and to compensate for this, twice as much iron catalyst was used.

The results of this catalyst comparison study are summarized in Table 3. The addition of either catalyst resulted in a dramatic increase in coal conversion and heptane insoluble conversion, but had little effect on the non-distillable conversion. The coal conversion and heptane insoluble conversion without the addition of catalyst was 66.6 wt-% and 21.3 wt-%, respectively. The coal conversion and heptane insoluble conversion increased to 81.1 wt-% and 63.9 wt-% with the iron catalyst and increased further with the UOP catalyst to 92.2 wt-% and 81.3 wt-%, respectively. The non-distillable conversion (510^{o}C+) ranged from 69.3 to 73.6 wt-% for these three tests.

TABLE 3

Autoclave Catalyst Comparison Study
(Lloydminster 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, wt-% of MAF Coal	66.6	81.1	92.2
Heptane Insoluble	21.3	63.9	81.3
Non-Distillable (510^{o}C+)	69.3	73.6	72.1
Hydrogen Consumption, wt-%	1.8	1.7	2.7

The comparison of the Co-Processing process using no catalyst, an iron oxide catalyst and the UOP catalyst should also include factors such as hydrogen consumption and product quality. The differences between these systems becomes more apparent when these factors are also included as part of the evaluation. The product properties of the total liquid product for each catalyst system tested are summarized in Table 4.

TABLE 4

Autoclave Catalyst Comparison Study Total Liquid Product Properties

(Lloydminster Vacuum Resid, Illinois Coal No. 6)

Catalyst Type	None	Fe_2O_3	UOP
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
Heptane Insolubles, wt-%	37.03	14.52	7.37
Carbon Residue, wt-%	14.6	16.5	15.1
Vanadium & Nickel, wt-ppm	19	9	23

---

* Estimated.

The UOP catalyst has the best hydrogenation capabilities of the three systems tested. As previously shown in Table 3, the hydrogen consumption with the UOP catalyst was 2.7 wt-%, compared to 1.8 wt-% and 1.7 wt-% for the screening tests using no catalyst and the iron catalyst, respectively. This higher hydrogen consumption yields a liquid product with a higher API gravity, higher hydrogen content and a lower heptane insoluble content. From an upgrading viewpoint, this higher API gravity product is advantageous, because for products with the same boiling range, the product with the highest API gravity is less aromatic and more like petroleum fractions. The lower heptane insoluble content, on the other hand, means that the material would have a lower tendency to poison or foul conventional upgrading catalysts, thus making it more economically attractive to upgrade.

The effect of feedstock selection was evaluated by testing each of the resids with the Illinois coal and each of the coals with the Lloydminster resid at the base conditions previously mentioned. The results of the resid reactivity study are shown in Figure 3. In this figure, conversions, expressed as coal, non-distillable, heptane insoluble, and 371°C+, as well as the hydrogen consumptions, are plotted versus the API gravity of the petroleum feedstocks. Except for the 371°C+ conversion, the conversions are relatively independent of the petroleum feedstock used. Since the lower API gravity feedstocks contain less hydrogen, the hydrogen consumption does increase as the API gravity decreases.

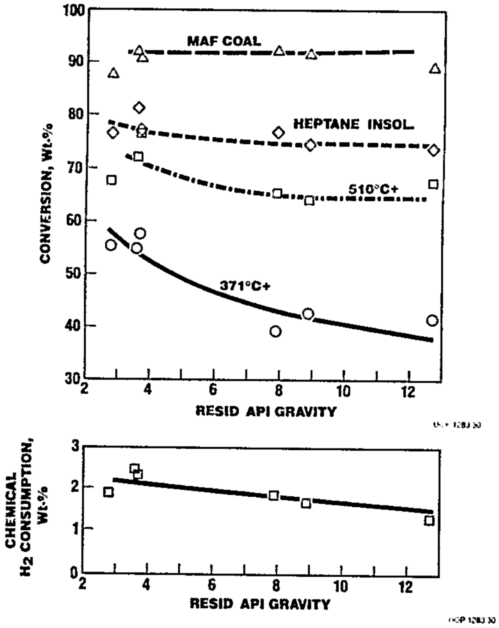

Figure 3. Resid Reactivity Screening
(Illinois Coal No. 6)

The coal reactivity screening test results are summarized in Figures 4 and 5. The observed conversions for the three bituminous coals and the dried sub-bituminous coal followed no particular trends. However, it appears that the high moisture content (14.7 wt-%) of the as-received sub-bituminous Wyodak coal does effect the activity of the catalyst, as the coal conversion and heptane insoluble conversion decreased by 12.0 wt-% and 14.3 wt-%, respectively, when compared to the test results with the dried Wyodak.

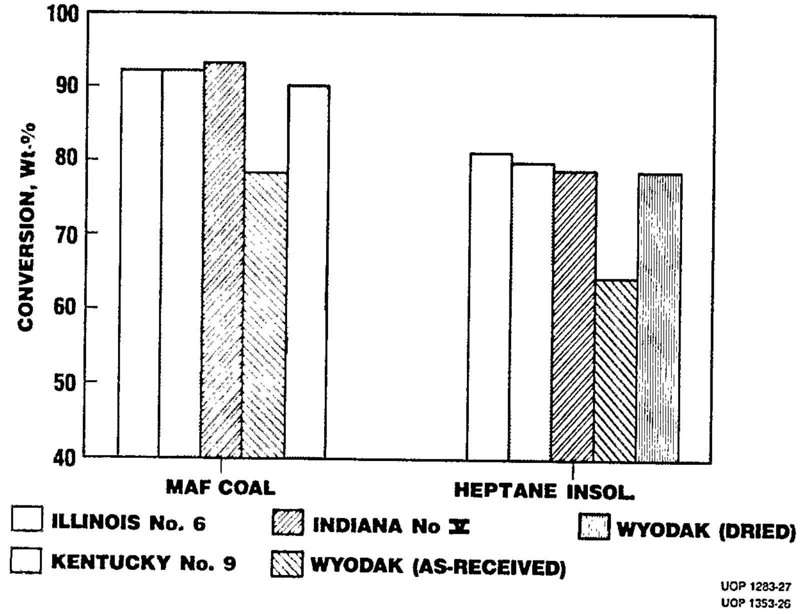

Figure 4. Coal Reactivity Screening
(Lloydminster Resid)

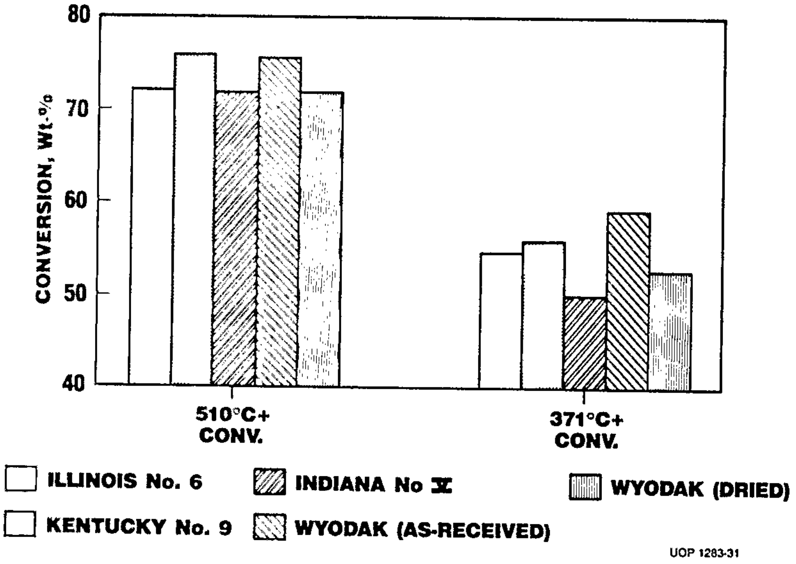

Figure 5. Coal Reactivity Screening
(Lloydminster Resid)

CONTINUOUS PILOT PLANT OPERATION

The results of the autoclave tests indicated that the concept of Co-Processing is feasible. The next stage of development of the Co-Processing concept involved continuous pilot plant processing of coal and resid blends. The primary objectives of the continuous pilot plant operations have been to direct its development towards maximizing the coal concentration in the resid/coal feedstock and to produce the greatest distillate yield when integrated with a conventional refinery. After the continuous pilot plant operations have been completed, the experimental data collected will provide a basis to conduct an economic evaluation of a conceptual commercial Co-Processing facility.

The feedstocks used for the continuous pilot plant work have been blends of Lloydminster vacuum resid and Illinois Coal No. 6. Tables 5 and 6 summarize the properties of the Lloydminster vacuum resids and Illinois No. 6 coals used in the continuous pilot plant work to date. These components were not exactly the same as those used during the autoclave studies, but are very similar.

TABLE 5

Pilot Plant Petroleum Resid Feedstocks

Resid Name	Lloyd-minster Sample No. 1	Lloyd-minster Sample No. 2
API Gravity	3.2	6.5
Specific Gravity	1.0505	1.0254
Distillation, D-1160, °C		
IBP, vol-%	387	369
5	481	432
EP	481	523
% Over at EP	5.0	26.5
Analysis, wt-%		
Carbon	81.9	83.7
Hydrogen	10.3	10.0
Oxygen	-	-
Sulfur	5.20	5.14
Nitrogen	0.62	0.48
Carbon Residue	22.9	17.3
Heptane Insolubles	18.4	13.9
Ni + V, wt-ppm	389	248

TABLE 6

Pilot Plant Coal Feedstocks

Coal Name	Illinois No. 6 Sample No. 1	Illinois No. 6 Sample No. 2
Ultimate Analysis, wt-%		
Ash	9.36	10.56
Carbon	69.25	68.77
Hydrogen	4.80	4.84
Nitrogen	1.35	1.37
Sulfur	2.65	3.34
Oxygen (Diff.)*	8.93	7.03
Proximate Analysis, wt-%		
Moisture	3.66	4.09
Ash	9.36	10.56
Volatile Matter	38.70	39.90
Fixed Carbon (Diff.)	48.28	45.45

---

* Excludes moisture.

The initial continuous pilot plant test runs were conducted to identify any operational problems with the continuous unit and to verify the observations made during the autoclave screening tests. The pilot plant results from two early tests, as well as those obtained in an autoclave reference test using the same blend, are summarized in Table 7. As seen in this table, the results obtained at the initial operating conditions were not as good as the autoclave results, with the coal, heptane insoluble and non-distillable conversions being significantly lower than the autoclave test results. This was not entirely unexpected as the initial operating conditions were selected only as a starting point in establishing the base operating conditions in the continuous pilot plant.

TABLE 7

Continuous Pilot Plant Operations

Run	Initial Operating Conditions	Revised Operating Conditions	Autoclave
Conditions	Base	Reduced Space Velocity	Base
Lloydminster Resid	------------	Sample No. 1	---------------
Illinois No. 6 Coal	------------	Sample No. 1	---------------
Conversions			
Coal, wt-% of MAF Coal	85.9	85.2	93.2
Heptane Insoluble, wt-%	56.3	70.7	81.6
Non-Distillable, wt-%	57.3	61.2	70.8

In an attempt to achieve conversions similar to the autoclave test runs, the space velocity in the continuous pilot plant was reduced, as it was thought that the initial operating conditions were not severe enough. All other test conditions were kept the same. The results from these revised operating conditions improved, although they were still well below those obtained in the autoclave screening test.

At the conclusion of the pilot plant operations at the revised operating conditions, the entire pilot plant was inspected. This inspection disclosed that the poor pilot plant performance was not caused by the selection of the operating conditions, but rather was caused by catalyst dispersion problems in the feed tank system. The pilot plant feed system consists of two tanks. The first, larger tank is used to make the feed blend and can hold up to two weeks of blended charge stock. This tank is equipped with a mixer and a feed recirculation system so that a uniform feed blend is maintained. There were no signs of a catalyst dispersion problem in this tank and the good autoclave results, summarized in Table 7, that used feed samples taken from this tank confirm this.

The second, smaller tank is a daily charge tank that allows the feed rates to be measured more accurately. This tank is located on a scale and relies on a feed recirculation system to maintain a uniform feed blend. Inspection of this second tank revealed that a large amount of material had deposited in the bottom of this tank. Analysis of this material indicated that it was primarily catalyst.

The quantity of catalyst recovered in the bottom of this tank was enough to significantly reduce the fresh feed catalyst concentration charged to the pilot plant, thereby reducing the performance of the Co-Processing unit. This also accounts for the good autoclave test results and the poor pilot plant performance, since the catalyst had deposited out in the second tank and not in the first.

To minimize the catalyst dispersion problem, a conical bottom and a mixer were added to the second, smaller tank. Following these modifications, the pilot plant was operated at the initial operating conditions. The test results obtained at these conditions using the modified feed system are summarized in Table 8. In this table, these results are compared to a second autoclave reference test that used the same feed blend and to the earlier pilot plant run which used a slightly different blend. As seen in this table, the results of the modified feed system test compare very favorably with the autoclave test results, with coal conversion 0.7 wt-% lower, heptane insoluble conversion 2.2 wt-% higher and non-distillable conversion 3.9 wt-% lower. When the two pilot plant results in Table 8 are compared, the overall conversions obtained after the feed system modifications were much better, with coal conversion increasing to 91.8 wt-%, heptane insoluble conversion increasing to 82.2 wt-% and non-distillable conversion increasing to 64.2 wt-%.

TABLE 8

Continuous Pilot Plant Operations

Run	Initial Operating Conditions	Modified Feed Tank	Autoclave
Conditions	Base	Base	Base
Lloydminster Resid	Sample No. 1	Sample No. 2	Sample No. 2
Illinois No. 6 Coal	Sample No. 1	Sample No. 2	Sample No. 2
Conversions			
Coal, wt-% of MAF Coal	85.9	91.8	92.5
Heptane Insoluble, wt-%	56.3	82.2	80.0
Non-Distillable, wt-%	57.3	64.2	68.1

Future test runs will evaluate the effects of changing the coal type an concentration, as well as catalyst type and concentration. Samples will be collected during the pilot plant runs so that a deasphalting study and a catalyst recovery study can be conducted. Following the experimental work, UOP will assess the economic incentives of the Co-Processing technology.

CONCLUSIONS

The UOP Co-Processing scheme has been successfully demonstrated both in laboratory batch experiments and in the continuous pilot plant. Also, the Signal Research Center autoclave tests have proved to be valuable tool for setting the target conversion levels for the pilot plant unit and for conducting the reactivity screening studies. After successfully modifying the feedstock system to correct for a catalyst dispersion problem, the continuous pilot plant test results have verified the autoclave test results.

ACKNOWLEDGMENT

The authors express their thanks to Burton H. Davis of the Kentucky Center for Energy Research Laboratory for the acquisition and preparation of the coal samples and to the U.S. DOE for supporting this study. Work presented in this paper has been performed under DOE Contract DE-AC22-84-PC70002, "Coal Liquefaction Co-Processing".

REFERENCES

1. J. G. Gatsis, U.S. Patent 3,705,092, "Solvent Extraction of Coal by a Heavy Oil," (1972).

2. J. G. Gatsis, et al., "Coal Liquefaction Co-Processing," Proceedings of DOE Direct Coal Liquefaction Contractor's Review Meeting, November 19-21, 1985.

HRI'S COAL/OIL CO-PROCESSING PROGRAM - PHASE I

J. B. MacArthur, J. E. Duddy and J. B. McLean
Hydrocarbon Research, Inc.

HRI's COAL/OIL CO-PROCESSING PROGRAM - PHASE 1

by

J. E. Duddy, J. B. MacArthur and J. B. McLean
Hydrocarbon Research, Inc.
(A Subsidiary of Dynalectron Corporation)
P. O. Box 6047
Lawrenceville, New Jersey 08648

ABSTRACT

Coal/oil co-processing has the potential to significantly reduce the cost of liquid fuels from coal. Hydrocarbon Research, Inc. (HRI) is developing an advanced catalytic two-stage process to liquefy coal while simultaneously upgrading heavy crudes or petroleum residua. Phase 1 of HRI's coal/oil co-processing program has been completed. The program features feedstock characterization, microautoclave reactivity screening, autoclave reactivity screening, continuous bench unit operations, product characterization studies, economic screening studies and commercial planning studies. As a result of this program proposals have been made by Ohio-Ontario Clean Fuels, Inc. (OOCF) to the State of Ohio and the United States Department of Energy for support of the design, construction and operation of a prototype commercial coal/oil co-processing plant. Phase 1 of the program was sponsored by the Electric Power Research Institute (EPRI), Ontario-Ohio Synthetic Fuels Corporation Ltd. (OOSFC), Alberta Research Council (ARC) and Dynalectron Corporation. Phase 1 Program results are presented in this paper.

INTRODUCTION

Although coal/oil co-processing is not a new concept (HRI did co-processing experiments in the 1960's) 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 while simultaneously upgrading poor quality heavy crudes or petroleum residua. Some of the factors which contribute to reducing the cost of liquid fuels from coal via coal/oil co-processing include:

- A lower investment compared to direct coal liquefaction.
- Ability to use existing refinery capacity and infrastructure.
- Better economics at smaller plant sizes compared to direct coal liquefaction.

In addition to the economic incentive, coal/oil co-processing has two other 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 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 a significant portion 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 that contribution (deposition of metals) to catalyst deactivation is reduced.

HRI's COAL/OIL CO-PROCESSING TECHNOLOGY

HRI's coal/oil co-processing technology uses the ebullated-bed reactor. The derivation and development of this 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 exciting new developments in Catalytic Two-Stage Liquefaction (CTSL).(1)

Figure 1 shows a simplified process flow diagram for HRI's coal/oil co-processing technology. 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 single- and 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. The configuration shown is for once-through operation. 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.

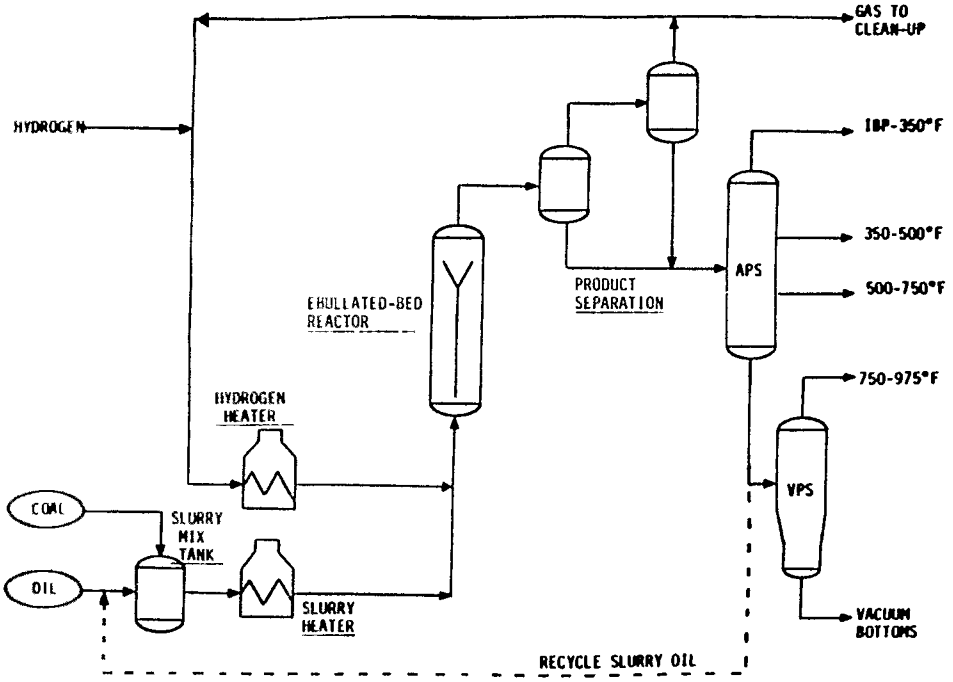

FIGURE 1. SINGLE-STAGE CO-PROCESSING - SCHEMATIC FLOW DIAGRAM

HRI's 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, which has recently been completed, was sponsored by:

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

The State of Ohio's Coal Development Office supported Phase 1 of 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 is the initial step in a coordinated program for coal/oil co-processing development. It is concentrated on feedstocks of current commercial interest. Specific elements of the Phase 1 program are:

- Feedstock Characterization
- Reactivity Screening
  - Microautoclave
  - Autoclave
- Continuous Bench-Scale Operations
- Product Characterization
- Economic Screening
- Commercial Planning

PHASE 1 PROGRAM RESULTS

Phase 1 of HRI's coal/oil co-processing program was initiated in April 1985 and was recently completed. Highlights of results from each of the technical tasks follows:

Feedstock Characterization

Four coals and four oil feedstocks were selected for this program. The feedstocks were selected based on current or near term commercial interest in North America. The feedstocks included:

Coals

1. Eastern, Appalachian Bituminous Coal (Ohio No. 5/6)
2. Low Sulfur, Sub-Bituminous Coal (Alberta)
3. High Sulfur Bituminous Coal (Illinois No. 6)
4. U. S. Gulf Coast Lignite (Martin Lake, Texas)

Oils

1. High Metals Residuum (Mexican Maya)
2. Western Canadian Heavy Feedstock (Cold Lake Residuum)
3. U. S. Gulf Coast Residuum (Western Texas Sour)
4. Great Lake Residuum (Interprovincial Pipeline)

The coal analyses performed includes proximate, ultimate, petrographic and mineral analyses. For the oils elemental analysis as well as physical and chemical characterizations were performed. Table 1 summarizes some of the feedstock characterizations. This table shows that of the coals tested, Ohio No. 5/6 coal and Illinois No. 6 coal are similar. The Ohio coal has a lower ash content and higher hydrogen content. The Alberta sub-bituminous coal is similar to typical Wyoming sub-bituminous coals. The Texas lignite has a relatively low ash content, but otherwise is typical of lignite from that region.

The oil characterizations show that the Cold Lake and Maya feedstocks are considerably poorer in quality compared to the IPL and West Texas Sour. They are much higher in sulfur, metals, RCR and asphaltenes.

An overview of the feedstock testing performed in the Phase 1 Program is provided in Table 2. This table shows the scale of testing (characterization, microautoclave, autoclave, bench) done on each feedstock and combination of feedstocks. After the feedstock characterizations were completed, batch reactivity screening tests were executed to provide an indication of the reactivity of a given feedstock or feedstock combination. Two levels of testing were done. Microautoclave tests, using 20cc microautoclave, provided the first level of reactivity screening, indicating relative coal and 975°F^+ conversion levels at specified severities. Autoclave tests, using a 1-liter stirred autoclave, provided more detailed information including approximate yields and product qualities. As shown in Table 2 all of the individual coal and oil feedstocks were screened at the microautoclave scale, as well as five feedstock combinations. At the autoclave scale two coals and one oil, and two feedstock combinations were evaluated.

TABLE 1

FEEDSTOCK ANALYSES

COALS	OHIO NO. 5/6	ILLINOIS NO. 6	ALBERTA SUB-BITUMINOUS	TEXAS LIGNITE
Carbon, W %	75.3	69.9	67.9	63.3
Hydrogen, W %	5.6	4.9	4.7	5.3
Nitrogen, W %	1.6	1.4	1.4	1.2
Sulfur, W %	3.0	3.7	0.5	1.2
Ash, W %	6.8	11.7	8.2	12.0
Oxygen, W % (by difference)	7.7	7.8	17.3	17.0
H/C Atomic Ratio	0.89	0.84	0.83	1.00
OILS	**COLD LAKE**	**IPL**	**MAYA**	**WEST TEXAS SOUR**
°API	6.9	14.5	4.1	14.7
W % 975°F^+	70	68	85	65
Hydrogen, W %	10.1	10.8	9.7	11.5
Nitrogen, W %	0.5	0.4	0.7	0.3
Sulfur, W %	5.2	1.3	5.0	2.4
Nickel and Vanadium, Wppm	330	44	637	62
RCR, W %	18.4	12.3	24.1	8.3
Oils, W %	39	55	30	58
Resins, W %	41	36	39	38
Asphaltenes, W %	20	9	31	4

TABLE 2

CO-PROCESSING PROGRAM FEEDSTOCKS - PHASE 1

	CHARACTERIZATION	M/A(1)	A(2)	BENCH
COALS				
Ohio No. 5/6	x	x	x	
Alberta	x	x	x	(3)
Illinois No. 6	x	x		(3)
Texas Lignite	x	x		
OILS				
Cold Lake	x	x	x	(3)
West Texas Sour	x	x		(3)
Maya	x	x		
IPL Residuum	x	x		
COAL/OIL COMBINATIONS				
Ohio No. 5/6/Cold Lake		x	x	x
Ohio No. 5/6/West Texas Sour		x		
Ohio No. 5/6/Maya		x		
Alberta/Cold Lake		x	x	(3)
Texas Lignite/West Texas Sour		x		

(1) M/A = Microautoclave
(2) A = Autoclave
(3) Bench run done under separate program.

Microautoclave Reactivity Screening

Over 200 single-stage microautoclave tests were conducted studying severity, feedstock ratio and catalyst effects. Descriptions of the microautoclave equipment and procedures used are available elsewhere.(2)

Figure 2 shows the relative reactivities of the four oils tested for 975°F$^+$ conversion. Their relative reactivity can be summarized as follows:

Cold Lake < IPL < Maya < West Texas Sour

Figure 3 shows the relative reactivities of the four coals tested for 975°F$^+$ conversion. Their relative reactivity can be summarized as follows:

Alberta < Ohio No. 5/6 < Illinois No. 6 < Texas lignite

Co-processing microautoclave tests were done on the following coal/oil feedstock combinations:

1. Alberta/Cold Lake
2. Ohio/Cold Lake
3. Ohio/Maya
4. Ohio/West Texas
5. Texas Lignite/West Texas

Figure 4 shows the relative reactivites for 975°F$^+$ conversion for these feedstock combinations. The reactivity screening results are based on a 1:1 oil-to-coal ratio, or 50 W % coal in the fresh feed. The figure shows the actual reactivity obtained in the microautoclave tests, as well as the predicted conversion, based on the individual feedstock reactivities. This comparison shows the synergy of coal/oil co-processing on overall 975°F$^+$ conversion. The actual 975°F$^+$ conversions obtained are greater than those predicted based on the individual feedstock reactivities for all but one (the most reactive pair) feedstock combination.

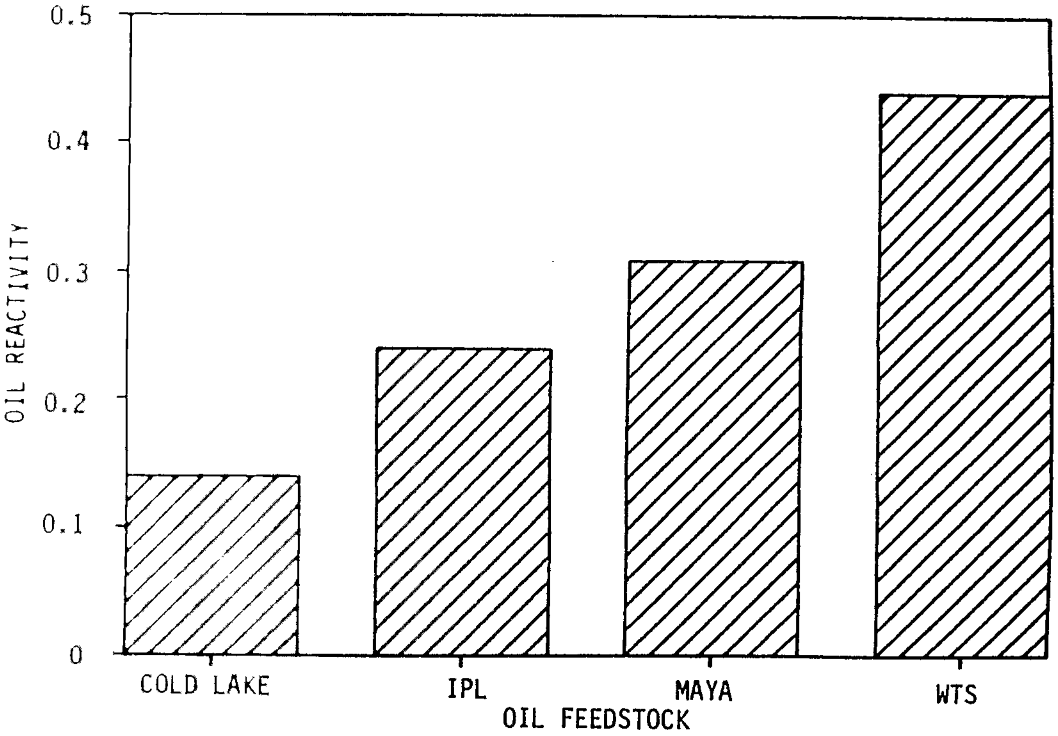

FIGURE 2. OIL REACTIVITY FOR 975°F$^+$ CONVERSION

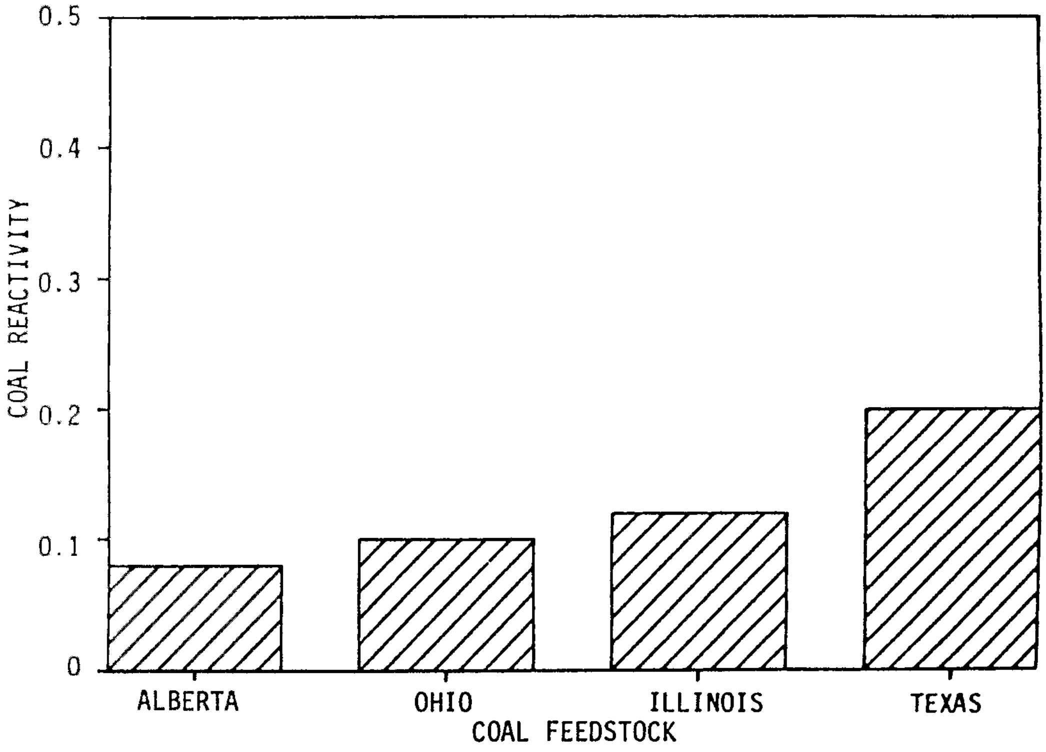

FIGURE 3. COAL REACTIVITY FOR 975°F+ CONVERSION

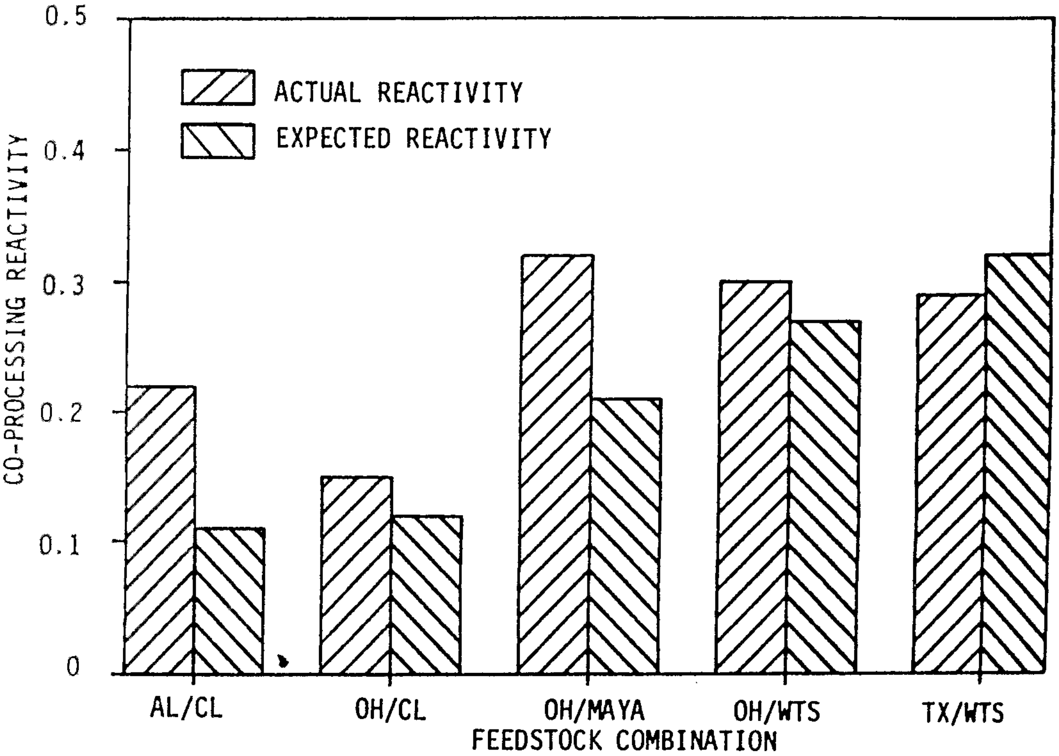

FIGURE 4. CO-PROCESSING REACTIVITY FOR 975°F+ CONVERSION

This observed process synergy was further studied by evaluating 975°F$^+$ conversion versus the oil-to-coal feedstock ratio, or percent coal in the fresh feed. This effect is shown in Figure 5 for the Alberta/Cold Lake feedstock combination. Both coal and 975°F$^+$ conversion are plotted versus percent coal in the fresh feed. This figure shows that coal conversion increases with coal concentration and that the overall 975°F$^+$ conversion is greater than would be predicted from the individual 975°F$^+$ conversion of the feedstocks.

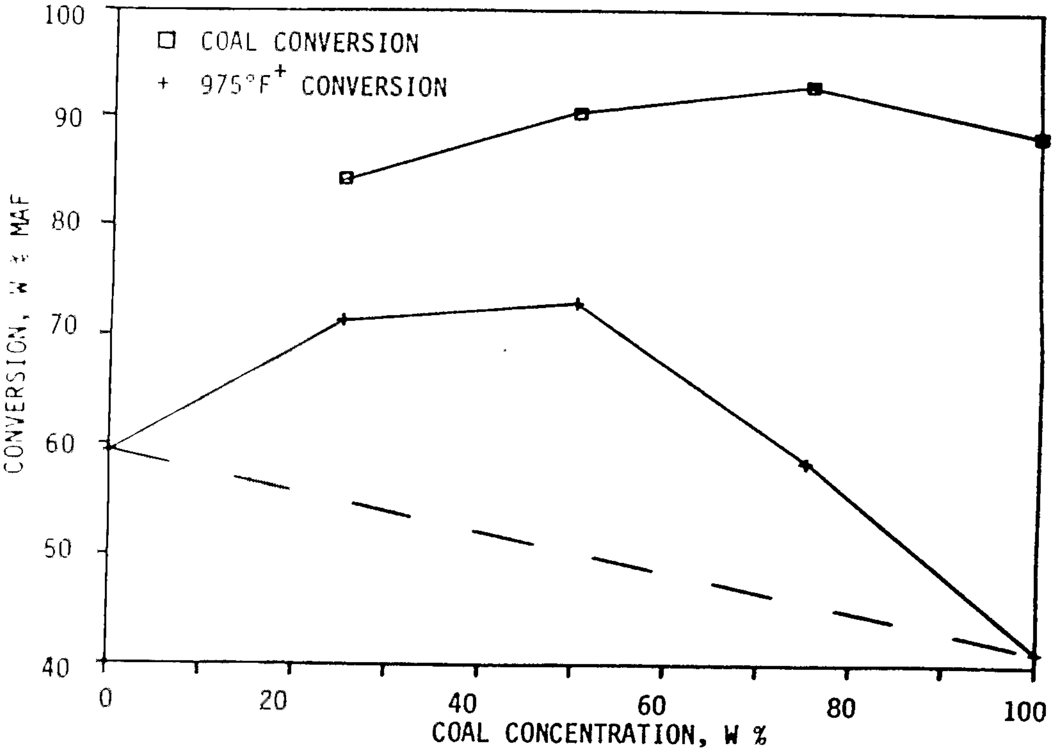

FIGURE 5. EFFECT OF COAL CONCENTRATION ON AL/CL

The same plot is presented for the Ohio/Cold Lake feedstock combination in Figure 6. This plot shows the same effect of coal concentration on coal conversion, but reveals a surprising result on 975°F$^+$ conversion. At high coal concentrations the 975°F$^+$ conversion is actually lower than would be predicted by the individual feedstock reactivities. That is, there is a negative interaction occurring between these feedstocks at high coal concentrations.

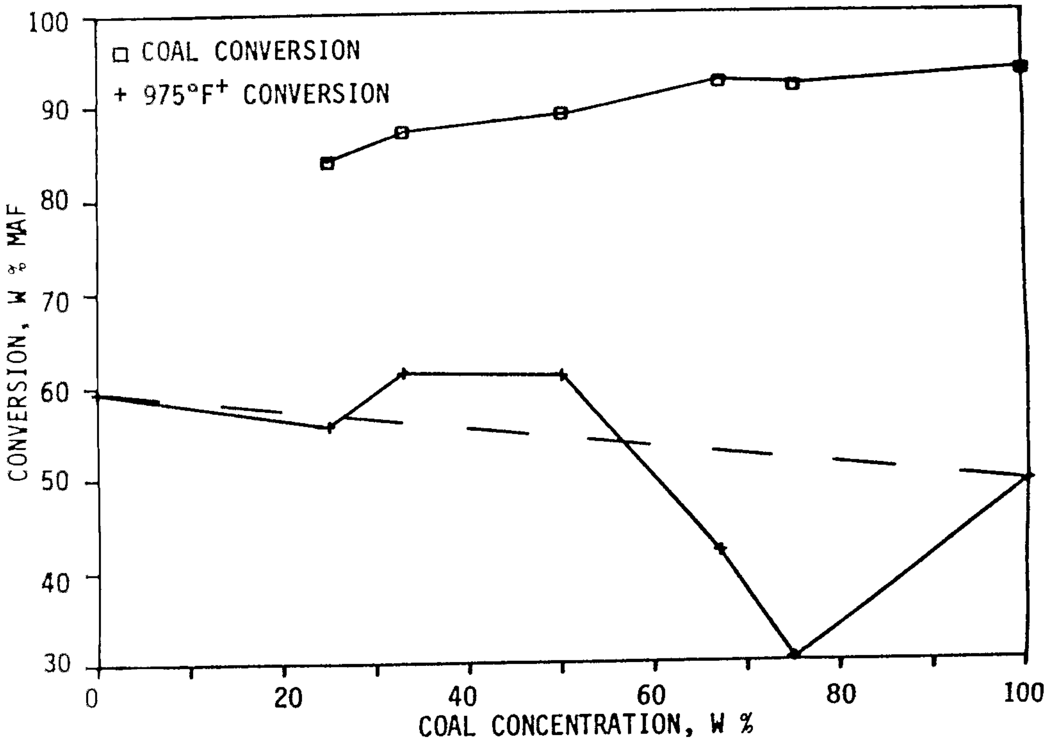

FIGURE 6. EFFECT OF COAL CONCENTRATION ON OH/CL

The most likely explanation for this phenomenon is that the presence of the petroleum derived oils sufficiently reduces the solvent quality in this range to cause a large drop in the conversion of the coal residua. At lower coal concentrations this effect is offset by the improved conversions of the petroleum residua. As shown previously, it should be noted that the ratio studies with the other feedstock combinations do not show this same negative behavior, but in all cases the response to coal concentration is non-linear, with maximum conversions occurring at about 50 W % coal.

Autoclave Reactivity Screening

Fourteen autoclave reactivity tests (all single stage) were conducted to screen oil reactivity (Cold Lake), coal reactivity (Ohio and Alberta) and co-processing reactivities. The autoclave tests also evaluated the use of supported catalyst versus a slurry phase catalyst (pyrite). Key autoclave results showed the same reactivity trends noted in the microautoclave reactivity screening. The autoclave results also showed that the supported catalyst was greatly superior for 975°F+ conversion and provided distillate liquid products with very low sulfur and nitrogen contents.

Continuous Bench Unit Operations

Two process variable bench runs were completed in the Phase 1 Program. Both runs used the Ohio No. 5/6 coal and Cold Lake atmospheric residuum. The first run was done using a single-stage process configuration to:

- provide baseline data for evaluation of major process variables and comparison to subsequent two-stage operations.
- gain experience in co-processing the selected feedstocks so that potential operating problems could be better anticipated for two-stage testing.
- allow direct comparison with HRI's extensive H-Oil® Process data base on the selected oil feedstock over a similar range of operating conditions.(3)

The second bench run was done using a two-stage process configuration. Conditions were selected based on the single-stage results to:

- obtain high 975°F$^+$ conversion, in the range of 90 W % MAF, such that the bottoms from vacuum distillation would contain approximately 50 W % solids.
- obtain a high quality vacuum gas oil (650-975°F) product which would be suitable for use as a low sulfur fuel oil or a high quality turbine fuel.

Over fifty days of continuous bench unit operations were accumulated over the two bench runs. Sixteen process conditions were evaluated over a wide range of operating conditions including:

- Coal Concentration
- Temperature
- Space Velocity
- Recycle Rate
- Recycle Composition

Over the wide range of operating conditions evaluated, process performances in the following ranges were obtained:

- 59 to 92 W % MAF 975°F$^+$ conversion
- 89 to 96 W % MAF coal conversion
- 66 to 91% Hydrodesulfurization (HDS)
- 40 to 80% Hydrodenitrogenation (HDN)
- 81 to 99% Demetallization
- 55 to 79 W % MAF C_4-975°F Liquid Yield

Selected results from the continuous bench unit operations are shown in Tables 3, 4 and 5. Table 3 summarizes yields and process performance for three conditions from Bench Run No. 1 (single-stage). Operating conditions are identical for each set shown except for the coal concentration in the fresh feed (and recycle rate required). Table 4 summarizes the same data for two conditions from Bench Run No. 2 (two-stage). Table 5 compares product quality data from the two runs. The important information to note in these tables is the superior process performance and product quality obtained on the two-stage operations. Following is further analysis of the results of the continuous bench unit operations:

TABLE 3

CONTINUOUS BENCH UNIT OPERATIONS
Bench Run No. 1 - Single Stage

Feedstocks: Cold Lake Atmospheric Residuum
Ohio No. 5/6 Coal

CONDITION	5	2	4
W % Coal in Fresh Feed	33	50	67
YIELDS, W % DRY COAL PLUS OIL			
C_1-C_3	6.0	5.0	5.3
C_4-390°F	14.4	14.5	11.2
390-650°F	25.1	24.7	22.5
650-975°F	24.7	25.7	24.9
975°F$^+$	17.8	17.0	21.4
Unconverted Coal	2.8	3.2	3.7
Ash	2.4	3.5	4.6
H_2O, COx, NH_3, H_2S	9.4	9.5	9.6
TOTAL	102.6	103.3	103.3
PROCESS PERFORMANCE, W % MAF			
975°F$^+$ Conversion	74	75	70
Coal Conversion	91	93	94
Hydrodesulfurization	79	83	70
Hydrodenitrogenation	50	64	54
Demetallization	92	95	92
C_4-975°F			
W % MAF	66	67	61
B/T Total Feed	4.4	4.4	3.9
B/B Oil Feed	1.2	1.5	2.0

TABLE 4

CONTINUOUS BENCH UNIT OPERATIONS
Bench Run No. 2 - Two-Stage

Feedstocks: Cold Lake Atmospheric Residuum
Ohio No. 5/6 Coal

CONDITION	6	4
W % Coal in Fresh Feed	33	50
YIELDS, W % DRY COAL PLUS OIL		
C_1-C_3	8.0	6.2
C_4-390°F	21.4	17.6
390-650°F	36.4	34.1
650-975°F	19.7	23.2
975°F$^+$	4.5	6.7
Unconverted Coal	1.4	2.0
Ash	2.4	3.6
H_2O, COx, NH_3, H_2S	9.5	10.8
TOTAL	103.3	104.2
PROCESS PERFORMANCE, W % MAF		
975°F$^+$ Conversion	92	90
Coal Conversion	95	96
Hydrodesulfurization	91	86
Hydrodenitrogenation	78	80
Demetallization	99	99
C_4-975°F		
W % MAF	79	78
B/T Total Feed	5.4	5.1
B/B Oil Feed	1.4	1.8

TABLE 5

CONTINUOUS BENCH UNIT OPERATIONS

Feedstocks: Cold Lake Atmospheric Residuum
Ohio No. 5/6 Coal

	Single Stage			Two Stage	
CONDITION	6	2	4	6	4
W % Coal in Fresh Feed	33	50	67	33	50
LIQUID PRODUCT QUALITY					
NAPHTHA, IBP-390°F					
Gravity, °API	53.1	50.8	46.3	54.2	53.0
Hydrogen, W %	13.47	13.60	13.00	13.85	13.86
Sulfur, W %	0.10	0.08	0.11	0.04	0.02
Nitrogen, W %	0.14	0.07	0.15	0.15	0.06
DISTILLATE, 390-650°F					
Gravity, °API	28.3	28.9	25.8	30.5	28.7
Hydrogen, W %	11.77	12.02	11.46	12.13	11.76
Sulfur, W %	0.42	0.11	0.22	0.06	0.04
Nitrogen, W %	0.18	0.17	0.30	0.17	0.22
VACUUM GAS OIL, 650-975°F					
Gravity, °API	13.0	15.4	10.7	15.1	13.3
Hydrogen, W %	10.39	10.65	9.69	10.72	10.54
Sulfur, W %	0.90	0.34	0.43	0.22	0.17
Nitrogen, W %	0.41	0.36	0.48	0.36	0.35

- Coal Conversion increases with coal concentration in the fresh feed (Figure 7). In general, coal conversion was quite high, approaching those attainable in direct coal liquefaction. Coal conversions were higher in the two-stage process configuration.

- 975°F+ Conversion obtained in the single-stage bench run followed the same trend observed in the microautoclave and autoclave reactivity screening. As shown in Figure 8, the actual 975°F+ conversions obtained were higher than expected at 33 and 50 W % coal, and lower than expected at 67 W %.

- Liquid Product (C_4-975°F) Yields are plotted versus 975°F+ conversion in Figure 9. Over a range of about 60-90 W % MAF 975°F+ conversion, the yield of liquid product correlates quite well. The maximum liquid product yield was about 80 W % on MAF feed. Liquid product selectivities are shown in Figure 10 for both single- and two-stage operations versus coal concentration in the fresh feed. In the single-stage operations the selectivity to 390-650°F and 650-975°F was similar for each coal concentration. C_4-390°F yield was considerably lower at 67 W % coal in the fresh feed. Two-stage operations showed higher overall liquid product yields, due to the higher conversion levels, and a greater selectivity to C_4-390°F and 390-650°F, with correspondingly less 650-975°F.

- HDS, HDN and Demetallization - Percent removals of sulfur, nitrogen and metals (nickel plus vanadium) are plotted versus reciprocal relative space velocity in Figure 11. No adjustments have been made for temperature or catalyst age. Up to 90% HDS, 80% HDN and 99% demetallization were obtained. It is important to note that demetallization is defined here as metals removed from the liquid product, including unconverted 975°F+ residuum. A significant portion of the metals removed were with the coal solids, and not on the catalyst.

Overall the continuous bench unit operations have demonstrated the technical feasibility of coal/oil co-processing over a wide range of operating conditions and conversions, in both single- and two-stage process configurations. High 975°F+ conversions were obtained in the two-stage operations with excellent selectivity to liquid products and superior product quality.

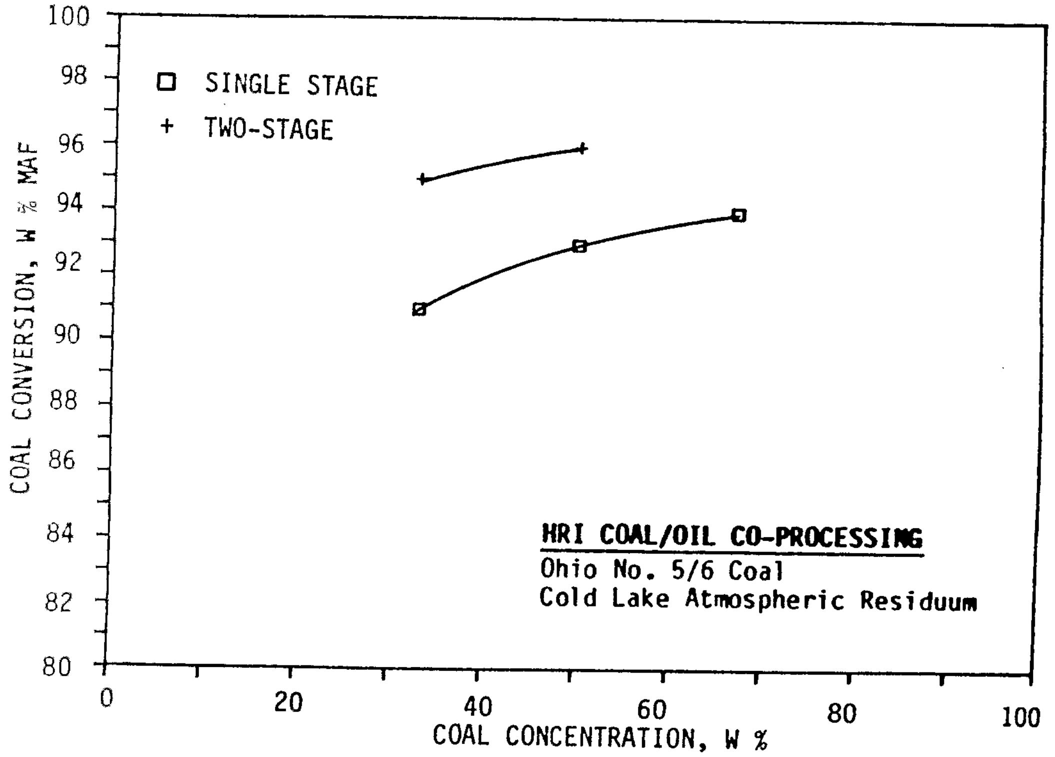

FIGURE 7. COAL CONVERSION

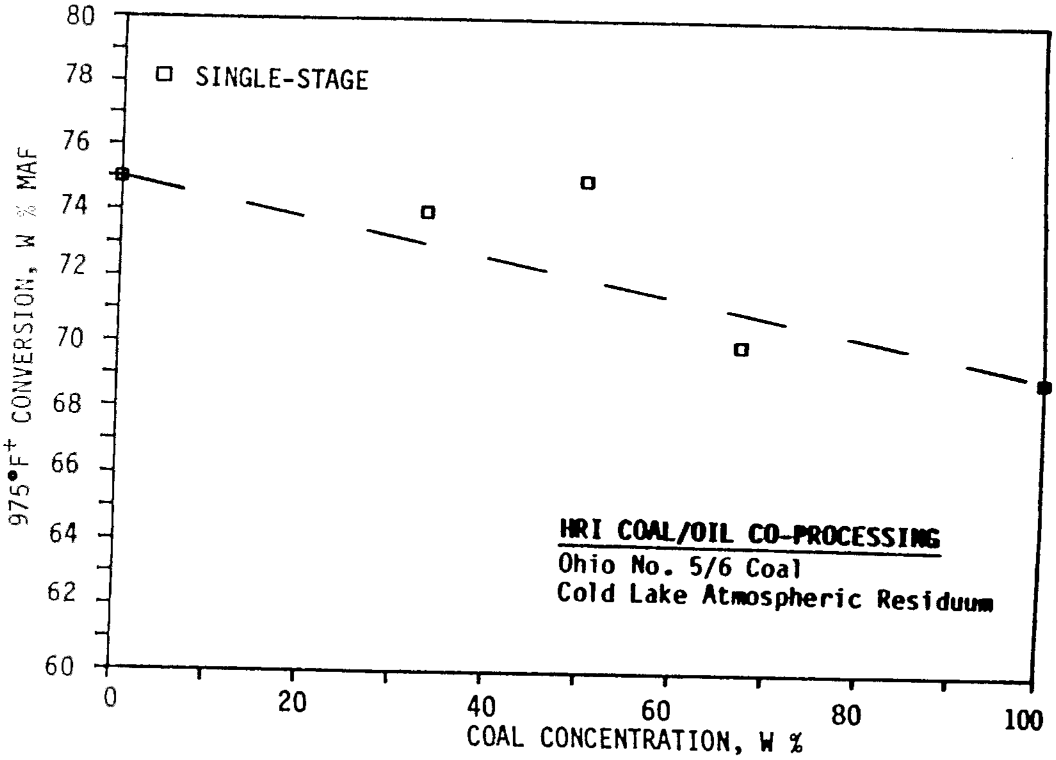

FIGURE 8. 975°F$^+$ CONVERSION

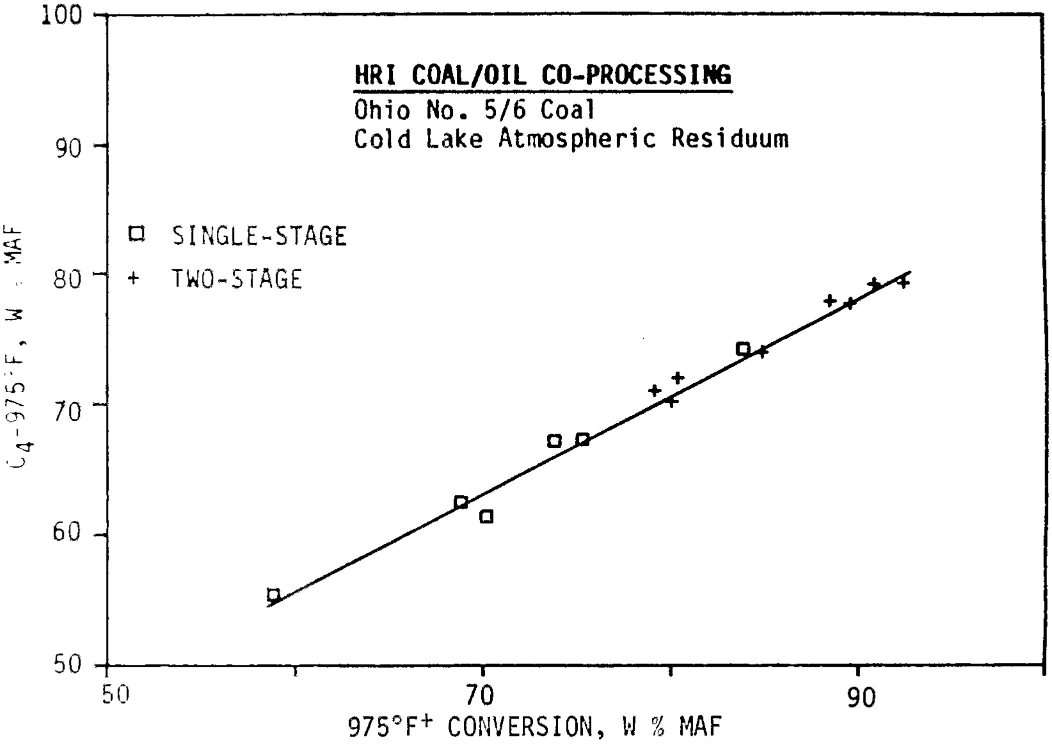

FIGURE 9. LIQUID PRODUCT YIELD

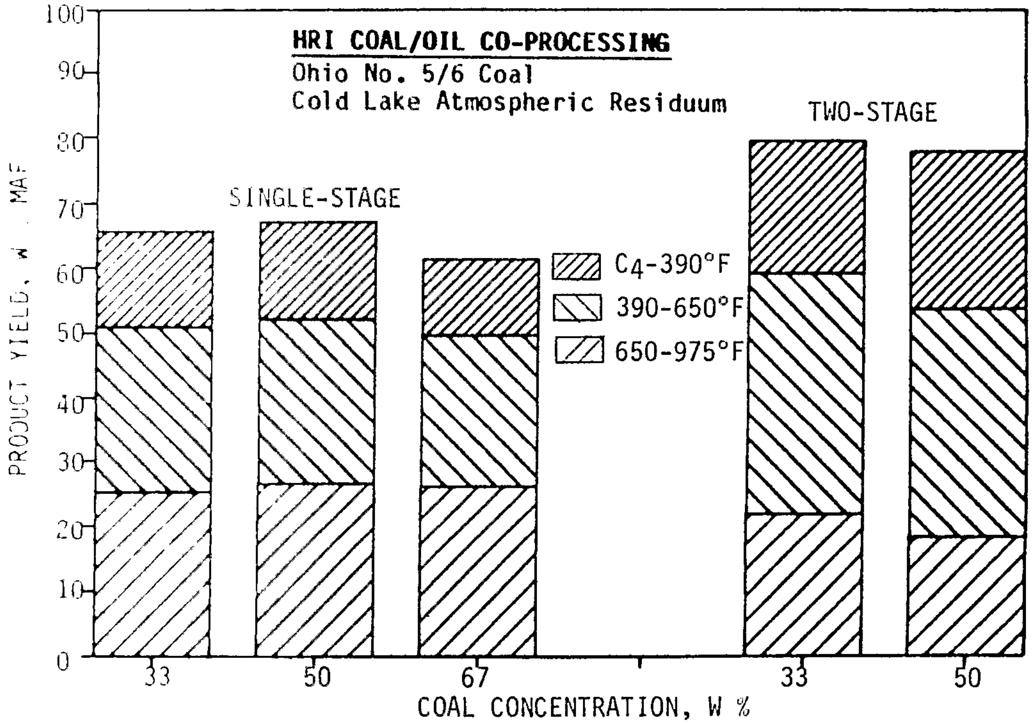

FIGURE 10. LIQUID PRODUCT YIELDS

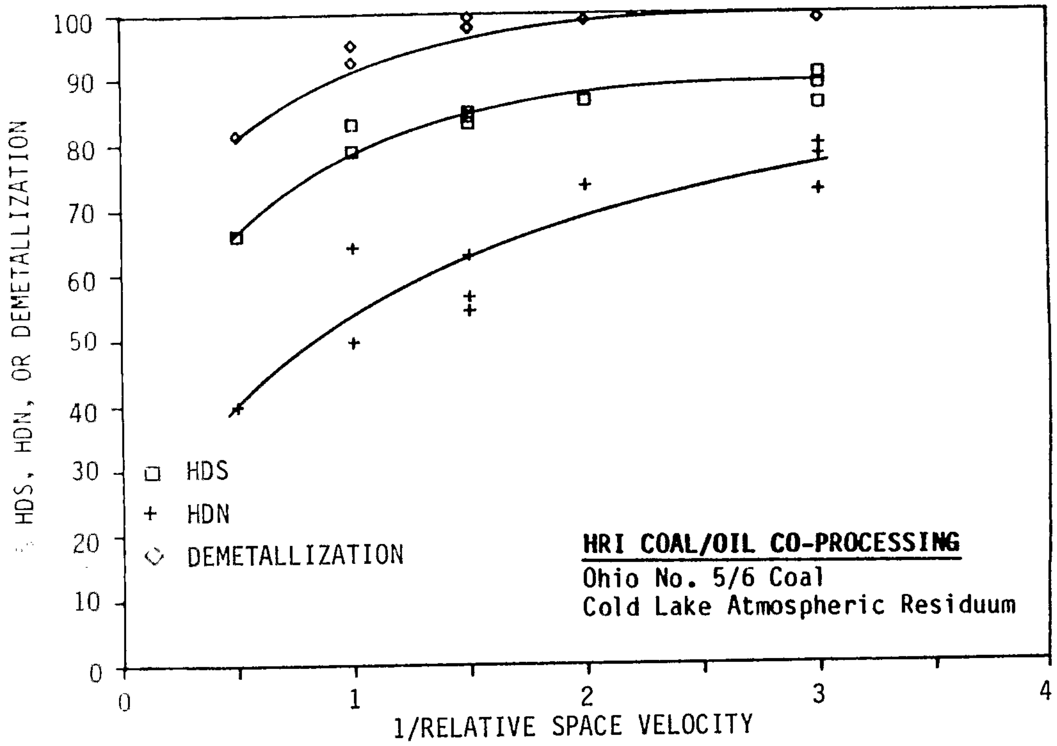

FIGURE 11. HDS, HDN, AND DEMETALLIZATION

Product Characterization

The products from coal/oil co-processing will fit into the existing markets for liquid fuels. An overview of the coal/oil co-processing products, their probable dispositions and possible further upgrading required, is shown in Table 6.

The naphtha from co-processing will go to gasoline blending pools. To prepare a high octane gasoline blendstock, the coal/oil co-processing naphtha will be hydrotreated and catalytically reformed. As shown in Figure 12, the coal/oil co-processing naphtha contains higher concentrations of naphthenes and aromatics compared to an H-Oil® Process naphtha derived from processing Cold Lake atmospheric residuum. The resulting product from catalytic reforming will have a higher octane number, with higher volumetric yield, at lower operating severity.

The mid-distillate and VGO products from coal/oil co-processing are extremely low in sulfur and considerably lower in nitrogen compared to products from direct coal liquefaction (see Table 7). These products could be combined and used as a low sulfur fuel oil or turbine fuel for utility application, without further upgrading.

TABLE 6

PRODUCT CHARACTERIZATION
OVERVIEW OF CO-PROCESSING PRODUCTS

Co-Processing Product	Nominal Boiling Range	Probable Disposition	Possible Further Upgrading
Naphtha	IBP-390°F	Gasoline	Hydrotreating and Catalytic Reforming
Mid-Distillates	390-500°F 500-650°F	Jet Fuel Diesel Fuel No. 2 Fuel Oil Turbine Fuel* No. 6 Fuel Oil	Hydrotreating
Vacuum Gas Oils	650-850°F 850-975°F	Conversion No. 6 Fuel Oil Turbine Fuel* Recycle to Reactor	Hydrotreating, Fluid Catalytic Cracking, Hydrocracking
Resid (Excluding Solids)	975°F+	No. 6 Fuel Oil Recycle to Reactor	
Resid (Including Solids)	975°F+	Partial Oxidation Direct Combustion Solids Separation Recycle to Reactor	Flaking, Fluid Coking

*Including oil-fired combined cycle electric power generation.

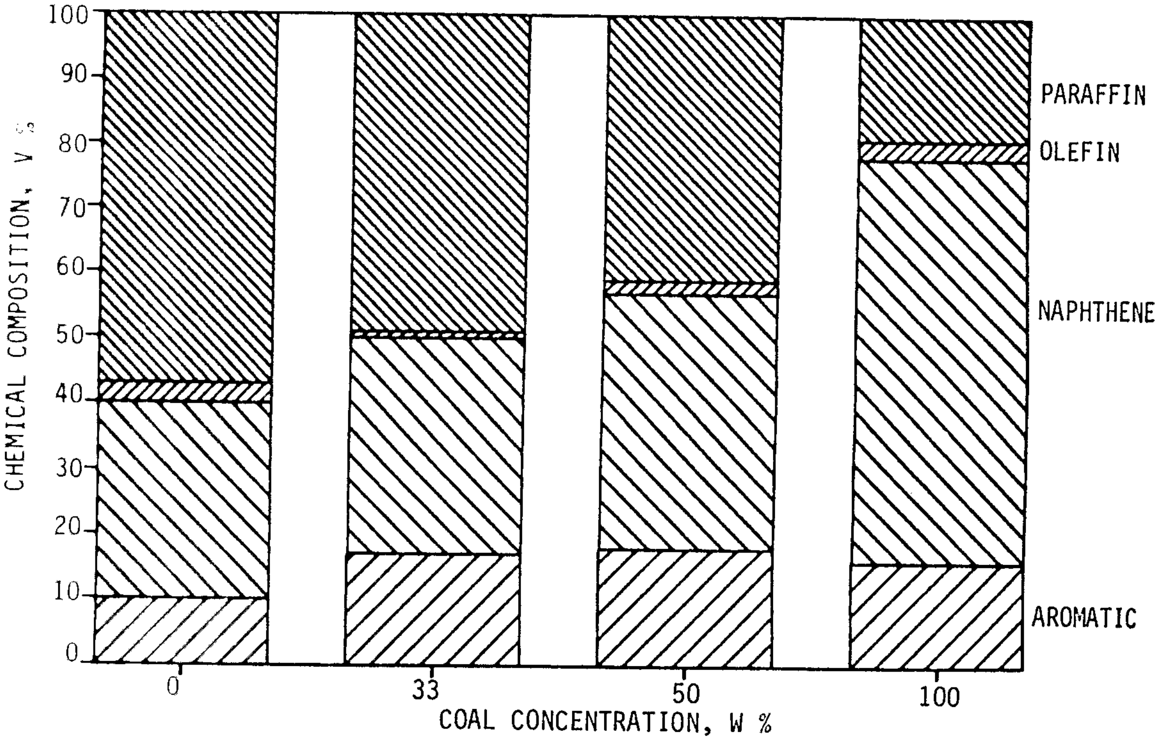

FIGURE 12. CHEMICAL COMPOSITION OF NAPHTHA

TABLE 7

PRODUCT CHARACTERIZATION

MID-DISTILLATE

% COAL FEED	0	33-50	100
°API	32	29	23
Hydrogen, W %	12.5	12.0	11.0
Sulfur, W %	0.7	< 0.1	<0.1
Nitrogen, W %	0.2	0.2	0.3
Cetane Index	41	36	28

VACUUM GAS OIL

% COAL FEED	0	33-50	100
°API	19	15	9
Sulfur, W %	1.3	0.2	<0.1
Nitrogen, W %	0.3	0.35	0.6

Economic Screening Studies

Screening studies were done to evaluate the relative economics of the coal/oil co-processing options demonstrated in Bench Run No. 1 (single-stage). The objective of this economic screening study was to identify the preferrred oil-to-coal feed ratio and operating conditions. Some coal/oil co-processing vacuum bottoms processing options were also evaluated.

The economic studies are based on evaluating coal/oil co-processing as an add-on to an existing petroleum refinery. It was assumed that residuum was available from the refinery and utilities and offsites were also available. It was further assumed that the refinery would accept the coal/oil co-processing products after appropriate upgrading.

All facilities required for the addition of coal/oil co-processing to the existing refinery were specified, including:

- Coal Preparation (including receipt, storage, crushing and drying).
- Co-Processing
- Bottoms Processing
- Hydrogen Manufacture
- Product Treating/Upgrading
- Utility/Offsite Tie-ins

A summary of the cases evaluated is provided in Table 8. In the base Cases 1-5 the bottoms from coal/oil co-processing are coked, and hydrogen is produced via steam reforming of natural gas. Each case is based on 3,000 TPSD of total coal plus oil feed. In Cases 1-3 the coal concentration increases from 33 to 67 W %, at otherwise constant operating conditions. Note that as the coal concentration increases, so does the amount of recycle required. Case 4 is based on high conversion at 33 W % coal and Case 5 is based on low conversion at 50 W % coal. Bottoms processing alternatives are evaluated in Case 4A (partial oxidation). In Case 4A the coal/oil co-processing bottoms are used to manufacture hydrogen. Results are summarized in Table 9.

TABLE 8

ECONOMIC SCREENING STUDIES
SUMMARY OF CASES

<table>
<tr><th>CASE</th><th>1</th><th>2</th><th>3</th><th>4</th><th>4A</th><th>5</th></tr>
<tr><td>Overall Feed Rate, TPSD</td><td colspan="6">< ------------------ 3000 ----------------- ></td></tr>
<tr><td>Percent Coal Feed</td><td>33</td><td>50</td><td>67</td><td>33</td><td>33</td><td>50</td></tr>
<tr><td>975°F$^+$ Conversion, W %</td><td>74</td><td>75</td><td>70</td><td>84</td><td>84</td><td>59</td></tr>
<tr><td>Co-Processing Bottoms Processes</td><td colspan="4">< -------- Coking ---------- ></td><td>POX</td><td>Coking</td></tr>
<tr><td>Hydrogen Source</td><td colspan="4">< ---- Steam Reforming ----- ></td><td>POX</td><td>Steam Reforming</td></tr>
<tr><td>Recycle, W % of FF</td><td>-</td><td>50</td><td>115</td><td>-</td><td>-</td><td>50</td></tr>
</table>

TABLE 9

ECONOMIC SCREENING STUDIES
SUMMARY OF RESULTS

<table>
<tr><th>CASE</th><th>1</th><th>2</th><th>3</th><th>4</th><th>4A</th><th>5</th></tr>
<tr><td>Percent Coal Feed</td><td>33</td><td>50</td><td>67</td><td>33</td><td>33</td><td>50</td></tr>
<tr><td>Feedrate, TPSD</td><td colspan="6">< ------------------ 3000 ------------------ ></td></tr>
<tr><td>C$_4$-975°F Product, BPSD</td><td>14100</td><td>14200</td><td>12750</td><td>14850</td><td>14000</td><td>12500</td></tr>
<tr><td>Estimated Investment, MM$</td><td>240</td><td>260</td><td>300</td><td>260</td><td>300</td><td>249</td></tr>
<tr><td>Operating Cost, MM$/Yr</td><td>93</td><td>89</td><td>87</td><td>97</td><td>93</td><td>87</td></tr>
<tr><td>By Product Revenues, MM$/Yr</td><td>(5)</td><td>(5)</td><td>(6)</td><td>(5)</td><td>(13)</td><td>(6)</td></tr>
<tr><td>Net Cost, MM$/Yr</td><td>88</td><td>84</td><td>81</td><td>92</td><td>80</td><td>81</td></tr>
<tr><td>First-Year Product Cost, MM$/B</td><td>23.03</td><td>22.24</td><td>24.87</td><td>22.89</td><td>22.39</td><td>24.01</td></tr>
</table>

Product costs are shown versus percent coal in the fresh feed in Figure 13. Product cost components (capital, other operating cost, residuum and coal) are shown separately. As the coal concentration increases, the relative contribution of feedstock costs decreases as the cost of coal ($1.25/MMBtu) is considerably less than the cost of residuum ($15/B or about $2.50/MMBtu). The cost of capital and other operating expenses (labor, maintenance, natural gas, utilities), however, increases with coal concentration. As shown in this figure, 50% coal is slightly preferred to 33% coal with product costs of about $22-23/Bbl. The product cost at 67% coal is considerably higher.

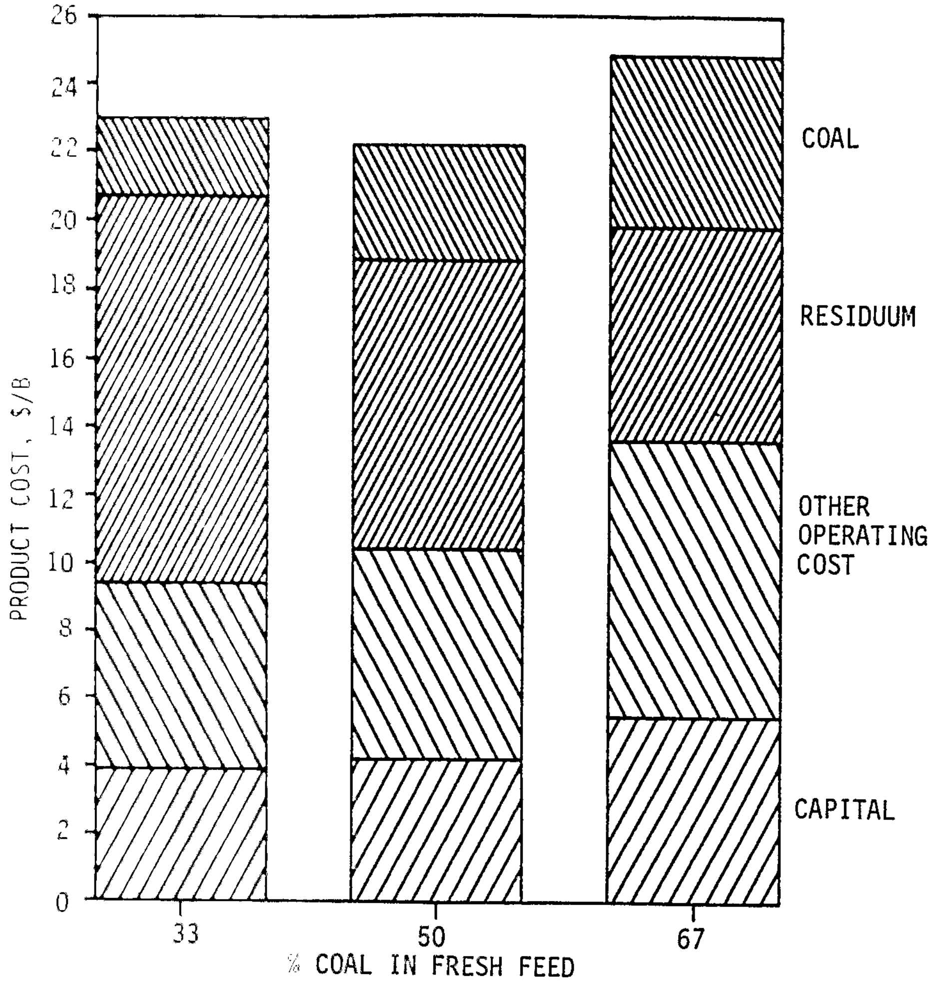

FIGURE 13. PRODUCT COST COMPONENTS

Product cost is shown as a function of 975°F$^+$ conversion in Figure 14. This figure shows that high conversion operations are preferred. The sensitivity of these results to the assumed price of residuum and coal is shown in Figures 15 and 16. These figures show that 33% coal is attractive with the cost of residuum below about $10/B.

The economic screening studies show that 50% coal in the fresh feed and high conversion operations are preferred. The economics at 33% coal are similar, however, they are very sensitive to the price of oil.

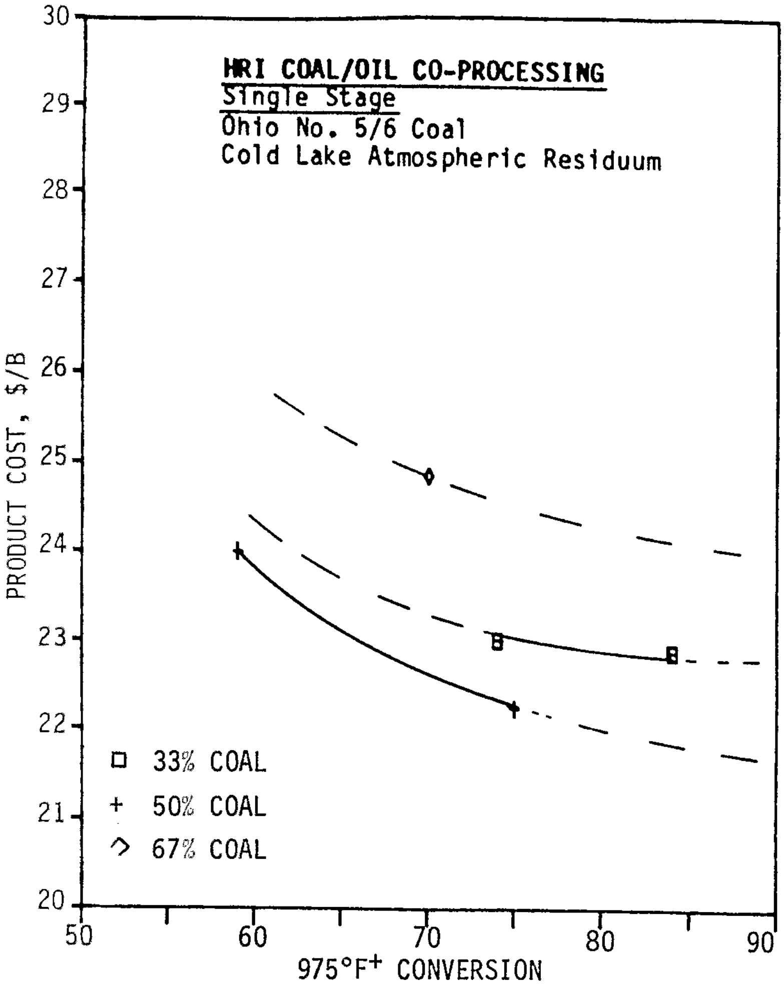

FIGURE 14. PRODUCT COST VERSUS 975°F$^+$ CONVERSION

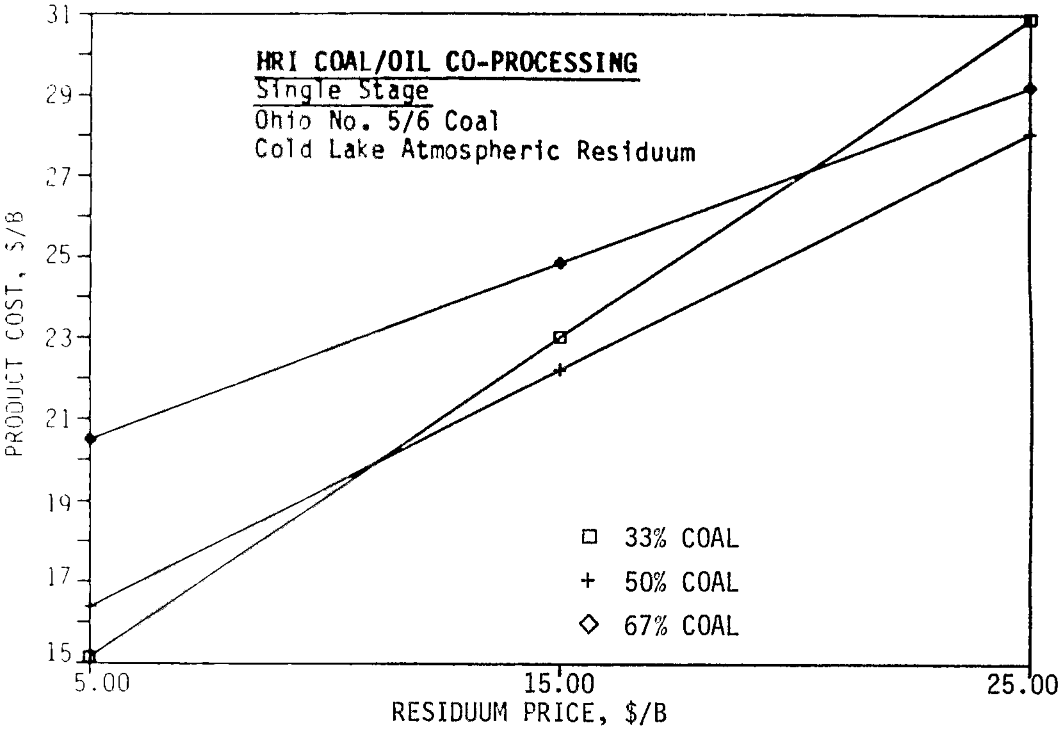

FIGURE 15. PRODUCT COST VERSUS RESIDUUM PRICE

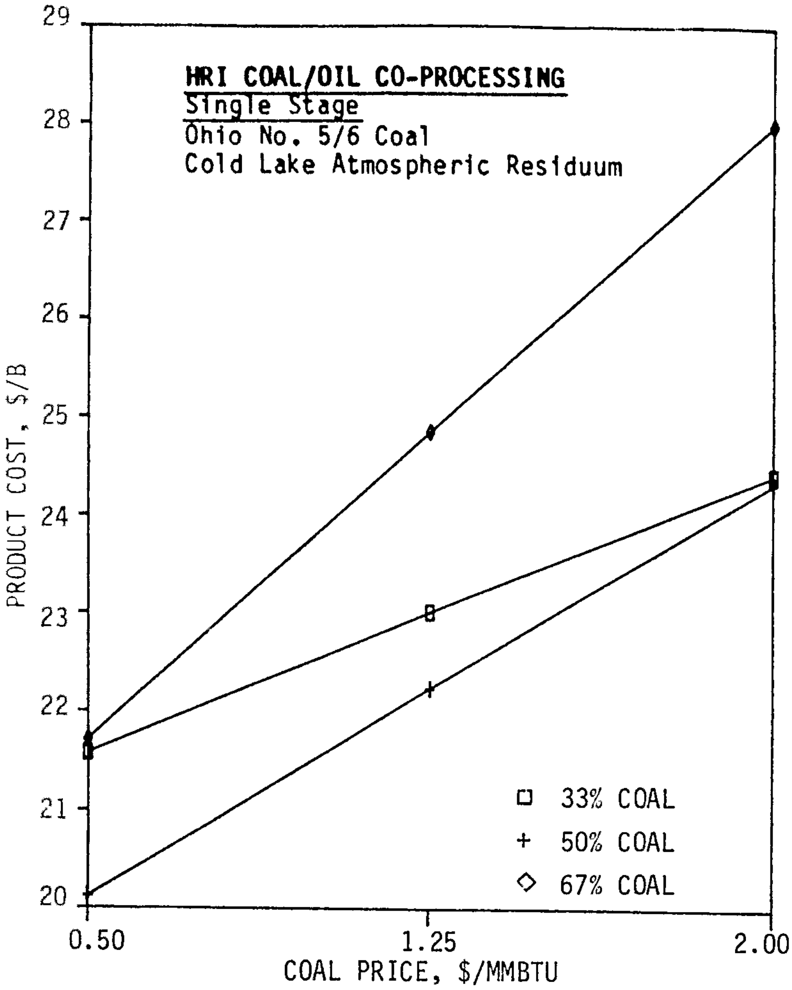

FIGURE 16. PRODUCT COST VERSUS COAL PRICE

Commercial Planning

The final technical task of HRI's Coal/Oil Co-Processing Program - Phase 1 was commercial planning studies. The purpose of these studies was to identify potential sites for the commercial application of coal/oil co-processing in the Great Lakes Region in terms of:

- The confluence of raw materials supply.
- Availability of construction and operating manpower, material, and expertise.
- Availability of coal handling, process, utility and offsite facilities.

The studies have identified a number of attractive locations in the Great Lakes Region, where all of the infrastructure required for coal/oil co-processing is currently in place and available. A single site in Warren, Ohio, has been identified for the location of a prototype commercial co-processing plant. Ohio-Ontario Clean Fuels, Inc. has teamed with HRI and Stearns Catalytic Corporation and submitted proposals to the U. S. Department of Energy and the Ohio Coal Development Office for support of this project.

CONCLUSIONS

Phase 1 of HRI's Coal/Oil Co-Processing Program has demonstrated the technical feasibility of coal/oil co-processing in both single- and two-stage process configurations. In continuous bench unit operations, 90 W % 975°F$^+$ conversion was achieved with up to 90% hydrodesulfurization and 80 W % hydrodenitrogenation. The two-stage configuration is technically preferred to achieve high 975°F$^+$ conversion (>90 W % MAF) and product quality. Economically, operation is also preferred at high conversion and at 50 W % coal in the fresh feed. Based on the excellent results obtained to date, plans for a prototype commercial plant have been developed.

ACKNOWLEDGEMENTS

HRI would like to acknowledge the contributions of EPRI, OOSFC and ARC to this program. ARC performed the feedstock characterizations and autoclave studies. OOSFC was responsible for the commercial planning activities. All parties participated in the technical management and direction of this program.

REFERENCES

(1) Comolli, A. G., et al, "New Technology Concept for Two-Stage Liquefaction of Coal", Final Summary Report, DE-60017-10, February 1986.

(2) Comolli, A. G., et al, "New Technology Concept for Two-Stage Liquefaction of Coal", Topical Report No. 1, DE-60017-TOP-1, August 1985.

(3) Wisdom, L. I., and J.J. Colyar, "High Conversion H-Oil Processing of Cold Lake and Lloydminster Residues in Support of Husky's Bi-Provencial Project", 3rd International Conference on Heavy Crude and Tar Sands - UNITAR/UNDP Information Center, July 1985.

CO-PROCESSING OF WYODAK SUBBITUMINOUS COAL AND COLORADO SHALE OIL

R. L. Miller and R. M. Baldwin

Colorado School of Mines

ABSTRACT

Results are reported for a series of single-stage batch reactor experiments in which Wyodak subbituminous coal and shale oil derived from medium grade Colorado shale were co-processed at both high severity and low severity reaction conditions. Distillate yields in excess of 60 wt% MAF coal were obtained at 825°F reaction temperature with hydrogen feed gas. Low severity runs at 600°F with carbon monoxide/water as reducing agent gave distillate yields in excess of 85 wt% MAF coal. Results from blank shale oil experiments at mild reaction conditions suggested that shale oil residuum reactivity was enhanced in the presence of coal or primary coal-derived products. Prehydrotreatment of the shale oil, feed coal reactivity, and use of a disposable coal dissolution catalyst were shown to affect process performance.

1. INTRODUCTION

The concept of simultaneously converting both coal and non-coal-derived residual oil to distillate products has intrigued researchers for many years (1-6). This type of once-through process, termed co-processing or liquefaction co-processing, has several potential advantages over conventional direct liquefaction processes:

- Two low grade feeds are converted to higher quality liquid products
- Recycle solvent requirements are reduced or eliminated resulting in lower capital investment and operating costs
- Existing petroleum refinery capacity can potentially be utilized with minimal process modification

Furthermore, as we will demonstrate, synergistic interactions between coal and heavy oil can result in larger distillate yields than could be expected from conventional coal liquefaction processes. However, liquefaction co-processing still suffers from some technical problems which must be solved before commercial development can proceed. Most non-coal-derived heavy oils derived from petroleum, oil shale, or tar sands are less aromatic than coal-derived liquids, and not surprisingly, have been shown to be rather poor coal dissolution and hydrogen donor solvents. To compensate, very severe thermal reaction conditions and/or expensive heterogeneous catalysts have been utilized in most prior co-processing studies to obtain sufficiently high levels of coal conversion. This has resulted in increased hydrogen consumption, excessive cracking of distillable liquids to gases, and overall poor process performance.

One important exception has been the studies of Ignasiak and co-workers who have reported results of a two stage co-processing scheme in which coal and bitumen are reacted in the first stage at mild reaction conditions using CO/H_2O as reducing gas (7). Further upgrading and hydrogenation of the liquid products is accomplished in a conventional catalytic hydrotreater using hydrogen gas. Evidence of a coal/bitumen synergistic effect in the first stage has been reported. This synergism acts to increase distillate yield, suppress coke formation, and reduce hydrocarbon gas make.

An alternate approach to the problem of increasing coal dissolution has been employed in the present study. Results of exploratory liquefaction co-processing experiments in our laboratory demonstrated that selected non-coal-derived heavy oils, each with a nitrogen content in excess of about 1.2 wt%, could be used to dissolve Wyodak subbituminous coal at typical coal liquefaction reaction conditions (8). This effect was not surprising, since partially hydrogenated quinoline-type nitrogen compounds such as tetrahydroquinoline (THQ) have been shown to greatly enhance coal dissolution in model compound studies (9-11). Based on encouraging results from the exploratory screening runs, additional co-processing studies using promising coal/heavy oil combinations were undertaken. Results of these experiments suggested that shale oil was one of the more promising non-coal-derived heavy oils for use as a liquefaction co-processing feed.

The objective of this paper is to report yield and conversion results from liquefaction co-processing experiments using Wyodak subbituminous coal and shale oil derived from medium grade oil shale. Runs were completed at both high and low severity reaction conditions using a single-stage one pass process scheme. The effects of feed coal reactivity, mild hydrotreatment of the shale oil prior to co-processing, and use of a disposable coal dissolution catalyst were studied. Experiments designed to demonstrate the existence of enhanced distillate yield via a coal/shale oil synergism were also completed.

2. EXPERIMENTAL PROCEDURE

MATERIALS

Coal

Wyodak subbituminous coal samples Wyo-1 and Wyo-3 were used as feed coals in the co-processing experiments. Selected properties of the coals are presented in Table I. These samples were obtained from the Canyon E and Anderson seams at Carter Coal Company's Rawhide Mine located in the Powder River Basin of north-eastern Wyoming. Sampling and preparation details of the coals have been reported (12,13). Previous reactivity studies performed on four Wyodak sub-bituminous coals including Wyo-1 and Wyo-3 indicated that Wyo-3 was a relatively reactive coal at typical direct liquefaction reaction conditions (14). The high degree of reactivity was primarily attributed to the high organic sulfur and reactive maceral (vitrinite and exinite) contents of Wyo-3 coal. Wyo-1 coal was found to be much less reactive at liquefaction reaction conditions (14). Coal samples were dried to less than 1.0 wt% moisture content before use in liquefaction co-processing experiments.

Shale Oil

Two shale oil samples were used in the liquefaction co-processing runs. Solvent A-5 was a full boiling range sample of shale oil obtained from the Western Research Institute (formerly the Laramie Energy Technology Center of the Department of Energy). This sample was produced from thermal retorting of medium grade (29 gal/ton) Colorado oil shale. Solvent A-6 was prepared by mildly hydrotreating a portion of sample A-5 in a two liter batch Autoclave Magnedrive II reactor at 650°F for one hour with an initial cold hydrogen pressure of 2000 psig. Nalcomo 477 cobalt molybdate catalyst was used to hydrotreat the shale oil. Catalyst samples were thermactivated at 1000°F for two hours in a muffle furnace prior to use. Approximately 0.6 wt% hydrogen was consumed by the shale oil during hydrotreating. Properties of shale oil samples A-5 and A-6 are presented in Table II. Approximately 50 wt% of the nitrogen in these samples existed in quinoline-type or hydroquinoline-type molecular structures.

Feed Gas

Liquefaction experiments were completed using either commercial grade hydrogen or carbon monoxide as feed gas. Each gas was fed to the liquefaction reactor via a hydraulic compression system.

Disposable Catalysts

Iron oxide provided by the Kerr-McGee Corporation and carbon disulfide were used as disposable coal dissolution catalysts in some co-processing runs using hydrogen as feed gas. Each of these materials was added to the reaction mixture in an amount equal to 5 wt% of the dry feed coal. Iron sulfate (5 wt% dry feed coal) was used as coal dissolution catalyst in selected CO/H_2O experiments.

EQUIPMENT AND PROCEDURES

A schematic diagram of the experimental methods used in this project is shown in Figure 1. Completion of these analyses allowed the product yields listed in Table III to be monitored for each liquefaction experiment.

The liquefaction co-processing experiments were carried out in a 60 cm^3 stirred microautoclave reactor system designed and constructed at the University of Wyoming. The reactor is similar to larger Autoclave batch reactors except that heating is accomplished with an external high temperature furnace. At the end of each run, the reactor and its contents are quenched with an icewater batch. This reactor system can provide the benefits of small tubing bomb reactors (quick heatup (~ 2 min. from room temperature to 850°F) and cooldown (~30 sec. back to room temperature)), while at the same time insuring sufficient mechanical agitation of the reactants with an Autoclave Magnedrive II stirring assembly to minimize hydrogen mass transfer effects. Figure 2 shows a typical time-temperature profile obtained using the microautoclave reactor system. The system is also designed so that the reactor pressure is very nearly constant throughout an experiment. Two iron-constantan thermocouples attached to a Fluke 2175A digital thermometer were used for temperature measurements. One thermocouple measured the temperature of the reactor contents, while the other measured the temperature of the reactor wall. Reactor pressure was monitored using a 0 - 5000 psi Marsh pressure gauge.

Co-processing experiments were completed at two distinct sets of reaction conditions as shown in Table IV. The high severity conditions are representative of conventional direct coal liquefaction processes using hydrogen gas as reducing agent. Runs using carbon monoxide and water as reducing agent were completed at lower reaction temperature where hydrogen production via the aqueous water-gas shift reaction is favored. In these runs, distilled water in an amount equal to 50 wt% of the dry feed coal was charged to each reactor run.

Gaseous products were analyzed using gas chromatography. Water and distillate yields were measured by distilling portions of the combined liquid-solid product mixture to an 850°F endpoint in a microdistillation apparatus. Additional portions of the liquid-solid product mixture were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and pyridine. Details of the experimental procedures used in this work have been reported (8).

3. DISCUSSION

Using data collected with the analytical procedures described, detailed yield and conversion results were computed for each liquefaction co-processing run. Details of the computational methods used in this study have been described previously (15). For purposes of the present discussion, process performance will be monitored using the following three parameters: C_4-850°F distillate yield (wt% MAF coal basis), hydrogen utilization efficiency, and pyridine conversion (wt% MAF basis). Hydrogen utilization efficiency is defined as the mass of C_4-850°F distillate produced per unit mass of hydrogen consumed. The value of this parameter provides a good indication of the overall efficiency of hydrogen consumption in the co-processing experiments. Pyridine conversion is defined as a measure of the extent of conversion of all feeds (coal and non-coal-derived heavy oil) to pyridine soluble products. However, since both A-5 and A-6 shale oil samples were completely soluble in pyridine, and negligible coking of the shale oil occurred at the reaction conditions studied, pyridine conversion values reported in this paper are a direct measure of the extent of coal conversion in the co-processing runs.

Approximately 15 high severity co-processing runs and 30 low severity co-processing runs were completed in this study. The following subsections discuss the results obtained at each set of reaction conditions.

RESULTS FROM HIGH SEVERITY CO-PROCESSING RUNS

Effect of Shale Oil Prehydrotreatment

The results from liquefaction co-processing experiments using Wyo-3 coal and A-5 or A-6 shale oil at 825°F and 2000 psig initial cold hydrogen pressure are shown in Figures 3 - 5. It is apparent from this data that mild hydrotreatment of the shale oil prior to co-processing greatly enhances process performance. Distillate yields of 55 - 60 wt% (MAF coal), hydrogen utilization efficiencies of about 20, and pyridine coal conversion values of 68 - 85 wt% were obtained using Wyo-3 coal and A-6 shale oil. Similar enhancement effects were seen using Wyo-1 feed coal. Previous co-processing studies by Kerr-McGee using Ohio No. 5

bituminous coal and Canadian Cold Lake bitumen have also demonstrated the beneficial effect of heavy oil hydrotreatment prior to co-processing (15).

At least two possible reasons exist for the effects shown in Figures 3 - 5. First, mildly hydrotreated A-6 shale oil acted as a more powerful hydrogen donor solvent than A-5 in promoting coal conversion and distillate production. Secondly, the quinoline-type nitrogen content of A-5 was approximately 0.7 wt%. Mild hydrotreatment of A-5 presumably converted a number of the quinoline structures to hydroquinoline structures. As mentioned earlier in this paper, hydroquinolines such as tetrahydroquinoline (THQ) have been shown to actively promote coal solvation in direct liquefaction. The data shown in Figures 3 - 5 suggest that a similar effect occurred during liquefaction co-processing with A-5 shale oil.

Effect of Feed Coal Reactivity

Figure 6 presents a comparison of yield results for co-processing runs using Wyo-1 and Wyo-3 coal and A-6 shale oil. These data show that liquefaction co-processing performance is a strong function of feed coal reactivity as measured by distillate production, extent of coal dissolution to pyridine soluble products, and hydrogen utilization efficiency. As shown in Figure 7, the detrimental effects of low feed coal reactivity can be partially offset by use of a disposable catalyst such as iron oxide/carbon disulfide. Thus, it appears that co-processing performance can be greatly enhanced by utilizing a feed coal which is quickly and easily dissolved at liquefaction reaction conditions. This result may help explain a previously observed synergism between coal and heavy oil. Several researchers have attributed this synergism to attack by coal-derived free radicals on selected weak linkages in the complex heavy oil molecular structure, which in turn helps increase heavy oil reactivity towards cracking to distillate.

RESULTS FROM LOW SEVERITY CO-PROCESSING RUNS

Several previous studies have reported the successful liquefaction of low rank coal at mild reaction conditions using carbon monoxide and water in place of hydrogen gas (7,16,17). In these runs, hydrogen was provided by the aqueous phase water-gas shift (WGS) reaction involving carbon monoxide and water. A number of catalysts such as alkali metal salts, alkaline earth salts, and organic nitrogen bases have been shown to catalyze the aqueous phase WGS reaction (18). In planning this series of low severity experiments, it was hypothesized that the basic nitrogen contents of A-5 and A-6 shale oils would also catalyze the WGS reaction to some extent. As shown in the following discussion, this hypothesis appears to be correct for the co-processing runs with A-6 shale oil.

Effect of Shale Oil Prehydrotreatment

Figure 8 shows distillate yield results from co-processing runs completed using Wyo-3 coal and either A-5 or A-6 shale oil at 600°F and 1500 psig initial cold CO pressure. This data clearly shows that mild hydrotreatment of the shale oil greatly enhances co-processing performance. Coal conversion also increased significantly when A-6 shale oil was used in place of A-5 shale oil. Distillate yields of over 85 wt% MAF coal (58 wt% MAF coal and 850°F+ shale oil) and pyridine soluble coal conversions of nearly 60 wt% MAF basis were obtained with A-6. The enhancement at low severity conditions can be attributed to: 1) increased hydrogen donor ability of the hydrotreated shale oils and, 2) increased concentration of partially hydrogenated basic nitrogen compounds such as tetrahydroquinoline and piperidinopyridine in the shale oil. As discussed earlier, these compounds are known to promote coal dissolution and catalyze the aqueous phase water-gas shift reaction.

Effect of Reaction Temperature

Figures 9 and 10 present yield and conversion results for co-processing runs completed with Wyo-3 and A-6 at 600°F and 650°F. These data show that process performance improves significantly at lower reaction temperature. This effect can be at least partially attributed to the favorable thermodynamic equilibrium of the water-gas shift reaction at lower temperatures.

Effect of Initial Carbon Monoxide Pressure

The effect of varying the initial CO pressure is illustrated in Figures 11 and 12. At 600°F reaction temperature, increasing the CO pressure from 1000 to 1500 psig more than doubled the distillate yield and greatly enhanced coal conversion over the entire range of reaction times studied.

These data indicate that relatively high pressure is required to achieve sufficient CO solubility in the aqueous phase for the water-gas shift reaction to proceed at a satisfactory rate.

Effect of Disposable Coal Dissolution Catalyst

As shown in Figure 13, the addition of $FeSO_4$ as a coal dissolution catalyst significantly improved distillate yield and coal conversion when co-processing Wyo-3 coal and A-6 shale oil. Similar improvement was noted with A-5 shale oil and at the other low severity reaction conditions studied. Several previous "blank" shale oil experiments had demonstrated that $FeSO_4$ showed no effect towards catalyzing shale oil cracking reactions. In addition, detailed material balance calculations indicated that the distillate yield increase was greater than could be accounted for solely by the increased level of coal conversion. These results also suggest that the key to successful liquefaction co-processing involves rapid and extensive dissolution of coal to primary products. If sufficient coal conversion can be achieved, overall co-processing performance appears very attractive.

Results from Blank A-6 Shale Oil Runs

In an attempt to estimate the amounts of distillate derived from coal and from shale oil, several blank shale oil runs (no coal added) were completed. Results from both high severity and low severity blank runs are shown in Figure 14. These data were then used to estimate the amount of distillate attributable to the shale oil feed in each co-processing run. Estimates of the coal-derived distillate production were computed by assuming that half of the total coal-derived cyclohexane soluble product was distillate. Results of these calculations are shown in Figure 15. Both low severity and high severity runs are included in this figure for comparison purposes. At each set of reaction conditions, additional distillate in excess of that predicted by the blank shale oil runs was obtained. Thus, it appears likely that the reactivity of shale oil residuum towards distillate production is enhanced in the presence of coal or primary coal-derived products.

4. SUMMARY AND CONCLUSIONS

A series of liquefaction co-processing experiments has been completed using two Wyodak subbituminous coals and two shale oil feeds. Both high severity (hydrogen gas) and low severity (carbon monoxide gas and water) reaction conditions were evaluated.

Results from the high severity runs indicated that distillate yields in excess of 60 wt% MAF coal could be achieved in a single-stage one pass process mode. Prehydrotreatment of the shale oil, feed coal reactivity, and use of a disposable coal dissolution catalyst each affect process performance at high severity conditions.

Over 85 wt% (MAF coal basis) distillate yield was obtained using Wyo-3 coal and A-6 shale oil at low severity reaction conditions. Prehydrotreatment of the shale oil, lower reaction temperature, higher reaction pressure, and use of a disposable coal dissolution catalyst all contributed to improved process performance in the low severity runs. Results from blank shale oil experiments suggested that distillate yield could be maximized by co-processing coal and shale oil rather than processing the two feeds separately.

5. REFERENCES

1. Yan, T.Y., and W.F. Espenscheid, Fuel Proc. Tech., 7, 121, (1983).

2. Shinn, J.H., A.J. Dahlberg, C.W. Kuehler, and J.W. Rosenthal, "The Chevron Co-Refining Process," Proceedings of the Ninth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California, (May 1984).

3. Kelly, J.F., S.A. Fouda, P. Rahimi, and M. Ikura, "CANMET Coprocessing: A Status Report," CANMET Coal Conversion Contractors' Review Meeting, Calgary, Alberta, Canada, (November 1984).

4. Curtis, C.W., J.A. Guin, M. Pass, and K.J. Tsai, ACS Fuel Chem. Preprints, 29, 5, 155, (1984).

5. Moschopedis, S.E., R.W. Hawkins, and J.G. Speight, Fuel Proc. Tech., 5, 213, (1982).

6. Miller, R.L., "Use of Non-Coal-Derived Heavy Solvents in Direct Coal Liquefaction," Proceedings of the Tenth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California, (April 1985).

7. Ignasiak, B., G. Kovacik, T. Ohuchi, L. Lewkowicz, and M.P. duPlessis, "Two-Stage Liquefaction of Subbituminous Alberta Coals in Non-Donor Solvents," CANMET Coal Conversion Contractors' Review Meeting, Calgary, Alberta, Canada, (November 1984).

8. Miller, R.L., "Use of Non-Coal Derived Heavy Solvents in Direct Coal Liquefaction," Interim Report for EPRI Project RP 2383-01, (November 1985).

9. Atherton, L.F., and C.J. Kulik, "Advanced Coal Liquefaction," presented at the 1982 AIChE Annual Meeting, Los Angeles, California, (November 1982).

10. McNeil, R.I., D.C. Young, and D.C. Cronauer, Fuel, 62, 806, (1983).

11. Broderick, T.E., "Liquefaction of Wyodak Coal in Tetrahydroquinoline," M.S. Thesis, University of Wyoming, Laramie, Wyoming, (1984).

12. Miller, R.L., "Effect of Wyodak (Wyoming) Coal Properties on Direct Liquefaction Reactivity," Ph.D. Dissertation, Colorado School of Mines, Golden, Colorado, (1982).

13. Silver, H.F., R.G. Corry, and R.L. Miller, "Coal Liquefaction Studies," Final Report for EPRI Projects 779-23 and 2210-1, (December 1982).

14. Miller, R.L., and R.M. Baldwin, Fuel, 64, 1235, (1985).

15. Rhodes, D.E., "Comparison of Coal and Bitumen-Coal Process Configurations," Proceedings of the Tenth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California, (April 1985).

16. Ross, D.S., J.E. Blessing, Q.C. Nguyen, and G.P. Hum, Fuel, 63, 1206, (1984).

17. Hodges, S., and D.E. Creasy, Fuel, 64, 1229, (1985).

18. Elliott, D.C., and L.J. Sealock, I & EC Prod. Res. Dev., 22, 426, (1983).

Table I

PROPERTIES OF WYODAK
SUBBITUMINOUS COALS

Sample	Wyo-1		Wyo-3	
Mine	Rawhide		Rawhide	
Seam	Canyon E		Anderson	
Ultimate Analysis (wt% dry basis)				
Carbon	69.8		58.2	
Hydrogen	4.7		4.3	
Nitrogen	0.8		0.8	
Sulfur	0.3		2.9	
Sulfate		0.0		0.8
Pyritic		0.0		0.8
Organic		0.3		1.3
Oxygen (difference)	18.3		13.9	
Ash	6.1		19.9	
Total	100.0		100.0	
Proximate Analysis (wt% dry basis)				
Ash	6.1		19.9	
Volatile Matter	47.8		45.1	
Fixed Carbon	46.1		35.0	
Total	100.0		100.0	

Table II

PROPERTIES OF FEED SHALE OILS

Feed	A-5	A-6
Wt% Distilled		
Water	0.7	0.1
350°F-	4.2	10.3
350°-500°F	9.6	18.3
500°-650°F	18.8	22.5
650°-850°F	39.0	29.8
850°F+	27.7	19.0
Ultimate Analysis (wt% dry basis)		
Carbon	83.3	84.7
Hydrogen	12.1	12.9
Nitrogen	1.4	1.2
Sulfur	0.5	0.4
Oxygen (difference)	2.7	0.8
Ash	0.0	0.0
Cyclohexane Solubility, wt%	100.0	100.0
Toluene Solubility, wt%	100.0	100.0
Pyridine Solubility, wt%	100.0	100.0

Table III

PRODUCTS MONITORED IN LIQUEFACTION CO-PROCESSING EXPERIMENTS

- Gases

  CO, CO_2, H_2
  $C_1 - C_3$

- Water

- C_4-850°F Distillate

- 850°F+ Pyridine Soluble Residuum

  Oils
  Asphaltenes
  Preasphaltenes

- Pyridine Insoluble Organic Matter (IOM)

Table IV

LIQUEFACTION CO-PROCESSING REACTION CONDITIONS

	High Severity Reaction Conditions	Low Severity Reaction Conditions
Reaction Temperature (°F)	825	600-650
Feed Gas	H_2	CO
Reaction Pressure (psig)	2000	1000-1500
Reaction Time (min)	30-60	15-60
Feed Coal	Wyo-1, Wyo-3	Wyo-3
Feed Shale Oil	A-5, A-6	A-5, A-6
Disposable Catalyst	Fe_2O_3/CS_2	$FeSO_4$

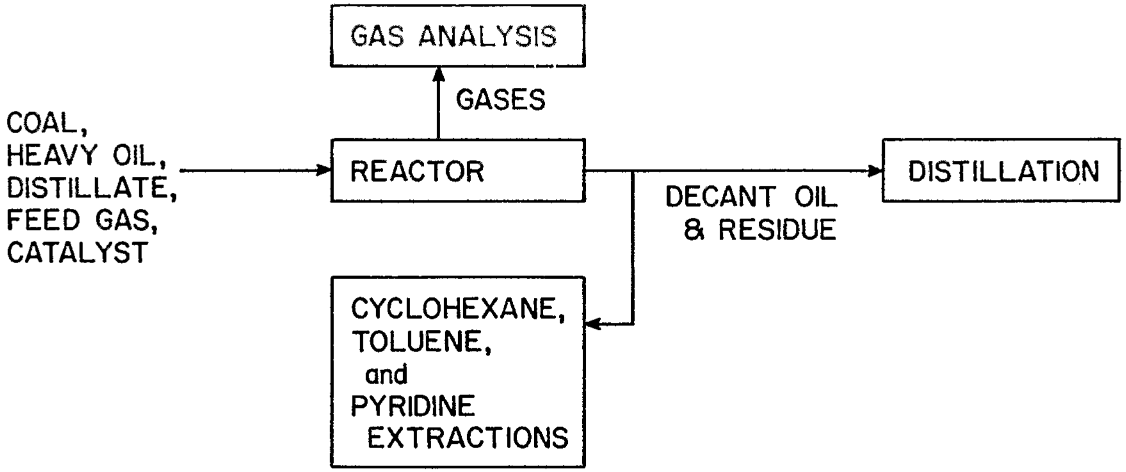

Figure 1. Schematic Diagram of Experimental Procedure

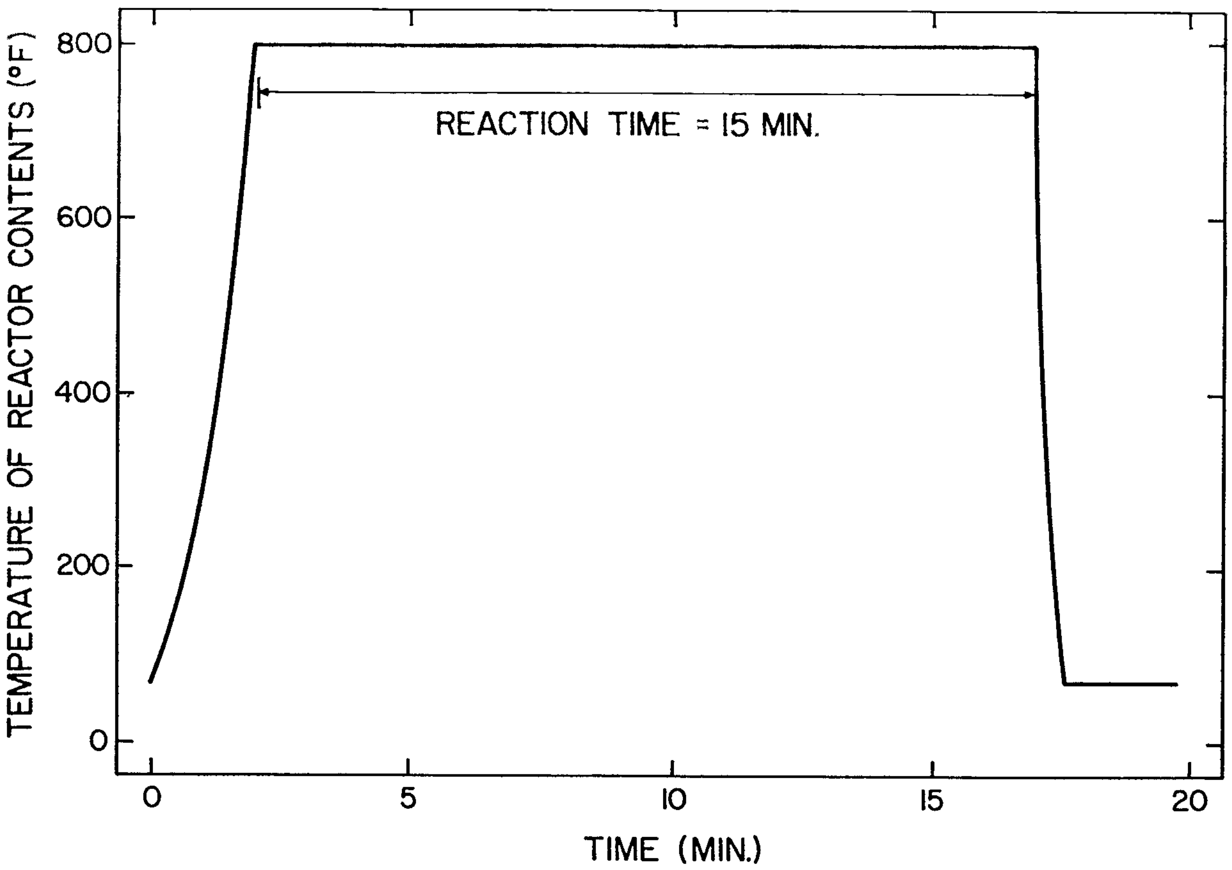

Figure 2. Diagram of Example Time-Temperature Profile for $60\ cm^3$ Microautoclave Reactor System ($800^{\circ}F$ Reaction Temperature, 15 min. Reaction Time)

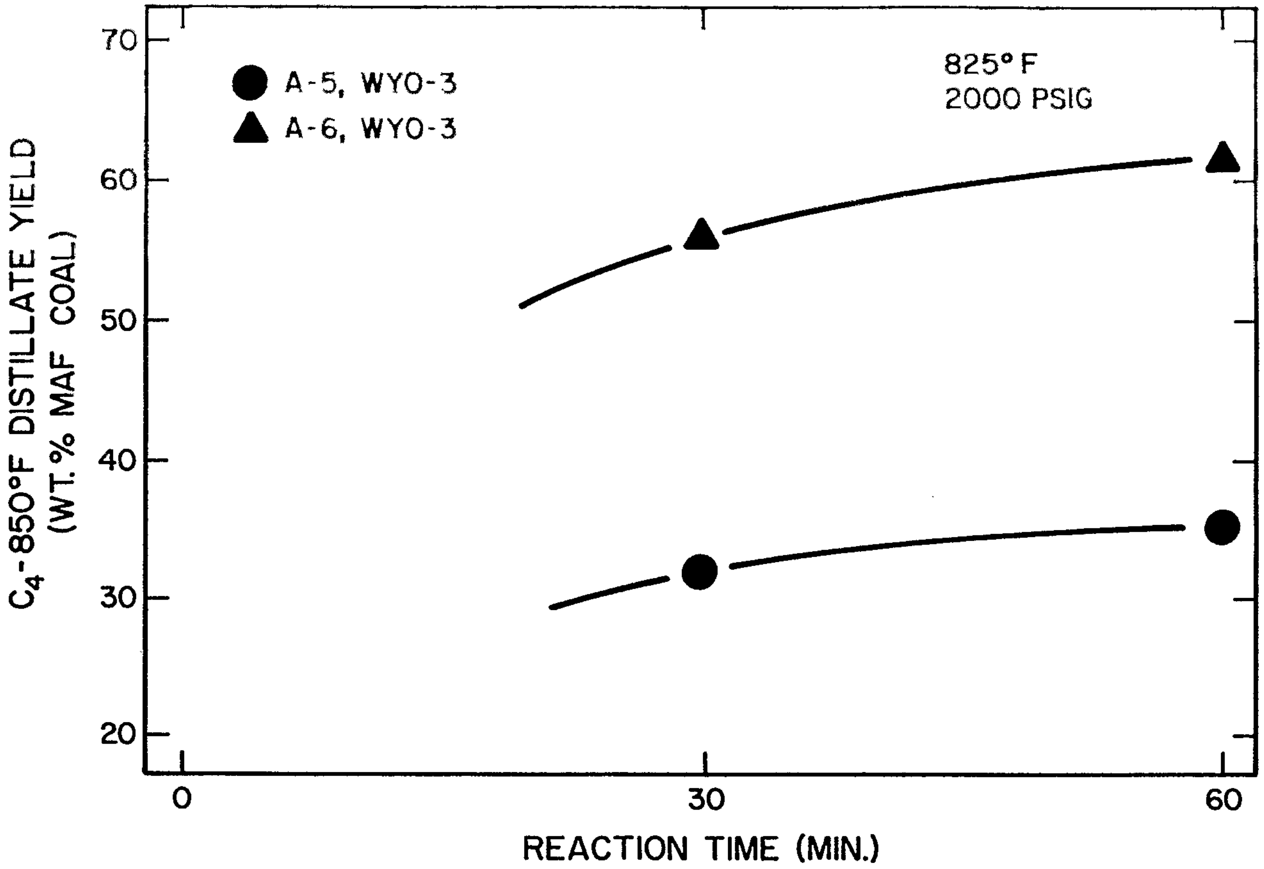

Figure 3. Distillate Yield as a Function of Reaction Time and Shale Oil Feed - High Severity Reaction Conditions

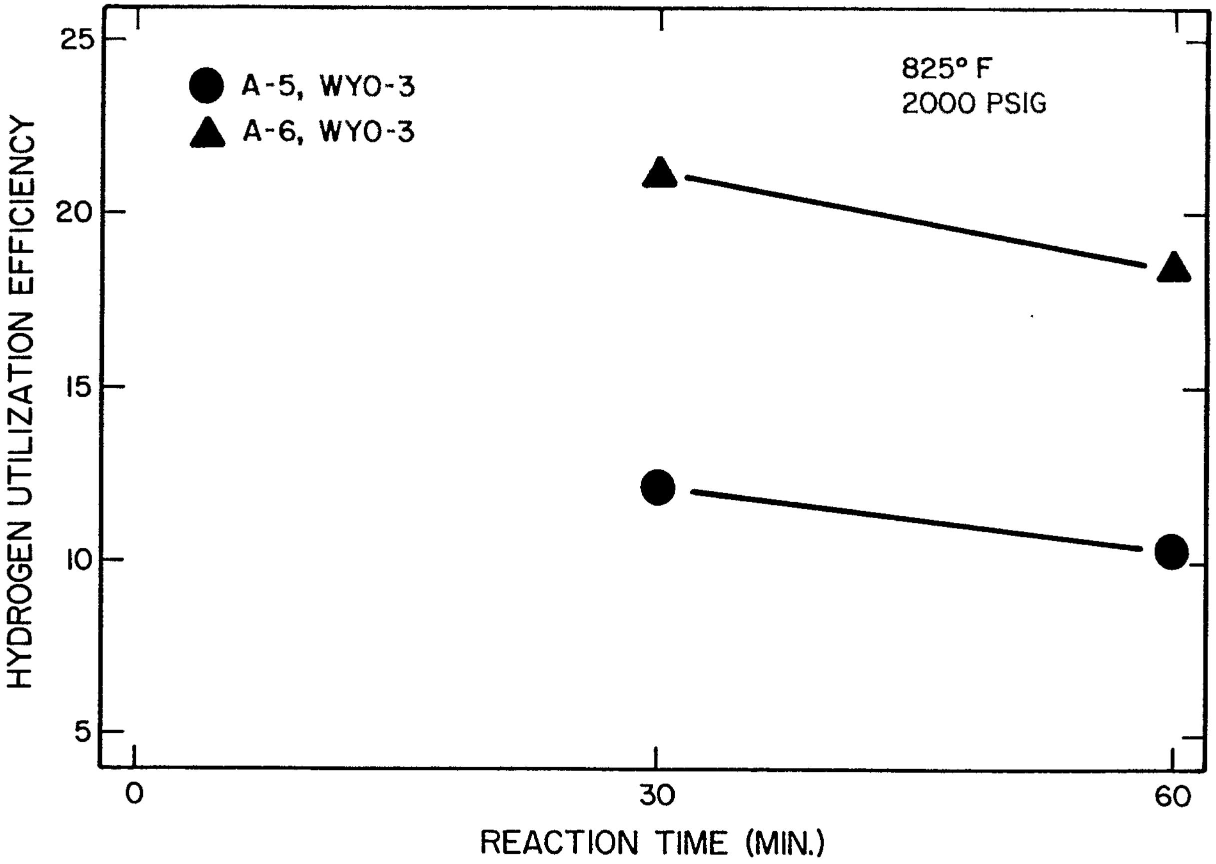

Figure 4. Hydrogen Utilization Efficiency as a Function of Reaction Time and Shale Oil Feed - High Severity Reaction Conditions

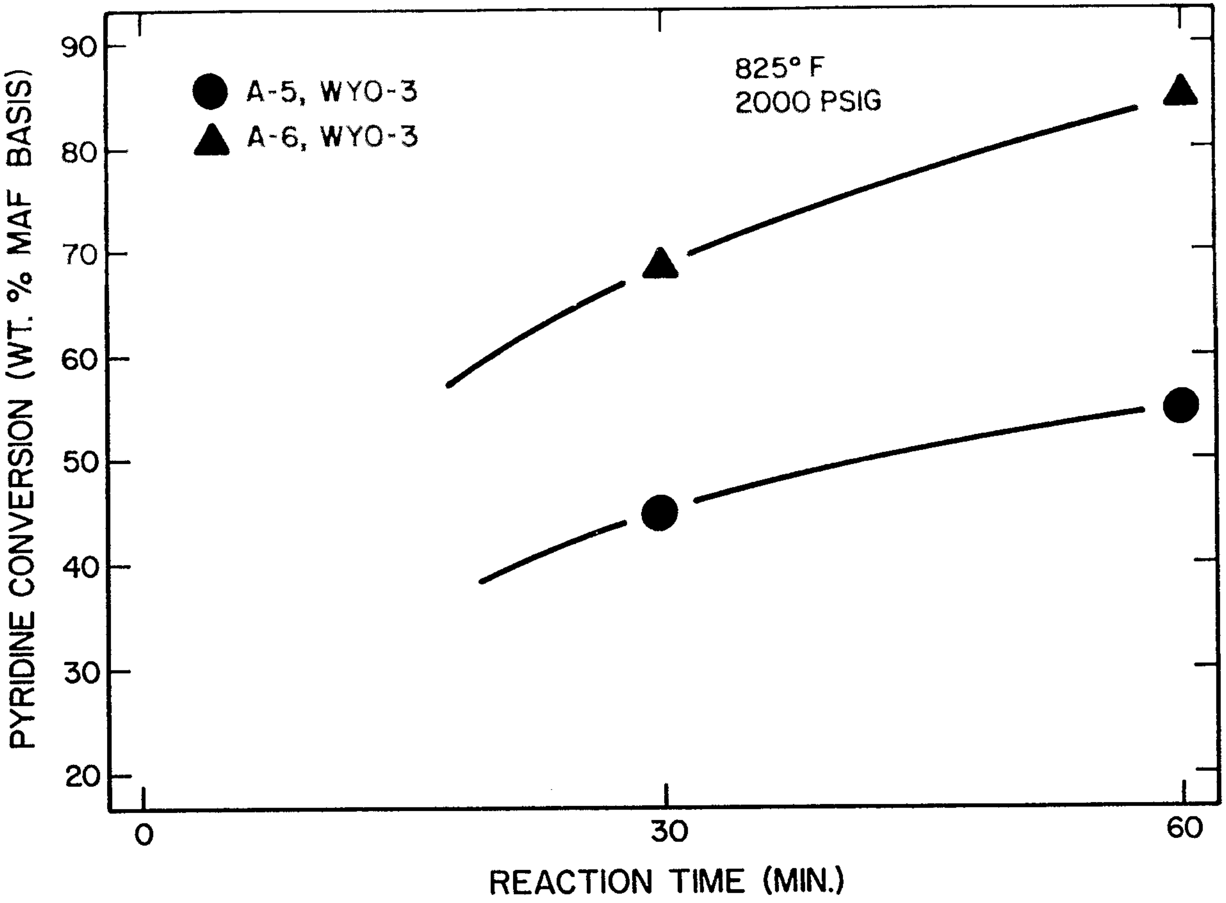

Figure 5. Pyridine Conversion as a Function of Reaction Time and Shale Oil Feed - High Severity Reaction Conditions

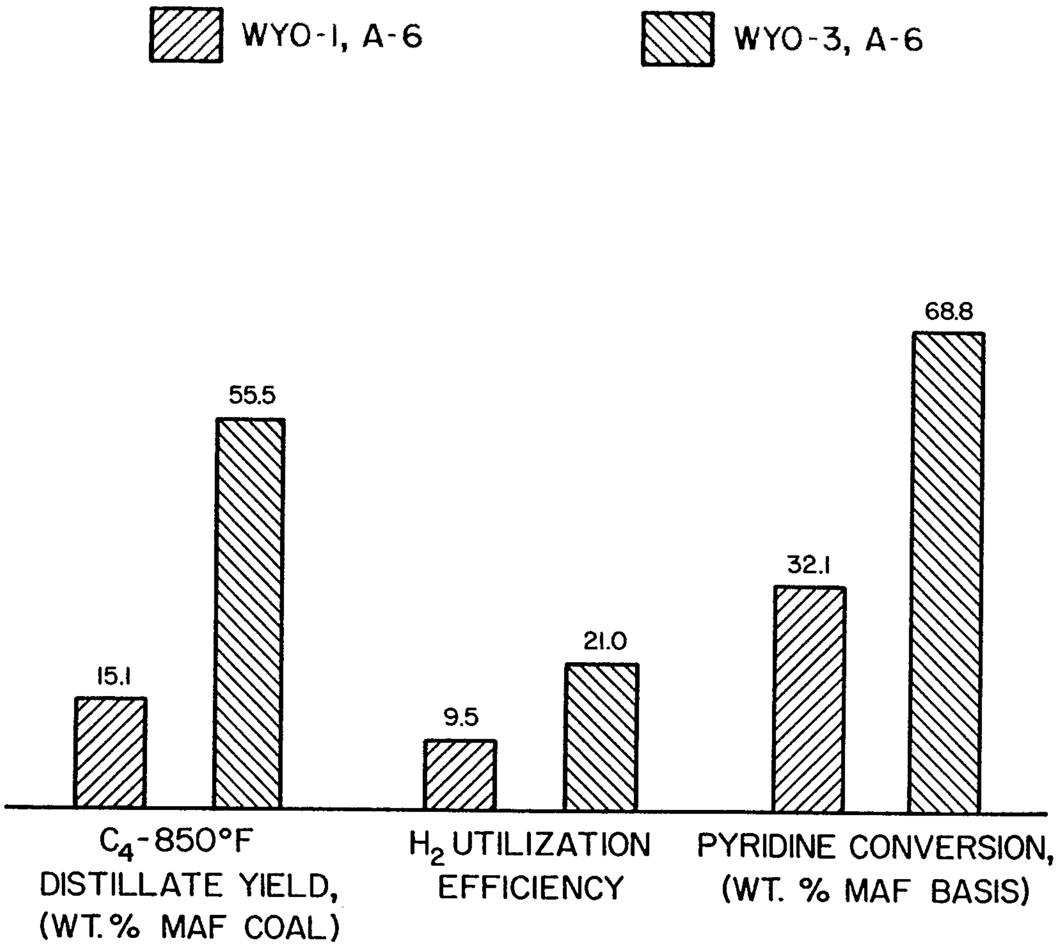

Figure 6. Effect of Feed Coal Reactivity on High Severity Process Performance (Reaction Conditions: 825°F, 2000 psig H_2, 30 min.)

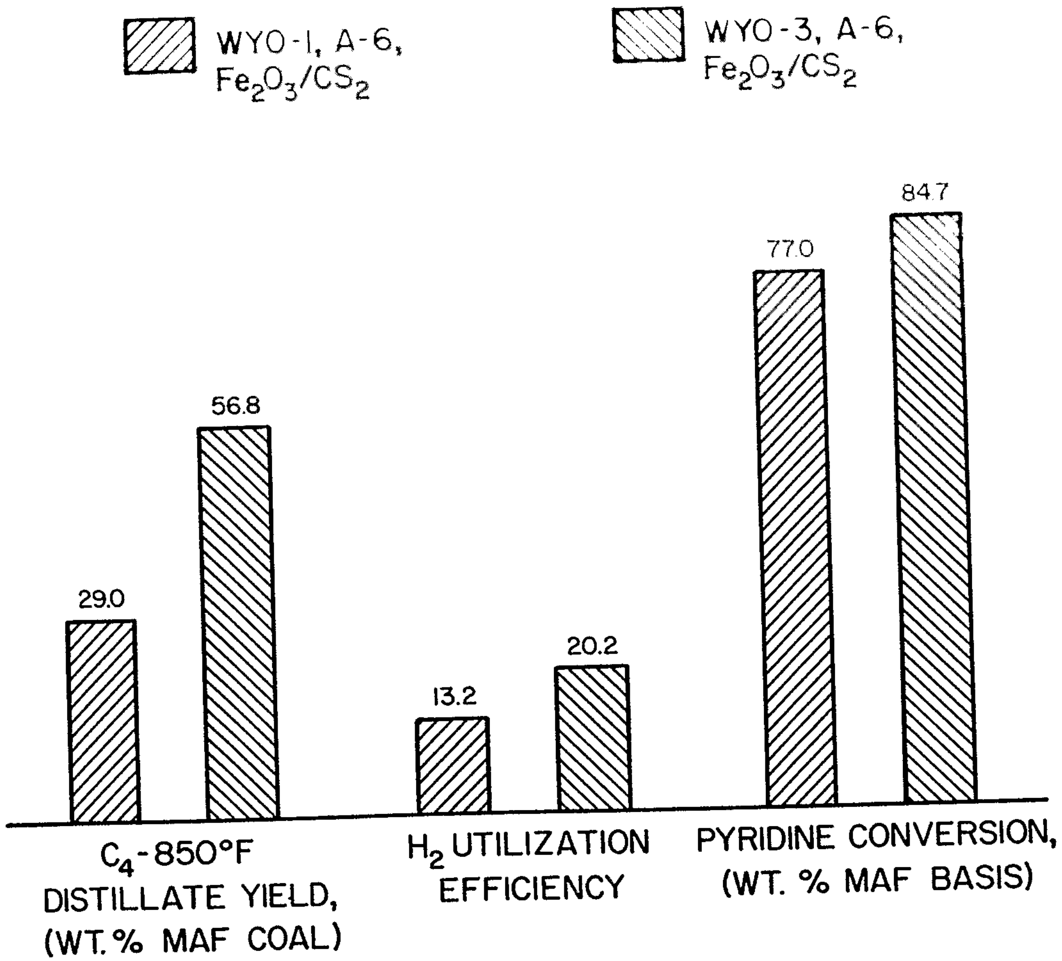

Figure 7. Effect of Feed Coal Reactivity on High Severity Process Performance (Reaction Conditions: $825^{0}F$, 2000 psig H_2, 30 min., Fe_2O_3/CS_2 Catalyst)

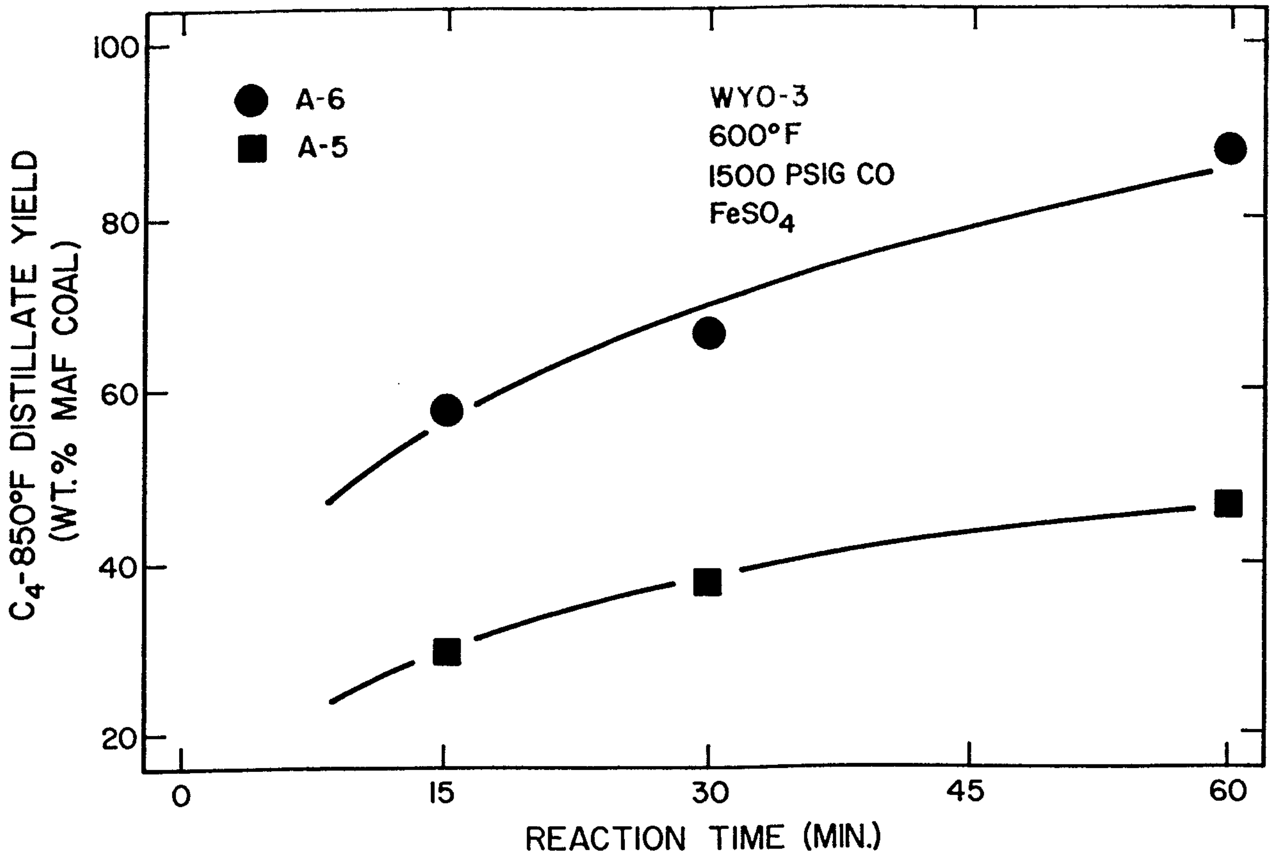

Figure 8. Distillate Yield as a Function of Reaction Time and Shale Oil Feed - Low Severity Reaction Conditions

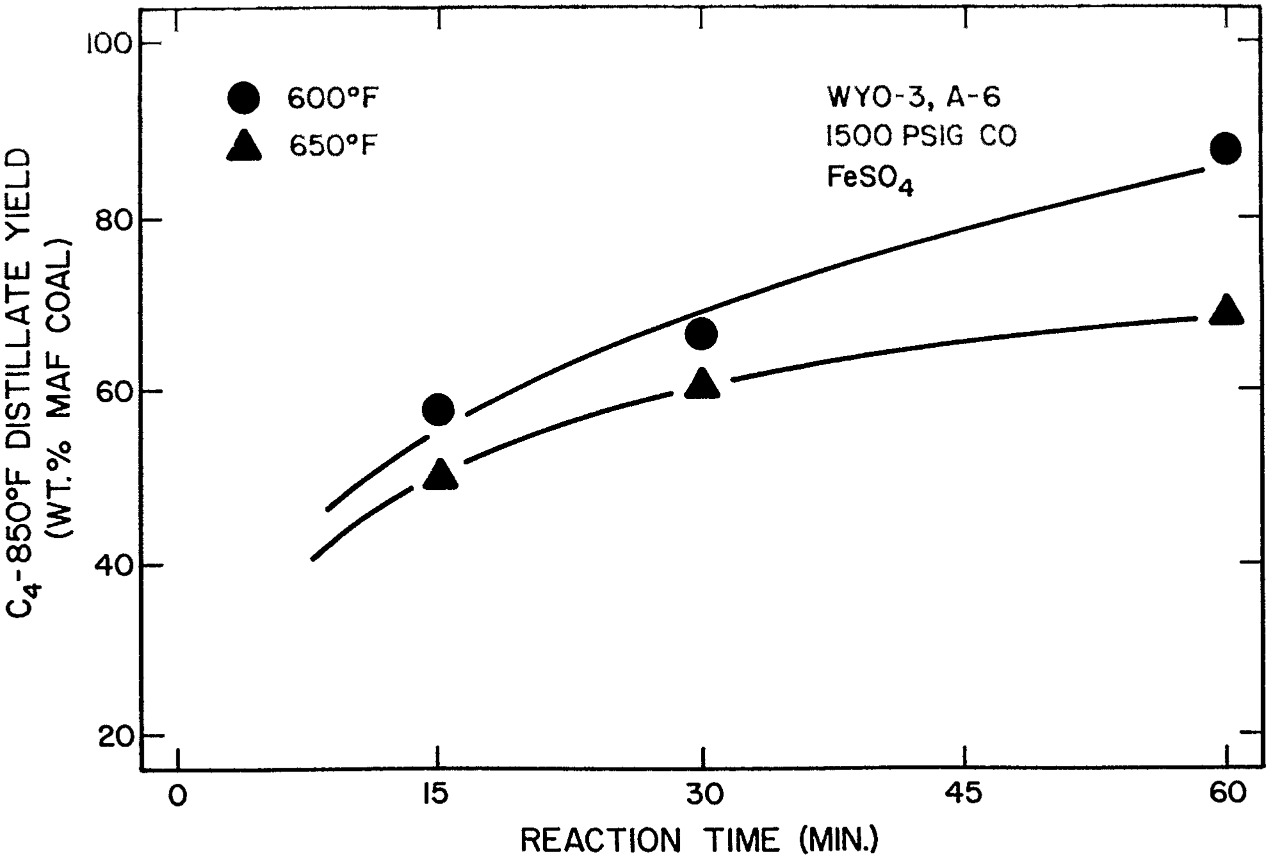

Figure 9. Distillate Yield as a Function of Reaction Time and Temperature - Low Severity Reaction Conditions

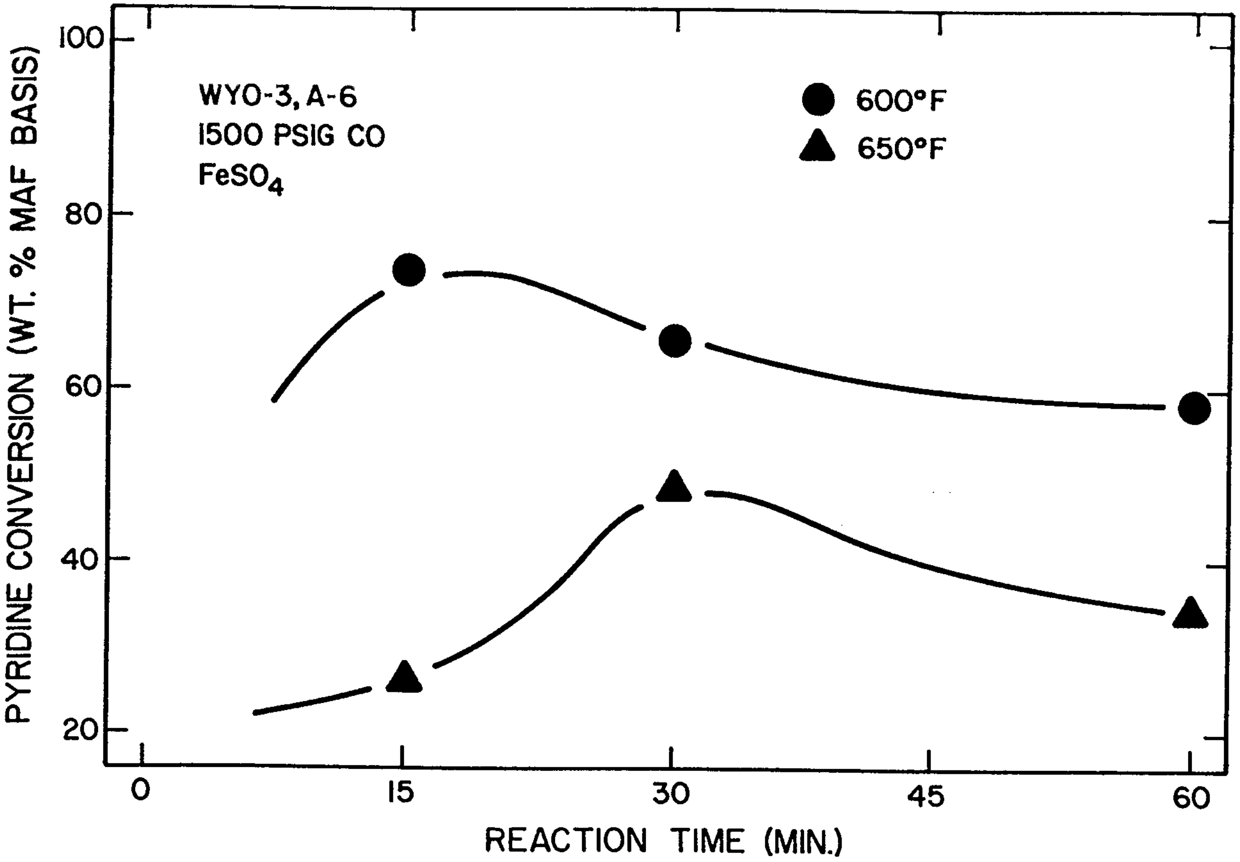

Figure 10. Pyridine Conversion as a Function of Reaction Time and Temperature - Low Severity Reaction Conditions

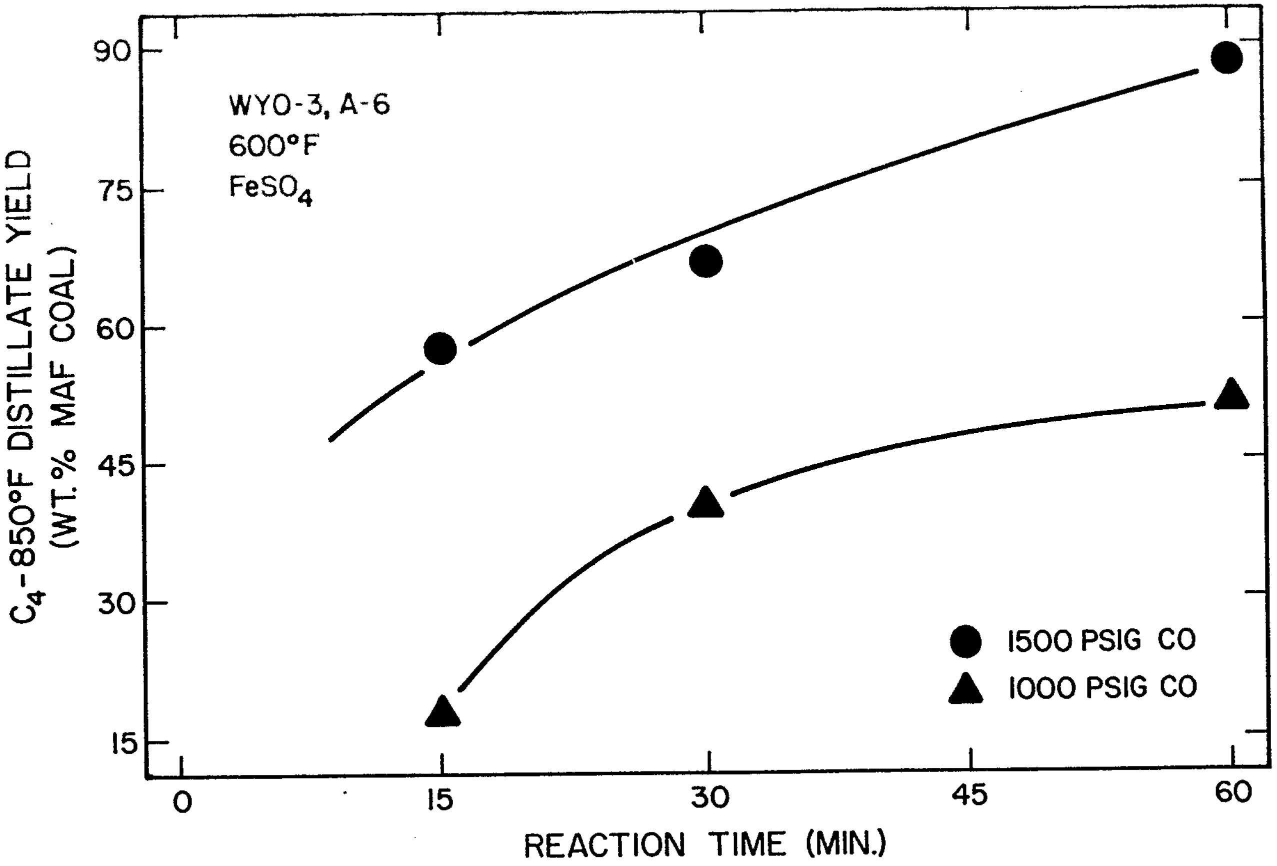

Figure 11. Distillate Yield as a Function of Reaction Time and Carbon Monoxide Pressure - Low Severity Reaction Conditions

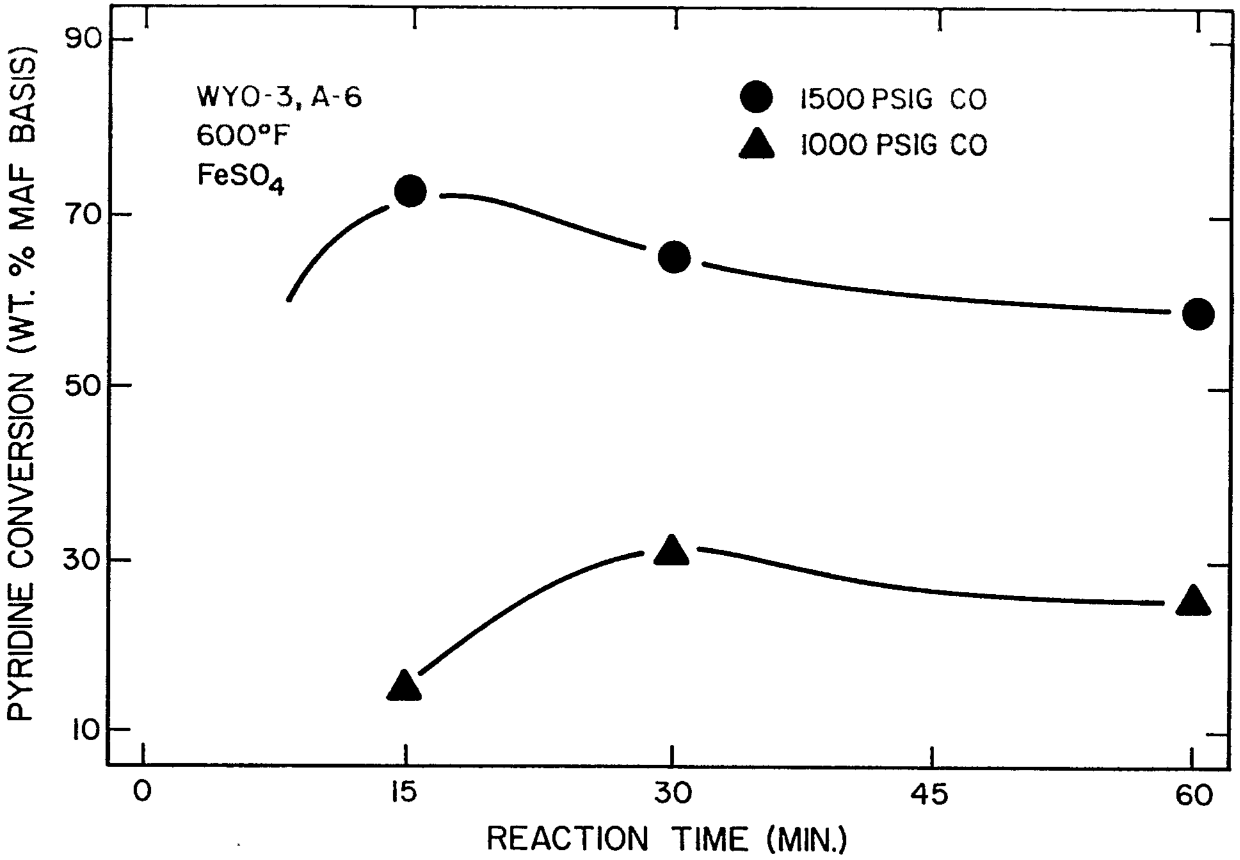

Figure 12. Pyridine Conversion as a Function of Reaction Time and Carbon Monoxide Pressure - Low Severity Reaction Conditions

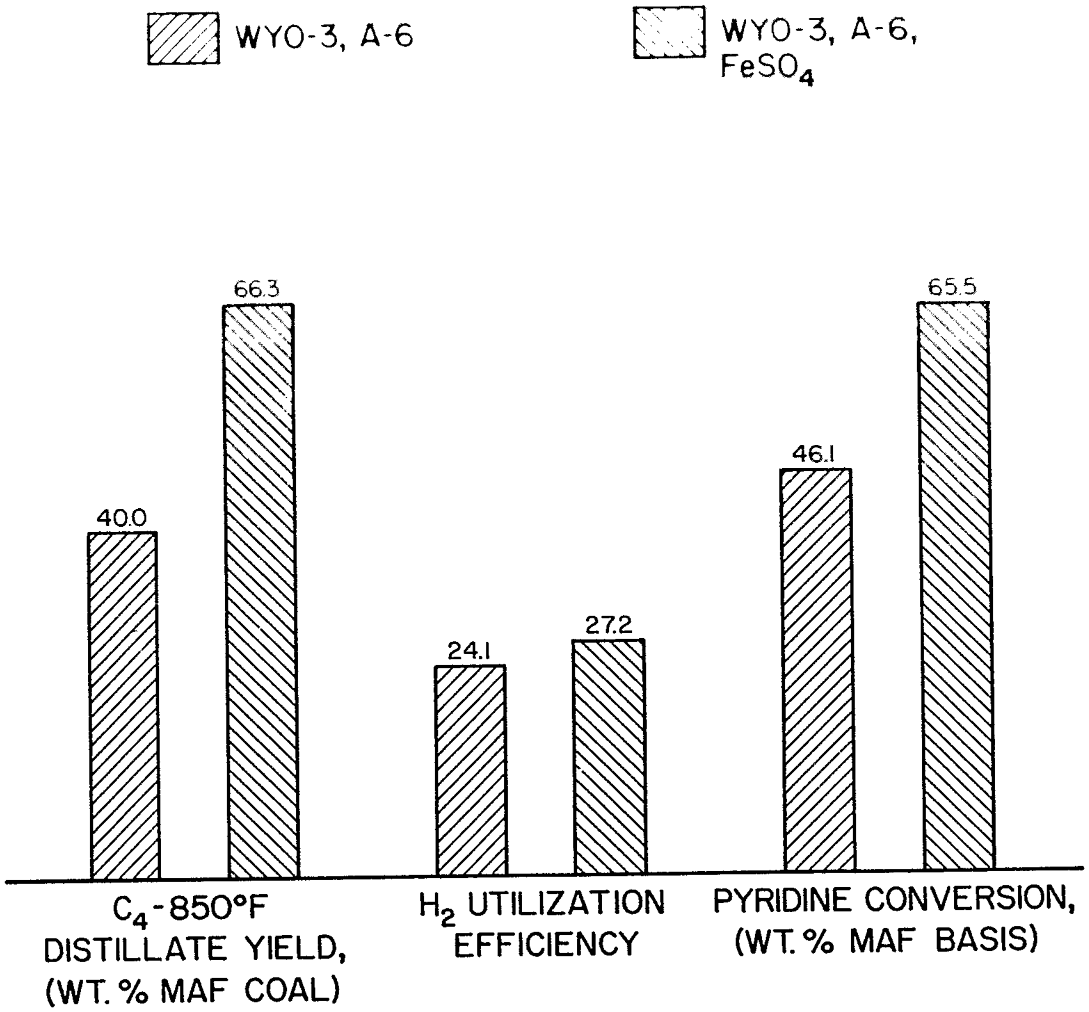

Figure 13. Effect of Disposable Coal Dissolution Catalyst on Low Severity Process Performance (Reaction Conditions: 600°F, 1500 psig CO, 30 min.)

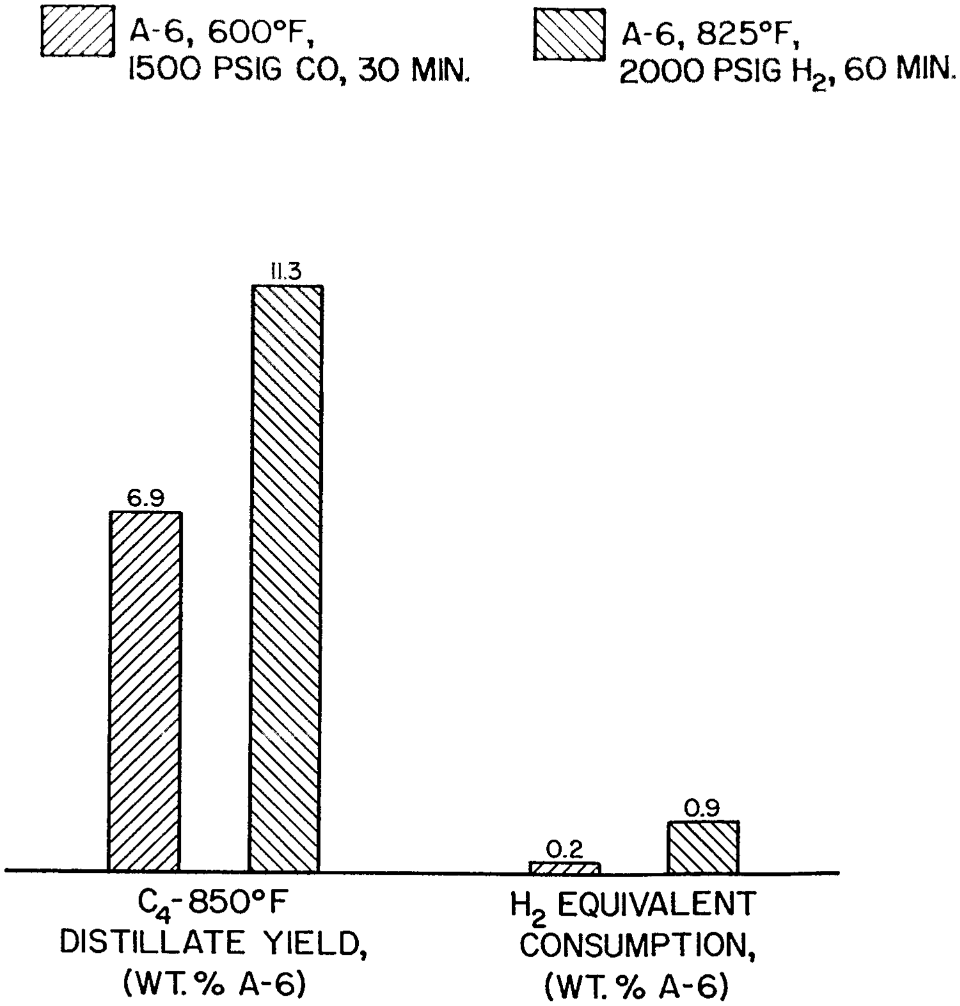

Figure 14. Results from Blank Shale Oil Runs at Low and High Severity Reaction Conditions

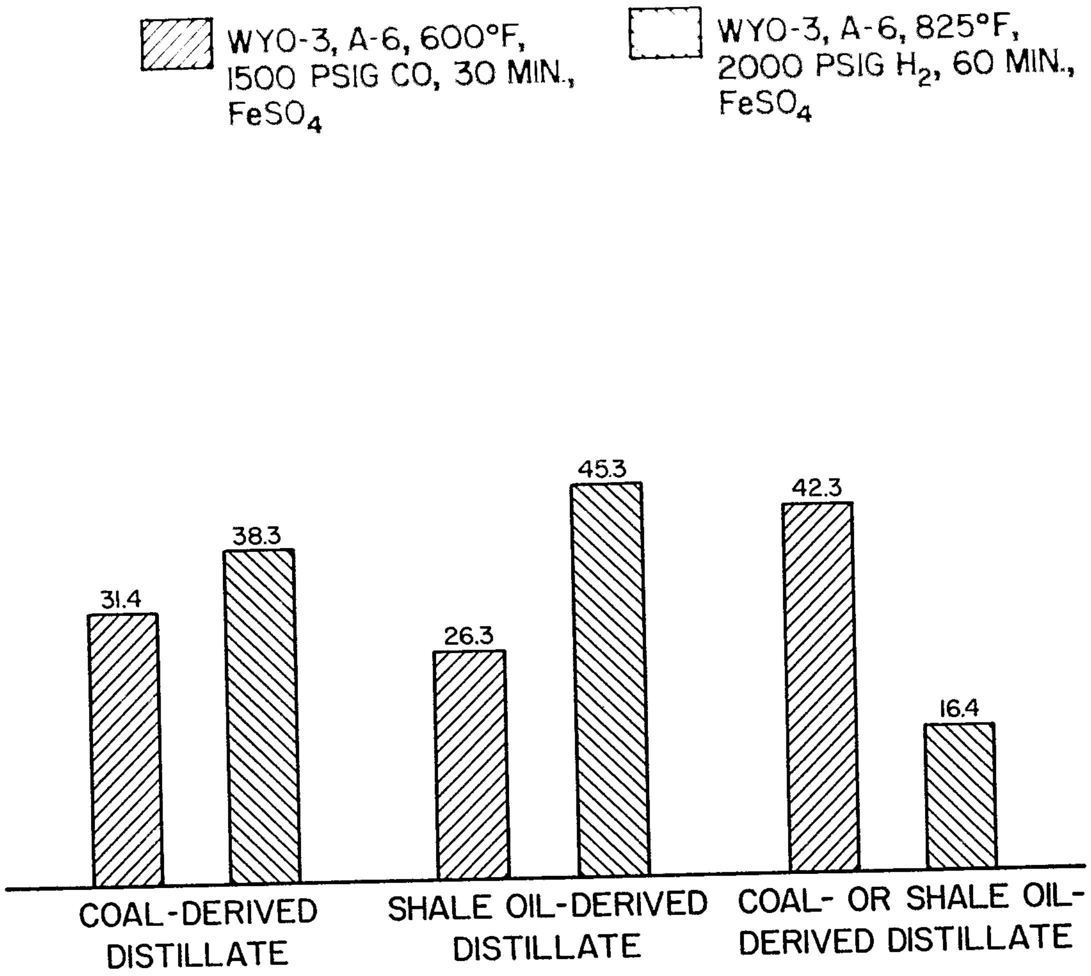

Figure 15. Estimated Distribution of Distillate Production from Wyo-3 Coal and A-6 Shale Oil at Low and High Severity Reaction Conditions

STABILITY AND COMPATIBILITY OF RESIDUAL FUEL OILS

R. Anderson, J. Goetzinger and J. Reynolds

National Institute for Petroleum and Energy Research (NIPER)

STABILITY AND COMPATIBILITY OF RESIDUAL FUEL OILS

R. P. Anderson, J. W. Goetzinger, and J. W. Reynolds

National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma 74005

ABSTRACT

In recent years there has been a marked decrease in the quality of residual fuel oils available to the electric utility industry. Experience has shown that conventional fuel oil analyses are inadequate to allow utilities to prevent or predict handling difficulties due to problems with instability or incompatibility with these lower quality fuels. A number of "problem" and "nonproblem" fuel oils supplied by utilities have been analyzed in an attempt to understand the reasons for the reported problems. In addition to chemical and physical characterization, these and additional fuels and blends have been subjected to baseline tests for determining instability or incompatibility. These baseline tests have been used as a basis for initial evaluation of rapid tests which utilities might use for the prediction of potential problems due to instability or incompatibility.

ACKNOWLEDGMENT

This paper is based on work jointly supported by the U.S. Department of Energy under Cooperative Agreement DE-FC22-83FE60149 and the Electric Power Research Institute under Agreement RP2527-1.

INTRODUCTION

Recent years have seen a drastic decline in the quality of residual fuel oils available to the electric utility industry. Concern with this decline in quality and the inadequacy of current specifications to prevent or predict problems in handling and burning these oils were recently evidenced by the utilities participating in an EPRI-sponsored workshop on Fuel Oil Utilization (1). Problems with fuel quality are in no way limited to residual fuels but are also being observed in distillate fuels with discoloration and the formation of insoluble gum and sediment on storage (2,3).

The decline in residual fuel oil quality is due to a combination of factors which were recently reviewed by Mueller (4). Foremost among these factors is the decline in crude oil quality; i.e., the increased use of heavy crudes. This is shown in figures 1 and 2 which show the declining API gravity of U.S. refinery feedstocks and the increased level of heavy crudes; i.e., crudes of API gravity <20. The heavy crudes, which are generally of high heteroatom content, high metals content, and high asphaltene content, are particularly deleterious to both processing and product quality.

A second factor responsible for decreased residual fuel oil quality is in changes in refinery processing. While refinery feeds were becoming heavier, product demand was shifting toward lighter products and away from heavy residual fuels. Residual fuel oil consumption decreased by 50% from 1977 to 1983 (4), and the decrease has continued (5). This has led the refiner to more severe processing in trying to convert the bottom of the barrel to distillate products. As will be discussed later in this paper, more severe processing can lead to increased problems with stability and compatibility. Other factors, such as growth of "jobbers" and the spot market at the expense of long-term supply contracts with refiners, have also contributed to the decline in fuel oil quality.

A residual fuel is usually made of two components: a resid (the bottoms from either an atmospheric or vacuum distillation) boiling above about 650° F (atmospheric resid) or about 950° F (vacuum resid) and a lighter flux component boiling above about 350° F which is used to control viscosity and, to a lesser extent, to adjust sulfur content. The residual material may be either straight-run or cracked. Residual fuels produced from the smaller, simpler refineries (many of which are now closed) were typically straight-run bottoms made from relatively high-quality crudes; this source of high-quality residual fuels has largely disappeared. Stability problems are more significant with cracked materials than with straight-run materials; instability is more severe with thermally cracked material than with catalytically cracked material. In this time of low demand for residual fuel and high demand for distillate, the refiner commonly resorts to visbreaking (thermal cracking) to decrease the viscosity of the resid, thereby lowering the requirement for addition of more valuable distillates to lower the viscosity.

This project addresses problems associated with storage and handling of residual fuels as opposed to problems of combustion. In particular, the problems of concern are instability and incompatibility. Both phenomena lead to difficulty in handling; i.e., formation of solids or sludge which may solidify in tanks, foul heaters, plug strainers, cause pumps to fail, or plug lines. The traditional definitions of instability and incompatibility are as follows:

Instability. The tendency of a fuel to produce a deposit in storage or on heating. Instability may also be observed via other changes in the fuel; e.g., via increases in viscosity.

Incompatibility. The tendency of a fuel to produce a deposit on dilution or on blending with other fuels.

The distinction between the two phenomena may be clear cut in some instances; however, in other instances it may not be readily apparent whether a problem was due to instability or incompatibility. Examples discussed in this paper provide instances where the problem was clearly instability, where the problem was clearly incompatibility, and where it was not clear which of the phenomena was responsible for the reported problem.

The overall objective of this project is to provide rapid practical tests which utilities can use to predict whether a particular fuel or blend is likely to lead to problems during its utilization. A general change in the direction of the project has taken place since the presentation at last year's conference (6). The initial approach was to perform detailed analyses of problem and nonproblem fuels; learn the type of components which were responsible for the observed problems; and, based on that information, develop rapid practical tests for utility usage. Emphasis has shifted from detailed chemical analyses initially undertaken towards more general chemical characterization of utility supplied "problem" and "nonproblem" fuels and, most recently, toward evaluation of simple empirical tests which may correlate with problem behavior and which can be utilized in utility laboratories.

EXPERIMENTAL AND RESULTS

RESIDUAL FUEL OIL DATA BASE

One part of this project encompassed the establishment of a residual fuel oil data base independent of the instability/incompatibility work. Nine residual fuel oils, most of which were supplied by utilities and were generally not defined as problem fuels, were subjected to a set of analyses including elemental composition, ash composition, distillation (both ASTM D 1160 and simulated distillation by GC), carbon residue, asphaltene content (by several methods), viscosity versus temperature, flash point, and burning profile (a Babcock and Wilcox thermogravimetric method). These results will not be discussed in detail here, but some analyses will be provided to indicate the range of compositions observed in commercial residual fuels. A summary of the analyses is provided in table 1.

A wide range of product qualities is readily apparent. For example, asphaltene content ranges from as little as 1.3% to as high as 12.1%, API gravity from as low as 5.5 to as high as 20.5, hydrogen from 9.3 to 12.4%, and sulfur from 0.34 to 4.34%. The level of nondistillable residue (boiling point >1000° F) ranges from 38 to 61% and the viscosity from 60 to 465 SFS at 122° F. Strong correlations between many of these properties are apparent, but these are beyond the scope of this paper.

ANALYSIS OF UTILITY SUPPLIED PROBLEM/NONPROBLEM RESIDUAL FUELS

Utilities have provided a number of samples characterized as "problem" or "nonproblem" samples. In most cases, a utility supplying a problem sample also supplied a companion sample with which the problem was not experienced. A general description of the utility supplied samples and their designation as "problem" or "nonproblem" is provided in table 2.

Analysis of the first problem sample (strainer plugging) was reported last year (6) and will not be discussed in detail here. In that case, the problem appeared to be due to addition of used motor oil to the residual fuel; the material plugging the strainer appeared to consist primarily of a polymeric material which was believed to be a viscosity index improver included in the motor oil formulation.

The next sample set is identified as the "line-plugging" problem set. In this case, a row of burners in a boiler was operated in a cyclic manner. Flow of fuel through the line would be stopped, and the burners would not be operated for about an eight-hour period. On trying to restart the burners, it would sometimes not be possible to reestablish flow through the lines. A sample taken at a time when flow was difficult to reestablish constitutes the problem sample, and the nonproblem sample was taken at a time when problems in reestablishing flow were not evident.

The next sample set is identified as the "heater-plugging" problem set. A heater used to heat the fuel to atomization temperature would plug to the extent that flow through the heater could not be maintained. A sample believed to be associated with the plugging behavior was provided as the problem sample; another residual fuel purchased to the same specifications was supplied as the nonproblem sample.

The final sample set of the problem/nonproblem fuels is identified as the "viscosity instability" problem set. In this case, three samples associated with a shipment of fuel which exhibited severe viscosity instability were provided. Only in this case could the problem reported by the utility (and the lack of the problem in the companion sample) be verified in the laboratory.

Some of the more conventional analyses for the above samples are summarized in tables 3 and 4. Analyses on the whole residual fuel are provided in table 3. Where sufficient amounts of material were available, the fuel was subjected to thin-film distillation to provide a distillate and residue for analysis. Thin-film distillation was used to minimize the thermal stress to which the sample was subjected. Distillation results and analyses of the distillate and residue fractions are summarized in table 4.

In general, the conventional analyses do not provide a definitive explanation for the problem versus nonproblem behavior. The two samples in the line-plugging set (1956-1964) were quite similar; both of these low sulfur (0.35%) fuels would be considered high-quality residual fuels. They are of high API gravity and low viscosity. They are high in hydrogen and low in sulfur, nitrogen, asphaltenes, and ash. The samples are of high pour point, and the distillates are waxy. It is conceivable that if sufficient cooling in the lines took place, the problem with reestablishing flow could be related to the waxiness of the fuels. High wax contents were apparent from the physical appearance of the distillates and from the presence of high molecular weight n-paraffins in the simulated distillation spectra (figure 3). This does not account for the reported variation between the problem and nonproblem samples, however, unless the problem is strictly related to environmental conditions at the time of sampling.

The next set of samples (heater-plugging set, 1954 and 1980) are 1% sulfur fuels. The lower quality of these fuels is shown by their higher sulfur content, lower API gravity, lower hydrogen, higher nitrogen, higher asphaltenes, higher carbon residue, and higher ash. In this case, the problem sample is of higher viscosity and higher asphaltene content than the nonproblem sample. With the available information, it is not possible to know if the heater plugging problem is associated with the higher asphaltene content of the problem fuel. It was not possible to reproduce the plugging problem in an Alcor Thermal Fouling Tester.

Other than the high viscosity itself, there is nothing in the data from the viscosity instability set (2021 and 1861) to indicate a stability problem with the problem sample. Asphaltene content is high, but this alone is not indicative of problem behavior.

It is apparent that the conventional analyses (and a number of other analyses which are beyond the scope of this paper) fail to allow the prediction of problem behavior for these fuels. Other analyses of the above fuels, including stability testing and various methods of determination of sediment, are discussed in the following sections.

Enlarged Sample Data Base

For the development of stability and incompatibility tests discussed in the following sections, it was necessary to increase the number of samples subjected to testing. Additional samples included are shown in table 5. A complete description of these samples is beyond the scope of this paper.

STABILITY TEST METHOD DEVELOPMENT

Baseline Stability Test

Some uncertainty exists with the samples discussed above as to whether the problem samples are inherently "bad" fuels and the nonproblem samples are inherently "good" fuels or whether other factors are of overriding importance. As the problem or nonproblem behavior reported by the utility is dependent on mechanical and physical considerations unique to a particular situation, a fuel which is not a problem in one situation may become a problem sample in another application, and vice versa. Consequently, it was decided that the development of predictive tests for instability or incompatibility must be tied to a baseline test which will definitively demonstrate, in the laboratory, whether or not a fuel exhibits instability (or incompatibility on blending).

As a baseline determination of stability, residual fuels were subjected to long-term aging at elevated temperature (80° C and, to a lesser extent, 100° C), and changes in the fuel were monitored. Aging was carried out for periods up to 24 weeks at 80° C (equivalent to approximately 22 years at 25° C, assuming doubling of reaction rates with every 10° C increase in temperature). Changes in viscosity, asphaltene content, sediment via hot filtration, and carbon residue were monitored. Changes in Conradson carbon (carbon residue) were quite small and will not be discussed further.

The technique used for determination of sediment formation during aging at elevated temperature is based on the new method of the Institute of Petroleum, Test for Total Sediment in Residual Fuel Oils, IP-375. This method involves filtration of the fuel at 100° C through a glass fiber filter paper, washing the sediment with an aliphatic solvent, drying, and weighing. At the time our work was initiated, the method had not been formally adopted, and two variations (using single or double filter papers) were under consideration. Our initial work used the single paper method which was subsequently found to be inferior to the double paper method in which the bottom filter paper is used as a blank.* Results for the first two problem sets are shown in figure 4 (single filter paper method). Initial sediment levels are low (< or equal 0.1%). Results through the first several weeks of aging are erratic, probably due in part to inaccuracies in the sediment determination method at low levels of sediment. However, after long periods of aging, the levels of sediment do become quite large. At 24 weeks, sediment levels ranged from 0.2% to over 2%. By eight weeks, the levels of sediment for the four samples were in the same order as at 24 weeks.

The sediment formation on long-term 80° C aging did not correlate with the problem/nonproblem behavior reported by the utilities. For the heater-plugging set, the nonproblem sample (#1980, 2.2% sediment) showed a much higher level of sediment formation that the problem sample (#1954, 0.28% sediment). For the line-plugging set, the problem sample did show a higher level of sediment formation (1956, 0.96% sediment) than the nonproblem sample (#1964, 0.23% sediment). Sediment could not be determined for the viscosity instability samples (#2020-22) as they were not filterable.

Viscosity changes are shown in figure 5. In addition to the samples discussed previously, samples of a visbroken Mayan resid and a hydrocracked residual fuel oil sample are included. A wide range of stability behavior is noted. For example, the utility fuel sample exhibiting the viscosity instability (sample #2021) increased by 290% (from 140 to 540 centistokes at 180° F) in two weeks. Although substantially less severe, other samples which showed high viscosity instability include the visbroken Mayan resid, the hydrocracked sample (#2103)

---

*Sediment by hot filtration for the unaged samples was rerun by the dual filter method. As expected, these values are lower than those from the single filter method.

and nonproblem utility sample #1768. These samples all underwent viscosity increases of about 50-75% during four weeks of aging at 80° C. Sample 1954 showed a low viscosity at four weeks but probably is of similar instability as shown by viscosity determinations for other aging periods. Very high viscosity stability was noted by the line-plugging problem set (#1956 and #1964) which increased by less than 10% during four weeks of aging.

It should be noted that there is not a correlation between instability as noted by viscosity increases and instability as noted by sediment formation. For example, the sample showing the highest degree of viscosity stability (#1956, whose viscosity increased only 20% on 24 weeks of aging) had the second highest amount of sediment formation.

Changes in asphaltene content on 80° C aging are shown in figure 6. There is a rough correlation between increases in viscosity and increases in asphaltene content. The following comparisons are made for the asphaltene content increases for the first four weeks of aging. Significant increases in absolute asphaltene contents were observed for the visbroken Mayan resid (#2032, from 16.6 to 20.5% asphaltenes), the viscosity instability sample (#2021, from 13.6 to 16.5% asphaltenes), and nonproblem sample #1768 (from 3.6 to 7.3% asphaltenes). These samples also exhibited significant increases in viscosities. Small increases in absolute asphaltene contents were observed for the line-plugging samples (#1956 and #1964, from 1.3 to 1.9 and from 0.8 to 1.3, respectively). These latter two samples also showed only small increases in viscosity.

Rapid Test Methods for Prediction of Instability

The methods discussed above indicate the stability or instability of a fuel on long-term aging at elevated temperature. These methods requiring long aging times are obviously not suited for routine usage but should be considered baseline tests against which rapid predictive tests can be compared. Tests which have been considered as possible predictors for long-term instability include electron spin resonance spectroscopy (ESR), coke content, the Shell accelerated dry sludge test, and acid-base contents. These will be discussed in turn.

Electron Spin Resonance Spectroscopy

Samples which have been severely treated during processing are more likely to exhibit instability problems. A possible indication of severe processing is the presence of free radicals. Free radicals (a chemical species containing an unpaired electron) may be produced during the severe temperature conditions used in refinery cracking processes. Free radicals are unstable and are generally short lived. However, due to the low mobilities of large species found in resids and the opportunity for extensive electron delocalization, long-lived free radicals may exist in residual materials. The concentrations of free radicals may be expected to show a correlation with severity of processing and with instability of a sample. Such a correlation has been observed. This correlation is most readily evident in the correlation of free radical concentrations with viscosity instability.

ESR data are summarized in table 6. For this discussion, we are concerned only with the carbon free radical concentrations; the concentrations of vanadyl radicals can be obtained from the same ESR run but will not be considered further. The carbon free radical concentrations are in arbitrary but self-consistent units. The increase in carbon free radical concentration which may occur during processing is shown by the Mayan resid visbreaking run; concentration in the feed (#1735) was 13.4, while concentration in the visbroken product (#2032) was 22.5. This sample and the viscosity instability sample (#2021) had the highest free radical concentrations and both showed significant increases in viscosity on aging. Intermediate concentrations of free radicals (and intermediate levels of viscosity instability) were noted for samples #1768, #1954, and the hydrocracked sample #2103 (free radical concentrations of 15.9, 16.2, and 15.8, respectively).

The samples which had the greatest viscosity stability on aging (the line-plugging set, #1956 and #1964) also had the lowest free radical concentrations (7.7 and 9.3, respectively).

Although there does appear to be a correlation between instability and concentration of carbon free radicals, ESR spectroscopy is not a technique regarded as suitable for use in utility quality control laboratories; hence, a more simple method of predicting instability was sought.

Coke Determination

Another method which may indicate a history of severe processing and, hence, the potential for instability is in the presence of insoluble coke-like material. Hot filtration methods as discussed above determine the presence of material insoluble in the residual fuel. These insolubles may be largely precipitated asphaltenes which are insoluble in the residual fuel but soluble in an aromatic solvent. ASTM D 473, Sediment in Crude Oils and Fuel Oils by the Extraction Method, determines the amount of material which is insoluble in an aromatic solvent (toluene). The insolubles could include inorganic contaminants as well as coke-like material. Determination of sediment by extraction followed by determination of carbon and hydrogen contents of the toluene insolubles can provide an indication of the level of coke-like material.

Results for the determination of coke-like material for the viscosity instability problem set are summarized in table 7. In this case, the toluene insolubles were isolated by Soxhlet extraction with toluene rather than the ASTM method. A comparison of the viscosity instability samples (#2020-2022) and their companion nonproblem sample (#1861) shows a high level (0.4-0.8%) of toluene insoluble material in the problem samples compared to a very low level (0.04%) for the companion nonproblem sample. The high carbon and low hydrogen contents (88% and 5%, respectively, for sample #2021) show this to be primarily a coke-like material. In comparison, hydrogen contents of vacuum resids have run in excess of 10%, and hydrogen contents of petroleum asphaltenes run about 8%.

A correlation of high coke content and viscosity instability was also observed for the visbroken Mayan resid.

Due to this potential correlation between the presence of coke and viscosity instability, a number of additional samples were subjected to determination of the presence of coke-like material (ASTM D 473 followed by determination of carbon and hydrogen if a sufficient level of insolubles were present). Results are summarized in table 8. Only the samples discussed above (#2021, the viscosity instability sample, and #2032, the visbroken Mayan resid) show large amounts of coke-like material.

In conclusion, the presence of a large amount of coke-like material in a residual fuel may be an indicator of viscosity instability. However, the absence of a significant amount of coke-like material does not necessarily indicate that there will not be problems with viscosity instability. For example, sample #2035 (a high asphaltene content fuel from the residual fuel oil data base, table 1) underwent a 150% increase in viscosity during four weeks of aging at 80° C but contains only 0.01% sediment by extraction.

Shell Accelerated Dry Sludge

Shell has recently reported on an accelerated test for the determination of potential dry sludge content (7). This test (SMS 2696-83, Accelerated Dry Sludge Content of Residual Fuel Oils) involves the addition of a small amount of poor solvent (10 parts residual fuel, 1 part cetane) and aging at 100° C for one hour followed by the determination of sediment by hot filtration. The technique for determination of sediment after the cetane addition is similar to the IP method for sediment by hot filtration but differs in a number of minor respects.

Preliminary results indicate a correlation between sediment formation on long-term aging and the Shell accelerated dry sludge test. In figure 7 the sediment present after 24 weeks of aging at 80° C (IP single filter method) is compared with our initial results for the Shell accelerated dry sludge test. These limited data show a correlation between the two methods. A further evaluation of the correlation between sediment formation on long-term aging and the Shell accelerated dry sludge test is currently underway. The results obtained to date indicate that there is a correlation between the sediment present after four weeks of aging at 80° C and the results of the Shell accelerated dry sludge test. If the correlation between the two methods continues to hold, it suggests that the sediment formation on long-term aging may be as dependent on simple precipitation or flocculation of asphaltenes as on chemical reactions (oxidation, condensation, polymerization) leading to materials of decreased solubility.

Acid-Base Contents

Residual fuels in the original problem/nonproblem sample sets were subjected to separation into strong acids, weak acids, strong bases, weak bases, and neutrals via a nonaqueous ion exchange technique developed at NIPER (8). Where sufficient size samples were available, the separation was conducted on the distillate and residue fractions following thin-film distillation. Where inadequate samples were available, the separation was carried out on the whole residual fuel. Differences between various fuels were markedly lower for the whole fuels, but these are the results which will be compared as they are available for all of the fuels. Results are summarized in table 9, and selected results are plotted in figure 8. Strong acids have often been implicated in problem behavior. For this data set, the strong acid contents of the problem fuels are higher than the strong acid contents of the companion sample (problem and nonproblem samples from one sample set are connected by lines in figure 8). It was also found that the weak base contents of the nonproblem samples were higher than those for the corresponding problem samples (figure 8). It may be a coincidence, but many of the commercial antioxidant additives are basic.

Separation of fuels into fractions as described above is beyond the capabilities of utility quality control laboratories. The above samples plus additional samples are currently being subjected to determination of strong and weak acids and strong and weak bases by nonaqueous potentiometric titration--a method which could be adopted by utility laboratories. The acid-base contents determined via potentiometric titration will be evaluated for potential correlations with reported problem/nonproblem behavior and with observed stability and compatibility behavior.

INCOMPATIBILITY TEST METHOD DEVELOPMENT

As has been noted in the literature, incompatibility is easily recognized once it has occurred; it is not so easily predicted, and better methods for predicting incompatibility are needed (9). Instances of severe problems of incompatibility on blending of residual fuels have been noted in the literature. In the example cited by Holmes (9), after fuels were blended for transport, a tar-like precipitant formed, settled, and partially solidified. A very similar incident was experienced by a utility during the course of this project. Unfortunately, samples from this incident were not available.

Incompatibility can be anticipated by making laboratory scale blends and determining whether they contain sediment by hot filtration. In our work, we have prepared blends by heating the components to 60 to 80° C, blending, heating the blend to 100° C for one hour, and determining sediment by the IP method. Although the above method is satisfactory for predicting incompatibility problems, it is desirable to be able to predict incompatibility from characteristics of the potential blend components. This may, for example, allow the development of specifications which could preclude purchasing a fuel which could lead to incompatibility problems.

Incompatibility usually results from blending one fuel of high asphaltene content with another fuel or diluent which is of too low solvent power (aromaticity too low) to keep the asphaltenes in solution. Thus, it should be possible to predict incompatibility by consideration of two factors: first, the aromaticity of the solvent fraction of the residual fuel and, second, the quality of solvent required to keep the asphaltene fraction of the fuel in solution.

Griffith and Siegmund of Exxon have developed a compatibility test (10,11) based on the Scatchard-Hildebrand equation of solubility behavior and the solubility parameters for asphaltenes and nonasphaltenes. The solubility parameters of asphaltenes were determined from the solubility of the resid fraction of the residual fuel in mixtures of toluene and heptane (toluene equivalence, reference 12), and the solubility parameter of the nonasphaltenes was found to correlate with the aromaticity as determined by the Bureau of Mines Correlation Index (BMCI, reference 13). BMCI is used as a measure of an oil's solvency, in particular its aromatic content; high BMCI is indicative of a highly aromatic oil, and low BMCI indicates a more paraffinic oil. Toluene equivalence (TE) is a measure of a fuel or resid's "solvent requirement," or the amount of aromatic character required of a diluent to completely dissolve the asphaltenes in a fuel/solvent mixture.

We have evaluated these techniques to predict incompatibility based on characterization tests which: 1) determine the quality of solvent required (solvent quality demand) to dissolve the asphaltene fraction of the residual fuel and 2) the aromaticity (i.e., solvent quality) of the overall blend. Toluene equivalence (applied to the total residual fuel, not just the resid portion) was found to be a satisfactory measure of solvent quality demand.

The solvent quality or aromaticity has been determined from the BMCI which is based on the 50% distillation point and the specific gravity. Solvent quality measurements attempted besides the BMCI included determination of saturates and aromatics by high performance liquid chromatography (HPLC) and detailed structural information by a combination of proton and C-13 nuclear magnetic resonance (NMR) spectra. Although these methods may provide significantly more information than the BMCI, they are significantly more complex and do not appear to be better predictors of incompatibility than the BMCI.

BMCI is designed to be a measure of aromaticity of a solvent and ranges from zero for hexane to 100 for toluene. It is calculated from the following equation:

$$\mathrm{BMCI} = 87552/(\mathrm{ABP} + 460) + 473.7\ \mathrm{SG} - 456.8$$

where:

ABP = Average Boiling Point, °F
SG = Specific Gravity, 60/60 °F

BMCI may also be estimated from other parameters (14), but these have not been used in this work.

The BMCI for actual commercial residual fuels analyzed in this project ranged from a low of 46-48 for the line-plugging problem set (1956 and 1964) to as high as 77 for one of the highly aromatic fuels in the residual fuel oil data base (#2035). More extreme BMCI's were observed for various materials prepared at NIPER; from 41-43 for resid from highly aliphatic Nigerian and Ekofisk crudes to 84 for visbroken Mayan resid, and 85-103 for blends containing high levels of fluid cat cracker recycle oil or slurry oil.

Toluene equivalence is the percentage of toluene required in a blend of toluene/hexane to completely dissolve a fuel or resid. Complete solubility is determined by application of a drop of solution to a filter paper and the appearance of the resulting spot. In the Exxon papers, the toluene equivalence was measured on residual material. We have applied the test to the total residual fuel as the utility will generally not have ready access to the resid alone.

As with the BMCI, a wide range of toluene equivalences was observed for the commercial residual fuels; from low values of 4-6 for the line-plugging problem set (1956 and 1964) to as high as 85 (for the viscosity instability problem sample #2020). The range is widened by including the resids from the Nigerian and Ekofisk crudes (TE = 0) and visbroken Mayan resid (TE = 100).

In the work of Griffith and Siegmund, they concluded that a blend of two components would be compatible (would not precipitate asphaltenes) if the blend met the conditions (BMCI - TE) > K. Their value for K was in the range of 7 to 14. Therefore, by knowing the values of BMCI and TE of a potential blend, both of which can be calculated from these properties of the blend components, one should be able to predict if incompatibility will occur.

We determined the BMCI and TE of a number of oils and blends and determined the level of sediment via the IP hot filtration method (dual filter). Results of this work are summarized in table 10. The utility of the BMCI and TE measures for predicting incompatibility is apparent by evaluation of the data in table 10. We have set a standard of satisfactory compatibility as a hot filtration sediment value of ≤0.1 wt % and a (BMCI - TE) of >10 as a predictor of satisfactory compatibility. In examination of the values in table 10, one finds 12 oils with (BMCI - TE) <10. Of these 12, 11 of them have sediment values >0.1 wt %. Of the 16 samples with (BMCI) >10, all but two have sediment values <0.1%.

In conclusion, measures of solvent quality and solvent quality demand can be used to predict problems of incompatibility for potential blends with a high probability of success.

CONCLUSIONS

- The commonly used tests for characterization of residual fuel oils are inadequate to allow prediction of handling problems.
- Problems with fuel oils experienced by utilities could in some cases be reproduced in the laboratory and correlated with fuel properties. In other cases, the problem reported by the utility could not be reproduced or satisfactorily explained.
- A baseline test for determination of stability of residual fuels involving long-term aging at 80° C was developed; this test involved monitoring changes in sediment (determined by hot filtration), asphaltene content, and viscosity.
- Concentration of carbon free radicals as determined by electron spin resonance spectroscopy (ESR) correlates with viscosity instability.
- Residual fuel oils containing significant levels of coke may exhibit viscosity instability; however, the absence of coke does not assure that the sample will not undergo large increases in viscosity on aging.
- Additional data are required to evaluate a potential correlation between sediment formation on aging with the Shell accelerated dry sludge test.
- A baseline test for incompatibility involved preparation of blends followed by determination of sediment by hot filtration.
- In most cases, incompatibility of residual fuel oils can be predicted by consideration of two factors: the solvent quality and the solvent quality demand. Solvent quality is adequately determined by BMCI and solvent quality demand by toluene equivalence.
- Potential correlations between acid-base contents and problem behavior require further evaluation.

REFERENCES

1. Proceedings of the 1985 Fuel Oil Utilization Workshop, Atlanta, GA, June 19-20, 1985. EPRI Report AP-4431, February 1986.

2. Wright, Bob W., Don R. Kwalkwarf, Richard D. Smith, Dennis R. Hardy, and Robert N. Hazlett. "Storage Stability of Diesel Fuel Marine: Relation to E.S.R. Measurements." Fuel, Vol. 64, 1985, p. 591.

3. Stavinoha, L. L., and C. P. Henry, editors. "Distillate Fuel Stability and Cleanliness." ASTM Special Technical Publication 751, 1981.

4. Mueller, Howard. "Residual Fuel Oil Markets: The Source of Changes In Resid Quality." Proceedings of the 1985 Fuel Oil Utilization Workshop, Atlanta, GA, June 19-20, 1985. EPRI Report AP-4431, February 1986.

5. Beck, Bob. "Stocks to Play Smaller Role in Meeting Winter Fuel Demand." Oil and Gas Journal, December 2, 1985, p. 27.

6. Anderson, R. P., J. W. Goetzinger, and D. W. Brinkman. "Storage Stability and Compatibility of Heavy Fuel Oils." Proceedings of the Tenth Annual EPRI Contractors' Conference on Clean Liquid and Solid Fuels. EPRI Report AP-4253-SR, October 1985.

7. Lewis, C. P. G., R. Quillet, and T. Schreuder. "Resid Fuel-Oil Stability, Cleanliness Test Improved." Oil & Gas Journal, April 8, 1985, p. 73.

8. Green, J. B., R. J. Hoff, P. W. Woodward, and L. L. Stevens. Fuel, Vol. 63, 1984, p. 1290.

9. Holmes, J. W., and J. A. Bullin. "Fuel Oil Quality Probed." Hydrocarbon Processing, September 1983, p. 101.

10. Griffith, M. G., and C. W. Siegmund. "Controlling Compatibility of Residual Fuel Oils." ASTM Marine Fuels Symposium, Miami, FL, December 7-8, 1983.

11. Griffith, M. G., and C. W. Siegmund. "Controlling Compatibility of Residual Fuel Oils." Proceedings of the 1985 Fuel Oil Utilization Workshop, Atlanta, GA, June 19-20, 1985. EPRA Report AP-4431, February 1986.

12. Exxon Analytical Method - Specification 79-004 (March 1979). Revised April 1980. Exxon Research and Engineering Company, P.O. Box 191, Linden, NJ 07096.

13. Smith, H. R. "Correlation Index to Aid in Interpreting Crude Oil Analysis." Bureau of Mines Technical Paper 610, U.S. Government Printing Office, Washington, DC, 1940.

14. Abbott, M. M., T. G. Kaufman, and L. Domash. Canadian Journal of Chemical Engineering, Vol. 49, 1971, p. 379.

Table 1

RESIDUAL FUEL OIL DATA BASE

Test	1768	1861	1953	1964	1980	2033	2035	2041	2103
°API Gravity	16.2	17.8	12.2	20.5	14.7	11.3	10.6	5.5	10.0
Elemental, wt%									
Carbon	84.79	86.70	85.94	86.40	86.68	84.32	84.74	88.63	85.98
Hydrogen	11.82	11.94	10.60	12.44	11.30	10.52	10.34	9.32	10.17
Nitrogen, Kjeldahl	0.45	0.34	0.47	0.26	0.38	0.45	0.53	0.25	0.41
Sulfur, Leco	1.02	0.34	2.47	0.35	1.00	4.34	2.51	0.98	1.35
Carbon Residue, wt%									
Conradson	12.97	11.10	17.94	7.18	12.99	18.09	19.25	13.60	21.13
Fuel Asphaltene, wt.%									
D 3279	3.78	4.05	10.35	1.29	4.69	11.96	12.12	5.60	9.64
Pentane	7.14	6.16	15.44	1.94	7.15	17.84	17.42	10.04	14.58
Flash Point*, ° C	136.5		73.5	149.5	114.5	66.0	84.5	96.5	72.5
Ash Content, wt%	0.045	0.043	0.075	0.010	0.043	0.066	0.086	0.063	0.020
Ash Composition									
X-ray, qualitative	Ca,V, Ni,Zn	Ni,Fe	V,Ni, Fe,Pb	Fe, Ni	V,Fe,Ni	V,Ni	V,Ni	Ca,V,Ni, Fe,Pb,Zn	V,Ni, Fe
Viscosity, SFS, 122°F	235	130	159	59.6	112	465	338	120	238
Residue, wt.% (D 1160)	55	61	53	38	40	53	42	38	60

* By Pensky-Martens Closed Cup (ASTM D 93)

Table 2

UTILITY SUPPLIED "PROBLEM" AND "NONPROBLEM" SAMPLES

Identification #		Problem
"Problem" Sample	"Nonproblem" Companion	
1761-62	---	Strainer Plugging
---	1768	---
1956	1964	Line Plugging During Cyclic Boiler Operation
1954	1980	Fuel Heater Plugging
2020-2022	1861	Viscosity Instability

Table 3

GENERAL ANALYSES OF UTILITY SUPPLIED PROBLEM/NONPROBLEM FUEL OILS

Property	1768, Nonproblem	1956, Problem	1964, Nonproblem	1954, Problem	1980, Nonproblem	2021 Problem	1861 Nonproblem
Specific gravity @ 60°/60° F	0.958	0.924	0.931	0.963	0.968	0.950	0.948
Gravity, ° API	16.2	21.6	20.5	15.4	14.7	17.5	17.8
Kinematic viscosity,							
cSt @ 122° F	499.2	88.5	124.2	426.1	237.1	1299.	275.3
@ 180° F	82.7	23.6	30.3	65.6	47.4	139.3	57.9
Pour Point, °F	65.	85.	90.	90.	55.	65.	90.
Elemental, wt %							
Carbon	84.79	86.50	86.40	86.60	86.68	86.00	86.70
Hydrogen	11.82	12.53	12.44	11.50	11.30	11.55	11.94
Sulfur, (Leco)	1.02	0.35	0.35	0.93	1.00	0.41	0.34
Nitrogen, (Kjeldahl)	0.45	0.23	0.26	0.35	0.38	0.50	0.34
Asphaltenes, wt %							
n-Pentane	7.14	1.56	1.94	11.92	7.15	17.70	6.16
n-Heptane, by ASTM D3279	3.78	0.77	1.29	9.84	4.69	13.65	4.05
n-Heptane, by Speight recommendations	7.17	2.02	3.77	10.05	6.46	15.16	8.02
Carbon Residue, wt %							
(Ramsbottom)	10.50	4.57	5.40	11.53	10.52	12.48	8.76
(Conradson)	12.97	6.16	7.18	14.06	12.99	15.06	11.10
Ash, wt %	0.04	0.019	0.010	0.053	0.030	0.073	0.042
Biological Activity	Anaerobic	Aerobic and Anaerobic	Aerobic	None	None	None	Anaerobic

Table 4

GENERAL ANALYSES OF DISTILLATES AND RESIDUES PRODUCED FROM UTILITIES SUPPLIED PROBLEM/NONPROBLEM FUEL OILS

Original Fuel Oil	1768 (Nonproblem)		1956 (Problem)		1964 (Nonproblem)		1954 (Problem)		1980 (Nonproblem)	
Fraction	Distillate	Residue	Distillate	Residue	Distillate	Residue	Distillate	Residue	Distillate	Residue
Yield	32.12	65.28	56.20	41.79	47.13	49.74	48.20	49.40	46.88	50.27
Specific Gravity @ 60°/60° F	0.8826		0.8987		0.9008		0.9137		0.9267	
API Gravity	28.8		25.9		25.6		23.4		21.2	
Carbon Residue, wt.% (Conradson)		19.46		13.88		13.50		23.61		22.37
Elemental Analysis, wt%										
Carbon	84.83	85.50	86.54	86.18	86.74	86.20	85.42	85.66	86.86	85.25
Hydrogen	12.76	10.94	12.89	11.91	12.85	12.06	12.20	10.41	11.84	10.43
Sulfur (Leco)	0.726	1.28	0.274	0.504	0.217	0.422	0.689	1.33	0.849	1.37
Nitrogen (Kjeldahl)	0.067	0.621	0.075	0.391	0.074	0.416	0.088	0.589	0.112	0.617
Pentane Asphaltenes, wt.%		11.88		4.59		3.78		25.94		15.68
Heptane Asphaltenes,* wt.%		8.54		2.18		2.02		17.67		9.59
Calculated**		6.20		1.84		2.59		19.91		9.32

* ASTM D 3279

** Calculated from asphaltene content of original residual fuel oil and distillates results.

Table 5

ADDITIONAL SAMPLES FOR INSTABILITY/INCOMPATIBILITY TESTING

ID#	Source	Comment
1953	Residual Fuel Oil Data Base	See Table 1
2033	Residual Fuel Oil Data Base	See Table 1
2035	Residual Fuel Oil Data Base	See Table 1
2041	Residual Fuel Oil Data Base	See Table 1
2103	Residual Fuel Oil Data Base	See Table 1
2114	Blend 30% 2035, 70% 2111	Blend high asphaltene fuel with highly aliphatic fuel (Nigerian)
2115	Blend 70% 2035, 30% 2111	Same as 2114 except blending ratio
2116	Blend 70% 2035, 30% 2112	Blend high asphaltene fuel with highly aliphatic fuel (Ekofisk)
2117	Blend 30% 2035, 70% 2112	Same as 2116 except blending ratio
2118	Blend 50% 2109, 50% resid from 1954	Blend cat cracker heavy recycle oil and +1000° F resid for relatively high asphaltene 1% S fuel oil
2119	Blend 50% 2110, 50% resid from 1954	Same as 2118 except cat cracker slurry oil
2120	Utility fuel oil	Reported as high in sediment

Table 6

ELECTRON SPIN RESONANCE

Sample #	Description	Vanadyl Radical Concentration	Carbon Free Radical Concentration
1735	Mayan Resid	1.45	13.40
2032	Visbroken Mayan Resid	1.28	22.50
2021	Viscosity Instability	0.00	22.10
1861	Nonproblem Companion	0.00	15.61
1954	Heater plugging sample	0.31	16.20
1980	Nonproblem	0.12	11.80
2103	Hydrocracked Sample	0.01	15.80
1768	Nonproblem Sample	0.27	15.90
1956	Line plugging sample	0.00	7.70
1964	Nonproblem	0.00	9.29

Table 7

COKE DETERMINATION FOR THE VISCOSITY INSTABILITY PROBLEM SET

	Toluene Insolubles	Insolubles Analysis				
		%C	%H	%N	%S	Total
2020 (P)	0.47	81.95	4.94	1.67	0.47	89.03
2021 (P)	0.76	88.44	5.13	1.81	0.45	95.38
2022 (P)	0.41	92.71	5.28	2.03	0.22	100.02
1861 (NP)	0.04	Insufficient Sample				

Table 8

SEDIMENT BY EXTRACTION AND VISCOSITY STABILITY

Sample I.D. #	Viscosity, Centistokes at 180°F after Aging at 80°C			Sediment by Extraction
	0 Weeks	4 Weeks	% Change	
2021	139.3	921.4	560	0.44
2035	97.8	245.9	151	0.01
2032	186.2	325.0	75	~1.00
1768	82.7	143.6	74	0.00
2033	134.9	200.7	55	0.00
2103	69.6	104.9	51	0.02
2041	39.1	57.3	47	0.02
1953	66.4	97.1	47	0.01
2120	42.2	57.2	36	0.06
1980	47.5	58.3	23	0.01
1954	65.6	78.0	19	0.01
1964	30.3	32.5	7	0.01
1956	23.6	24.4	3	0.01

Table 9

ACID-BASE-NEUTRAL FRACTIONATION OF TOTAL FUEL OILS

	Strong Acids	Strong Bases	Weak Acids	Weak Bases	Neutrals	Totals
1768 Nonproblem	1.20	12.70	6.02	7.88	73.33	101.13
1956 Line Plugging	2.90	5.59	4.79	2.81	85.44	101.53
1964 Nonproblem	2.28	10.32	5.28	6.59	77.68	102.17
1954 Heater Plugging	3.87	11.11	4.79	1.67	80.27	101.71
1980 Nonproblem	3.08	9.06	9.26	5.17	74.82	101.39
2020 Viscosity Instability	6.22	16.30	8.30	5.70	68.07	104.59
2021 Viscosity Instability	7.56	16.57	8.69	5.63	67.31	105.76
2022 Viscosity Instability	5.30	16.19	9.10	6.52	67.35	104.46
1861 Nonproblem	4.49	12.07	9.05	6.95	76.05	108.61
2032 Visbroken Mayan	12.47	7.74	3.26	2.42	72.99	98.88

Table 10

BMCI, TE, AND SEDIMENT HOT FILTRATION

Oil No.	BMCI	TE	BMCI-TE	Sediment by Hot Filtration Wt. Pct.
1768	54	24	30	0.00
1956	46	6	40	0.02
1964	48	4	44	0.01
1954	61	5	56	0.00
1980	65	46	19	0.05
2020	74	85	-11	0.16
1861	52	5	47	--
1953	69	44	25	0.00
2033	73	24	49	0.00
2035	77	61	16	0.02
2103	75	66	9	0.27
2032	84	100	-16	U
2113	55	54	1	U
2114	52	76	-24	U
2115	65	67	-2	1.57
2116	66	63	3	3.41
2117	55	66	-11	3.24
2118	85	27	58	0.02
2119	103	37	66	0.02
2120	74	85	-11	0.16
2122	78	100	-22	13.12
2133	50	43	7	0.31
2134	58	10	48	0.00
2135	55	34	21	0.30
2136	54	34	20	0.07
2137	54	52	2	0.01
2138	58	32	26	0.00
2139	69	54	15	0.50

U = unfilterable

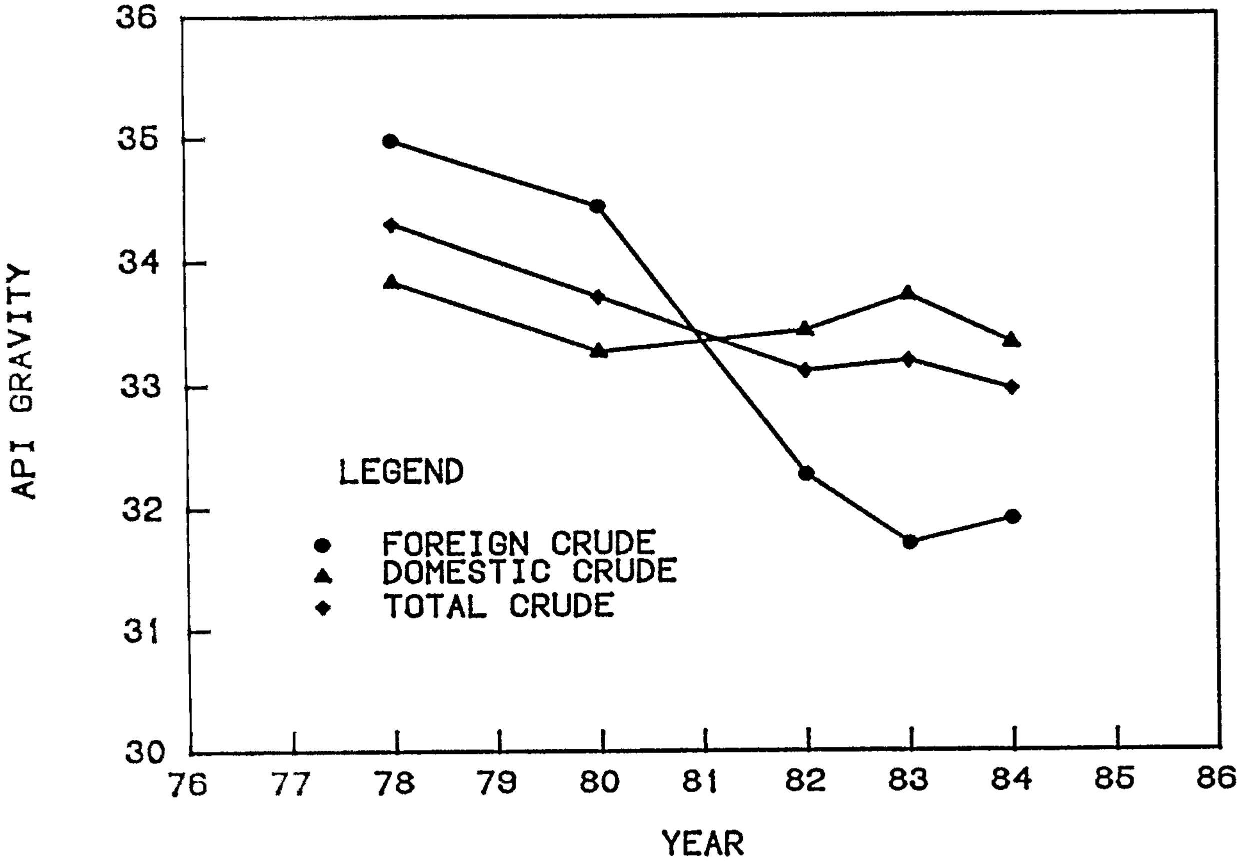

Figure 1. U. S. refinery crude feedstock API gravity.

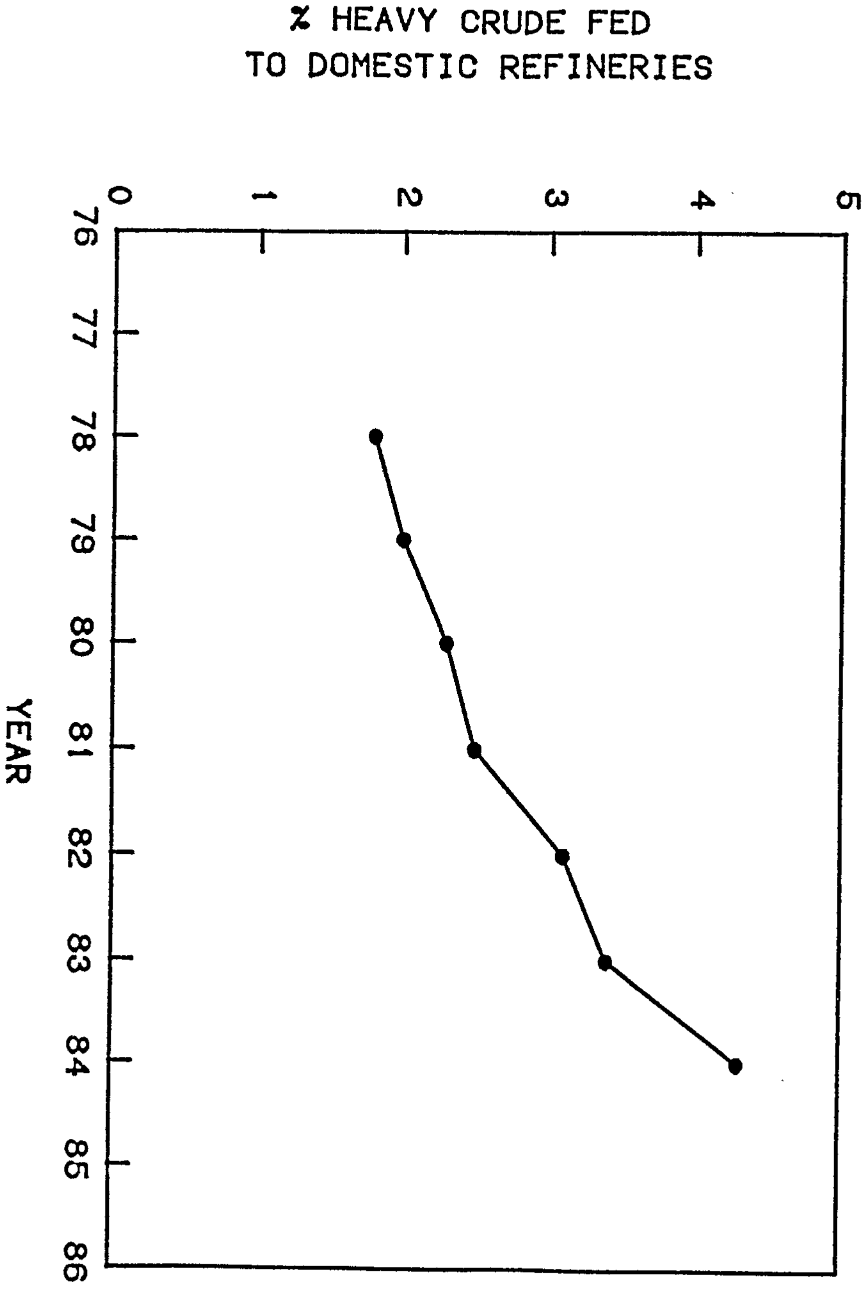

Figure 2. Percent heavy crude processed by U. S. refineries.

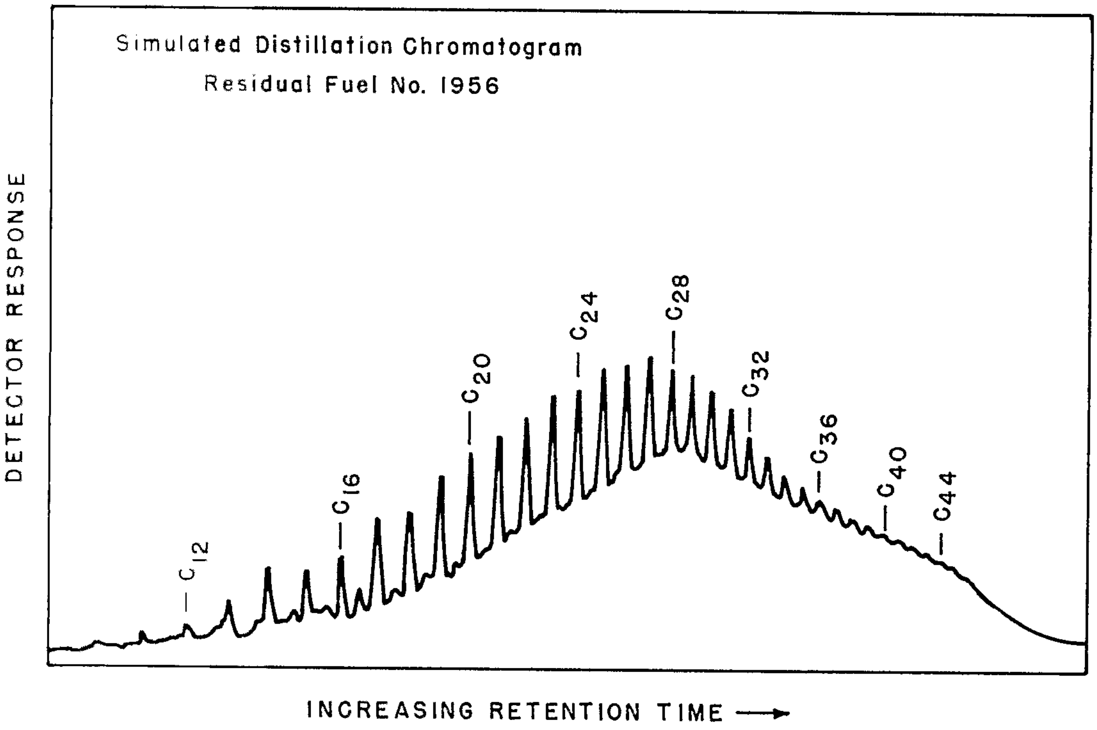

Figure 3. Simulated distillation chromatogram for the problem fuel No. 1956.

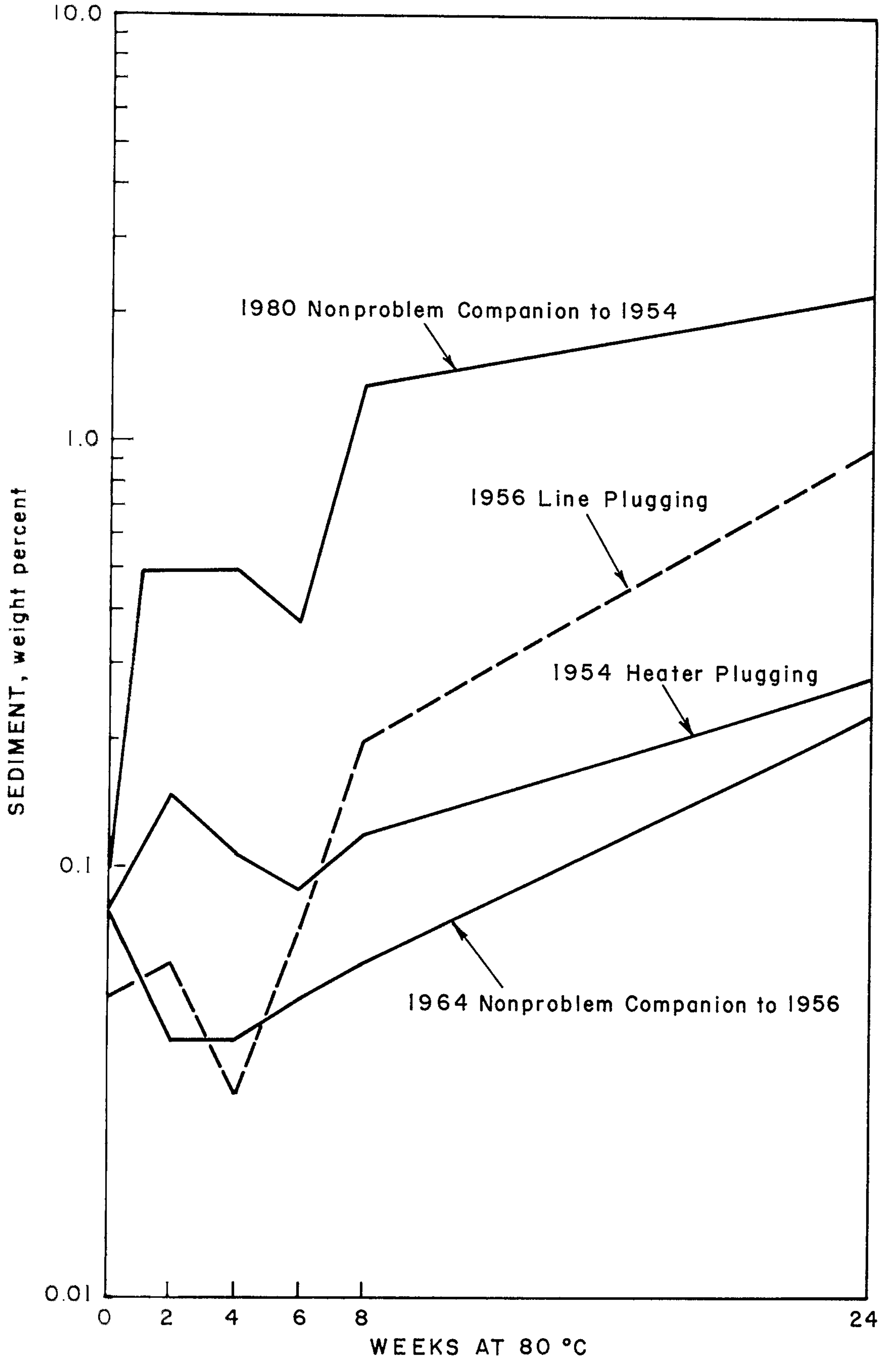

Figure 4. Sediment formation on 80° C aging.

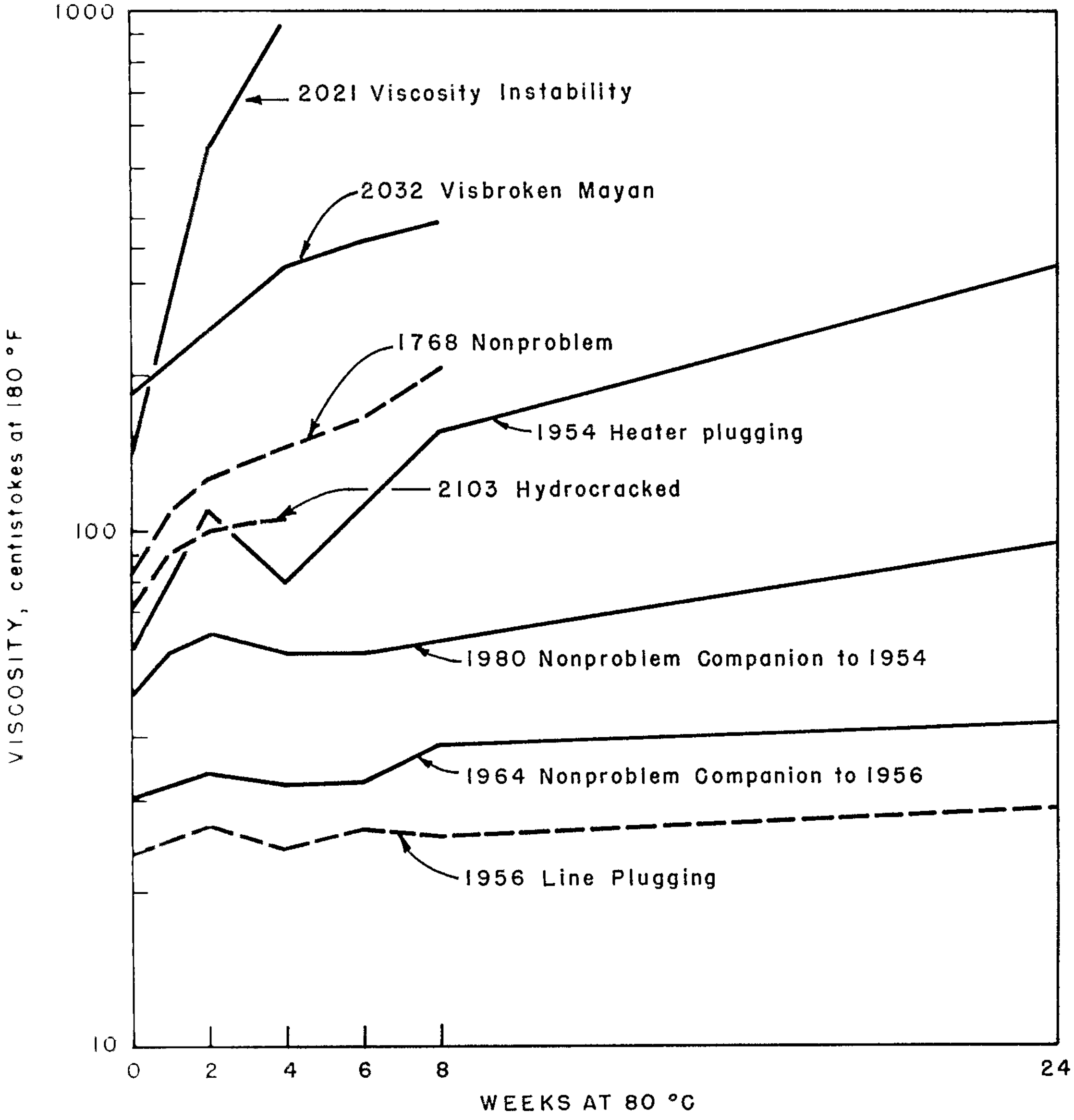

Figure 5. Viscosity change on 80^0 aging.

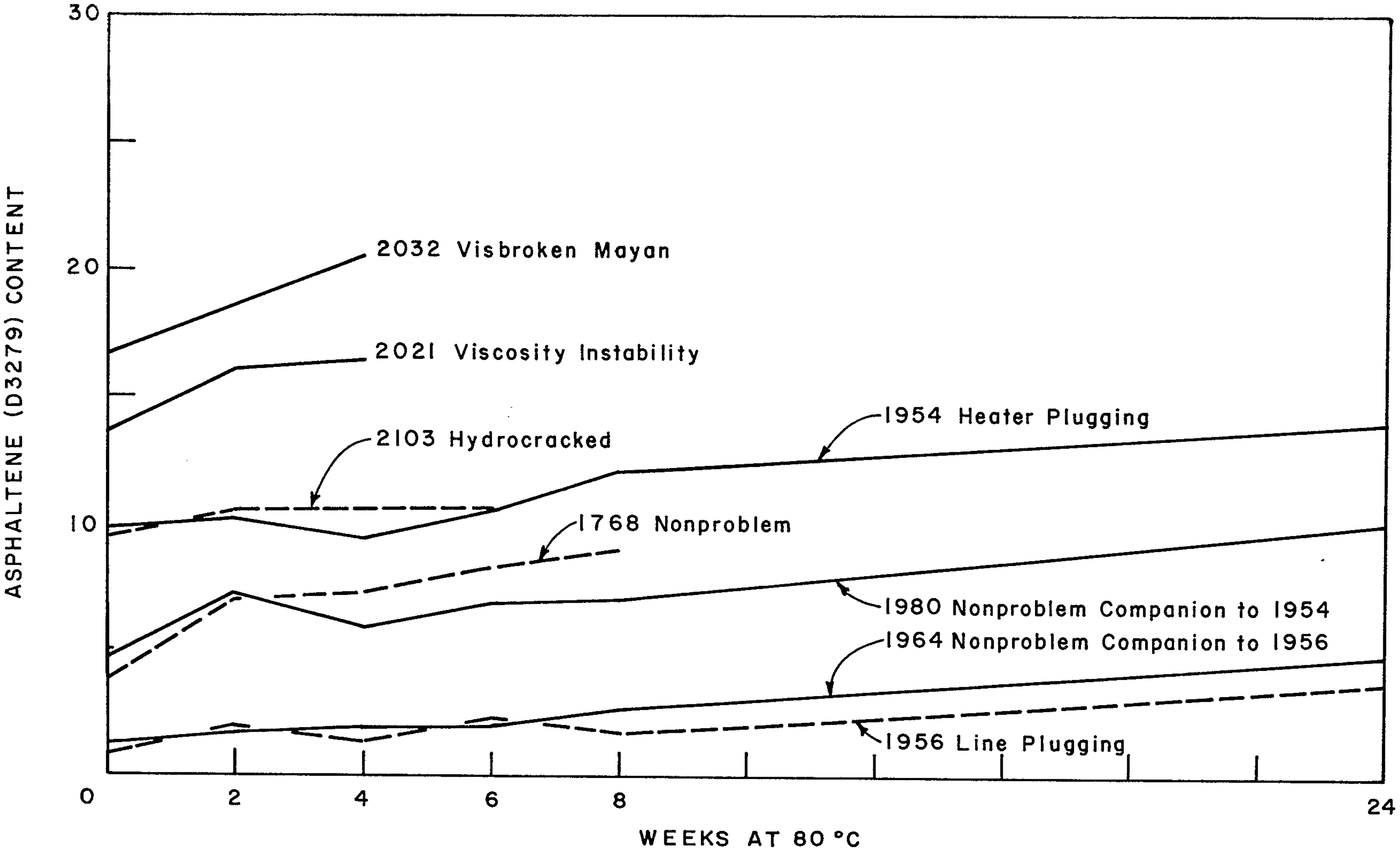

Figure 6. Asphaltene content change on 80^{o} aging.

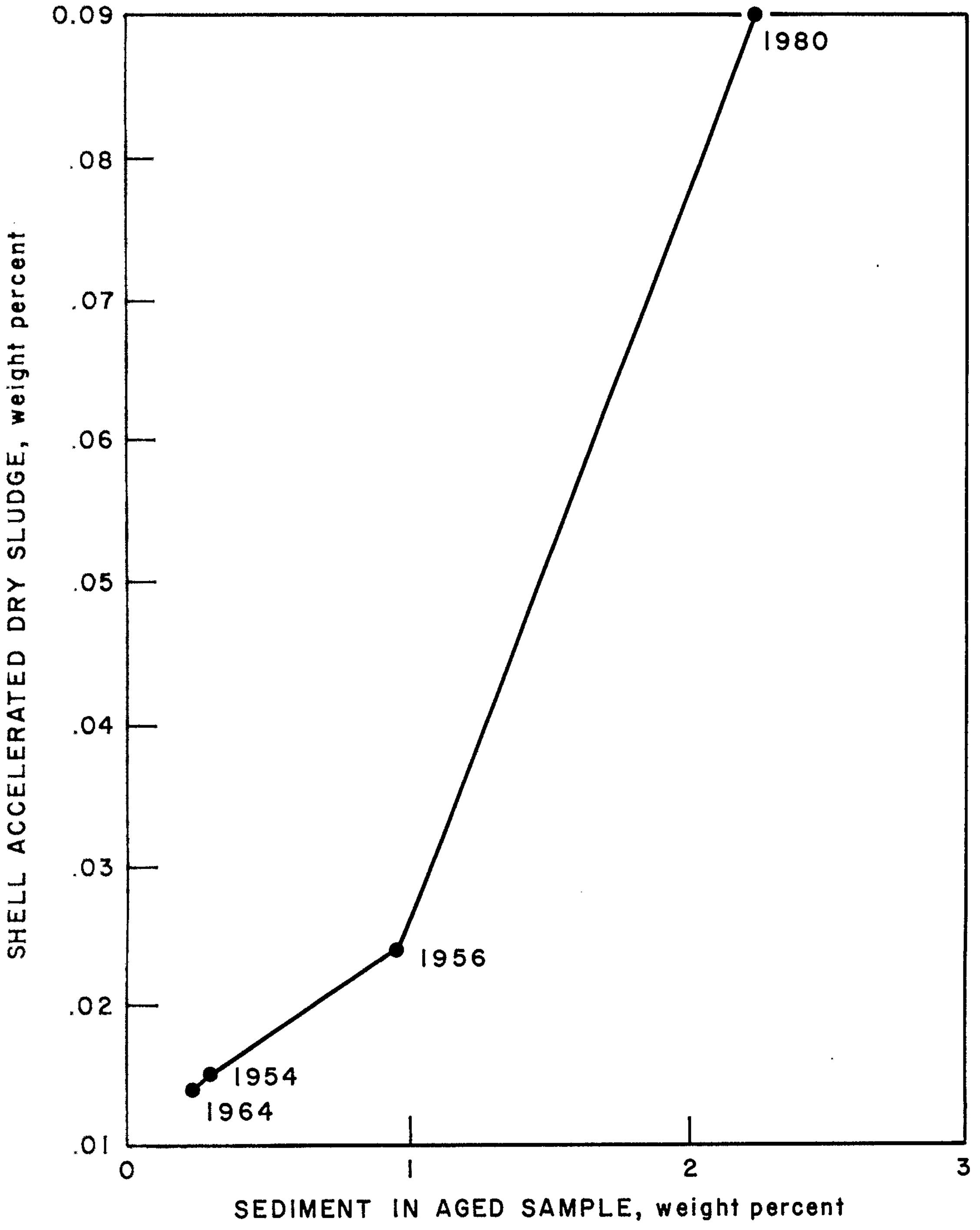

Figure 7. Correlation Shell accelerated dry sludge with sediment on 80^0 C aging.

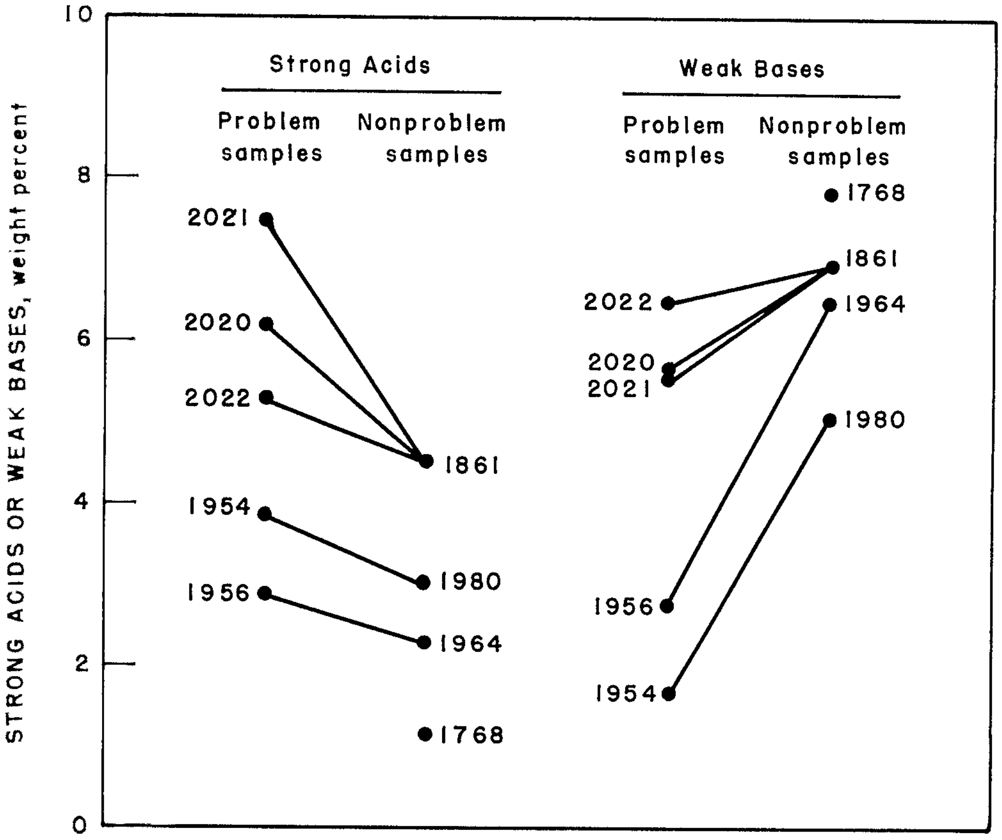

Figure 8. Strong acid and weak base content for problem/nonproblem fuels.