COAL-OIL COPROCESSING AT HTI

Development and Improvement of the Technology

DOE Contract No. DE-AC22-94PC91036

(September 1994 - September 1997)

<u>R.H. Stalzer</u>
L.K. Lee
J. Hu
A. Comolli

Hydrocarbon Technologies, Inc.
PO Box 6047
New York & Puritan Avenues
Lawrenceville, NJ 08648

COAL AND GAS CONVERSION CONTRACTORS' REVIEW CONFERENCE

AUGUST 29-31, 1995

INTRODUCTION

Co-Processing refers to the combined processing of coal and petroleum-derived heavy oil feedstocks. The coal feedstocks used are those typically utilized in direct coal liquefaction: bituminous, subbituminous, and lignites. Petroleum-derived oil is typically a petroleum residuum, containing at least 70 W% material boiling above 525°C. The combined coal and oil feedstocks are processed simultaneously with the dual objective of liquefying the coal and upgrading the petroleum-derived residuum to lower boiling (< 525°C) premium products. HTI's investigation of the Co-Processing technology has included work performed in laboratory, bench and PDU scale operations.

The concept of co-processing technology is quite simple and a natural outgrowth of the work done with direct coal liquefaction. In direct coal liquefaction, a feed coal slurry is produced by mixing pulverized coal with a process-derived recycle oil. This slurry allows the coal feedstock to be pumped and preheated to reaction conditions. The concept of coprocessing is to replace the process-derived recycle oil with an external, petroleum-derived residue which also needs to be upgraded. This eliminates costs and equipments associated with preparation and handling of the recycle slurry oil and should, therefore, reduce the cost of liquid fuels from coal.

A 36 month program to evaluate new process concepts in coal-oil coprocessing at the bench-scale was begun in September 1994 and runs until September 1997. Included in this continuous bench-scale program are provisions to examine new improvements in areas such as: interstage product separation, feedstock concentrations (coal/oil), improved supported/dispersed catalysts, optimization of reactor temperature sequencing, and in-line hydrotreating. This does not preclude other ideas from DOE contracts and other sources that can lead to improved product quality and economics.

Direct Coal Liquefaction Technology Background: Hydrocarbon Technologies, Inc. (HTI) has a very strong background and experience in performing research and development in catalytic direct coal liquefaction technology. The personnel of HTI have conducted research on coal liquefaction for more than 25 years. During this time, they have evaluated both thermal-catalytic and catalytic-catalytic coal liquefaction configurations with several alternative reactor designs and process operating conditions. A simplified flow diagram of a catalytic two-stage direct coal liquefaction (CTSL) technology is shown in *Figure 1*. This research work has led to important findings which significantly increased liquid yields, improved product quality, and improved process economics. The following process changes led this to improved performance:

- Staging coal liquefaction reactions
- Lower temperature and higher residence times
- Low-High and high-low temperature mode of operations in Catalytic Processing
- Heavier (343°C$^+$) boiling recycle solvents
- Coal concentration in feed slurries increased from ca. 30 W% to ca. 53 W%
- Deep coal cleaning
- Continuous sulfiding for low-rank, low-sulfur coals
- In-Line hydrotreating
- Use of synthesis gas in first stage instead of pure H_2
- Use of interstage product separation
- Combined processing of coal, resid, waste oils and plastics

With all these process improvements, the CTSL Process, in an extinction recycle mode of operation, provides a much better overall performance (for both bituminous and sub-bituminous coals) than the H-Coal Process, developed in the early 1980's (*Table 1*).

Coal/Oil Co-Processing Technology Background: HTI's approach to coal-oil coprocessing uses a two-stage reaction system with either extrudate catalyst in both reactors or a combination of a dispersed and a supported catalyst in the reactor stages. A simplified process flow-diagram for coal-oil coprocessing is shown in *Figure 2*. So far, HTI's personnel have been involved in a significant number of coprocessing research, development, and pilot-scale demonstration projects. A total of about 450 days of experience operating coal-oil coprocessing programs in continuous bench-scale units (25 kg/day throughput) has been accumulated. The distribution of this experience as per the types of feedstocks is shown in *Table 2*. This bench-scale operating experience has helped them build a bench-scale database covering not only feed coals and oils with varying properties but also a range of operating conditions and process configurations with the corresponding data on process performance. Coal and residuum conversions as high as 97 and 93 W% maf feed, respectively, have been achieved (*Table 3*) with C_4-525°C distillate yields of above 80 W% maf feed. Significant metal and heteroatom removals have also been obtained. All these achievements have improved the overall economics of coal liquefaction via coal-oil coprocessing. At present, coprocessing promises to be 25-30 % more economical than direct coal liquefaction, thus making noticeable headway towards reducing the cost of liquid fuels from coal to below $25 per barrel.

Low/High Temperature Staging and Interstage Separation: One of the prime factors that limits the capacity of a reaction train in ebullated-bed reactors, and therefore adds to product cost, is the velocity of the gas passing through a reactor. The higher this gas velocity, the greater is the gas holdup and consequently the lower is the effective reactor liquid volume. Reactor train sizing is performed by setting the gas velocity at the maximum operable level. This determines the reactor diameter and the required reaction severity determines the height. *Table 4* provides an illustration of hydrogen management options for two-stage reactor configurations. It is assumed that one unit of hydrogen is consumed in the reaction and that 4 units are supplied to the reactors to maintain adequate hydrogen partial pressure. Cases 1 and 1A are for equal reactor temperatures while cases 2 and 2A are for low/high temperature staging. The A cases include the use of an interstage separator between the first and second reactor. Previous experience has shown that for a two-stage system operating at equal temperatures approximately 75-80% of the hydrogen is consumed in the first stage. The low and high temperatures are selected such that 50% of the hydrogen is consumed in each stage.

In cases 1 and 1A, where 80% of the hydrogen is consumed in the first stage, 80% of the fresh hydrogen is supplied to the first stage. This results in a total supply of 3.2 units to the first stage and either 3.2 or 0.8 units to the second stage, depending on whether or not the interstage separator is used to remove all the first stage gases. In cases 2 and 2A, where 50% of the hydrogen is consumed in the first stage, 50% of the fresh hydrogen is supplied to the first stage. This results in a total supply of 2.0 units to the first stage and either 3.5 or 2.0 units to the second stage, depending on whether or not the interstage separator is used to remove all the first stage gases. For equal reactor temperatures the limiting gas velocity is 3.2 with or without the use of interstage separation. For low/high temperature staging the limiting gas velocity is 2.0 with interstage separation (3.5 without separation). Temperature staging with interstage separation could yield a maximum increase in capacity per reaction train of 60% (3.2/2.0=1.60).

Coal/Oil Coprocessing Synergy: Process synergy is an oft discussed but little understood aspect of coal/oil coprocessing. Process synergy, in terms of enhanced 525°C+ conversion, has been identified in coal/oil coprocessing from batch reactivity screening. It is more difficult to directly detect the synergy in bench scale operations as different modes of operation are employed in coal only liquefaction as opposed to oil only processing. It is possible to infer synergy on coprocessing bench operations with a few assumptions. If it is assumed that the conversion at 10 W% coal is a good representation of oil only operation and that the conversion at 40 W% coal provides an upper limit on conversion for coal only operation, inferences can be made regarding process synergy. As *Figure 3* shows, conversion at 20, 33 and 40 W% coal is significantly higher than would be expected if there was no synergy. At 33 and 40 W% coal, the conversion is 6 W% higher than would be expected.

The other aspect of process synergy in coal/oil coprocessing is demetallization by solids. Petroleum derived oil feedstocks contain metals contaminants, primarily nickel and vanadium, at concentrations as high as 500-1500 wppm. In oil only processing, these metals deposit on the catalyst as metal sulfides permanently poisoning the catalyst. The higher the level of metals in the feed, the higher the rate of catalyst deactivation. In coprocessing a large portion of the metals are deposited in the product solids. As can be seen in Figure 4, which shows the metals concentration in the product solids over the course of a test, these concentrations increase with catalyst age. Over the course of this test 99% of the metals were removed from the liquid product. Of this demetallization, over 90% occurred on the coal solids.

OBJECTIVES

The overall objective of this proposed research and development program is to further develop and improve coal/oil co-processing technology with an emphasis on better integration to existing refinery operations. Improvements can be realized in terms of increased selectivity to distillate products, improved product quality and increased reactor space velocity. These improvements will lead directly to improved economics and the potential for early commercialization of direct coal liquefaction technology. The specific objectives of this program are:

- To enhance co-processing reaction rates through utilization of improved catalysts and optimization of the first- and second-stage temperatures.

- To perform catalyst activity screening, including new high activity ebullated-bed catalysts, dispersed catalysts and combinations of extrudate and dispersed catalysts.

- To study reactant/product and coal-derived liquid/petroleum-derived residuum solubility ranges over a range of coal loadings in this reactor and process configuration.

- To maximize liquid product yields and product quality in an optimized two-stage co-processing system with in-line hydrotreating.

- To assess and optimize the operation of catalytic two-stage coal/oil co-processing technology, operating with interstage separation.

- To provide guidance to ongoing research by performing economic assessments of proposed modifications to the reactor configurations.

PROJECT STATUS

Microautoclave Test Program: The microautoclave unit is composed of two tubular reactor bombs which are mechanically shaken in a heated, fluidized sand bath. The reactors are charged with specific amounts of materials and can be pressurized to 13.5 MPa or greater. The bombs are plunged into a sand bath maintained at a predetermined temperature, then agitated for a specified amount of time. After reaching the desired temperature, the bombs are removed, plunged into a water bath for cooling, and the contents analyzed.

This part of the program serves as the initial screening of new catalyst types, coal/oil combinations, and operating conditions as they affect the reactivity. The microautoclave provides a very rough indication of relative reactivities. Gram quantities of feedstock, diluent and catalyst are charged to the microautoclave reactor. Information can be obtained on 525 °C+ conversion via thermogravimetric analysis, to simulate product distillation, and on coal conversion via extraction with tetrahydrofuran (THF) and ash analysis. In this program, the following microautoclave determinations, approximately 70-80 tests, are planned:

- Co-Processing Feedstock Reactivity - 2 coals and 3 oils will be evaluated (6 feedstock combinations). Reactivity will be evaluated at constant operating conditions (432 °C and 90 minutes residence time) for coal concentrations of 0, 10, 30, 50 and 100 % coal. A total of 25 tests are planned, including repeats and duplicates.

- Effect of Hydroaromatic Solvent Addition on Oil Reactivity - Solvents rich in hydroaromatics will be added to a selected petroleum feedstock to help elucidate process synergy effects in a hydrocracking atmosphere. 10 tests are planned.

- Product Reactivity - Co-Processing vacuum bottoms product reactivity will be evaluated for selected products which represent a range of conversion levels over a range of severity. 15 tests are planned.

- Alternative Catalyst Screening Evaluation - Alternative extrudate catalysts (such as high activity supported hydrocracking catalysts for heavy resids, noble metal-based supported catalysts, etc.) and catalyst systems (dispersed and dispersed/extrudate) will be screened. Dispersed catalysts (based on iron, molybdenum, tin, and vanadium) developed in-house at HTI will be tested in this program. 20 tests are planned.

The first set of microautoclave test are presently in progress. The performance of dispersed catalysts in coprocessing will be compared to that of a supported catalyst, AKZO AO-60, on the basis of 525°C+ conversion. Molyvan A (or L) and $Mo/Fe_2O_3/SO_4$, developed at HTI, will be employed in these microautoclave runs. The effect of catalyst concentration on the product yield (THF soluble and cyclohexane soluble) will be investigated. The hydroaromatic solvents, FCC decant oil and coal-derived oil, will be used to help elucidate process synergy effects in a hydrocracking atmosphere.

Laboratory Scale CSTR Test Program: A continuous two-stage gradient-less, catalytic, stirred autoclave reactor system commonly known as the Robinson-Mahoney reactor system (Unit 245), was recently modified by the HTI scientists to change the internals, especially the catalyst baskets' configuration, to better simulate ebullated bed operation. The modified two-stage CSTR system, now known as the Lee-Faupel-Canas (LFC) reactor system, has two 1000 cc reactors in series and can handle feed rates in the range of 5 to 25g per day. It can operate at temperatures up to 454°C and pressures up to 20.3 MPa. HTI has developed an internally propelled fluid-bed catalyst basket to increase the catalyst loading to a level that more closely simulates an ebullated bed. The flow-patterns and mixing-behavior very closely approach those in a fully ebullated-bed system. It is used for catalyst testing, feedstock screening, and evaluation of process improvements. It can be used as a single-stage or two-stage system with coal slurry or oil feedstocks. This part of the program evaluates the best results obtained from the microautoclave program using a continuous stirred autoclave reactor system, LFC reactor.

Run 1 will provide a baseline operation at conditions selected to tie in to existing bench-scale co-processing data base. It will also confirm operating procedures for coal slurry processing in this unit. Runs 2-4 will evaluate catalysts. Catalysts selected will be based on HTI experience with new high activity hydrocracking catalysts and results from microautoclave catalyst screening study. Two high activity extrudate catalysts will be selected for testing. One test will be devoted to a dispersed catalyst or dispersed/extrudate catalyst test. These tests will be performed in two segments, an initial 3-day catalyst break-in condition, followed by 7-days of operation at a severity representative of projected commercial operations.

Runs 5-6 will be performed to optimize operating conditions for low/high temperature two-stage operation. The preferred catalyst system from the catalyst screening task will be used. Multiple operating conditions, lasting 3-4 days will be evaluated. Run No. 7 will be carried out to study the interstage separation of products. Since the LFC system has no provisions for interstage sampling, this test condition will be simulated by performing two single-stage runs. Products from the initial segment of the run will be cut to remove low boiling materials prior to feeding to the second segment.

The first LFC test is just starting up using a New Mexico coal from the McKinley Mine and a California heavy oil. This baseline test investigates the effect of adding a hydroaromatic solvent, FCC decant oil and a coal-derived liquid, on coal conversion, 524°C+ conversion and on product quality. The initial and final conditions of this test are identical so that catalyst deactivation can also be evaluated. The operating conditions have been selected to provide a tie point to HTI's previous experience in coprocessing.

Bench Scale Test Program: The two continuous bench scale units at the R & D center, designated by the numbers 227 and 238, consist of two-stage reactors each in series and can be operated to exhibit either plug-flow or CSTR kinetics. These reactors are each 2000 cc in volume, with a nominal diameter of one-inch and can be operated either as ebullated catalyst beds or simply as back-mixed reactors with unsupported dispersed slurry catalyst. It is also possible to close-couple the two bench systems in such a way that more than two reactors can be used at the same time if the objectives of the run demand such a configuration. Each unit has two reactors in series with reactor temperatures controlled by electrically-heated fluidized sand baths. The reactors are close-coupled as the effluent from stage one flows directly into stage two without product separation. Provisions can be made to add an interstage separator to unit 227. The units are fully integrated in terms of providing coal slurry mixing, feed preheat, reaction and product separation/recovery as part of the continuous operation. Both units are capable of operating at temperatures up to 485°C and pressures as high as 20.3 MPa. They can process coal, coal/oil, oil only feed, as well as other hydrocarbon mixtures

This part of the program represents the focal point for all of the process improvements identified by economic screening and the smaller scale experimental work. As the bench-scale products can be completely characterized, and interstage samples can be obtained commercial performance can be projected.

Run 1 will evaluate in-line hydrotreating. The objective of adding in-line hydrotreating is to produce co-processing products which can be processed in existing refineries with no separate processing prior to refining. This will improve the acceptability of co-processing to refiners and allow introduction of co-processing to conventional refineries. The in-line hydrotreating of the process distillates (IBP-399°C) from HTI's direct coal liquefaction bench-scale and PDU-scale units has been successful in producing net distillates with high H/C atomic ratios (> 1.8) and very low amounts of heteroatoms (less than 10 ppm of nitrogen and sulfur). The advantage of such a processing is that the feed-stream to the hydrotreater is already at a high temperature and contains sufficient partial pressure of hydrogen for further refining and heteroatom removal. During coprocessing Bench-Run No. 1, an in-line hydrotreater with a fixed-bed of conventional Ni-Mo/Al_2O_3 trilobe catalyst will be employed and the effect of temperature will be studied over a range of 363-379°C. It is also planned that an in-line hydrotreater will be made an integral part of bench-scale processing for the subsequent bench runs. This test is planned for August 1995.

Run 2 will use an improved catalyst. The catalyst, whether extrudates in both stages or a combination of dispersed/extrudate systems, will be based upon the results of catalyst-screening carried out in the microautoclave and CSTR systems. In general, the supported extrudate catalysts will be the high activity resid hydrocracking catalysts based on Ni-Mo or Co-Mo on alumina, while the dispersed catalysts will be based on iron and/or molybdenum.

Run 3 will be performed with low/high temperature staging. So far, most of the continuous bench-scale and PDU-scale co-processing operations at the HTI R & D facility have been carried out in two equal-temperature, catalytic, ebullated-bed reactor stages. The optimization of reactor temperature profiles for direct coal liquefaction led to a fully catalytic two ebullating-bed system with low temperature first stage for recycle solvent generation by hydrogenation and a higher temperature second stage for upgrading of the first stage products by hydrocracking. Low-high reactor temperatures will be in the range of 413-427°C for the first stage and between 441-449°C for the second stage reactor.

Run 4 will determine the effects of interstage separation. Separation of light distillates and off-gases between the reactor stages has been employed successfully during our ongoing catalytic multistage direct coal liquefaction program. In this process configuration, the feed stream entering the second stage reactor is more concentrated in the reactive components and has a higher hydrogen partial pressure. Thus, a distinct kinetic advantage is obtained. The interstage hot separator will be maintained at around 343°C during Run 4, and the effects of feed space velocity and reaction severity on overall process performance will be studied.

Run 5 will study the thermal/catalytic configuration with dispersed catalyst in the first stage back-mixed thermal reactor. In this run, a combination of a dispersed and an extrudate supported catalyst will be used, i.e., the first stage will have a high surface area, fine dispersed catalyst, while the second stage will be an ebullated-bed reactor with a supported catalyst. The performance data obtained during this run will be compared with that from one of the earlier bench runs employing a catalytic-catalytic reactor system.

With the exception of Run 5, which is for 12 days, each run is scheduled for 15-days at target operating conditions. The total bench-scale program includes 72 operating days at target conditions. A typical bench-scale operation of 15 days will include evaluation of multiple operating conditions. A minimum length of evaluation for a single condition is 3 days. Depending upon specific operating conditions some conditions will be maintained for 4-6 days. A 15-day run will usually evaluate 3-5 conditions.

Material balances are preformed each day of the bench-scale operation. Typical material recoveries are in the range of 98-102 %. Coal conversion is calculated each day except for transition days, where a given operating condition is being changed. Normalized yields and conversions are typically calculated 2 or more times per condition, depending upon the length of the condition.

TABLE 1. CTSL PROCESS PERFORMANCE IMPROVEMENTS

Coal	Illinois (Bituminous)		Wyoming (Subbituminous)	
Process	H-Coal	CTSL	H-Coal	CTSL
Coal Conv., W% MAF	94	97	91	93
524°C^+ Conv., W% MAF	73	94	75	89
C_4-524°C Liquid Yield				
W% MAF Coal	51	78	48	66
Bbl/Ton Coal	3.3	5.0	3.1	4.3

TABLE 2. COAL/OIL COPROCESSING TECHNOLOGY BENCH-SCALE EXPERIENCE (OPERATING DAYS)

Feedstock (Oil)	Cold Lake	Lloydmin.	Maya	Kuwait	Orinoco	Hondo	Shengli	Assam	Total
Coal	Canada	Canada	Mexico	Kuwait	Venezuela	US	China	India	
Lignan (Canada)		35							35
Westerholt (Germany)	29								29
Ohio (US)	82		15		24				121
Illinois (US)				5					5
Taiheiyo (Japan)			25						25
New Mexico (US)						21			21
Texas Lignite (US)	3		105		4	3			115
Black Thunder (US)	5								5
Forestburg (Canada)	41								41
Yanzhou (China)							25		25
Assam (India)								24	24
Total	160	35	145	5	28	24	25	24	446

TABLE 3. HRI COAL/OIL COPROCESSING TECHNOLOGY SUMMARY OF BENCH-SCALE DATABASE

COAL FEEDSTOCK PROPERTIES	MINIMUM	MAXIMUM
Ash, W% Dry Coal	3.9	17.5
H/C Atomic Ratio	0.68	1.03
O/C Atomic Ratio	0.05	0.24
Sulfur, W%	0.3	4.7
OIL FEEDSTOCK PROPERTIES		
°API Gravity	1.8	10.5
H/C Atomic Ratio	1.36	1.54
Sulfur, W%	0.6	5.7
Ni+V, Wppm	11	982
W% 525°C	68	94
OPERATING CONDITIONS*		
W% Coal Feed	10	67
Space Velocity	0.8	2.4
Temperature, °C		
First Stage	400	440
Second Stage	400	440
Recycle/Feed Ratio	0	1.15
525°C+ in Recycle, W%	0	70
PROCESS PERFORMANCE		
525°C+ Resid Conversion, W%	59	93
Coal Conversion, W%	81	97
HDS, W%	66	98
HDN, W%	40	88
C_4-525°C Yield, W%	55	83
C1-C3 Yield, W%	3	9
Hydrogen Consumption, W%	2	5

* The preferred operating conditions include: 25-40 W% coal in feed, a space velocity of 1.0, first and second stage reactor temperatures in the range of 430-440°C with no recycle.

TABLE 4. HYDROGEN MANAGEMENT IN TWO-STAGE REACTOR SYSTEMS

Case	1	1A	2	2A
Hydrogen Consumed				
Reactor 1	0.8	0.8	0.5	0.5
Reactor 2	0.2	0.2	0.5	0.5
Total	1.0	1.0	1.0	1.0
Hydrogen Supply to Reactor 1	**3.2**	**3.2**	**2.0**	**2.0**
Hydrogen Supply to Reactor 2				
From Reactor 1	2.4	0.0	1.5	0.0
Fresh	0.8	0.8	2.0	2.0
Total	**3.2**	**0.8**	**3.5**	**2.0**

FIGURE 1. HTI'S CATALYTIC TWO-STAGE COAL LIQUEFACTION PROCESS

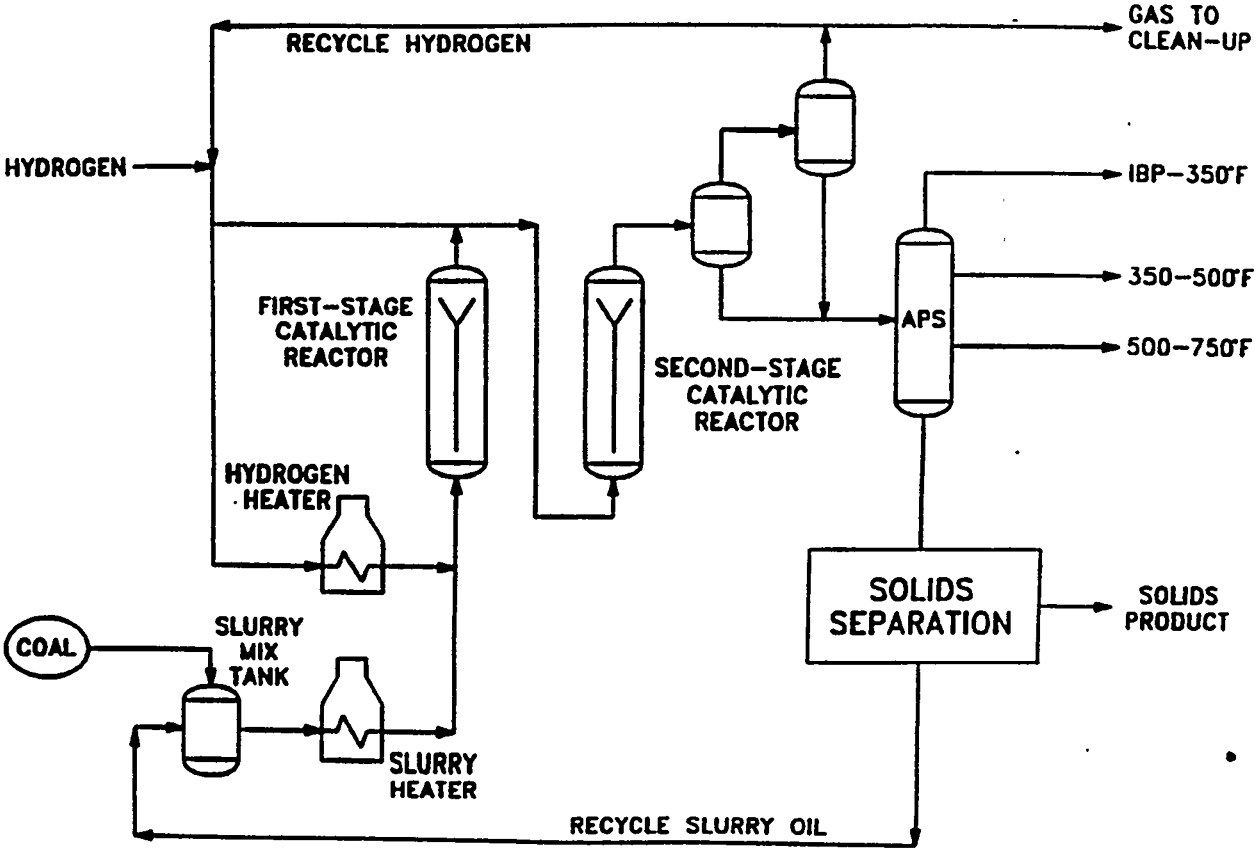

FIGURE 2. HTI'S CATALYTIC TWO-STAGE COAL/OIL COPROCESSING TECHNOLOGY

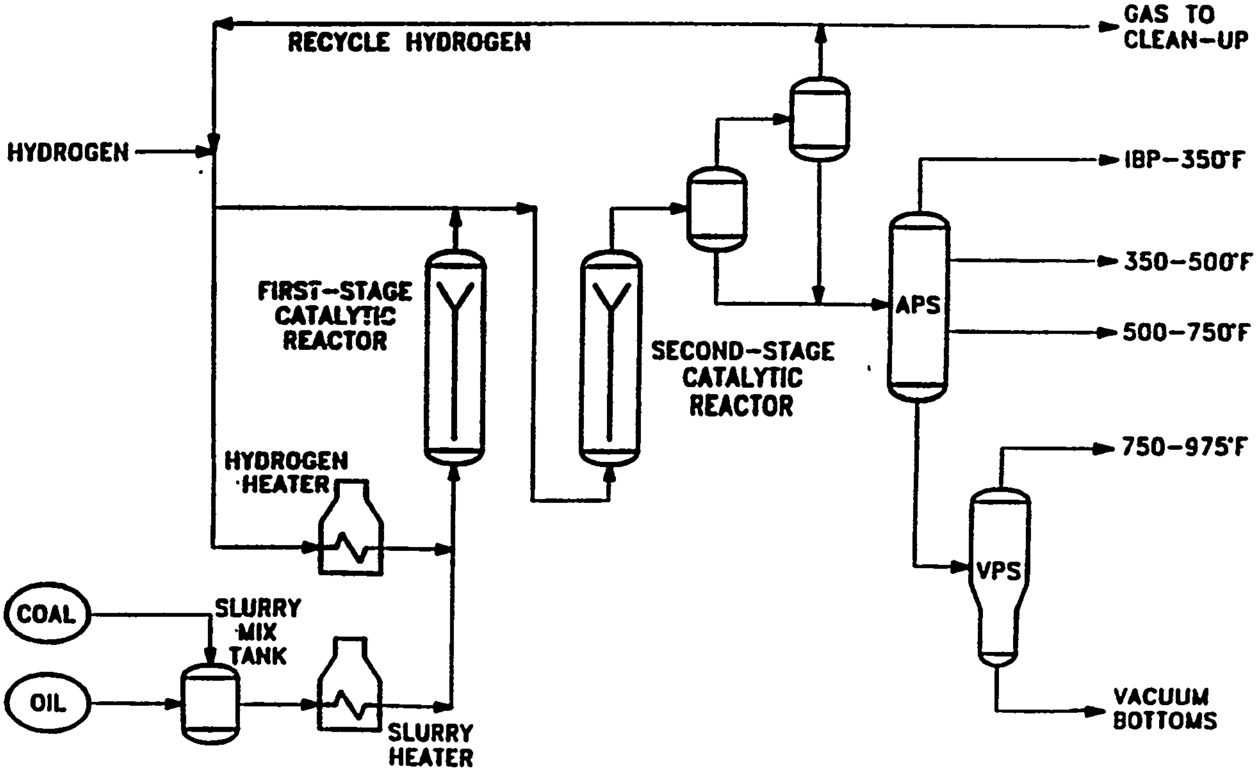

FIGURE 3. COAL/OIL COPROCESSING SYNERGY ON 524 C+ CONVERSION

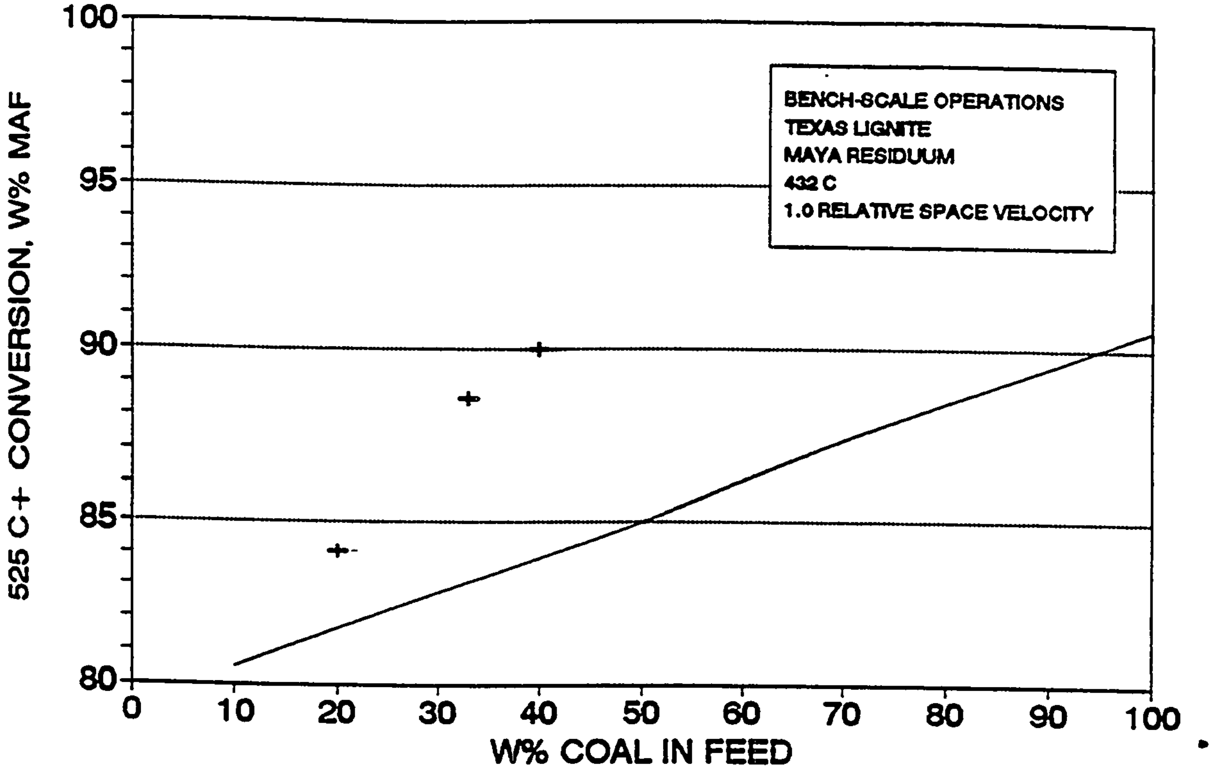

FIGURE 4. COAL/OIL COPROCESSING METALS CONCENTRATION IN PRODUCT SOLIDS