APPLICATION OF CARBON MONOXIDE/STEAM AND COUNTERFLOW REACTOR TECHNOLOGIES TO COAL LIQUEFACTION

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BACKGROUND AND OBJECTIVES

In this project, two technologies have been coupled in an attempt to improve the economics of coal liquefaction. Carbon monoxide/steam is used to solubilize and remove some heteroatoms from the coal, and the product from this step is then further hydrogenated to produce distillable oil. Counterflow reactor technology developed by Canadian Energy Developments Inc. is used in both steps. A one kilogram per hour integrated continuous flow bench scale unit has been constructed and operated. It is expected that sufficient data will be obtained from this bench scale unit to permit a preliminary economic evaluation of the process.

The counterflow reactor system has been successfully demonstrated at the 0.25 ton/day scale for the coprocessing of Alberta heavy oil and Alberta subbituminous coal(1,2) and on a five ton/day pilot plant with heavy oil only(3). The features of this system which are expected to lead to improved economics are:

1. capital cost reduction through low recycle gas rates
2. lower operating cost through more efficient heat utilization
3. minimal catalyst costs

Much work has been done on carbon monoxide/steam technology over the years at the Alberta Research Council and elsewhere. Studies on Alberta subbituminous coal done at the Alberta Research Council showed that a two stage process based on carbon monoxide/steam solubilization followed by a hydrocracking step offered the best route for the liquefaction of Alberta subbituminous coals(4,5). It was concluded, therefore, that the use of counterflow reactors to carry out these two stages was worthy of investigation. The two year project, supported by the Department of Energy, started in August 1992.

Agglomeration technology developed at the Alberta Research Council was also considered for initial deashing of the coal, if it could be demonstrated that it would be economically beneficial. The two coals examined, Illinois #6 and Black Thunder, both had relatively low ash content (12.6 and 5.2 percent, respectively) and laboratory agglomeration tests indicated that only marginal ash removal (10-30%) was obtained. Our initial conclusion is that, with these coals at least, a prior agglomeration step is not likely to be economically beneficial.

Autoclave studies done prior to, and in support of the bench scale unit operation have provided some basic information on the particular feedstocks being used and have guided the selection of operating conditions for the continuous unit. The key parameters which are important for the selection of operating conditions are: coal solubility, carbon monoxide conversion, hydrogen consumption, heteroatom removal and product quality. It is not certain at this point that maximum coal solubility is required in the first stage to provide the best operating scenario. Obtaining the correct balance of conversion between the first and second stages for optimum economic benefit is, therefore, a key objective for the bench scale study. Detailed knowledge of the effects of operating conditions on the product slate from the first stage was required.

EXPERIMENTAL PROGRAM

Autoclave Studies

A matrix study using a three-level Box-Behnken type program was completed in a 1 litre autoclave. The variables examined were temperature, pressure, and residence time. The ranges of these variables were based on previous experience with Alberta subbituminous coals. All experiments were conducted with Black Thunder coal and a Black Thunder derived solvent. An initial charge of 120g solvent, 80g coal, 4g potassium carbonate and 13-27g water depending on the initial carbon monoxide pressure was loaded into the autoclave. The results for coal conversion, carbon monoxide conversion, hydrocarbon gas yield and hydrogen consumption are shown in Figures 1-4. Better than 80% coal conversions are achieved at temperatures of 390°C+, initial carbon monoxide pressures of 600 psig +, and the residence time of at least 30 minutes. The highest carbon monoxide conversion and hydrogen consumption are also found under these conditions. A qualitative estimation of heteroatom removal also confirmed that the above conditions are the most favourable. The results also show, however, that at 410°C, a penalty is paid due to increased hydrocarbon gas yield, particularly at 60 minutes residence time. It was concluded, therefore, that, initially at least, the conditions for the bench unit in first stage should be 390°C and 30 minutes residence time. The carbon monoxide pressure was selected at 2500 psig for the bench unit operation. This was necessary because it was initially planned to have a higher pressure in the first stage than in the second stage to permit transfer of product from one stage to the other.

While our initial studies have concentrated on 100% carbon monoxide as the gas feed to the first stage, it was realized that commercially a synthesis gas would probably be used. The effect of using different levels of carbon monoxide in the gas feed was therefore explored. The results are shown in Figure 5. Carbon monoxide conversion is unaffected by the level of carbon monoxide in the feed gas, but coal conversion and hydrogen consumption both dropped with lower concentrations.

A third aspect to the autoclave work on the first stage of the process related to catalyst. Potassium carbonate was chosen for the bulk of the work, since this is generally regarded as the catalyst of choice, but the effects of using other catalysts, and no catalyst was explored. These results are shown in Figure 6. Interestingly, coal conversion was not greatly affected by the choice of catalyst system. As expected carbon monoxide conversion and hydrogen consumption were reduced when catalysts with limited or no shift capability were used.

Finally, the two stage process was also investigated in the autoclave. In these experiments the first stage was completed, and then the first stage gas removed at about 250°C, and replaced by hydrogen. The two catalysts, potassium carbonate (4g) for the first stage and iron sulphide (4g) for the second stage, were both introduced into the original slurry feed. For one run iron sulphide (FeS) was replaced by ammonium tetrathiomolybdate (ATM)(120mg) as second stage catalyst. The conditions for the first stage were held constant at 390°C, 30 mins residence time, and 600 psig cold carbon monoxide pressure. Conditions were varied in the second stage. The results are shown in Figure 7. Coal conversions in excess of 90% were obtained in all cases, and carbon monoxide conversions were also constant at 80%. Hydrogen consumption, however, increased with temperature, and was, as expected, higher with the more active second stage catalyst, ammonium tetrathiomolybdate.

The increased hydrogen consumption is consistent with the increased conversion of asphaltene and preasphaltenes to oils (Figure 8). Gas yields, as expected, increased with increasing temperature.

Bench Unit Program

An existing bench scale unit from the Nisku facilities of the Alberta Research Council was moved, and reassembled at ARC's new Devon research facilities. The bench scale unit (BSU) has a nominal capacity of 1 kg coal/oil feed per hour and is designed to operate at a maximum pressure of 2500 psig and a maximum temperature of 500°C. The BSU (Figure 9) consists of the slurry feed system, the coal solubilization stage, and the hydrogenation stage. Both reactor stages use a counterflow reactor.

In the slurry feed system, the coal/oil slurry feed is prepared (V-110) and recirculated (P-110) to maintain a uniform composition and to supply the high pressure feed pumps (P-130, P-140). Also, the catalyst solution is injected via P-161B.

In the coal solubilization stage the feed slurry is injected together with the catalyst into the top of counterflow reactor R-200. R-200 has an inside diameter of 34 mm and a volume of 0.68 litres. Flowing downward against the upward flowing $CO/CO_2/H_2$ (products of the shift reaction) and water, coal is solubilized, and together with solvent, unconverted coal and ash is withdrawn from the bottom via level controller LIC-200. LIC-200 adjusts the rotation of P-200 for control of the liquid level in R-200. Gases and vaporized solvent are removed from the top of R-200. After cooling in HE-210, the condensable material (mainly water and some oil) is withdrawn from V-210 under level control (LIC-210), and the remaining gases are withdrawn via back-pressure controller PIC-210.

In the hydrogenation stage the bottom stream from R-200 is injected into the top of the counterflow reactor R-300. R-300 has an inside diameter of 34 mm and a volume of 1.47 litres. Flowing downward against upward flowing hydrogen and vaporized reaction products, more coal is solubilized, and solubilized coal is hydrogenated to distillable and non-distillable oils. Also, some conversion of the solvent occurs. The bottom stream of R-300 is withdrawn under level control (LIC-300). Gases and vaporized products are removed from the top of R-300. After cooling and condensing in HE-310, the condensible materials are withdrawn from V-310 under level control (LIC-310) while the remaining gases are removed via back pressure controller PIC-310.

The BSU is controlled with a computerized digital control system which also logs all relevant operating conditions including data for mass balance purposes.

The BSU has been commissioned during a period of about three to four months. During that time, a number of mechanical and operational difficulties have been resolved. It was originally anticipated to mix the first and second stage catalysts with the feed slurry. As it turned out, this could not be done as the first stage catalyst (potassium carbonate) precipitated as a crystalline solid plugging pipe lines and valves. This phenomenon was first observed at the outlet of feed preheater HE-235 which repeatedly plugged with material having a high concentration of potassium carbonate. Since injection of the potassium carbonate as an aqueous solution after HE-235, no plugging in the feed lines or in HE-235 has been observed. Three successful runs have been completed in the first stage mode with the R-200 bottom product by-passing R-300.

It was originally planned to operate the first stage at a higher pressure than the second stage so that a simple control valve or valve arrangement for liquid level control in R-200 could be used. However, after a number of attempts with single and multiple valves did not succeed, it was decided to operate the first stage at a lower pressure and to use an interstage pump between the first and second stage. This would also allow a more economic design as the first stage would be designed for the lowest possible pressure determined from optimization between the two stages as outlined earlier. The interstage pump P-200 is equipped with a variable speed drive for level control in R-200 and raises the pressure of the first stage bottom stream to the operating pressure of the second stage. With this arrangement, the BSU was operated continuously both with oil feed only and with coal/oil slurry as long as no potassium carbonate was introduced. In all attempts with potassium carbonate, the check valves of the interstage pump P-200 plugged about 1.5 hours after the potassium carbonate was introducd. After the potassium carbonate was replaced with sodium aluminate as catalyst for the first stage shift reaction, no plugging of the BSU has been observed.

Recently, the BSU has been operated continuously for about one week in the fully integrated two stage mode with a feed slurry containing about 35 wt% of coal. Mass balances are in a range of 95% or better.

First Stage Operation: Autoclave vs Bench Unit

Initial operations on the bench unit were confined to a study of first stage operation only. As discussed earlier, initial operating conditions for the bench unit were selected as 390°C with a residence time of 30 minutes. Operating pressure was set at 2500 psig, since at that time it was intended to use a higher pressure in the first stage so as to drive the first stage product into the second stage. The potassium carbonate level was the same as in the autoclave (2% wt on feed), but the carbon monoxide and steam rates were increased in order to provide mixing in the bottom of the counterflow reactor.

The feed rates of carbon monoxide/steam for the two systems, based on moles per 100gm MAF coal feed, are shown in Figure 10. The feed rates in the bench unit were 4-5 times higher on this basis than in the autoclave. However, the gas residence time is much lower in the bench unit (about 2 mins.). Although carbon monoxide conversions in the bench unit were only 10-15%, carbon monoxide conversions and hydrogen consumption were very comparable in both systems based on moles per 100gm of MAF coal feed. Coal conversions at apparently equivalent conditions in the bench unit were lower than those predicted from the autoclave program (Figure 11). Factors which could explain these differences include: process severity measurement, residence time distribution (gas and liquid), and mixing effects.

Two Stage Operation

The results from recent two stage operations are currently being evaluated, and will be reported at a later date.

FUTURE PLANS

Problems with bench unit operation when potassium carbonate is used as a shift catalyst have created a need for additional autoclave work to explore alternative options for a shift catalyst. In addition, it is planned to run Illinois #6 coal with an Illinois #6 derived solvent as part of the bench unit program. A small autoclave program will, therefore, also be required in support of this activity.

The future bench unit program will be directed towards process development and optimization for both Black Thunder and Illinois #6 coals. Also, as mentioned earlier a preliminary economic evaluation will be performed.

ACKNOWLEDGEMENTS

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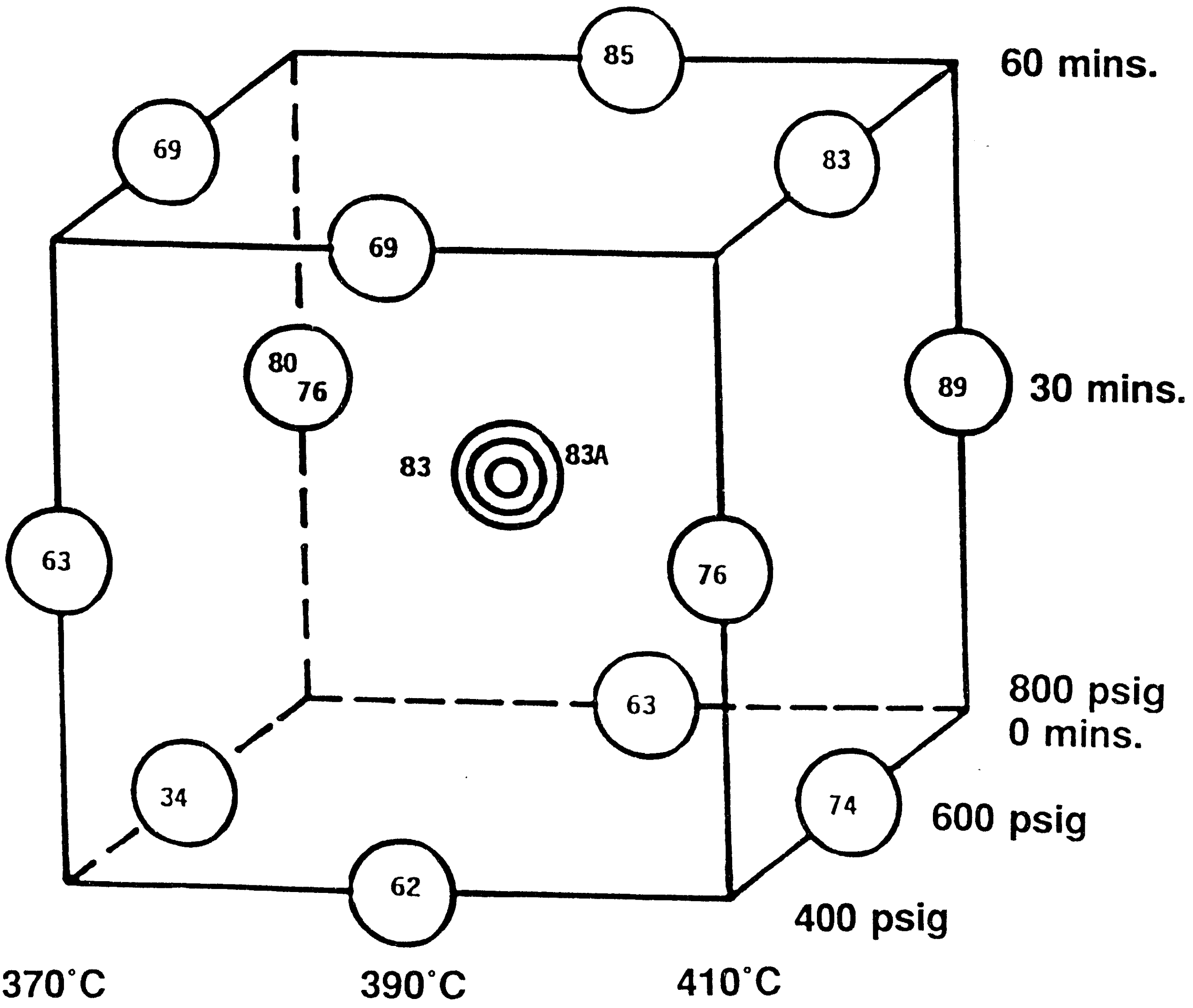
Figure 1

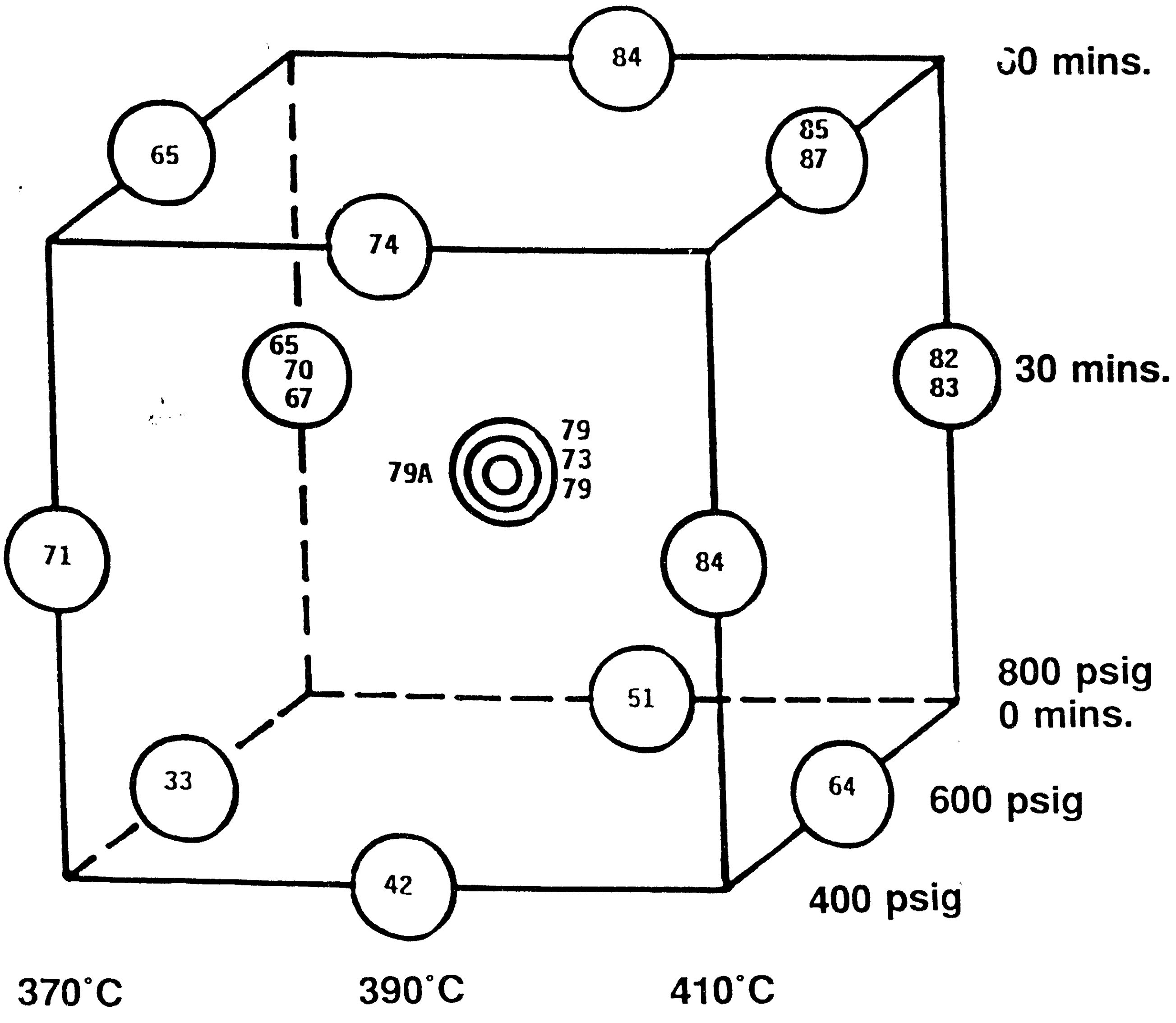
COAL CONVERSION
(MAF WT%)



A - Agglomerates as feed

Figure 2

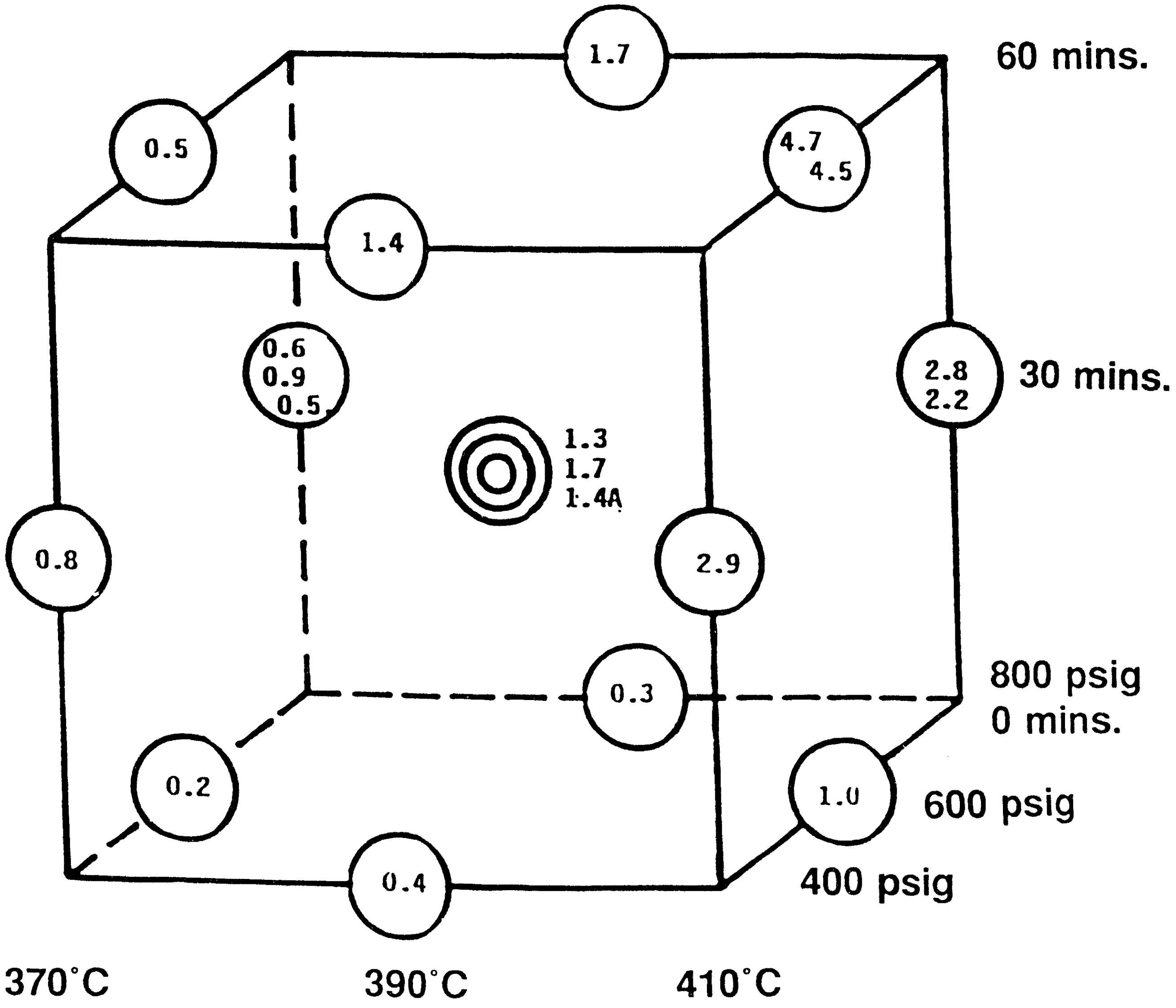
CARBON MONOXIDE CONVERSION (MOLE %)



A - Agglomerates as feed

Figure 3

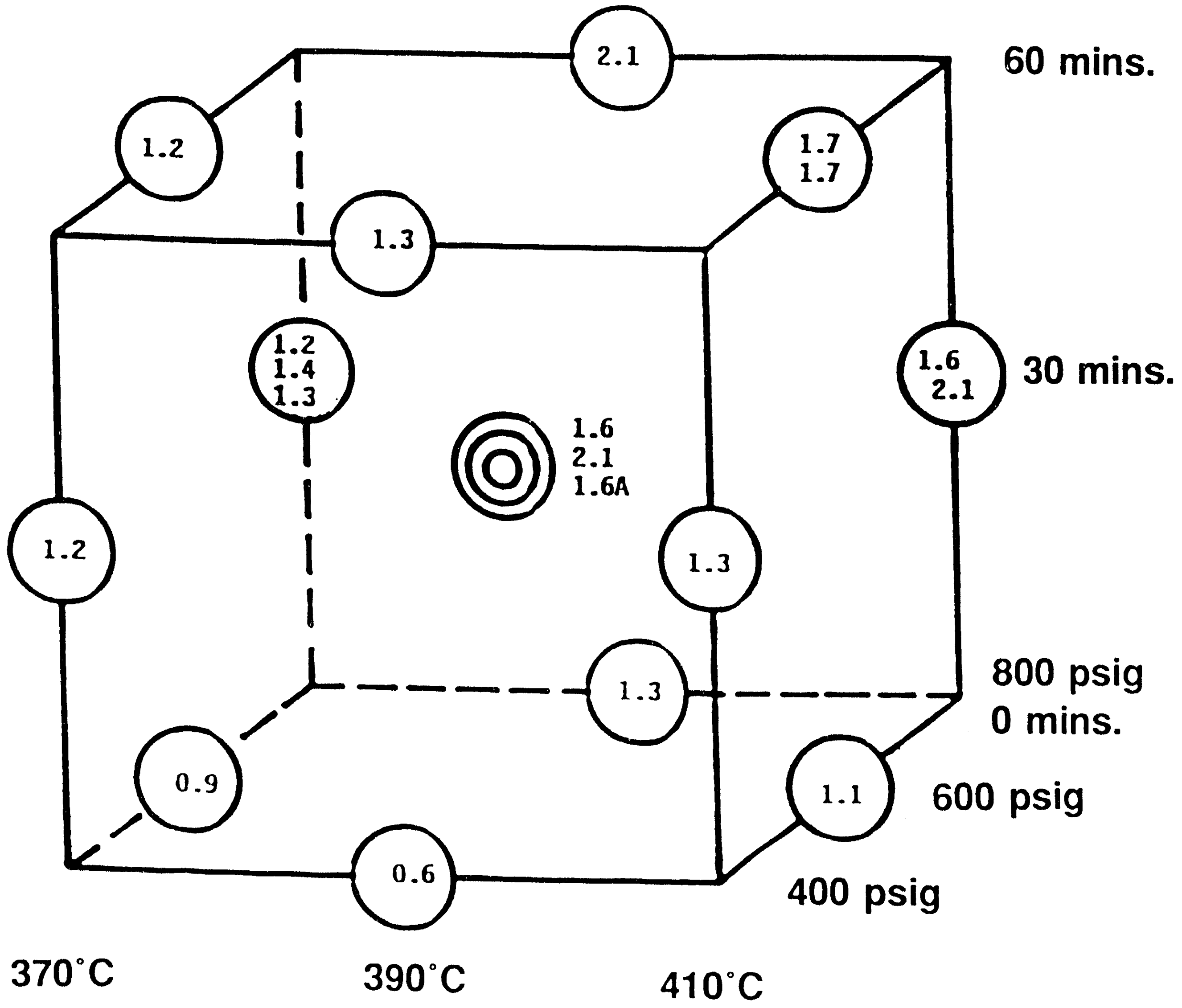
HYDROCARBON GAS YIELD (g/100g MAF COAL)



A - Agglomerates as feed

Figure 4

HYDROGEN CONSUMPTION
(g/100g MAF COAL)



A - Agglomerates as feed

Figure 5

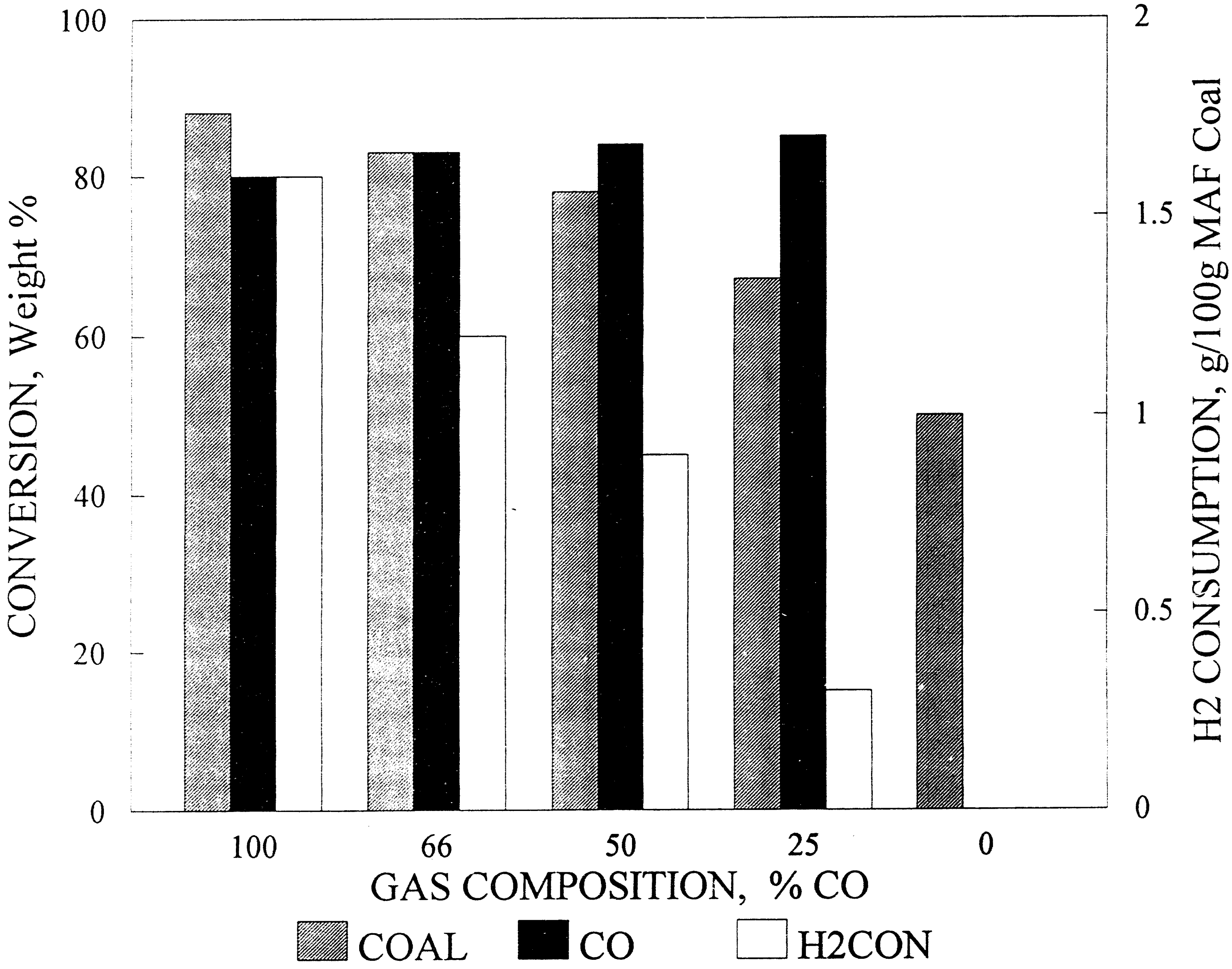

CONVERSION, Weight %
0
20
40
60
80
100
H2 CONSUMPTION, g/100g MAF Coal
0
0.5
1
1.5
2
100
66
50
25
0
GAS COMPOSITION, % CO
COAL
CO
H2CON

Figure 6

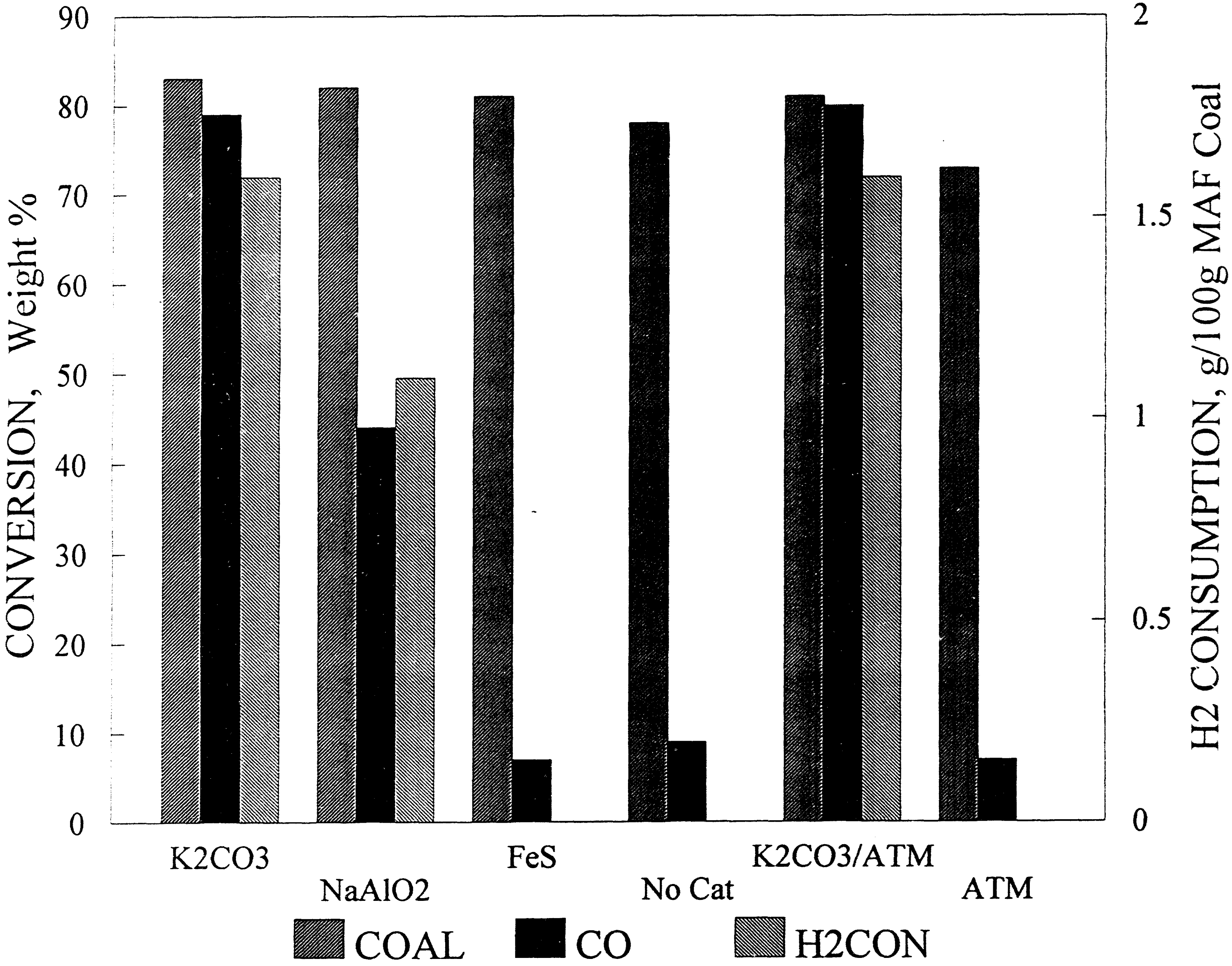

CONVERSION, Weight %
0
10
20
30
40
50
60
70
80
90
H2 CONSUMPTION, g/100g MAF Coal
0
0.5
1
1.5
2
K2CO3
NaAlO2
FeS
No Cat
K2CO3/ATM
ATM
COAL
CO
H2CON

Figure 7

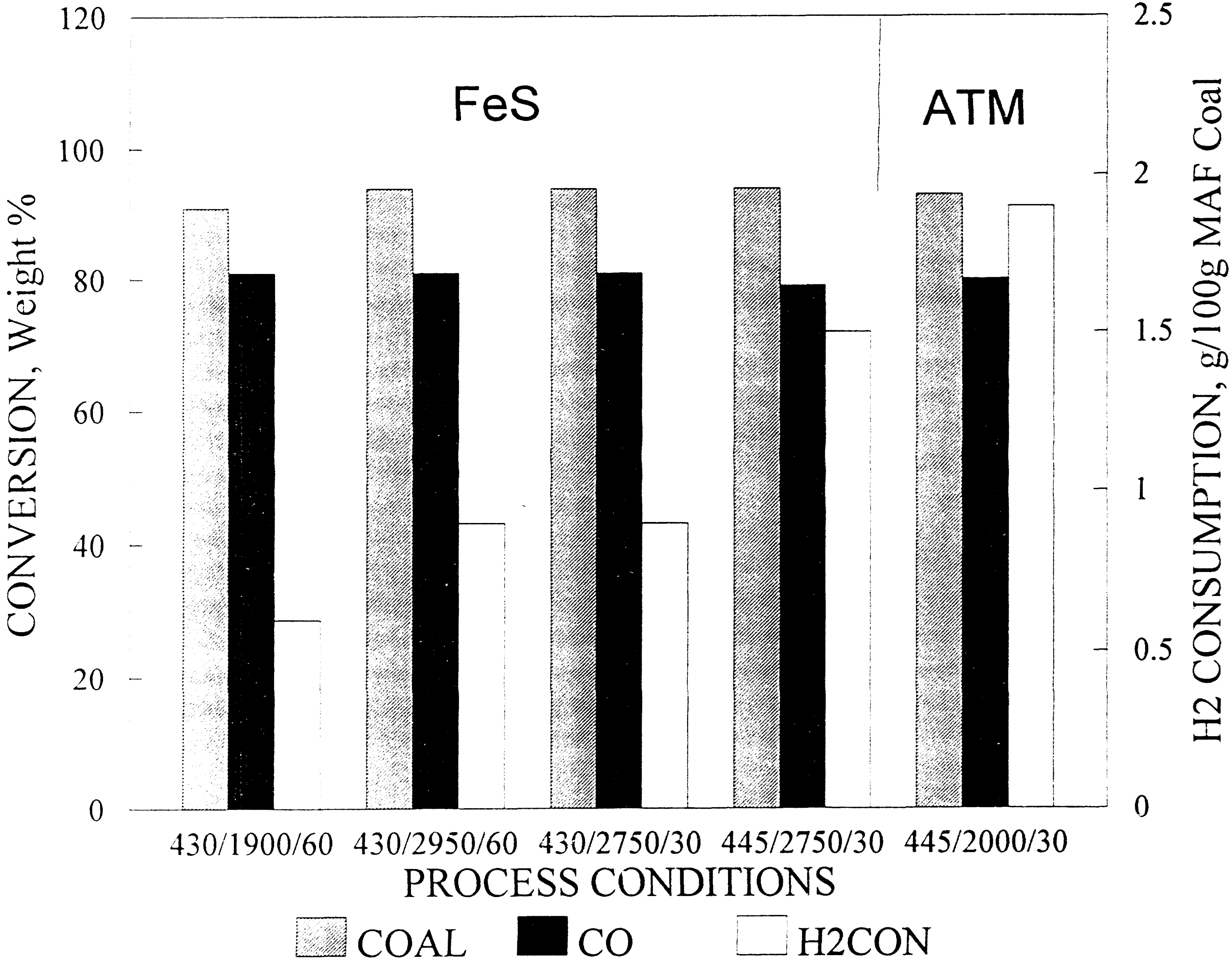

120
100
80
60
40
20
0
CONVERSION, Weight %
2.5
2
1.5
1
0.5
0
H2 CONSUMPTION, g/100g MAF Coal
FeS
ATM
430/1900/60
430/2950/60
430/2750/30
445/2750/30
445/2000/30
PROCESS CONDITIONS
COAL
CO
H2CON

Figure 8

PRODUCT DISTRIBUTION

(weight % on MAF coal)

	GAS	OILS	ASPHALTENES	PREASPHALTENES	IOM
First Stage	1	5	45	24	12
Second Stage			FeS Catalyst		
430°C/60 mins	7	30	38	7	6
430°C/30 mins	8	37	34	4	5
445°C/30 mins	11	33	34	5	6
			ATM Catalyst		
445°C/30 mins	12	41	26	3	7

Figure 9

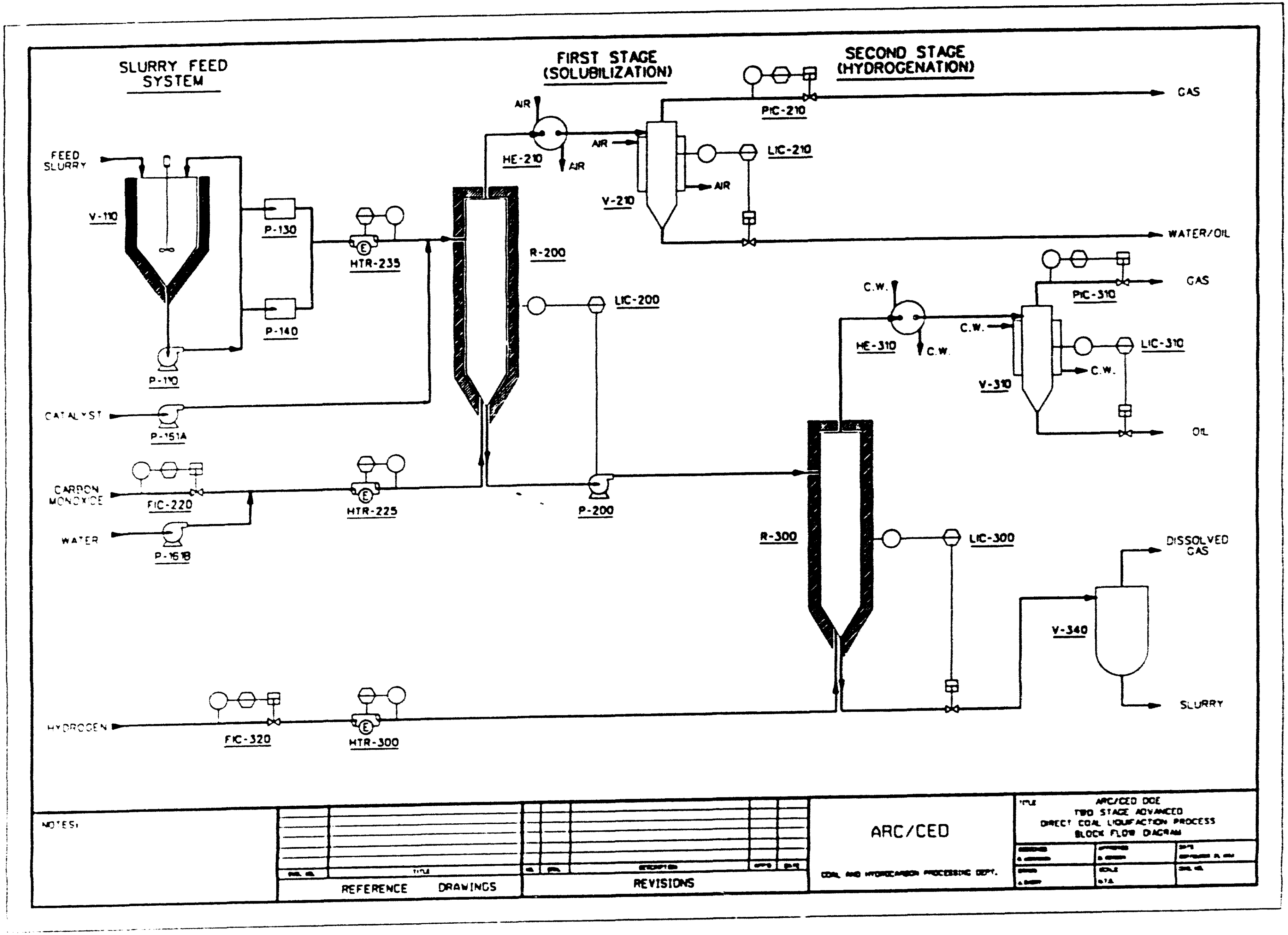

SLURRY FEED SYSTEM
FIRST STAGE (SOLUBILIZATION)
SECOND STAGE (HYDROGENATION)
FEED SLURRY
V-110
P-130
P-140
P-110
HTR-235
R-200
AIR
HE-210
AIR
AIR
V-210
AIR
PIC-210
LIC-210
GAS
WATER/OIL
LIC-200
CATALYST
P-151A
CARBON MONOXIDE
FIC-220
WATER
P-161B
HTR-225
P-200
C.W.
HE-310
C.W.
C.W.
V-310
C.W.
PIC-310
LIC-310
GAS
OIL
R-300
LIC-300
DISSOLVED GAS
V-340
SLURRY
HYDROGEN
FIC-320
HTR-300
NOTES:
REFERENCE DRAWINGS
REVISIONS
ARC/CED
COAL AND HYDROCARBON PROCESSING DEPT.
TITLE
ARC/CED DOE
TWO STAGE ADVANCED
DIRECT COAL LIQUEFACTION PROCESS
BLOCK FLOW DIAGRAM

Figure 10

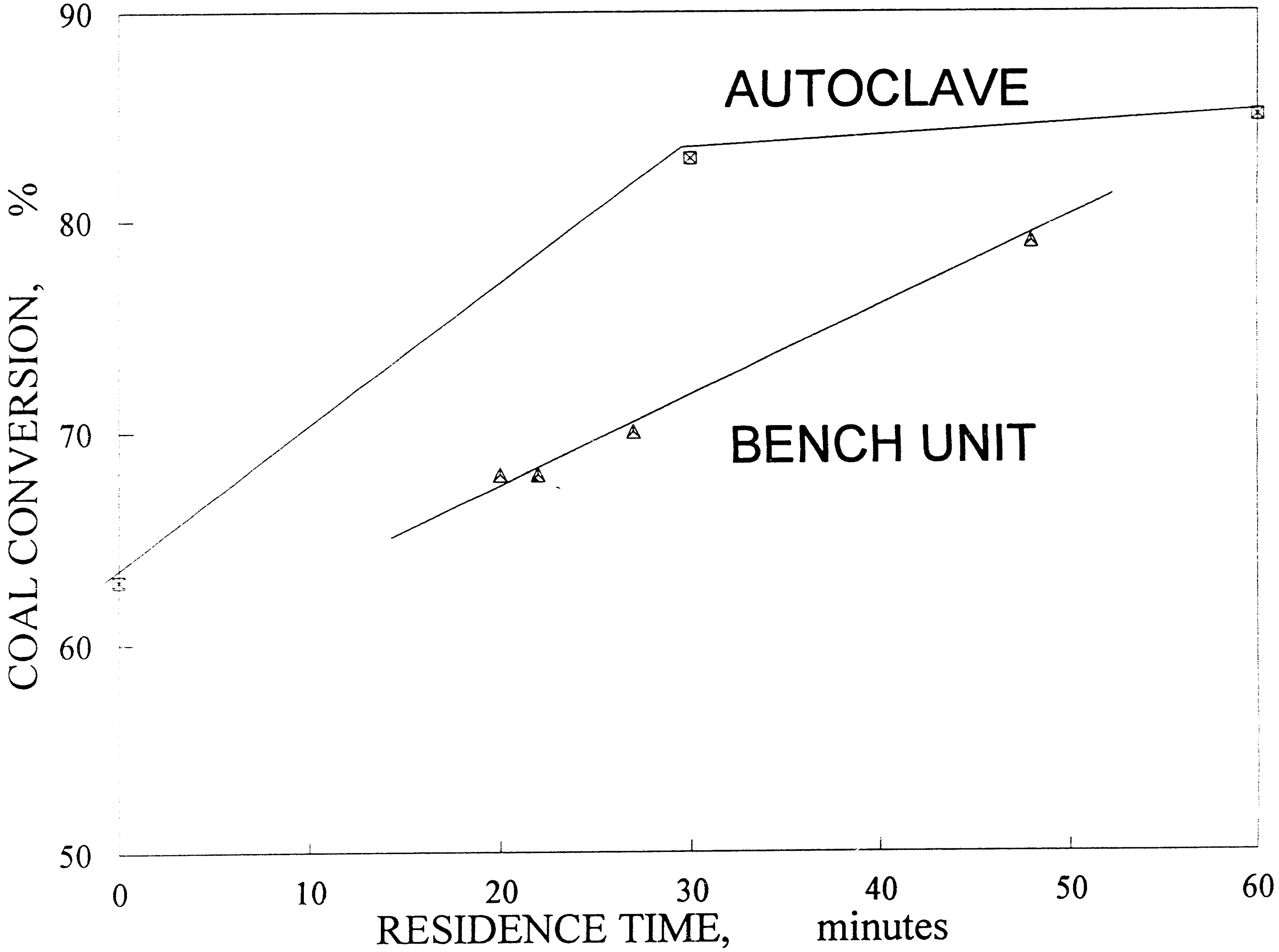
FIRST STAGE OPERATION

390°C/30 MINS

	AUTOCLAVE	BENCH UNIT
FEED		
CO	2.2	9.8
H_2O	2.5	7.9
PRODUCTS		
CO converted	1.5	1.4
CO_2 produced	0.3	0.3
H_2 consumption	0.8	0.6

Units: moles/100g MAF coal

Figure 11


90
80
70
60
50
COAL CONVERSION, %
0
10
20
30
40
50
60
RESIDENCE TIME, minutes
AUTOCLAVE
BENCH UNIT

INVESTIGATION OF ADVANCED LIQUEFACTION CONCEPTS

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ABSTRACT

Our approach to enhance liquefaction yields and quality of product slate is to utilize highly dispersed catalysts and variations in liquefaction atmosphere such as a CO/H_2 mixture. The purpose of the dispersed catalysts is to better control retrogressive reactions and avoid char formation, while the purpose of the of the CO is to improve the economics by simplifying or totally eliminating a separate water-gas-shift step and perhaps help remove oxygen in the product slate. We have shown, using highly dispersed molybdenum catalysts, liquefaction yields in an inert solvent such as hexadecane can be as great as in a good H-donor solvent such as tetralin. The advantage of the dispersed catalyst over a conventional supported catalyst is that highly dispersed catalysts have a more intimate contact with the coal molecules and have higher surface areas so smaller quantities of catalyst are needed. Ideally the catalyst is active at preconversion conditions to limit the amount of retrogressive reactions that occur in the initial stages of coal liquefaction. We are in the process of investigating the effects of types of dispersed catalysts and process conditions on the product slate for conversions of a Black Thunder subbituminus coal and corresponding recycle vehicle.

PROJECT OBJECTIVES

Several areas in the conversion technology have been identified that, if improved, could make coal conversions to oil more cost competitive with petroleum products. The objectives of this project are to address possible improvements in the economics by utilizing low-rank coals, dispersed catalysts and processing variations such as using a syngas atmosphere.

INTRODUCTION

Integrated processes to liquefy coal have evolved to the current two-stage coupled catalytic configurations now being used at Wilsonville.[1-4] Several areas in the conversion technology have been identified that, if improved, should make coal conversions to oil more cost competitive with petroleum products. These areas include pretreatment and cleaning methods, choice of feedstock, novel catalysts, and processes to improve hydrocarbon recovery. The objective of this project is to address possible improvements in the economics by utilizing low-rank coals, dispersed catalysts and processing variations such a syngas atmosphere.

Most work at Wilsonville has involved bituminous coals, which are much easier to convert than lower-rank coals such as Wyodak and lignites.[5] The lower-rank coals are more abundant and cheaper, and conversions lead to a higher quality product with less heteroatom content.[6] However, the yield of liquid products is low. The low conversion of these coals has been attributed to their high oxygen content, and the carboxyl groups are thought to cause free radical reactions during the conversion process, which in turn cause retrograde reactions.[7,8] The self-coupling of polyhydroxy aromatic structures is also thought to be an important retrogressive reaction.[9,10] Developing a process for utilizing these coals in high conversions would greatly improve the economics of coal conversion. Many of these retrogressive reactions can be eliminated, or at least minimized, by having a suitable H-donor source or hydrogen transfer medium,[11-13] by use of hydrogen with a good catalyst, or catalytically removing the phenolics or carboxylates. However, good donor solvents are not always feasible. A logical alternative would be a highly dispersed catalyst that can rapidly transfer hydrogen during coal liquefaction.

Many workers have investigated nonsupported high dispersion catalysts to impregnate the coal and solvent so that the hydrogen will be effectively utilized and rapidly transferred to the coal molecules.[14-22] Such a scheme should prevent retrogressive reactions by providing a readily available source of hydrogen. Such catalysts could act either to break coal linkages directly or to produce an active solvent species that would then break the weak links in coal. With a highly dispersed catalyst of very high surface area, very small amounts of catalyst would be necessary. Generally, efforts to use dispersed catalysts during coal liquefaction utilize precursors that are not activated until high temperatures.[23-26] For instance, molybdenum is often added as either as the oxide or thiolate water soluble salts, or as molybdenum naphthenate; although the most active catalyst is molybdenum disulfide.[27] Sulfur must be added to molybdates to form the trisulfide, which is finally transformed to the disulfide. However, the conversion of the molybdenum trisulfide to disulfide occurs only under high temperatures, and the conversion has been reported to require temperatures as high as 350°C.[28] Recent work has shown that instead of soluble molybdenum catalysts, ultrafine molybdenum sulfide particles are likewise extremely effective in coal liquefaction.[29] Dispersed iron catalysts have been extensively studied, since they are relatively inexpensive catalyts. Andres et al.[30] and Charcosset et al.[31] have found marked increases in coal conversions with decreasing particle size iron oxides. The active catalyst is generally thought to be pyrrhotite and the transformation is thought to be particle size dependent, suggesting ultrafine iron particles would be the most active in coal liquefaction. Numerous efforts have been made to prepare ultrafine iron based catalysts for coal liquefaction using methods such as surfactants and laser pyrolyses to produce catalysts in the range of Angstroms.

Process conditions such as carbon monoxide atmospheres have also been postulated to help the liquefaction process by removing oxygen, and possibly reduces the retrogressive reactions. The use of CO can also save hydrogen by undergoing the water-gas-shift reaction and can thus aid in the economics of coal liquefaction by saving a separate gas purification step prior to the coal liquefaction process. McKeough has suggested that the use of CO to remove oxygen can make the use of lower-rank coals more attractive.[32] The following section describes our approach to assess these potential improvements for a coal liquefaction process.

APPROACH

The approach to this work is in two phases, in the first phase we are conducting screening tests using a variety of potential liquefaction catalysts, and in the second phase we will evaluate the products after a final upgrading step. These screening tests are being conducted in batch autoclaves at temperatures up to 425°C, using either model coals in synthetic solvents or using a Black Thunder subbituminus coal with the corresponding recycle solvent, obtained from Wilsonville. In these screening tests we are evaluating several catalysts, emphasizing the iron based catalysts, and various process conditions such as carbon monoxide atmospheres with and without the addition of water. The iron based catalysts include iron oxide (from Wilsonville), sulfated iron oxide, iron carbonyl, thiolato iron carbonyl, and will include some of the ultrafine iron catalysts. We are initially concentrating on obtaining the optimal CO/H_2 conditions using the iron carbonyl catalyst, and then will determine the effects of other types of catalysts.

EXPERIMENTAL PROCEDURES

Catalysts

Iron oxide used in the Black Thunder conversions was obtained from Wilsonville. The organometallic molybdenum catalyst was $(C_5H_5)_2Mo_2(\mu\text{-}SH)_2(\mu\text{-}S)_2$, referred to as Mo(OM), and was prepared by modification of the method of Dubois et al.[33] Pentacarbonyl iron was obtained from Aldrich, and the sulfur-containing iron cluster, $(\mu\text{-}S_2)Fe_2(CO)_6$, referred to as Fe_2S_2, was prepared by the method of Bogan et al.[34] Ammonium tetrathiomolybdate, (MoS_4), was obtained from Alfa Chemicals. Nickel biscyclooctadiene $[Ni(COD)_2]$ was obtained from Organometallics Inc.

Model Coal Conversions

The model coal liquefaction experiments were conducted in a 300 mL Autoclave Engineers stirred reactor using 5.0 g of coal, 3 mmol of catalyst, 30 g of solvent, and 500 psig (cold) hydrogen. Reaction temperatures were held at either 400°C or 425°C for 20 minutes. The product was filtered through a medium porosity filter and separated into toluene soluble (TS) and insoluble (TI) fractions. Conversions were calculated from the amount of toluene-insoluble material and are on a daf basis and on a carbon basis for the Lignite conversions. The coals used were PSOC 1098 Illinois #6, and Beulah-Zap seam North Dakota lignite from the Argonne Premium coal bank.[35]

Black Thunder Conversions

The screening experiments were conducted in a 300 mL autoclave with conversions being run at 425°C for 1 hour . The feedstock consisted of 2.5 parts by weight of recycle vehicle (50g) from Wilsonville run #263 to 1 part Black Thunder coal (20g). The total gas charge was up to 1000 psi (cold), and contained 3% H_2S. CO concentrations ranged from 20% to 50%. The coal was dried at 76°C under <1 torr vacuum to reduce the water content. The analyses of the coal and recycle vehicle are listed in Table 1. After conversions the products were fractionated into THF-insoluble, THF-soluble/toluene-insoluble, toluene-soluble/hexane insoluble, and hexane soluble fractions. The THF-soluble/toluene insoluble fraction is referred to as preasphaltenes, the toluene-soluble/hexane-insoluble fractions, as asphaltenes, and the hexane soluble fractions is referred to as oils.

Table 1. Analyses of Black Thunder Coal and Recycle Solvent

Ultimate Analysis (Wt%)	Black Thunder (As Received)	Black Thunder (Dried at 76°C)	Recycle Solvent
Carbon	55.07	63.56	88.08
Hydrogen	6.22	4.96	7.09
Nitrogen	0.79	0.80	0.99
Sulfur	0.34		
Chlorine	<0.07		
Ash	5.87		
Oxygen (by diff)	31.71		
Proximate Analysis (Wt% As Received)			
Moisture	21.21		
Volatile Moisture	35.30		
Ash	5.87		

ACCOMPLISHMENTS AND CONCLUSIONS

Model Coal Results

Data from coal conversions in tetralin and hexadecane solvent systems are presented in Table 2. The first four liquefaction experiments listed were conducted at 400°C and include a non-catalyzed conversion, and conversions using molybdenum (MoS_4 and Mo(OM)) catalysts on an Illinois #6 coal. The remaining four experiments were conducted at 425°C for an Argonne Lignite coal, and compare various soluble iron and nickel based catalysts. Since conversions in tetralin appeared to moderate the effects of the catalysts, we were prompted to utilize a non-reacting, non-donor conversion medium that would not interfere with the study of the catalysts. In order to achieve this goal, conversions were conducted in n-hexadecane so that solvent interactions should be minimal. In previous work we have observed no decomposition of n-hexadecane under these conditions. Most of the conversions are quite low, as expected. For instance in the absence of catalyst the Illinois #6 coal was converted to 25% toluene soluble material. However, in the presence of the molybdenum catalysts, the conversions were greatly enhanced. The coal impregnated with MoS_4 of 41% and the organometallic molybdenum-impregnation [Mo(OM)] resulted in a conversion of 54%, which is nearly as great as when tetralin was used as the conversion medium. Thus we suggest that if the catalyst dispersion is great enough, and does not require high temperature activations, good liquefaction solvents are not necessary.

The last four conversions are of an Argonne Lignite. As shown in the table both the soluble organometallic iron complexes ($Fe(CO)_5$ and ($FeS_2(CO)_2$) are very effective for low rank coals, giving conversions in the range of 40%; however, when the nickel catalyst was used, the conversions increased to 60%. Iron catalysts are well known to be effective for liquefaction of low rank coals. However, nickel has been rarely used. Since low rank coals are high in carboxylates, and nickel is known to aid in decarboxylations, it would seem that dispersed catalysts containing nickel should also be examined for low rank coals.

Table 2. Conversion to Toluene Soluble Products in Hexadecane[a]

Catalyst	Coal	T(°C)	% TS[b]
None	Illinois # 6	400	25
Mo(Aq)	Illinois #6	400	41
Mo(OM)	Illinois #6	400	54
Mo(OM)[c]	Illinois #6	400	61
None	Lignite	425	24
$Fe(CO)_5$	Lignite	425	41
Fe_2S_2	Lignite	425	39
$Ni(COD)_2$	Lignite	425	60

[a] Reaction conducted in a 300-mL autoclave with 5 g coal, 3 mmol catalyst, 30 g solvent and 500 psi H_2 for 20 min at temperature.

[b] Yields calculated on daf basis for Illinois #6 coal and on a carbon basis for lignite.

[c] Reaction run in tetralin under identical conditions.

Black Thunder Conversions

We are currently in the process of screening several types of dispersed catalysts under hydrogen and/or hydrogen/carbon monoxide atmospheres in a batch autoclave for liquefaction of a low rank coal (Black Thunder Wyodak coal) using the corresponding recycle vehicle obtained from Wilsonville. The emphasis of the project is to compare iron based catalysts, with the goal of developing catalysts which can be easily transformed into the most active form during the coal liquefaction experiment. For the screening tests using the Black Thunder Coal we are comparing conversions using catalysts such as iron oxide (used by Wilsonville), organometallic iron complexes (such as iron carbonyl and a thiolato iron carbonyl) and sulfated iron oxide, in the presence of H_2 atmospheres and H_2/CO atmospheres. The liquefaction products are fractionated into preasphaltenes, asphaltenes, and oils.

The combination of low pressures of hydrogen and a low H/C ratio recycle vehicle (1.055) gave very modest conversions. Nevertheless, such conditions should emphasize the better catalysts. As shown in Table 3, for the conversions at 1000 psi the iron carbonyl catalysts gave the best conversions to soluble products when either H_2 or CO(20%)/H_2 atmospheres were used, as seen by the THF insoluble yields of 5.8% and

9.9%, respectively. When the reaction was conducted at 850 psi H_2 the conversion to THF soluble products was considerably reduced; however when iron oxide was used under those conditions it was difficult to maintain proper temperature control and severe retrogressive reactions apparently occurred. Nevertheless, when the lower partial pressure of hydrogen was supplemented with CO to 20% CO, conversions increased close to when pure hydrogen was used. When the partial pressure of CO was increased to 50%, conversions were still quite good and the final products exhibited increased oil yields. As shown in Table 4, the products from these CO reactions showed reduced oxygen content which would most likely make the final product more easily upgraded into usable fuels. It is interesting that the CO underwent water-gas-shift activity even though the coal was previously dried prior to the conversion. Efforts to increase the water-gas-shift reaction by addition of water actually proved to be detrimental, and appeared to decrease oil yields. Thus under these conditions, the use of CO in the coal liquefaction process appears to be feasible without the addition of water, and the problems associated with water such as emulsions, corrosion and high pressures can be avoided. However the optimal partial pressures of hydrogen and carbon monoxide need to be determined to assess the impact in a coal liquefaction process.

Table 3. DAF Yields of Fractionated Products[a]

Catalyst	Atmosphere[b]	THF Insol	Preasphaltene	Asphaltene	Oils
Recycle	1000 psi H_2	6.9	4.6	53.2	30.9
Fe_2O_3	1000 psi H_2	12.4	13.3	37.8	19.1
Fe_2O_3	1000 psi CO/H_2	19.6	10.4	28.6	18.1
$Fe(CO)_5$	850 psi H_2	21.9	6.8	31.3	14.9
$Fe(CO)_5$	1000 psi H_2	5.8	7.5	54.9	21.7
$Fe(CO)_5$	20% CO/H_2	9.9	5.0	40.1	21.5
$Fe(CO)_5/H_2O$	20% CO/H_2	14.2	11.9	54.9	4.6
$Fe(CO)_5$	50% CO/H_2	15.4	19.2	35.8	26.1
$Fe(CO)_5/H_2O$	50% CO/H_2	14.3	14.4	47.6	7.4
$Fe_2O_3 \cdot SO_4$	1000 psi H_2	12.4	11.6	41.2	17.7

[a] Reaction conducted in a 300-mL autoclave with 20g Black Thunder Wyodak coal, 1.4 g iron metal in catalyst, 50 g Recycle solvent and at 425°C. Atmosphere contained 3% H_2S in either H_2 or CO/H_2.

[b] CO/H_2 mixtures contained 3% H_2S, 79% H_2, and 18% CO.

Table 4. Effect of CO on Oxygen Content[a]

Atmosphere	% O in Asphaltene	% O in Oil
H_2	4.78	2.37
50% CO/H_2	2.74	1.74

[a] Reaction run with $Fe(CO)_5$ as catalyst

PLANS

During the coming year we plan to complete our screening tests and determine the optimal ratio of CO to H_2 required in order to maximize the coal conversion. We plan to utilize model systems studies in order to determine the effect of the catalyst and process on the functionalities in the coal. We also plan to include an upgrading step and evaluate the product profile in order to assess the possible effects that catalysts and process conditions will have on the overall economics of the coal conversion process.

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ADVANCED CONCEPTS IN COAL LIQUEFACTION - OPTIMIZATION OF REACTOR CONFIGURATION IN COAL LIQUEFACTION

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INTRODUCTION

HRI has conducted research on coal liquefaction for more than 25 years. During this time, HRI evaluated both thermal-catalytic and catalytic-catalytic coal liquefaction configurations with several alternative reactor designs and process operating conditions. The research work led to important findings which significantly increased liquid yields, improved product quality, and improved process economics. The following process changes led to improved performance:

- Staging coal liquefaction reactions
- Lower temperature and higher residence times
- Heavier (650°F$^+$) boiling recycle solvents preferred
- Low-High Temperature mode of operation in Catalytic Processing
- Coal concentration in feed slurries increased from ca. 30 W% to ca. 53 W%
- Deep coal cleaning improved feedstock quality for liquefaction
- Continuous sulfiding for low-rank, low-sulfur coals
- In-Line hydrotreating for product quality improvement
- Use of synthesis gas in first stage instead of pure H_2 improved net hydrogen utilization

With all these process improvements, HRI's CTSL Process (shown in Figure 1), in an extinction recycle more of operation, yields 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).

HRI has been selected by the U.S. Department of Energy to study the optimization of reactor configurations with a goal of developing a feasible cost-effective processing scheme that will result in an increased overall yield of higher quality distillates. Since the high pressure-high temperature reactors and associated equipment for a coal liquefaction plant can comprise up to 20% of the capital costs of a grass roots plant, significant savings can result from improved reactor configurations and a decreased reactor volume requirement. It is also expected that improved reactor configurations will lead to improvements in the product selectivity, product slate, and hydrogen utilization. The reactor configurations/concepts studied in this Project are:

- Incorporation of a fixed-bed plug flow reactor after partial conversion and micronization of coal in an upstream CSTR (or an ebullated bed reactor)
- Comparison of different conceptual reactor schemes/configurations
- Interstage concentration of unreacted materials for improved kinetics in the two (or three) stage back-mixed reactor system.

MODELLING BACKGROUND

The HRI CTSL Process uses a relatively low first-stage temperature (750-775°F) and a higher second-stage temperature (815-825°F). The first stage with more favorable hydrogenation conditions, regenerates the H-donor capacity of the recycle solvent, while accomplishing a significant degree of coal conversion and production of distillate liquids. The second stage with higher temperature, to promote cracking, completes the conversion of coal with production of additional distillable and low-heteroatom containing liquids. The CTSL Process employes an ebullated bed of catalyst that maintains an expanded condition of catalyst and permits passage of large solid particles and avoids problems in dealing with highly viscous liquefied material especially in the first stage of the coal liquefaction reactions. Inspite of all the advantages an ebullated bed reactor system offers from the liquefaction process viewpoint, it has a severe kinetic disadvantage, unless the problem is mitigated by the multi-staged reactor configuration. The Table 2 weighs advantages and debits of an ebullated bed reactor system:

An ebullated bed reactor, with a good mixing of the reactants, has relatively uniform concentration of the reactive phases throughout the reactor (corresponding to the product stream concentration). Such a mode has a kinetic disadvantage relative to a plug flow (fixed or packed bed) mode where the reaction potential declines progressively throughout the reactor only reaching that of the product stream composition at the outlet of the reactor.

We have developed first order mathematical models, using CSTR kinetic equations and analysis of coal conversion results from the CTSL and various modes of coal liquefaction experience at the HRI's R&D Center. Application of such a model requires identification of species with different reactivity from coal, more or less corresponding to the maceral types identified by the petrographic analyses, although the actual correlating proportions of different reactive coal species have been developed from the two-stage CTSL or the single-stage H-Coal liquefaction results. Classification of coal as a reactant, into three species (one unreactive) has proven adequate to rationalize the CTSL experimental results giving coal conversions between 30 and 97 % maf coal. Hydrogen-transfer reactions from the donor-solvent in the liquid phase are a factor in coal conversion; however, in the correlation of CTSL results, where donor-solvent is generated *in situ*, inclusion of donor-solvent contribution is not deemed necessary in correlating the results. Although the quality of donor-solvent changes with the catalyst age, only small changes in conversions have been observed as a result of the catalyst age in CTSL Bench Experiments. These correlations were used in the current program to project and compare the performances of different reactor configurations or processing schemes under consideration. HRI's current mathematical model based on the first order kinetics of the CTSL Bench Scale data is shown in Figure 2.

Using the first order kinetic modelling, different reactor configurations can be compared relative to a two-stage CSTR performance, with either coal or residuum (975°F+) conversion as the basis for such comparison. Figure 3 compares reactor volumes necessary to achieve certain coal conversions with Illinois No. 6 coal. This comparison indicates that a system following first-order kinetics at 95 % conversion would require 130% greater reactor volume as a two-stage CSTR than as a plug-flow fixed bed system, all other kinetic factors being equal. Based on the initial CTSL modelling projections, the optimum reactor configurations or processing schemes studied in this program (Figure 4) were as follows:

(I) Fixed Bed Finishing Reactor

The application of fixed-bed reactors for direct coal liquefaction was extensively tested in Synthoil process as a first stage. Problems occurred with plugging, coking, and rapid deactivation of the catalyst. Our goal is to use a fixed-bed hydrocracker as a finishing reactor (second or third stage) where the unconverted coal and ash average from 10-20% and particle size is generally less than 325 mesh (44 microns) as compared to typical feed concentrations of 35-50% coal and a size of 50 mesh (300 microns). Use of such a finishing reactor at low temperature using trilobe catalyst for low pressure drop should have minimum plugging problems and exothermicity can be taken care of by cold gas quenching methods. A simple first order model with identical rate constants and a conversion of 95% in two stages indicates that the CSTR-Fixed Bed combination would require only 55% of the reactor volume as the CSTR-CSTR configuration. In modelling the CSTR-Fixed Bed and CSTR-CSTR configurations on Black Thunder Mine Wyoming coal, the plug-flow option with an isothermal second stage could raise coal conversions by about 3.4%, lower the bottoms plus gas yield by 3.9%, and improve the distillate liquid yield by 4% with a 0.3% lower hydrogen consumption.

(II) Three Stage CSTR System

The addition of a third ebullated bed in series to the CTSL configuration would assuredly result in closer approach to plug-flow fixed-bed reaction potential and involves virtually no processing uncertainties. The ebullated bed configuration in series differs from the previous three stage concepts in control of stage temperatures to obtain an optimum interrelation of hydrogenation and cracking functions. It is recognized that three-stage ebullated CSTR system does not present a radical innovation, since from the inception of the ebullated bed development, it was recognized that the CSTR kinetic effect of the ebullated bed system can be overcome in part by staging the reactor systems, two, three or more reactors. This program involves three ebullated bed configuration largely as a reference for other essential innovations of this program such as the use of a fixed-bed as the third reactor stage, or the incorporation of a practical method of reconcentration of heavy reactants before entering the next reactor stage. A simple first-order kinetic model, with equal temperatures in the stages, indicates that a three-stage system would require 25% less total reactor volume than the two-stage system at a conversion level of 95%. The three-stage concept can be improved further through interstage product separation and reactant concentration and/or incorporation of a fixed-bed upgrading stage.

(III) Product Stream Concentration

The concentration of primary reactants declines progressively in a plug-flow system and is lower stage-by-stage in a close-coupled, multistage CSTR system. More effective use of the reaction space for the conversion of liquid and solid phase reactants can be promoted if their concentration in the liquid phase could be maintained at higher levels and the hydrogen partial pressure increased. For example, in a three-stage CSTR system with simple first-order kinetics, attaining 95% conversion, the primary reactant concentration being fed to the third stage is about 15% of that in the feed to the first stage. Nominally, if the third stage feed concentration were raised to that of the original feed, the proportion of the reaction in the third stage could be correspondingly increased. Calculations based on simple first-order model indicate that a three-stage system of CSTRs with reconcentration of the second stage product going to the third stage (to obtain the same content of the reacting components as in the first stage feed) would require only 43% as much reactor volume to attain 95% conversion as would be needed in a conventional two-stage system with no interstage product concentration. Use of an interstage vapor/liquid separator offers an opportunity to increase the reactant (650°F+ slurry) concentration, increasing the subsequent hydrogen partial pressure and decreasing the production of by-product light hydrocarbon gases from further cracking of 650°F- liquids.

OBJECTIVE

An overall objective of this project is to develop a coal liquefaction process that can generate an all-distillate slate of high quality transportation fuels at a cost approaching $ 25 per barrel of crude oil equivalent, by studying different optimum reactor configurations. A more specific objective was to study the kinetics of coal liquefaction at different stages of coal conversion and improve the first order mathematical model based on the overall (2-stage) CTSL Bench Operations' data and use this model for an improved reactor configuration or processing scheme.

EXPERIMENTAL

The feedstocks required for evaluating different reaction configuration concepts and the processing schemes experimentally, were obtained as either the interstage or the product samples from HRI's CTSL Bench-scale and PDU-studies on Wyoming Black Thunder Subbituminous and Illinois No. 6 bituminous coals.

The principal experimental systems that are being used in this project are:

- A fixed-bed microreactor with continuous liquid (slurry) and gaseous feeds (Figure 6).
- A rapidly agitated microautoclave, 20 cc in volume, with rapid heating and cooling. This apparatus, used as a batch operation, with and without catalysts, is in a kinetic regime similar to a fixed-bed plug-flow reactor (Figure 5).
- A Robinson-Mahoney agitated reactor, containing a fixed annular catalyst basket, with a 1000 cc volume. This system as a continuous flow operation corresponds to a catalytic CSTR configuration of the CTSL system with somewhat greater flexibility and simplicity of operation.

Design of Experiments

In order to evaluate the advanced reactor configurations experimentally and therefore obtain the kinetic data on coal liquefaction at different stages of coal conversion, samples of partially converted coals (between 40-90% conversion) and coal-slurries were obtained from HRI's PDU scale and Bench Scale operations. These partially converted (synthetic or simulated) feedstocks were processed further using either a batch microautoclave system or a continuous fixed-bed reactor system to shed some light on the possible merits of the fixed-bed processing concepts, three-stage testing and the interstage stream concentration concept. An effort was made to study partially converted coal and slurry samples derived both from a bituminous Illinois No. 6 coal and a subbituminous Black Thnuder Mine Wyoming coal. Following were the partially converted coal and slurry samples we have evaluated so far in this program:

(i) Atmospheric bottom slurry (Tank O-47) from the PDU Run 260-03 carried out on Black Thunder Mine coal, designated as L-772.
(ii) Pressure filter liquid and pressure filter solid samples obtained from the Bench Run 227-76 (CC-16) Period E3; these were mild reaction severity samples collected when both the CTSL ebullated bed reactors were as 750°F.

The detailed analyses of these two simulated feedstock samples are given in Tables 3 and 4.

The partially converted samples thus collected, were found to have a high extent of coal conversion based on the THF-solubility (typically between 75-85 %); these samples were not adequate to provide any valuable information on kinetics of initial stages of coal conversion (i.e., when conversions are lower than 70 % or so). In order to obtain a partially converted coal sample with low degree of conversion, the samples had to be obtained from coal dissolution under relatively milder conditions (T < 370°F, reaction time < 30 min). Such samples of the mildly converted Illinois No.6 coal are being currently acquired from the Pittsburgh Energy Technology Center. The three-stage back-mixed reactor system and the interstage stream concentration concepts will be evaluated using a Robinson-Mahoney dual-reactors system; the plans of the continuous 16-days long run, simulating these concepts, is discussed in the later sections.

RESULTS AND DISCUSSION

A. Reactivity of the Partially Converted Coal and Coal Liquids: Effect of Stream Concentration

Microautoclave Screening Tests to Evaluate Reactivity of Partially Converted Filter Cake for Multistage Coal Liquefaction Concept:

A series of microautoclave tests (AC-01 through' AC-08) were carried out to assess the reactivity of partially converted coal samples to evaluate the possibility of multi-stage coal liquefaction. The partially converted coal was the THF washed cake of the pressure filter solids recovered from run 227-76 period E3. In spite of the relatively low severity (1st stage: 750°F and 2nd stage: 600°F) at which this sample was recovered, the coal conversion was fairly high (87.2 % based on THF solubility). Following were the reaction conditions for the microautoclave tests that were performed and the data on conversions, material balances, and product characterization were obtained.

THF Washed Cake (227-76-E3PFC):	2.0 g
Solvent (PFL 227-76-13):	8.0 g
Catalyst (Recovered AO-60 Cat*):	2.0 g
Pressure (H_2):	2000 psig at reaction temperature
Temperature:	750-825°F
Time:	15-60 minutes

* THF washed, second stage catalyst recovered from Run 227-76.

As indicated earlier the THF solubility of the partially converted coal sample was 87.2% and the resid (975°F+) conversion at the feed to the microautoclave tests was estimated to be 61.5 wt%. The results of coal and resid conversion relative to the starting materials and percent improvements in conversion levels are listed in Table 5.

Microautoclave Tests to Determine the Reactivity of 975 F+ Residuum from Illinois No. 6 Coal to Evaluate Interstage Stream Concentration Concepts

The pressure filter liquids obtained from Bench Run 227-76 Period E3 contained 38.27 wt% of 975°F+ resid material. The reactivity of this resid at different concentrations was tested to evaluate the interstage stream concentration concept. In order to alter the composition of the residuum fraction of this PFL, the following diluents were mixed with it in different proportions for the microautoclave tests:

Diluent B: IBP-850°F material from PFL (Period E3)
Diluent C: 850°F material from PFL (Period E3)

The results obtained from the microautoclave tests AC-8 through' AC-16 are presented in Table 6. The THF-washed recovered catalyst from the second stage of Run 227-76 was used in these tests.

It can be seen from Table 5 that a fair improvement is obtained in overall coal conversion (between 3-8 wt%) of the partially converted coal and more significantly it is the resid conversion that is enhanced considerably (as much as 32 wt%) by the additional processing of the partially converted coal. These results, therefore, seem to suggest that three-stage processing of coal definitely holds promise in improving the conversion levels, especially the resid conversion levels significantly. The partially converted coal sample used for these tests was originally 87.2 wt% soluble in THF. Considering this high solubility, there was no much room in the improvement in this number even though coal conversion levels, based on THF-solubility, of 95 wt% were obtained in these tests. A further series of microautoclave tests to evaluate the same concept (three-stage reactors) with mildly converted coal samples (THF solubility of less than 80 wt%) is planned.

Table 2 shows the effect of interstage stream concentration, in terms of the concentration of the 975°F+ residuum in pressure filter liquid feed charge for the microautoclave tests, on the percent resid conversion levels. Comparison of tests AC-08 and AC-12, both carried out at 800°F, indicates that AC-08 which has a higher concentration of resid in the feed charge, results in slightly better conversion levels (better resid conversion and lower char formation). Also, comparison of tests AC-10 and AC-15, both carried out at 825°F, indicates that AC-15 with higher concentration of residuum in the feed charge resulted in improved conversion levels. These results definitely seem to indicate the merit in the interstage stream concentration concept for enhanced kinetics of direct coal liquefaction.

B. Small Fixed Bed Reactor Tests: Evaluation of a Fixed-Bed as a Finishing Reactor

Two continuous flow tests were completed using a partially converted slurry (L-772) generated from the PDU Run 260-03 on a sub-bituminous Wyoming Black Thunder coal. Two different shaped and size, a 1/20" trilobe and a 1/32" extrudate, Ni-Mo supported catalysts were used in both upflow and downflow mode of operations. Results from these tests are discussed here.

The main purpose of these small-scale flow tests was to evaluate the viability of using a fixed-bed reactor as a "finishing reactor" in coal liquefaction. Also, the specific objective of the Runs ACL-01 and ACL-02 was to determine the space velocities at which solids in the feed slurry will not settle in the fixed-bed reactor. The test system consisted of two 3/8" i.d. fixed bed reactors connected either in upflow or downflow mode. as shown in Figure 6. The reactors were uniformly heated by a fluidized sandbath preheater. The slurry feed to the reactor system was provided by a positive displacement metering pump. This pump was initially sized for the lower end of the range of space velocity tested and subsequently boosted to a higher flow range by increasing both the gear ratio and the plunger diameter. Due to high stroke frequency at high flow rate, there were excessive leakages through the pump packing which affected the actual flow through the reactor substantially. Each Run had a total slurry feed duration of approximately 60 hours. However, there were five to six interruptions during each Run, mainly due to high pressure build-up as a result of solid deposition in the reactor or transfer lines. In most cases, the interruptions were immediately preceded by a reduction in the feed rates, or loss in slurry feed due to excessive leakage at feed or low-pressure circulating systems.

The Run summary for ACL-01 and ACL-02 is presented in Tables 7 and 8, respectively. In Run ACL-01, Shell-317 1/20" trilobe catalyst was tested. This catalyst was obtained from Wilsonville in a presulfided form. Three test conditions were evaluated in five mass-balance periods with run durations varying from 6.3 to 20.5 hours. The longest Run duration was achieved in Period 5 when the reactor configuration consisted of one reactor in the downflow mode. Periods 1 through 4 were in the upflow mode with two reactors connected in series. To simplify the operations, only one reactor was used in the Run ACL-02. Four test Conditions were tested. Periods 1 through 4 were in downflow mode of operation while Period 5 was in upflow mode. The space velocities investigated in this test were higher than those in ACL-01 ranging from 4900 to 8900 Kg/h/m^2. However, the temperature was around 370°F for majority of the products. Feed slurry used in these tests was partially converted coal slurry (L-772) from PDU-Run 260-03. It contained 12.06 and 3.35 W% of unconverted coal and ash (SO_3-free basis).

With the exception of ACL-02 Periods 1 and 2, most mass balances were low varying from 82.0 to 92.9 W%, as shown in Tables 7 and 8. This is mainly due to small scale operations and relatively short duration of each Period. The ash-balance for the Periods with an upflow mode of operations was typically low (< 40 W%); this was especially true at relatively low space velocities (<2500 Kg/h/m^2). At higher space velocities (> 4410 Kg/h/m^2), the ash-recoveries were much higher and closer to almost 100 W%, indicating that it was only at these higher space velocities that plugging problem was completely eliminated. The normalized product distribution for selected mass-balance Periods are presented in Table 9. The normalization procedure used in the calculation assumed that the low mass balances were mainly due to the over-estimation of the amount of feed slurry fed to the system. This is a reasonable assumption in view of the leakage or unaccountable loss at both the circulation and the feed pumps. Coal conversion of the fee slurry (L-772) was 74.6 W% in reference to the coal fed to the PDU. Due to relatively low reactor temperatures in all Periods the incremental conversion was minimum, less than 5 W%.

Based on the results of these two fixed bed tests, it appears that the downflow mode of operation is more preferable in terms of minimizing the solids settling and plugging the bed. Also, a space velocity of greater than 5000 Kg/h/m^2 is needed to sustain continuous operation. Due to the presence of solid matter in the feed, the fixed bed operation will be limited to a narrow range of operation parameters, e.g. a small turn-down ratio.

C. Theoretical Comparison of Different Reactor Configurations/Processing Schemes

In order to compare the different reactor configurations and processing schemes theoretically, a first-order kinetic model, based on the Bench-scale data was used. Coal and 975°F$^+$ residuum conversions were used as the basis of this comparison. Due to high proportion of the "reactive" fraction in the Illinois No. 6 bituminous coal, the simulated coal conversions for various reactor schemes under consideration were not much different. Due to this apparent insensitivity of the total coal conversion to the processing scheme, only 975°F$^+$ residuum conversions simulated by the model are used as the comparison-basis between different reactor configurations.

The following is the generalized expression for simulating the performance (in terms of either coal or residuum conversion) of any reactor configuration under consideration:

$$F_{Ci}=1.0-\left[\frac{(1-X_D-X_D*R)*(R+1)^{N-1}}{((1+R)*(1-X_D)+k\tau)^N-R*(R+1)^{N-1}}\right]$$

Where,

Fci is the fractional conversion of the species "i"
X_D is the fraction of product stream removed (by distillation) from the feed to the Nth reactor
R is the recycle ratio: Vol.flow rate of recycle stream/Vol.flow rate of feed stream
k is the rate constant for disappearance of species "i"
τ is the residence time of species "i" in the reactor system
[illegible] is the number of reactor stages (all equal volumes) in series.

[Constraint on simulation: Equal Reactor Stage Volumes and Equal Overall Systems' Volume.]

The results of simulation in terms of the 975°F$^+$ resid conversions are shown in Table 10. As shown in Table 10, the three-stage reactor configuration (Case # C) with almost similar overall reaction severity as the two-stage configuration (Case # A), results in about 4-5 W% higher resid conversion. Similarly, Cases D and E clearly show the benefit of interstage separation or product stream concentration, i.e., Cases D and E with 30 W% of product stream from Reactor 2 topped by distillation, show about 6 and 4 W% higher resid conversions than Case C, respectively. Increasing the fraction of product stream that is distilled to remove lighter materials, increases the residuum conversions further.

FUTURE WORK:

The future work in this Project is going to constitute the following:

(I) Studying the reactivity and kinetics of initial stages of coal conversion by using a partially converted coal (conversion less than 50 W%) as the simulated feedstock.
(II) A 16-day continuous run in a two-stage backmixed Robinson-Mahoney Reactor system to evaluate the three-stage and the interstage stream concentration concept and generate kinetic data for the technical assessment of these reactor configuration concepts.

The following are the details of our proposed 16-day continuous run:

Advanced Coal Liquefaction Concepts
Simulated 3-Stage Test

Objective: To evaluate the three-stage and interstage stream concentration concepts using Illinois No. 6 coal.

Background:

The addition of a third back-mixed catalytic ebullated bed reactor in series with two close-coupled stages will bring the performance of the system closer to the ideal plug flow case. An elementary first order kinetic model, with equal temperatures in the stages, indicates that a three-stage system would require 26% less total reactor volume than the two-stage system at a conversion level of 95%.

The concentration of primary reactants declines progressively stage by stage in a close-coupled, multistage CSTR system. More effective use of reactor space for the conversion of liquid and solid phase reactants could be maintained at higher levels and the hydrogen partial pressure increased. Projections based on the simple first-order model indicates that a three-stage system of CSTR reactors with reconcentration of the second-stage product going to the third-stage require only 43% as much total reactor volume to attain 95% conversion as would be needed to a conventional two-stage system with no interstage feed concentration.

Technical Objectives:

1. to determine the performance of a close-coupled two-stage CSTR system using the Robinson Mahoney reactor system (served as a base-case).

2. to determine the performance of a simulated, three-stage CSTR system

3. to evaluate the impact of interstage stream concentration on the performance of a simulated three-stage CSTR system.

System and Operation:

The two-stage Robinson Mahoney CSTR system is required for this run. The feed system shall be modified for continuous slurry charging rate ranging from 150 to 250 ml/hr (or 180 to 300 gm/hr for a slurry with a density of 1.2 gm/cc). In Part I, both reactor are charged with 128 cc of presulfurized Shell S-317 1/32" catalyst. These catalysts are to be removed at the end of Part I. For Part II, a new batch of presulfurized catalyst will be charged the remaining conditions (Conditions 3 and 4). Due to the shortage of feed materials for Part II, the amount of catalyst is reduced to 90 cc.

The run will be operated in an once-through mode (with no recycling of process solvent). The slurrying oil for the entire run is a blend of PFL collected from Run 227-78 (during shut-down and during different run-Periods) and L-769. The blending Ratio is going to be 75 W% of Run 227-78-PFL and 25 W% of L-769.

A mass balance period starts at 4:00 hour and ends at 4:00 hour of the following day. Each 24-hour mass balance period is further divided into **two** 12-hour sub-periods.

Operating Conditions:

This run consists of four conditions and extends over a duration of 16 days.

A brief description of each of the condition is given below:

Part I:

Condition #1 (Periods 1 through 8):
This is the first condition of Part I, a non-integrated three-stage configuration. Two close-coupled CSTRs are required. Temperature of Reactor 1 and 2 is set at 750° and 805°F, respectively, and with a space time velocity of 66 lb mf coal/h/ft_3 catalyst per stage. A solvent/coal ratio of 1.2 is selected to match that of the bench unit operations.

This condition produces feedstock for Conditions #3 and #4.

Condition #2 (Periods 9 through 11):
This is a basecase for evaluating the close-coupled two-stage configuration using the Robinson Mahoney system.

Temperatures:	K-1 at 750° F K-2 at 825° F
Space Velocity:	44 lb mf coal/h/ft_3 catalyst
Solvent/coal:	1.2

Part II:

This is Part II of the simulated, three-stage operation. Only one stirred tank reactor is required. A new batch of presulfurized Shell S-317 catalyst (90 cc only) is to be used.

Condition #3 (Periods 12 through 14):
The feed for this condition is the whole slurry product, collected from Condition #1 of Part I. A new batch of presulfided Shell-317 catalyst (only 90 cc) will be used in this Run-part. The dip-tube in the reactor will be shortened to maintain the same thermal/catalytic volume ratio. The simulated third stage shall be operated at the following conditions (Conditions for the simulated three-stage CSTR system are chosen such that total reaction severity remained the same as the close-coupled two-stage system as in Part I, Condition 2):

Temperature:	825° F
Space Velocity:	66 lb mf coal/h/ft_3

Condition #4 (Periods 15 to 16):
The process conditions chosen for this condition are identical to Condition 3. However, the feed to this condition will be topped separator bottoms from Condition #1 (to remove materials boiling below 650° F). The final selection of the cut point for topping is to be confirmed when analyses of product from Condition #1 become available.

The Run-Plan for the above operation is shown in Table 11.

SUMMARY

The reactor configurations/concepts being studied in this project include:

- Incorporation of a fixed-bed, plug-flow reactor after partial conversion and microionization of coal in an upstream back-mixed reactor (CSTR).
- Comparison (theoretical) of different conceptual reactor schemes/configuration.
- Interstage concentration of unreacted materials for improved kinetics in the two (or three) stage back-mixed reactor system.

In order to study these concepts, samples of partially converted coals and residua were obtained from the PDU as well as some bench runs at HRI. These samples were evaluated using a 20 cc batch microautoclave reactor system to shed some light on the possible merits of the interstage stream concentration and the three-stage back-mixed reactor system concepts. Incorporation of a fixed bed plug-flow reactor as a "finishing" stage in coal conversion, indicated that at space velocity values greater than a certain minimum, fixed bed reactor can be used successfully for coal liquids/slurries in the downflow mode of operation to minimize solid settling and subsequent plugging of the bed. Different reactor configurations and schemes have been compared on a theoretical basis using a simple first order kinetic model for the resid conversion, to provide a sound basis for experimental testing of concepts. A continuous flow operation to evaluate the three-stage CSTR and interstage stream concentration concepts is planned using a two-stage Robinson-Mahoney CSTR system to simulate the above process concepts.

ACKNOWLEDGMENTS

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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
$975^{\circ}F^{+}$ Conv., W% MAF	73	94	75	89
C_4-975°F Liquid Yield				
W% MAF Coal	51	78	48	66
Bbl/Ton Coal	3.3	5.0	3.1	4.3

Table 2. Credits and Debits of an Ebullated Bed Reactor System

Credits	Debits
• Near Isothermal operation, fully utilizes the heat of reaction	• CSTR kinetics, large volumes necessary
• Well-mixed system, intimate contact of gas, liquid and solids with constant chemistry of catalyst	• Catalyst volumes are limited by the hydrodynamics
• High solids-tolerance	• Catalyst attrition
• Low pressure drops	• Requires a customized pump
• Operates at catalyst equilibrium with constant activity for long periods	• Overall high equipment cost

Table 3. Feed Slurry (L-772) Inspection: Properties of Pressure Filter Liquid and Pressure Filter Solids.

Pressure Filter Liquid

Pressure Filtration, W%	
Filter Liquid	74.73
Filter Cake	25.27
Filter Liquid	
API Gravity	16.0
ASTM D-1160 Distillation, Vol% vs °F	
IBP	536
5	591
10	618
20	644
30	666
40	687
50	708
60	730
70	756
80	807
90	938
92	975
B.P. Distribution, W%	
IBP-650°F	20.42
650-850°F	62.30
850-1000°F	8.85
1000°F+	8.44
Elemental Analysis, W%	
Carbon	88.65
Hydrogen	11.14
Nitrogen	0.050
Sulfur	0.019
H/C Ratio	1.51

Pressure Filter Cake

	Weight %
Quinoline Solubles	39.03
Quinoline Insolubles (Ash-free)	47.71
Ash	15.21
Sulfur in Ash	5.14
SO3-free Ash	13.21
Coal/Ash (SO3-free)	3.60
Coal Conversion, maf W%	74.6
Mineral Analysis of Ash (W% of Ignited Sample)	
Silica, SIO2	33.33
Alumina, Al2O3	18.72
Titania, TiO2	1.40
Ferric Oxide, Fe2O3	7.86
Lime, CaO	19.92
Magnesia, MgO	3.96
Potassium Oxide, K2O	0.35
Sodium Oxide, NaO	0.50
Sulfur Trioxide, SO3	9.83
Phosphorous Pentoxide, P2O5	0.65
Strontium Oxide, SrO	0.10
Barium Oxide, BaO	1.62
Manganese Oxide, Mn3O4	0.07
Undetermined	1.63

Table 4. Analyses of Simulated Feedstock from Bench Run 227-76-Period E3: Pressure Filter Cake and Pressure Filter Liquid

ANALYSIS OF PRESSURE FILTER CAKE
(Run 227-76 Period E3)

Pressure Filtration:	
Filter Cake, W%	29.42
Filter Liquids, W%	70.58
Elemental Analysis, W%	
Carbon	16.0
Hydrogen	6.25
Nitrogen	1.70
Sulfur	0.85
SO_3-Free Ash	13.48
ASTM Ash	13.91
S in Ash	1.20
Quinoline Filtration, W%	
Insolubles (QI)	36.77
Ash in QI, W% PFC	14.60
S in QI Ash	1.03
Coal Conversion, W%	88.9

ANALYSIS OF PRESSURE FILTER LIQUID

(Run 227-76 Period E3)

API Gravity	1.3
Elemental Analysis, W%	
Carbon	89.51
Hydrogen	8.84
Nitrogen	0.54
Sulfur	0.22
Boiling Point Distribution, W%	
IBP	583°F
IBP-650	5.35
650-850	42.68
850-975	12.95
973^+	38.27
Loss	0.75

Table 5. Reactivity of Partially Converted Illinois No. 6 Coal

Test No. AC-	Temp. °F	Time Min.	%Increase in Coal Conversion	%Increase in Resid Conversion
01	750	15	3.2	-1.0
02	750	30	5.3	2.1
03	800	15	5.8	7.6
04	800	30	7.4	31.5
07	800	60	7.8	28.2
05	825	15	7.1	11.5
06	825	30	7.6	23.2

Table 6. Effect of Feed Concentration on Residuum Conversion

Test No. AC-	Reactants (gm)	Temp. °F	Time Min.	%975°F in Charge	%Resid Conversion
08	PFL (3)	800	30	38.27	29.7
12	PFL (2) & Dil. B (1)	800	30	25.51	27.2
10	PFL (3)	825	30	38.27	31.5
15	PFL (2) & Dil. C (1)	825	30	50.42	34.3
11	PFL (3)	800	60	38.27	37.0
16*	PFL (3)	800	30	38.27	22.7

* This test was carried out without any catalyst, i.e., a thermal background.

Table 7. Run Operating Summary for ACL-01 (254-01)

Fixed Bed Operation: Run 254-01
Shell S-317 1/20" Trilobe Catalyst (HRI-6030)

Run Summary

Condition	1	1	1	2	3
Period	1	2	3	4	5
No. of Reactor	2	2	2	2	1
Mode of Operation	Upflow	Upflow	Upflow	Upflow	Downflow
Duration, hours	9.4	6.3	12.8	11.5	20.5
Reactor Temperature (°C)*	402	417	416	404	369
Space Velocity Kg/h/M^2	2090	2650	2500	5040	4410
DMDS, W% Feed	2.8	2.8	2.8	2.8	2.8
Mass Recovery, W%	56.0	83.5	82.0	92.9	90.8
Ash Recovery, W%		18.3	31.7	35.4	93.8

---

[*] Mid-point temperature of the fluidized sandbath heater.

Table 8. Run Operating Summary for ACL-02 (254-02)

Fixed Bed Operation: Run 254-02
Shell S-317 1/16" Extrudate Catalyst (HRI-5903)

Run Summary

Condition	1	1	2	3	4
Period	1	2	3	4	5
No. of Reactor	1	1	1	1	1
Mode of Operation	Downflow	Downflow	Downflow	Downflow	Upflow
Duration, hours	9	21	11	4	9.4
Reactor Temperature (°C)*	372	371	396	372	407
Space Velocity Kg/h/M^2	5170	4890	5630	8870	8510
DMDS, W% Feed	2.8	2.8	2.8	5.0**	2.8
Mass Recovery, W%	95.5	110.0	92.4	88.0	88.8
Ash Recovery, W%		107.7	104.3		180

---

[*] Mid-point temperature of the fluidized sandbath heater.

Table 9. Normalized Product Distributions from Fixed-Bed Operations, ACL-01 and ACL-02

Fixed Bed Operations (Run ACL-01 & 2)

Normalized Product Distribution

(Basis: 100 part of L-772)

Run No.	1	1	1	1	2	2	L-772
Period No.[+]	2B	3B	4[++]	5B	2B	3B	Slurry
Gases							
C_1-C_3	1.77	2.03	1.00	0.38	0.49	0.38	
C_4-C_7	1.55	1.78	1.04	0.00	0.00	0.41	
H_2S	1.12	1.28	1.72	1.19	1.16	3.46	
Others	0.00	0.00	0.03	0.00	0.04	0.08	
Total	4.44	5.09	3.79	1.56	1.70	4.32	
Filtrate (PFL)							
IBP-650°F	24.24	31.12	24.07	14.03	16.37	19.34	15.26
650-850°F	48.69	41.62	46.00	44.24	42.67	40.70	46.55
850-975°F	19.00	9.54	13.41	7.10	5.83	7.67	6.61
975°F[+]	1.05	7.10		6.31	6.35	5.40	6.31
Total	92.98	89.37		3.15	72.21	73.10	74.73
Filter Cake (PFS)							
Quinoline Solubles	2.11	3.11	4.58	11.91	13.13	10.36	9.86
Quinoline Insolubles*	2.07	3.29	4.67	10.92	12.52	11.56	12.06
Ash (SO_3-free)	0.61	1.06	1.19	3.14	3.61	3.49	3.35
Total	4.79	7.45	10.44	25.97	29.26	25.42	25.27
Total Product**	102.2	101.9	102.3	100.7	102.2	102.8	100.0
Coal Conversion							
W% maf Coal ***	76.0	78.2	72.3	75.4	75.4	76.6	74.6
Incremental Conv.							
W% change over L-772	1.9	4.8	-3.1	1.1	1.1	2.7	0.0

[+] Each period was divided into two 12-hour sub-periods A and B.

[++] Averaged result using data from sub-periods A and B.

* Quinoline insolubles do not include ash.

** Total Product = 100 part of L-772 + 2.88 parts of DMDS + amount of H_2 consumed.

*** In reference to the coal feed to the PDU Run 260-03.

Table 10. Comparison of Different Reactor Configurations/Processing Schemes: Simulation of Performance

ASSUMPTIONS:
Recycle-to-fresh feed = 0.5
All Backmixed Stages
Activation energy = 32 kcal/gmol
Pre-exponential factor=2.86E1 lb/hr/ft3

Configuration	Study	Reactor Temperature, deg F			lb coal/hr/ft3 reactor	Distillation	% 975 F+ Residuum Conv. Predicted
	Case	Reactor 1	Reactor 2	Reactor 3	Space Velocity	Fraction	
Two-Stage	A	750	825		20.6	0	0.7743
Three-Stage	B	750	750	825	30.9	0	0.7485
	C	750	805	825	30.9	0	0.8194
	D	750	805	825	30.9	0.3	0.88
		750	805	825	30.9	0.4	0.9071
		750	805	825	30.9	0.5	0.9373
	E	750	805	810	30.9	0.3	0.86
		750	805	810	30.9	0.4	0.8898
		750	805	810	30.9	0.5	0.9251

Table 11. Run Plan
Robinson Mahoney Reactor System
Illinois No. 6 Coal (HRI-6107)
Shell S-317 Ni/Mo 1/32" Catalyst (HRI-5394)

Condition	1	2	3	4
Periods	1-8	9-11	12-14	15-16
No. of Reactor	2	2	1	1
Temperature, ° F				
Reactor #1	750	750	825	825
Reactor #2	805	825	n/a	n/a
Space Velocity lb mf coal/h/ft3 cat. per 1st stage	66	44	66	66
Feed Type	Coal	Coal	Cond. 1 Whole Product	Cond. 1 Topped Product
Solvent/Coal Ratio	1.2	1.2	n/a	n/a
<u>Coal and Solvent Flowrates:</u>				
Pat I				
dry coal, g/h	136	90	n/a	n/a
wet coal, g/h @ 3W% moisture	140	93	n/a	n/a
solvent, g/h	168	111	n/a	n/a
Total Slurry, g/h	308	204	n/a	n/a
Part II				
Slurry, (dry) g/h	n/a	n/a	195*	210**
Water,g/h	n/a	n/a	21*	n/a
<u>Hydrogen and Water Injection Rates:</u>				
Hydrogen, scfh	11	7.0	8.0	8.0
Water to Sep. Oultet g/h	50	50	50	50

* To be confirmed to match the production rate of separator bottoms from Condition #1.

** To match the production of topped separator bottoms from Condition #1

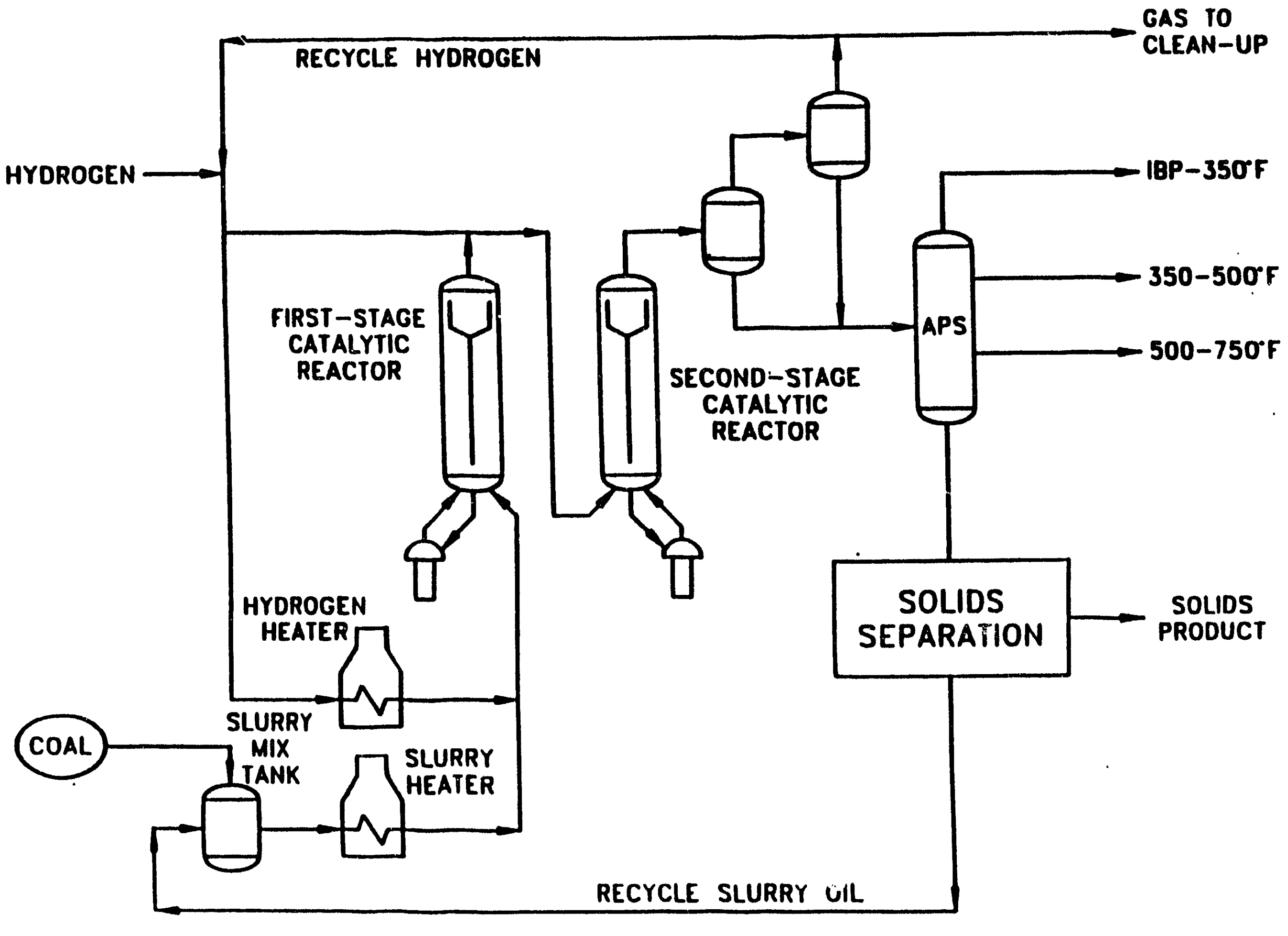


Figure 1. Schematic of HRI's CTSL Process

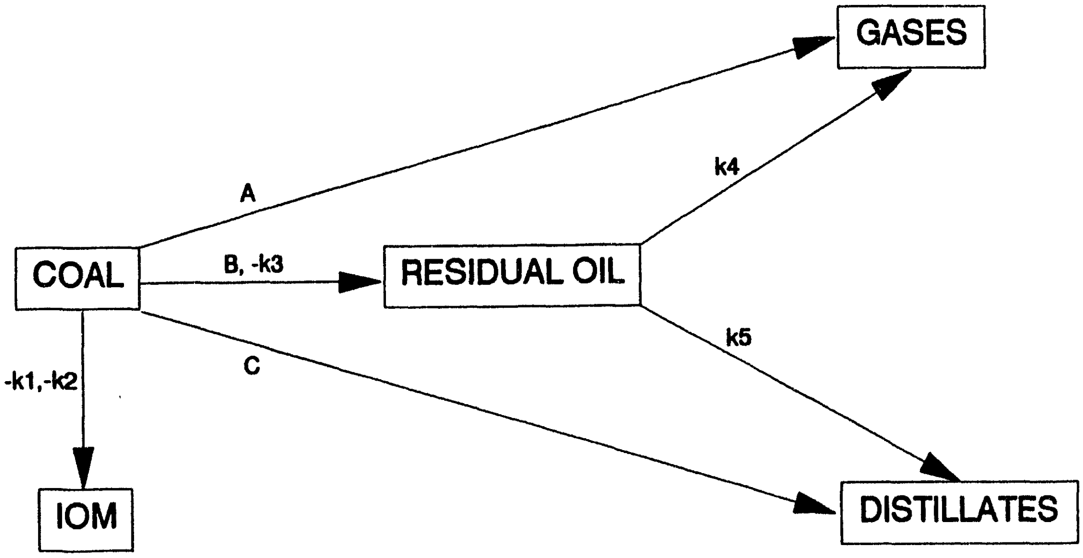


Figure 2. HRI's Current Kinetic Model for Direct Coal Liquefaction

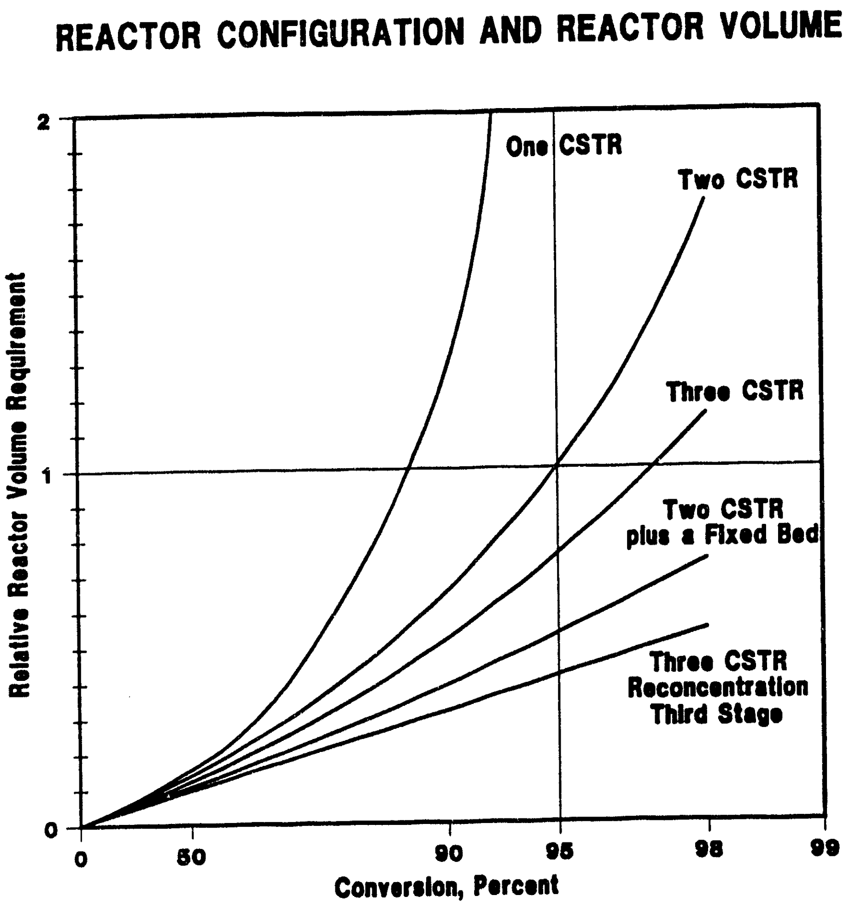
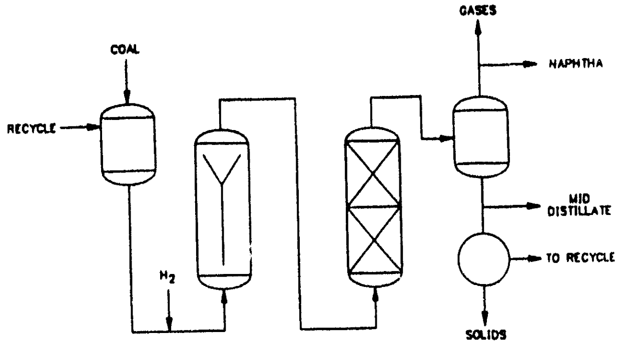
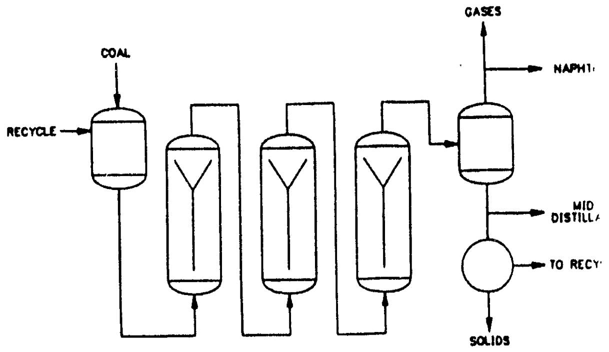


Figure 3. Relative Volume Requirements for Different Reactor Configurations

TWO STAGES
AN EBULLATED BED REACTOR
FOLLOWED BY A FIXED BED



THREE STAGE
THREE EBULLATED BED REACTORS



TWO STAGES
CONCENTRATION BETWEEN STAGES

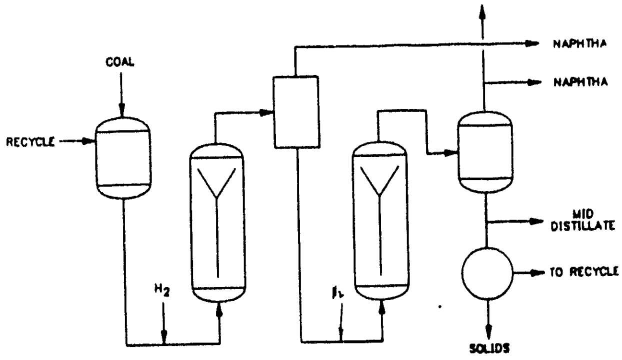
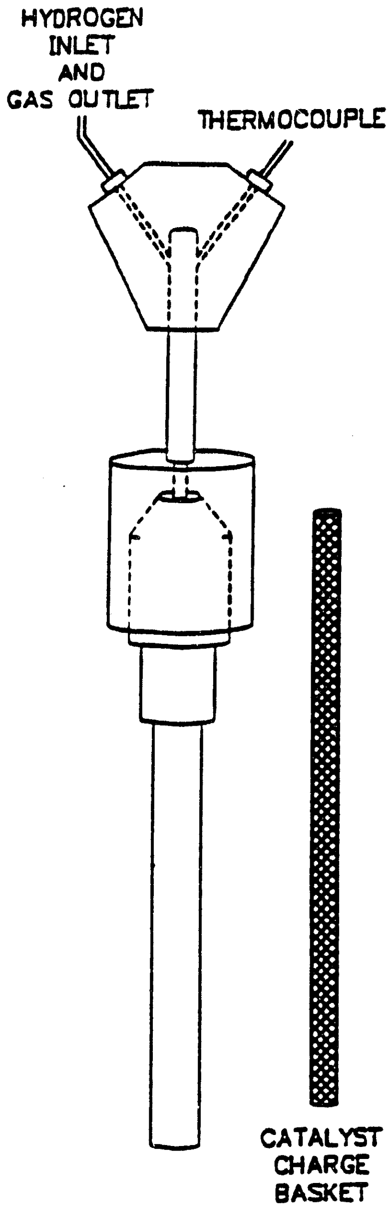


Figure 4. Reactor Configurations/Processing Schemes Being Studied in this Project



MECHANICAL DESIGN

- 20cc INTERNAL VOLUME
- MAXIMUM INLET HYDROGEN PRESSURE 3000
- OPERATIONS TO LIQUEFACTION TEMPERATUR
- THERMAL AND GAS INLET COUPLING
- 347ss MATERIAL OF CONSTRUCTION
- EXTERNAL CAP THREADS
- REACTOR CAP REDESIGN
- COLD TRAPS
- CATALYST BASKET
- UTILIZES WHOLE EXTRUDATE CATALYST
- GAS COLLECTION
- SHAKEN VERTICALLY IN A SAND BATH

TESTING CAPABILITIES

- THERMAL TESTS VARYING CHARGE, FEED RATIOS, TEMPERATURE, TIME
- CATALYTIC TESTS VARYING CHARGE, FEED RATIOS, TEMPERATURE, TIME

Figure 5. HRI's 20 cc Microautoclave Reactor System

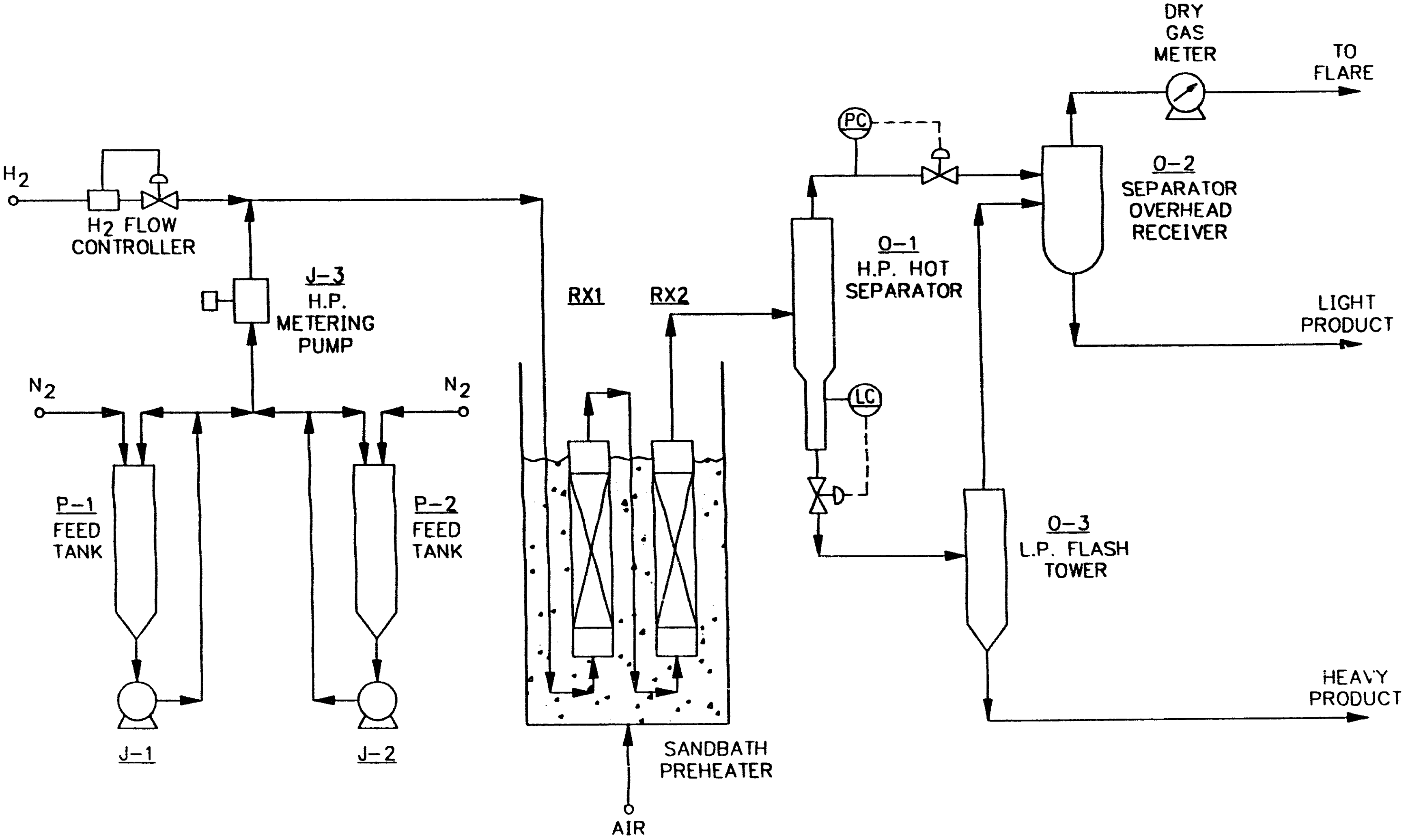


Figure 6. Fixed Bed System, Unit 254

COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION: AN ANALYTICAL CHARACTERIZATION CASE STUDY

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INTRODUCTION

The primary goal of this program is to improve the basic chemical understanding of direct coal liquefaction, and in so doing to provide a bridge between direct coal liquefaction and analytical chemistry. It is believed that the information gained in our endeavor to achieve this goal will advantageously influence the economics of direct coal liquefaction.

In this contract, CONSOL is participating in DOE's direct coal liquefaction process development program by providing analytical support to process developers. Established techniques are being used to characterize coal liquids produced from recent process development work. This ensures that relevant information is obtained from these materials, and that the properties of materials produced in the current program are understood within a framework of past development efforts. Early in the contract, approximately 25 techniques were identified to have the potential to provide additional analytical information useful for process development interests. These techniques are not necessarily new, but all were novel in their application to direct coal liquefaction feedstocks, intermediates, and products. In addition to the routine analyses, several of the most promising of those techniques were subsequently applied to material balance streams produced in the HRI, Inc. bench-unit Run CC-15. These special analyses include field ionization mass spectrometry and solid state ^{13}C-NMR spectroscopy. Additionally, standard petroleum inspection tests were used to evaluate the quality of the net product oils from the direct coal conversion process. Analytical data from this study, designed to demonstrate in a systematic manner application of these methods to support coal liquefaction process development, is discussed and interpreted in relation to Run CC-15 process conditions and performance.

HRI Run CC-15, which is more fully described below, had only three major operating variables, catalyst age, pretreater temperature and the use (or not) of iron-impregnated coal. Due to the relative simplicity of the run, data interpretation is comparably straightforward. This uncomplicated case study provides for a good demonstration of the usefulness of the techniques employed, and lays the groundwork for application of these techniques to more complex processing runs.

RUN DESCRIPTION[2,3,4]

Catalytic Two-Stage Liquefaction (CTSL) Run CC-15, also called Run 227-75, was made in HRI's two-stage ebullated bed bench scale unit 227. The run was divided into four operating conditions, each lasting several days. Each day is considered a run period. The objective of the run was to test a predispersed (impregnated) hydrated iron oxide catalyst prepared by the method of incipient wetness as developed by the U.S. Department of Energy (DOE)/Pittsburgh Energy Technology Center (PETC).[1] The feed coal was Wyodak and Anderson seam, Black Thunder Mine, subbituminous coal. The pretreated coal, which had an iron content of 0.57 to 0.65 wt % according to HRI (Table 1), was used in run periods 1-8 and 12-14 (Conditions 1,2, and 4). An untreated sample of the same coal was used in run periods 9-11 (Condition 3); the untreated coal had an iron content of 0.2 wt % according to HRI. The analyses of the coal and the pretreated coal can be found in Table 1. The pretreated coal has an elevated N content as a result of the catalyst incorporation procedure.[2]

Start-up and make-up oil for Run CC-15 was a filtered process-derived liquid produced in the HRI process development unit (Run 260-03). Black Thunder Mine coal was also used in Run 260-03. Analyses of the start-up oil are given in Table 2. The liquefaction tests were conducted in a 20 kg/day continuous flow unit (Figure 1). To activate the iron catalyst precursor (FeOOH), the impregnated Black Thunder Mine coal was pretreated with H_2S in a pretreatment reactor at 275°C (522 °F) in Condition 1 and 290 °C (570 °F) in Conditions 2 to 4. During the liquefaction, the first stage reactor temperature was maintained at about 427 °C (800 °F) and the second stage reactor temperature was held at about 413 °C (775 °F). Throughout the test, the first stage reactor was operated thermally. Shell S-317 NiMo catalyst was present in the second-stage reactor. The test was conducted using constant space velocity of about 43 lb coal/h/ft^3 of settled supported catalyst. Catalyst age increased as the run progressed. Operating conditions are given in Table 3.

Yields are given in Table 4 for four run periods (periods 5, 8, 11, 14) which correspond to Conditions 1, 2, 3, and 4, respectively. Process performance for those same periods is given in Table 5. Desulfurization was lower than anticipated, and HRI believes that it is due to high sulfur uptake by the solid residuals. It is presumed that the sulfur is trapped as iron and calcium sulfides in the pretreated Black Thunder Mine coal. This accounts for the negative desulfurization values (Table 5). Coal conversion and distillate yields in this run were higher in Conditions 1, 2, and 4 when iron-impregnated coal was used than in Condition 3 when it was not used. Although there was no apparent effect of catalyst deactivation on coal conversion as the run progressed, the catalyst deactivation is evident in the performance data for distillate yield and conversion of 975 °F$^+$ resid, which both decreased.

BENCH UNIT DESCRIPTION HRI RUN CC-15[2,5]

In the two-stage catalytic process configured for Run CC-15 (Figure 1), coal was slurried with process-derived heavy recycle oils and brought to the slurry preparation section on a bi-hourly basis. The slurry was pressurized, mixed with hydrogen, and fed to the pretreater. Sulfur was added in the form of liquefied hydrogen sulfide to ensure proper sulfidation of the catalyst precursor, as well as to maintain the supported catalyst in the sulfided state. The slurry then passed directly into the first-stage thermal reactor. Operation of the first stage was controlled at temperatures about 426 °C (800 °F).

The first-stage products pass directly to the second stage, without any separation, for hydrotreatment, liquefaction, and heteroatom removal. The severity of this stage can be regulated to control distillate yield and product selectivity. In Run CC-15, the second-stage temperature was maintained at about 413 °C (775 °F).

The two stages are conventional ebullated-bed reactors. They utilize 1/16" extrudate catalysts, which allow fluidized catalyst operation over a wide range of viscosity and density. In Run CC-15, the first stage was operated without supported catalyst. Slurry oil is composed of filtered atmospheric still bottoms. The solids and residual oil composition in the recycle stream can be varied for optimum process performance. Mass balance is performed every 8 or 12 hours and a daily (period) average is reported. Each of the conditions tested is maintained for a minimum of three days (periods) to ensure validity of the data.

SAMPLE DESCRIPTION

CONSOL received a suite of samples from HRI Run CC-15, including start-up solvent, coal, and process and product stream samples. In total, 55 samples from all four run conditions were examined by CONSOL. Of those 55 samples, three samples were first-stage oils. First-stage oils (also called interstage oils) are samples of the first-stage reactor inventory obtained from the recirculation stream on the ebullating bed. These three samples represented run conditions 2 (period 9), 3 (period 12), and 4 (period 15). Consequently, samples chosen for special analyses were chosen to represent the corresponding conditions and the run periods from which these three interstage samples were taken. Thus, a set of twelve samples were examined by FIMS and ^{13}C-NMR. The nine other samples included three pressure filter liquids (PFL), three pressure filter cakes (PFC), and three samples made by blending the two light net product oil samples, the separator overhead (SOH) and atmospheric still overhead (ASOH) sample. The pressure-filter liquid is a major second-stage product and the major component of the slurry oil. It is obtained by filtering the atmospheric-still bottoms through a pressure filter. The pressure filter cake is the retained material. The sampling procedure used by HRI is to take the PFL sample first, then to take the first-stage sample while maintaining constant operating conditions. As a result, any first-stage sample corresponds most closely to the PFL sample taken one period earlier. The separator overhead oil and the atmospheric still overhead oil are net distillate products. All oils are assumed to be solids-free for analytical purposes. Elemental analyses are given in Table 6 of the 12 samples obtained from run conditions 2, 3, and 4 which were further analyzed by the methods listed in Table 7. The SOH and ASOH oils were blended in the proportions in which they were produced and were analyzed as the blend to represent a net oil product.

The sample which was analyzed by petroleum inspection tests was a blend of ASOH and SOH from conditions 2, 3, and 4.

ANALYTICAL PROCEDURES

The analytical procedures used to provide a comprehensive data base of information about the samples obtained from Run CC-15, are listed in Table 7. They are divided into two groups, "base" methods and "exploratory" methods. The base methods were performed in-house at CONSOL R&D. The field ionization mass spectrometry (FIMS) was performed at SRI International. The ^{13}C solid-state nuclear magnetic resonance (NMR) spectroscopy was done at the University of Utah. Net oil product inspection tests were done at the National Institute for Petroleum and Energy Research (NIPER). Experimental methods for the in-house techniques have been published elsewhere.[6-11] Descriptions of the FIMS and ^{13}C-NMR methods applied to coal-derived materials can be found in CONSOL's topical reports[12-14] and the references contained therein.

SAMPLE PROPERTIES

CONSOL characterized 55 samples derived from HRI CC-15 by several of the "base" methods listed in Table 7. ^{1}H-NMR spectroscopy, phenolic -OH determination by Fourier transform infrared (FTIR) spectroscopy, and solvent quality determinations were performed on different samples as appropriate. The results of these analyses are presented in Figures 2 through 5 for several process streams. These results provide a general overview of the run.

PFL and PFC Samples

It is apparent from the ^{1}H-NMR data (Figure 2) that there is a general trend of increasing aromaticity of all PFL and PFC samples for the duration of the run. This reflects the dominant effect of supported catalyst deactivation with respect to hydrogenation. During Condition 3 (Periods 9, 10, and 11), there appears to be a significantly sharp increase in aromaticity of the PFL and PFC samples. This may reflect an increased rate of deactivation in the absence of the dispersed catalyst. However, during Period 9 an unusually large amount of makeup oil was required in the recycle feed (ca. 20 wt % of the recycle feed was makeup). This significant quantity of the less-aromatic makeup oil could decrease the aromaticity of the PFL sample obtained from period 9. The apparent increase is accounted for by a return in periods 10 and 11 to a lower make-up oil to process-derived oil ratio in the system.

Along with the general upward trend in aromaticity of the PFL samples, there are corresponding downward trends in hydroaromatics and paraffins. The cyclic beta protons, which are the cyclic hydrogen donors, and paraffins, which are represented by the sum of the alkyl beta and gamma protons, are shown in Figure 3. These trends can be expected to accompany the decreasing hydrogenation activity of the catalyst.

In Figure 4, it is evident that there is also a general trend of increasing phenolic -OH concentration of the PFL and PFC samples throughout the run. This reflects the dominant effect of catalyst deactivation with respect to deoxygenation. In contrast to the aromaticity results, the phenolic -OH concentration increases smoothly through the run, with no apparent irregularities.

Donor solvent quality of the whole PFL, as measured by a standard microautoclave assay, increased from the poor value of the start-up oil (56% MAF coal) to a moderately good value of about 80% MAF coal conversion by Period 8 (Figure 5). After Period 8, the donor quality of the whole PFL stayed relatively constant. A small decrease in Periods 11 and 12 may be related to the use of untreated coal in Periods 9 through 11.

Interstage, SOH and ASOH Samples

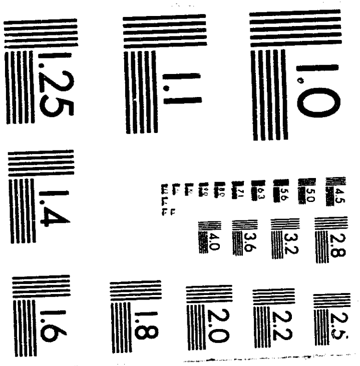
The trend showing an increased aromatic content of the SOH and ASOH samples as the run progressed is not as pronounced as the trend for the PFL and PFC samples; however, it is discernible (Figure 2). This, again, reflects the deactivation of the supported second-stage catalyst. The aromaticity of the interstage samples examined is significantly affected by the absence of the impregnated iron catalyst in Period 11. Hydrogen aromaticity for the Period 11 sample is 34% greater than that of the sample from Period 8 and 14% greater than that of the sample from Period 14 (relative basis).

The phenolic -OH content of the ASOH and SOH samples generally follows that of the corresponding PFL through the run. The ASOH samples are consistently higher in phenolic -OH than the corresponding whole PFLs. This arises from concentration of alkylated phenols in this particular boiling range product.[15] Evidence of this was seen previously in distillation fractions from Wilsonville Run 260[16] where it was observed that phenolic compounds were more concentrated in a certain net product fraction (kerosene cut) than the fractions boiling higher or lower than that fraction. Our recent analyses of the distillation fractions produced by NIPER[14] also confirmed this effect in the CC-15 product fractions.

Period 8, 11, and 14 Samples

As was described above, twelve samples representing Conditions 2, 3, and 4 (Periods 8, 11, and 14) were chosen for more comprehensive examination by in-house base methods and exploratory techniques. The twelve samples are the Interstage, PFL, PFC, and blended ASOH-SOH samples from these periods. Phenolic -OH concentrations, proton distributions, and solvent quality data for these twelve samples are given in Table 8.

The total proton aromaticity for the 12 samples is plotted in Figure 6. Included in the graph are data for the CONSOL-generated 850 °F$^-$ distillate and 850 °F$^+$ resid fractions of the whole interstage sample. The PFC and PFL aromaticity for the Condition 3 sample is consistent with a linear increase in aromaticity as the run progressed. The whole interstage sample from Condition 3 is substantially more aromatic than the samples from Conditions 2 or 4. The corresponding interstage distillate fraction shows no aromaticity increase from Condition 2 to Condition 3, however, the interstage resid shows a large aromaticity increase. This indicates that resid hydrogenation was less effective when the untreated coal was used in Condition 3, relative to the use of treated coal in Conditions 2 and 4. The effect was more pronounced in the interstage samples than in the PFL or


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3

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PFC samples because the supported catalyst in the second stage contributes to the hydrogenation of the process stream.

The condensed-ring aromatic hydrogen content of the PFC, PFL, whole interstage, interstage distillate, and interstage resid (Figure 7) show a significantly higher condensed aromatic hydrogen content in the Condition 3 whole interstage oil, as was discussed above, and interstage resid than in their Condition 2 and 4 counterparts. It is apparent that the suspension of the use of hydrated iron catalyst caused an increase in the condensed aromatic hydrogen content of the interstage oil by increasing the condensed aromatic hydrogen content of the resid component of the interstage oil. There is some increase evident in the PFC and PFL samples when the iron catalyst use is suspended. However, with the PFL and PFC samples the deactivation of the supported catalyst in the second stage obscures the effect of returning to treated coal in Condition 4.

The donor solvent quality as measured by microautoclave assay is shown in Figure 8 for the whole PFL and interstage samples representing Conditions 2, 3, and 4. There is a significant loss in donor solvent quality of the whole interstage oil during the operation with untreated coal (Condition 3). A small decrease in the PFL donor quality during Condition 3 may also be attributable to the use of untreated coal. The high aromaticity and low donor content (cyclic beta proton content, Table 8) of the interstage oil produced during Condition 3 account for its low donor solvent quality. The largest effects on aromaticity and cyclic beta were seen in the interstage resid fraction. The resid quality evidently significantly affects solvent quality.

The phenolic -OH content of the interstage sample is significantly lower in the sample obtained from Condition 3 than those measured in the samples from Conditions 2 and 4 (Table 8 and Figure 4). It is believed that the iron catalyst in use in Conditions 2 and 4 promotes fast cracking of the low rank coal and slow dehydroxylation to hydroaromatic structures; thus, the resultant higher phenolic -OH content. In the thermal case (Condition 3) cracking and dehydroxylation are competitive. The hydrogen depletion of the solvent, reflected in the poorer solvent quality and higher aromaticity, is also explained by this mechanism.[17]

NET PRODUCT OIL INSPECTION

In evaluation of the direct liquefaction process it is important to have a full understanding of the refining requirements of the raw liquid product. This information will eventually provide more accurate estimations of upgrading costs to specification fuels. Although it is acknowledged that the standard petroleum feedstock tests were not developed originally for the analysis of coal liquids, they are at least a starting point for these analyses. In this contract CONSOL examined three net product oils by standard refinery feed analyses and is in the process of evaluating a fourth sample. These analyses are comprised of over 30 individual tests. The first three samples were derived from Wilsonville Run 259 Period G, Wilsonville Run 260 Period D, and HRI CTSL Run CC-15. The fourth sample is from HRI Run CMSL-2. Analyses of the first two samples were provided by Conoco Petroleum Engineering. The third sample was evaluated by the

National Institute for Petroleum and Energy Research (NIPER). The sample obtained from HRI Run CC-15 will be discussed here.

Methodology

The methodology employed was to analyze the whole sample, which in the case of HRI Run CC-15 was a blend of the SOH and ASOH net products from Conditions 2, 3, and 4. The whole sample was fractionated into four distillation cuts; naphtha (IBP-380 °F), kerosene (380-510 °F), diesel (510-650 °F), and resid (650 °F$^+$). Each of the straight-run fractions was re-inspected using an appropriate suite of methods. The naphtha and kerosene fractions were then caustic washed for the removal of phenolic compounds. The washed fractions were then re-tested. The properties of the whole oil, the fractions and the caustic washed fractions are given in Tables 9 through 11.

Assessment of Analytical Data

The coal liquid product quality was assessed by comparison of the physical and chemical property test data for the distillation fractions (IBP-380 °F, 380-510 °F, and 510-638 °F) to the corresponding specifications for gasolines, aviation turbine fuels, diesel fuels or fuel oils, respectively.[14]

The IBP-380 °F (naphtha) fraction was compared to gasoline specifications. Simulated distillation results (Table 10) show that this material falls well outside gasoline specifications with a Reid vapor pressure (Table 9) below the maximum allowed for all classes of gasoline. The distillation boiling range requirements which require 10% off at a maximum temperature range of 122-158 °F for gasoline classes AA-E, and 50% off at 230 °F for class E and 250 °F for classes AA and A are not met (Table 10). The 90% off and end point specifications are met by this material. The IBP-380 °F fraction failed the copper strip corrosion test, existent gum test, and the oxidation stability test. The sulfur content did meet specifications. Hydrotreating would enhance this material and improve the octane rating. Caustic washing modestly improves the properties of this fraction (Table 11), lowering the acidity, and improving the oxidation stability, existent gum, and copper strip corrosion results. This procedure, therefore, makes this fraction more suitable for gasoline; however, its quality is still below specifications.

The 380-510 °F (kerosene) distillate fraction analyses are best compared to the specifications for aviation turbine fuels. This material met specifications for total sulfur content, acidity, copper strip corrosion, flash point, density, distillation final boiling point, residue and loss. It failed in aromatic content, mercaptan sulfur, 10 % off distillation temperature, freezing point, viscosity, net heat of combustion, smoke point, naphthalene content, and thermal stability. The high aromaticity of this distillate fraction, its most serious flaw, could be ameliorated by hydrocracking or hydrogenation. The caustic washing of this fraction significantly improves the mercaptan sulfur value. The high aromaticity of this material overshadows the modest improvements in other properties gained as a result of the caustic washing (Table 11).

The 510-680 °F distillation fraction was assessed using the specifications for diesel fuel oils and heating fuel oils. This fraction passed flash point, distillation, ash, sulfur, copper strip corrosion tests for all grades of diesel fuel, and cetane number for Grade No. 4-D diesel fuel oil. Viscosity was a little lower than the minimum requirement of 5.5 cSt at 104 °F. Cloud point was indeterminate due to the dark color of the sample. When the analytical data for this fraction were compared to that for heating or fuel oils it was found that this distillation cut met the specifications for flash point (except for No. 6 fuel oil). Its viscosity was within specifications for Grade No. 4 light oil. The material passed the specifications for all grades of fuel oil for ash, sulfur, and copper strip corrosion. The pour point of 35 °F is higher than allowable for Grades No. 2, 4 light, and 4 (specification value: 28 °F, maximum).

The >638 °F fraction (2.7% of the crude) of the coal-derived net product oil contained too high a concentration of nitrogen and metals to make it a good candidate for catalytic cracking. As a heavy heating oil, this fraction meets specifications for ash, sulfur, and copper strip corrosion.

EXPLORATORY METHODS

Two exploratory methods are being employed to examine the suite of twelve samples described above. These methods are field ionization mass spectrometry (FIMS) and solid state cross polarization/magic angle spinning (CP/MAS) ^{13}C-nuclear magnetic resonance (NMR) spectroscopy. Each of these methods was evaluated in projects under the Participants Program of this contract.[12,13] The FIMS work was done at SRI International and the ^{13}C-NMR project at the University of Utah. In each project the method showed a high potential for application to coal-derived materials.

FIMS was used to determine the molecular weight profile of complex coal-derived 850 °F^{+} distillation resid samples, and to identify in those samples some prominent components of the resid associated with decreased reactivity toward conversion and increased coking and catalyst deactivation behavior. The FIMS profiles were deconvoluted into two groups (high and low mass) with a simple data analysis method. Using this approach, quantified differences among samples could be related to the various process conditions of the run. The twelve samples obtained from HRI Run CC-15, described above, were examined by FIMS. Preliminary data from the FIMS analysis indicate that there are observable correlations between the molecular weight distributions and Run CC-15 process performance. Additionally, individual components, which are probable coke precursors, were identified in these samples. Although a bimodal (low/high) molecular weight profile could not readily be distinguished in these samples, shifting of the molecular weight distribution was apparent as a consequence of sampling location and/or of process performance. An analysis of the odd-mass and even-mass molecular weight profiles will allow for tracking of the nitrogen-containing heavy materials present in the process stream samples. Data analysis is continuing.

The solid state CP/MAS ^{13}C-NMR spectroscopy was demonstrated to provide a set of carbon structural parameters and molecular structural descriptors for coal liquefaction distillation resids. Comparison of these data for coal liquefaction distillation resids and that of feed coals from which the resids were derived can form the basis for a mechanistic model of coal liquefaction. The analysis by CP/MAS ^{13}C-NMR data of the twelve samples from HRI Run CC-15 discussed in this paper is continuing.

SUMMARY AND CONCLUSIONS

Base Method Analyses

Deactivation of the second-stage supported catalyst dominated most of the properties over the course of the run. Consequences of increased catalyst age were increases in aromaticity and phenolic -OH concentration and decreases in hydrogen donor content and paraffinic hydrogen content in most process streams, including product distillates. Donor solvent quality of the whole PFL increased through the early part of the run until Period 8 when it apparently stabilized. The effect of suspending the use of iron-impregnated coal in Condition 3 is most apparent in the interstage (first stage) samples. There is a decreased hydrogenation of the interstage sample (primarily in the resid portion of it) resulting in a higher aromaticity, lower phenolic -OH content in the solubles, and poorer solvent quality. These effects are all consistent with predicted properties of the iron catalyst in promoting fast cracking reactions and slow dehydration of the coal.[17] The presence of supported catalyst in the second stage largely mitigates this effect on the properties of the PFL, PFC and product distillate samples.

Net Product Inspection Tests

The properties of the net product oil and its distillate fractions, as determined by NIPER, show that the coal-derived material has some desirable qualities. The whole crude has a low sulfur content and boils below the maximum temperature allowed for the production of transportation fuels. The naphtha fraction (IBP-380 °F) is highly naphthenic and has a low benzene content. The naphtha fraction appears to be amenable to mild hydrotreating to produce a good gasoline blendstock. The kerosene (380-510 °F) fraction is much too cyclic for use as aviation fuel and it is recommended that this fraction be distributed into the two cuts on either end of it (diesel and gasoline feedstocks). The 510-680 °F fraction met most specifications as a heating fuel and diesel fuel. It appears that this material, after moderate hydroprocessing, could make a good diesel blendstock.

Exploratory Method Analyses

Both the FIMS and CP/MAS ^{13}C-NMR methods, currently being used to analyze the suite of twelve samples from HRI Run CC-15, are expected to provide chemical/molecular information to augment and extend the information provided by the base analyses. Preliminary information is encouraging.

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TABLE 1

ANALYSES OF BLACK THUNDER MINE COAL AND IRON-IMPREGNATED BLACK THUNDER MINE COAL HRI CTSL Run CC-15

	Untreated Coal (5828)		Iron-Treated Coal (L-780)	
HRI Sample No.	**HRI (a)**	**CONSOL (b)**	**HRI (a)**	**CONSOL (b)**
Moisture Content, wt %	8.41	5.59	8.81	11.20
Volatile Matter, wt % (MF)		43.21		43.51
Ash Content, wt % (MF)	6.95	7.15	7.15	6.58
Ash Content, SO_3-free, wt %	5.71	6.14	6.03	5.56
Ultimate Analysis, wt % (MAF, SO_3-free ash basis)				
Carbon	72.51	72.14	72.38	72.05
Hydrogen	4.08	4.88	4.31	4.92
Sulfur	0.51	0.51	0.49	0.47
Nitrogen	0.95	1.04	2.64	2.70
Oxygen (by difference)	21.95	21.43	20.18	19.86
Iron Content, wt % (MF)	0.20	0.33	0.57 -0.65	0.75
Elemental, wt % of Ash				
Na_2O		0.83		0.56
K_2O		0.44		0.24
CaO		19.86		20.77
MgO		3.96		4.23
Fe_2O_3		6.56		16.36
TiO_2		1.08		1.02
P_2O_5		0.89		0.79
SiO_2		36.17		27.22
Al_2O_3		15.26		11.46
SO_3		14.16		15.43
Unaccounted		0.79		1.92
Calorific Value, Btu/lb, dry basis		11528		11595

a Analyses reported in Reference 1
b Analyses performed by CONSOL R&D

TABLE 2

ANALYSES OF START-UP SOLVENT[1]
HRI CTSL Run CC-15

HRI No.	L-769
API Gravity	10.1
Elemental Analysis, wt %	
Carbon	88.95
Hydrogen	10.08
Sulfur	0.06
Nitrogen	0.34
ASTM D-1160 Distillation	
IBP	318°C
5, Vol %	339°C
10, Vol %	345°C
20, Vol %	358°C
30, Vol %	366°C
40, Vol %	376°C
50, Vol %	385°C
60, Vol %	398°C
70, Vol %	416°C
80, Vol %	449°C
90, Vol %	479°C
95, Vol %	517°C
96, Vol %	524°C

TABLE 3

OPERATING CONDITIONS[1,3]
HRI CTSL Run CC-15

Feed Coal: Black Thunder Mine (Wyodak and Anderson seams), Wyoming subbituminous

Conditions 1, 2, and 4: Treated with hydrated iron oxide

Condition 3: Untreated

Catalyst: Shell S-317 (NiMo on alumina), second stage only

Unit back pressure: 2500 psig

Oil/Solids Ratio: 1.4-1.7/1.0[a]

Start-up Oil: Filtered process oil from HRI PDU Run 260-03 (L-769)

		Temperatures, °F				
Condition	**Period**	**Pretreater**	**Stage 1**	**Stage 2**	**Coal Space Velocity[b]**	**Catalyst Age[c]**
1	1A-5C	523	799	775	42	144
2	6A-8C	567	801	776	41	228
3	9A-11C	567	801	774	43	316
4	12A-14C	566	801	774	43	403

(a) Additional solvent (PFL) equal to about 2.5% of recycle added through buffer pumps in pretreater and about 5.5% in stages 1 and 2

(b) Coal space velocity units: lb dry coal/hr/ft^3 on a settled catalyst volume basis

(c) Catalyst age units: lb MF Coal/lb Cat., Second Stage, given for last period of Condition

TABLE 4

PRODUCT YIELDS,[3] SELECTED PERIODS OF HRI CTSL Run CC-15

Condition	1	2	3	4
Run Period	5	8	11	14
Yields (est.), wt % of Dry Coal				
C_1 x C_3 gas	9.94	10.13	9.94	9.86
C_4 x C_7 gas	2.80	2.91	3.00	2.57
IBP x 390°F	16.26	16.36	15.61	14.69
390 x 500°F	13.67	13.30	12.22	11.12
500 x 650°F	17.55	1[illegible].59	14.98	15.70
650 x 850°F	10.04	7.99	6.66	10.08
850 x 975°F	1.81	2.07	1.66	2.43
Toluene Soluble 975°F$^+$	3.75	4.61	5.33	6.81
Toluene Insoluble 975°F$^+$	0.04	0.06	0.33	0.17
Unconverted Coal	6.50	6.87	9.40	6.85
Ash	6.03	6.03	5.71	6.03
Water	15.52	16.41	19.33	17.43
CO	0.74	0.67	0.80	0.74
CO_2	1.37	0.91	1.88	0.97
NH_3	2.71	2.62	0.73	2.49
H_2S	-0.02	-0.07	0.25	-0.10
Hydrogen Consumption, wt % MF coal	-8.72	-8.46	-7.82	-7.84

TABLE 5

PROCESS PERFORMANCE,[3] AND SELECTED PERIODS OF HRI CTSL Run CC-15

Condition	1	2	3	4
Run Period	5	8	11	14
Process Performance				
Coal Conversion, wt % MAF	93.1	92.7	90.0	92.7
975°F$^+$ Conversion, wt % MAF	89.1	87.7	84.0	85.3
C_4 x 975°F distillate yield, wt % MAF	66.1	64.1	57.4	60.2
Desulfurization, wt %	-3.1	-15.2	48.8	-19.8
Denitrogenation, wt %	90.0	87.1	66.6	82.6

TABLE 6

ELEMENTAL ANALYSES OF TWELVE SELECTED SAMPLES FROM HRI RUN CC-15

Condition	2				3				4			
Period	8ABC	8A	9A	8A	11ABC	11A	12A	11A	14ABC	14A	15A	14A
Sample	PFL	PFC	Inter-stage	SOH-ASOH	PFL	PFC	Inter-stage	SOH-ASOH	PFL	PFC	Inter-stage	SOH-ASOH
C, wt %, as det.	88.88	60.36	84.19	86.39	89.35	69.06	88.28	86.09	86.14	63.36	85.20	86.27
H, wt %, as det.	9.98	5.39	8.28	13.04	9.07	5.80	8.16	12.83	9.04	5.36	7.83	12.47
N, wt %, as det.	0.56	0.76	0.96	0.40	0.54	0.62	0.66	0.28	0.81	0.81	1.05	0.53
S, wt %, as det.	0.33	2.41	0.42	0.03	0.03	0.82	0.28	0.06	0.03	2.20	0.28	0.03
O, wt % by diff.	0.23	1.98	1.30	0.14	1.00	3.37		0.74	3.96	1.05	0.91	0.69
Ash, wt %, as	-----	20.14	4.93	-----	-----	20.33	3.72	-----	-----	27.20	4.71	-----

TABLE 7

ANALYTICAL PROCEDURES

BASE METHODS	EXPLORATORY METHODS
Solvent Quality	FIMS Analysis
Phenolic -OH by FTIR	^{13}C Solid-state and ^{1}H NMR Analysis
Solubility Fractionation	Inspection Tests on net product oils
Solution ^{1}H NMR	
Elemental Analyses	
Distillation	

TABLE 8

SUMMARY OF SAMPLE PROPERTIES: PROTON DISTRIBUTION, PHENOLIC -OH CONTENT, MICROAUTOCLAVE SOLVENT QUALITY COAL CONVERSION VALUES

Condition	2				3				4			
Period	8ABC	8A	9A	8A	11ABC	11A	12A	11A	14ABC	14A	15A	14A
Sample	PFL	PFC	Inter-stage	SOH-ASOH	PFL	PFC	Inter-stage	SOH-ASOH	PFL	PFC	Inter-stage	SOH-ASOH
Phenolic -OH, meq/g	0.21	0.28	0.61	0.17	0.23	0.31	0.49	0.20	0.30	0.43	0.62	0.25
Peak location, cm^{-1}	3308	3302	3301	3357	3305	3303	3298	3322	3306	3304	3301	3357
Cond. Aromatic, %	9.7	12.3	13.2	2.5	13.8	15.3	20.5	3.3	13.3	15.4	15.0	2.8
Uncond. Aromatic, %	5.1	3.7	6.4	4.2	4.7	4.6	5.8	4.6	6.2	5.0	8.0	4.4
Cyclic Alpha, %	12.0	13.8	12.8	7.4	15.8	14.8	11.2	8.4	13.9	14.5	13.9	7.5
Alkyl Alpha, %	7.5	7.8	8.6	6.6	8.6	8.6	7.7	7.4	8.4	8.6	8.9	7.0
Cyclic Beta, %	17.2	17.8	15.3	25.1	16.2	16.6	13.2	25.8	16.7	16.4	14.5	24.8
Alkyl Beta, %	31.9	29.0	28.5	31.3	27.2	26.8	26.8	31.4	27.6	25.4	25.6	30.8
Gamma, %	16.6	15.6	15.0	22.9	12.9	13.4	14.8	19.0	13.9	14.8	14.1	22.8
MAC[1], %	80.9	-----	74.4	-----	76.0	-----	62.2	-----	78.2	-----	75.7	-----
850 °F$^+$ Resid, wt %			36.8				37.1				41.2	
850 °F$^-$ Distillate, wt %			52.2				50.5				45.8	

[1] MAC = microautoclave solvent quality test, Modified equilibrium conditions (9 g solvent, 6 g coal, 750 °F, 30 min).

TABLE 9
INSPECTION TEST RESULTS FOR HRI CTSL RUN CC-16 COMPOSITE NET PRODUCT

Property	Sample				
	Total Dist.	<380 °F	380-510 °F	510-638 °F	>638 °F
Specific Gravity @ 60 °F (D4052)	0.8522	0.7798	0.8899	0.9223	0.9773
API Gravity	34.5	50.0	27.5	21.9	13.3
Elemental Analysis					
Carbon	86.77	85.93	87.12	87.63	87.93
Hydrogen	12.52	13.96	11.77	11.37	10.28
Sulfur	0.05	0.03	0.03	0.01	0.12
Nitrogen	0.25	0.09	0.33	0.22	0.81
Oxygen (by diff)	0.41	0.00	0.75	0.77	0.86
Basic Nitrogen (UOP269)	0.184	0.082	0.274	0.190	
Mercaptan Sulfur (D3227)		51.5	45.2		
Trace Metals,(D5185), Vanadium, ppm	12.2				
Nickel, ppm	15.0				
Iron, ppm	13.4				
Copper, ppm	14.6				
Ash (D482), wt %	0.004			<0.001	0.020
Viscosity (D445) cSt					
@70 °F	1.899			9.879	x
@100 °F	1.475			5.338	x
@-20 °C			10.80	x	
Refractive Index (D1218), 20 °C	1.46877	1.42882	1.49196	TOO DARK	TOO DARK
Freezing Point (D2386), °F	-24		-12		
Cloud Point (D2500), °F				TOO DARK	
Pour Point (D97), °F	<60			35	
Reid Vapor Pressure (D323), psi		2.54	<0.01		
Microcarbon Residue (D4530), wt %	0.06			0.00	1.95
Flash Point (D56, D93)[2], °C				x	x
Heptane Insolubles (D3279), wt %	0.39				
Group Analysis[3]					
Paraffins, vol %		38.0[1]	9.6	10.1	x
Naphthenes, vol %		45.7	43.1	34.5	x
Aromatics, vol %		8.7	41.4	52.1	x
Olefins, vol %		4.6	5.8	3.3	x
Benzene (PIANO, mod D6134)[3]		0.089			
Naphthalene (D1840), vol %			4.23		
Bromine Number (D1159)		3.62	5.08	2.70	
Aniline Point (D611), °F		103.8	71.5	88.3	
Smoke Point (D1322), mm			10.9		
Acidity (D3242), mg KOH/g	0.07	0.05	0.04	0.22	x
Copper Corrosion (D130)		3b(DARK)	1a(SLIGHT)	1a (SLIGHT)	1a(SLIGHT)
Existent Gum (D381), mg/100mL		11.2[2]	BP TOO HIGH[3]		
Oxidation Stability (D525), min		105			
Oxidation Stability (D2274), mg/100mL				0.9	
Thermal Stability (JFTOT)(D3341)			FAIL		
Distillation (ASTM D2892), wt %		40.2	33.4	22.5	2.7
Octane Number Motor Method (D2700)		60.7			
Octane Number Research Method (D2699)		61.6			
Cetane Index (D976)				34.2	

TABLE 10 (a)

ASTM D 86 AND SIMULATED DISTILLATION RESULTS, TEMPERATURE READINGS CORRECTED TO 101.3 kPA (750 mm Hg) PRESSURE

Sample	Total Distillate (b)		IBP-380 °F (c)		380-510 °F (c)		510-638 °F (d)	
Barometric Pressure (mm Hg)	779		777		773		766	
	°F	°C	°F	°C	°F	°C	°F	°C
Initial Boiling Point	97	36	135.5	57.5	408.2	209.0	474	246
5% recovered	172	78	177.8	81.0	425.6	218.7	507	264
10% recovered	200	93	190.7	88.2	428.1	220.1	518	270
20% recovered	268	131	205.8	96.6	433.0	222.8	532	278
30% recovered	333	167	220.4	104.7	437.7	225.4	541	283
40% recovered	388	198	235.7	113.2	442.7	228.2	549	287
50% recovered	430	221	253.4	123.0	448.1	231.2	561	294
60% recovered	469	243	275.3	135.2	454.4	234.7	573	301
70% recovered	507	264	297.8	147.7	461.6	238.7	586	308
80% recovered	539	282	317.4	158.6	470.4	243.6	603	317
90% recovered	589	309	336.0	168.9	478.9	248.3	624	329
95% recovered	633	334	344.8	173.8	486.8	252.7	637	336
End Point	803	428	359.2	181.8	507.9	264.4	666	352
Recovery, %	100.0		100.0		99.5		----	
Residue, %	0.0		0.0		0.0		----	
Loss, %	0.0		0.0		0.4		----	

(a) Taken from Reference 14.

(b) Simulated distillation results by ASTM D 5307 since the D 86 distillation was terminated at 32 mL due to smoking.

(c) D 86 distillation results

(d) Simulated distillation results by ASTM D 2887 since the D 86 distillation was terminated at IBP (533 °F) due to smoking.

TABLE 11

INSPECTION TEST RESULTS FOR HRI CTSL RUN CC-16 CAUSTIC WASHED FRACTIONS

Property	Washed Samples	
	<380 °F	380-510 °F
Caustic Wash Recovery , wt %	92.86	92.06
Phenol Recovery from Caustic Washed Sample, wt %	2.38	4.01
Specific Gravity @ 60 °F (D4052)	0.7775	0.8882
API Gravity	50.5	27.8
Elemental Analysis		
Carbon	86.12	87.75
Hydrogen	13.77	11.68
Sulfur	0.03	<0.01
Nitrogen	0.07	0.33
Oxygen (by diff)	0.01	0.23
Basic Nitrogen (UOP269)	0.058	0.264
Mercaptan Sulfur (D3227)	9.7	<0.1
Viscosity (D445) cSt		
@-20 °C		9.665
Refractive Index (D1218), 20 °C	1.42836	1.49072
Freezing Point (D2386), °F		-13
Reid Vapor Pressure (D323), psi	2.09	<0.01
Flash Point (D56, D93)[2], °C		82
Group Analysis[3]		
Paraffins, vol %	34.7[1]	9.1
Naphthenes, vol %	48.8	46.0
Aromatics, vol %	9.2	41.9
Olefins, vol %	4.2	3.0
Benzene (PIANO, mod D6134)[3]	0.078	
Naphthalene (D1840), vol %		3.74
Bromine Number (D1159)	2.37	2.69
Aniline Point (D611), °F	106.0	75.2
Smoke Point (D1322), mm		11.6
Acidity (D3242), mg KOH/g	<0.01	0.01
Copper Corrosion (D130)	2d(MODERATE)	1a(SLIGHT)
Existent Gum (D381), mg/100 mL	9.0[2]	BP TOO HIGH[3]
Oxidation Stability (D525), min	1440	
Thermal Stability (JFTOT)(D3341)		FAIL
Octane Number Motor Method (D2700)	58.1	
Octane Number Research Method (D2699)	60.2	

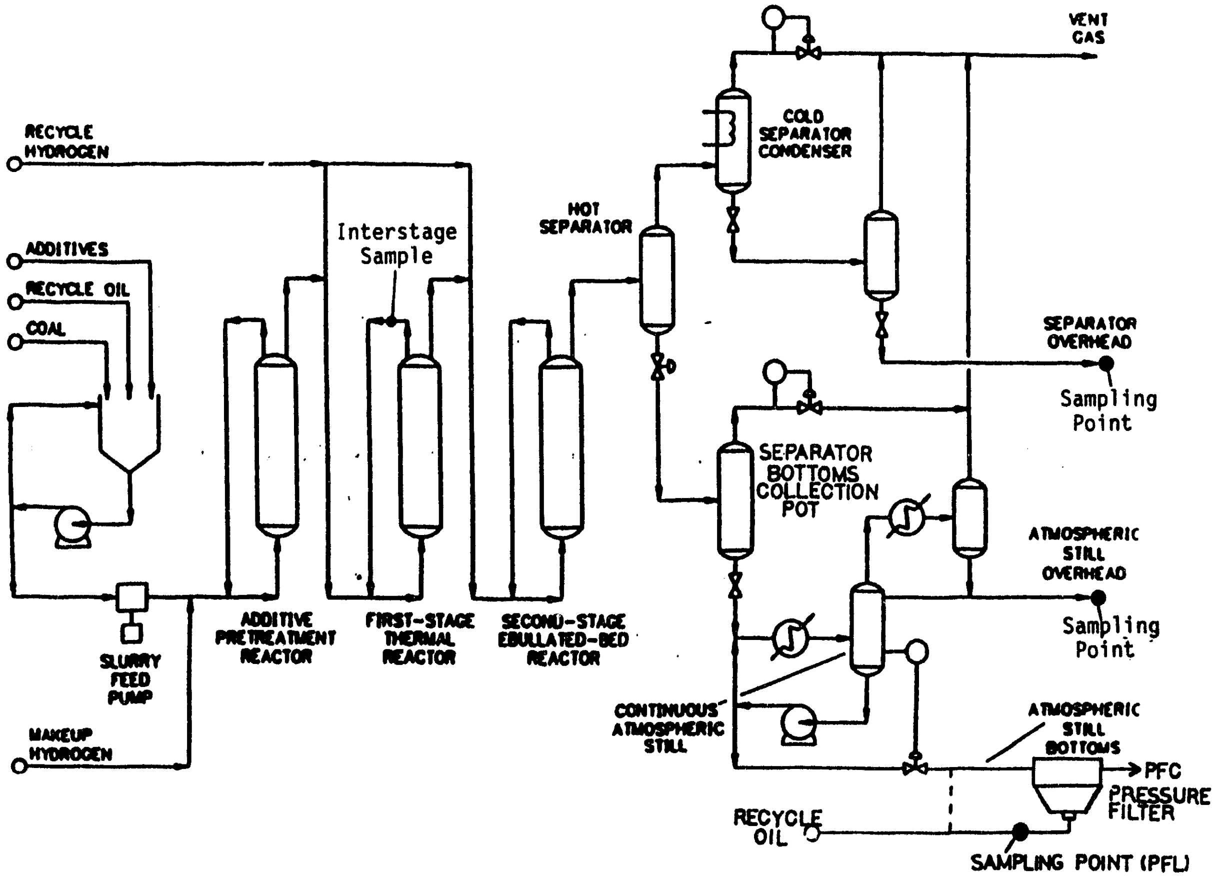
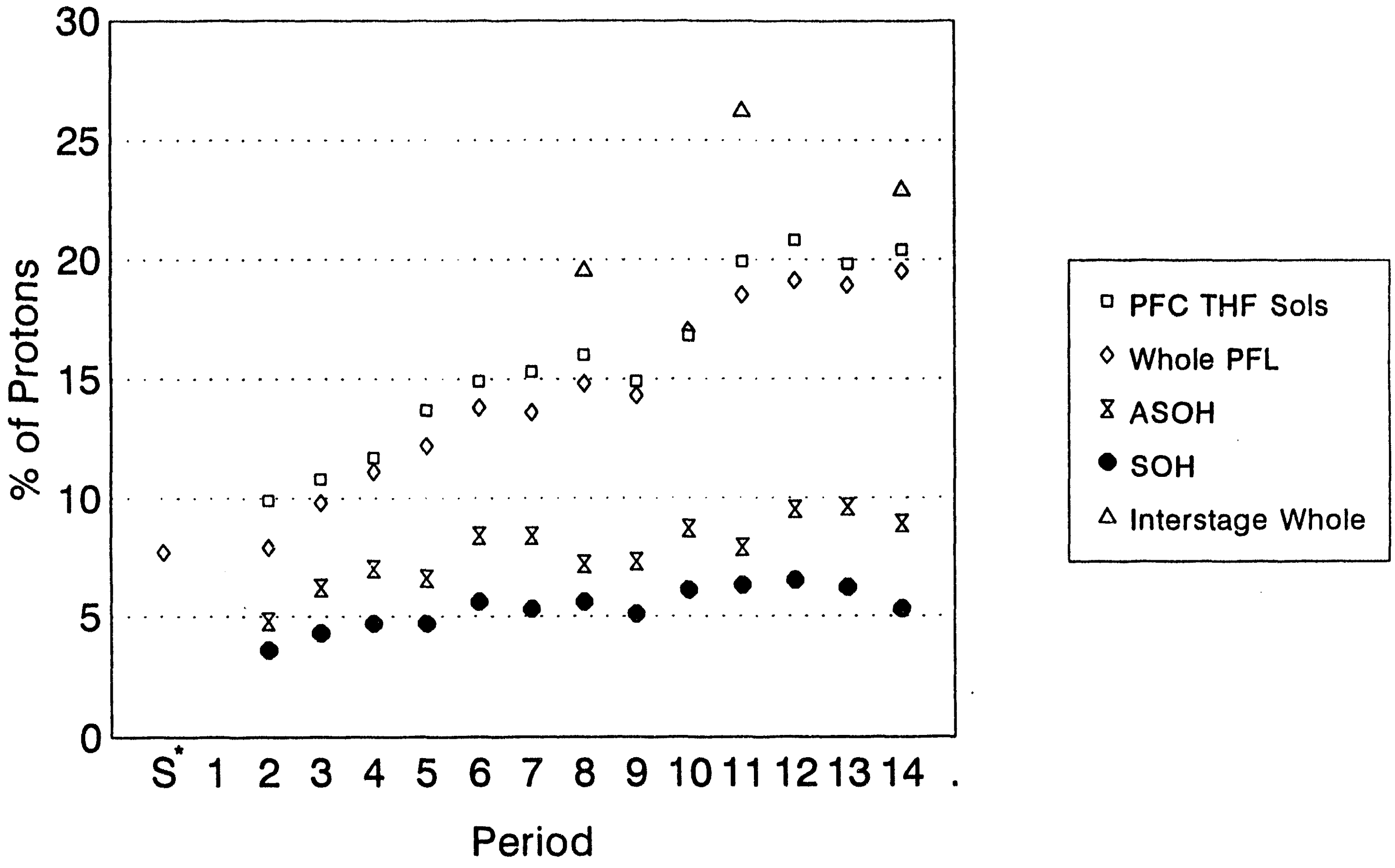
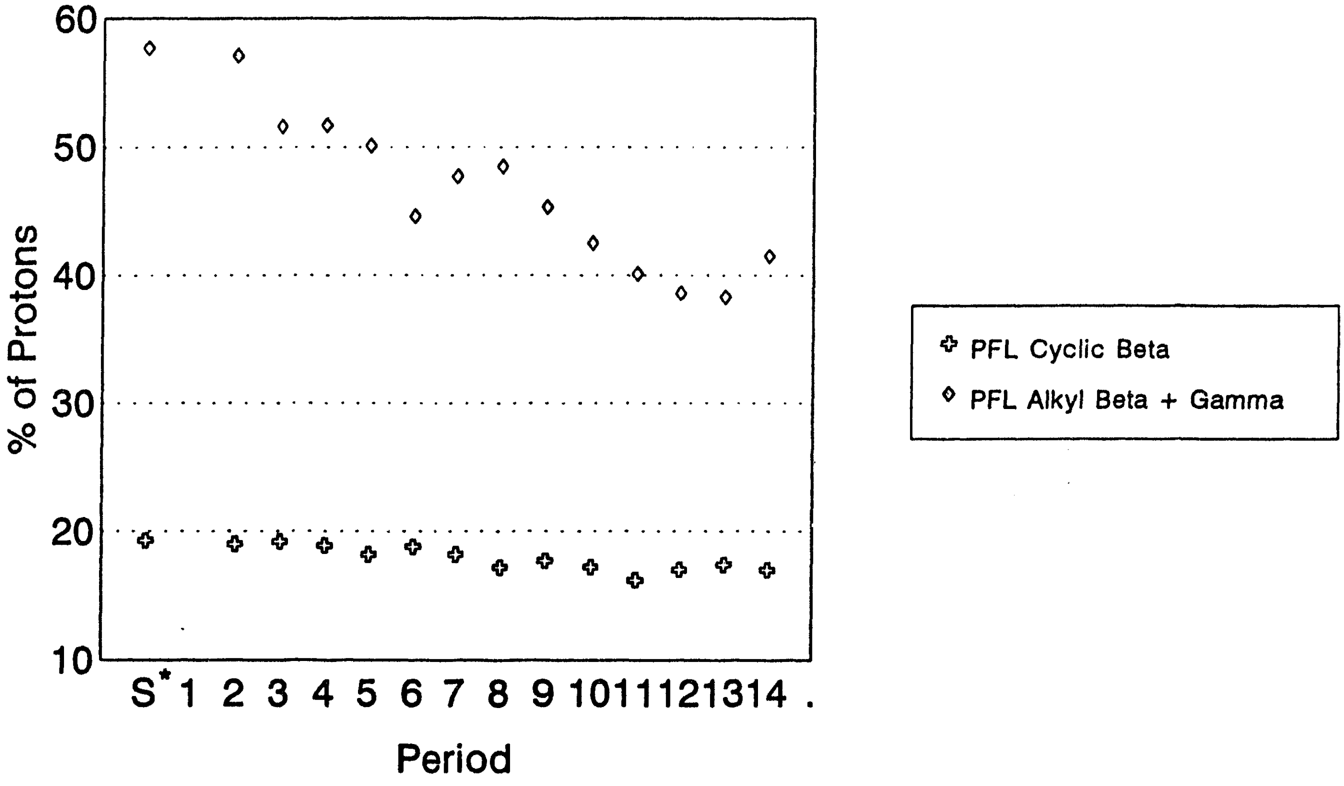


Figure 1. HRI Two-Stage Ebullated Bed Bench-Scale Unit 227 Configured for Run CC-15.



* S=Start-up

Figure 2. Proton Aromaticity.



* S=Start-up

Figure 3. Hydroaromatic and Paraffinic Proton Content.

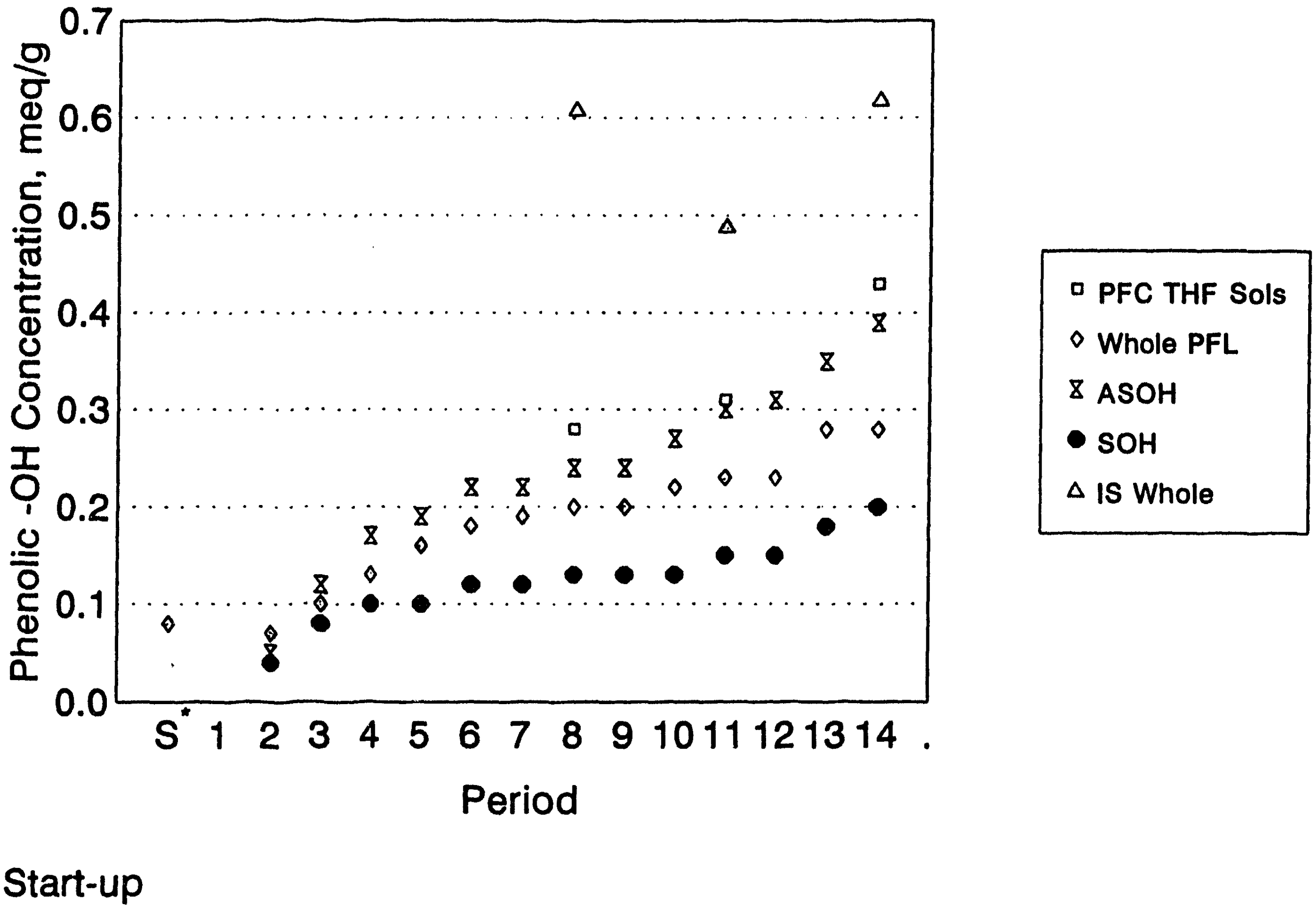


Figure 4. Phenolic -OH Concentration.

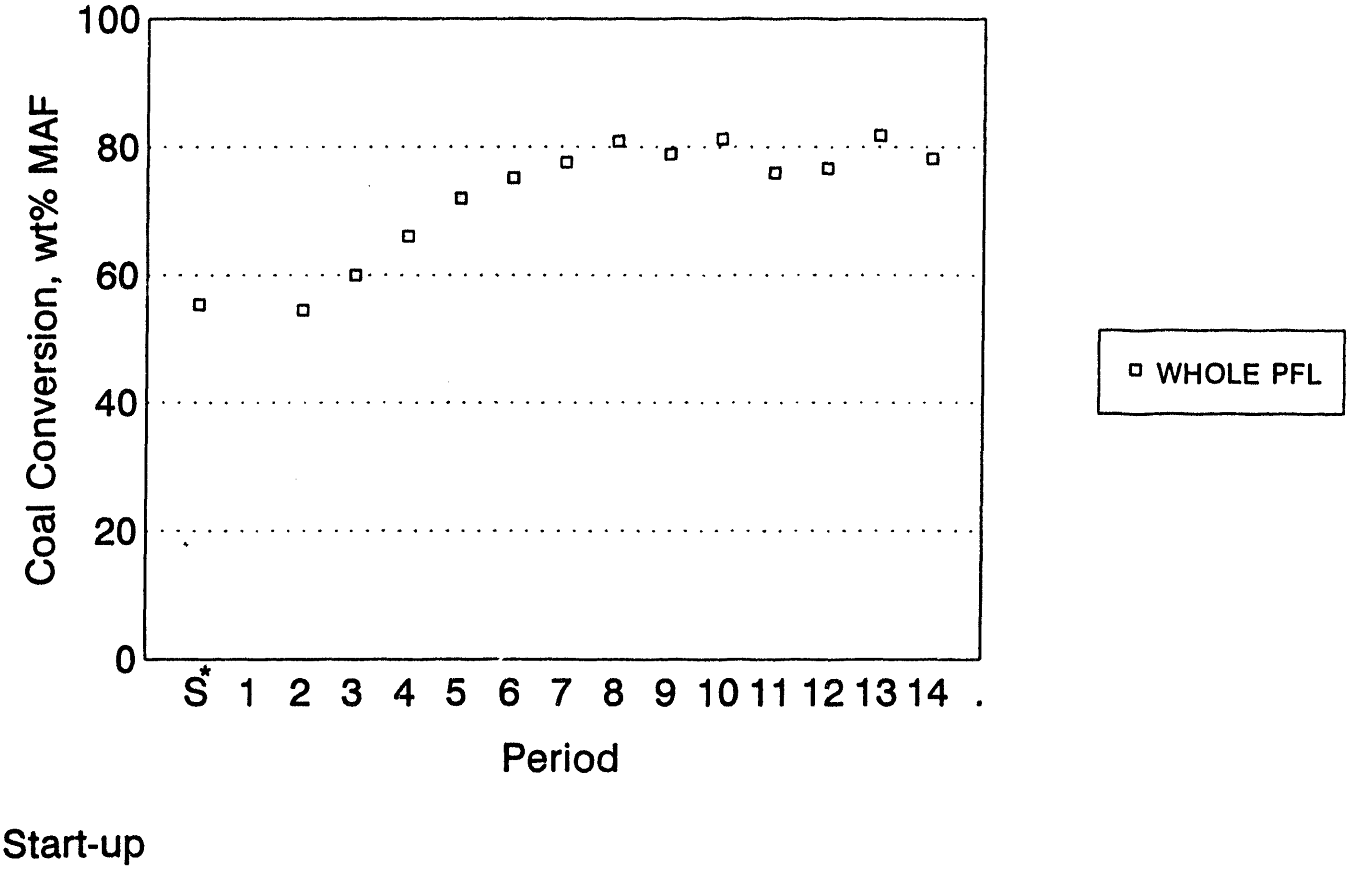


Figure 5. Donor Solvent Quality - PFL Samples.

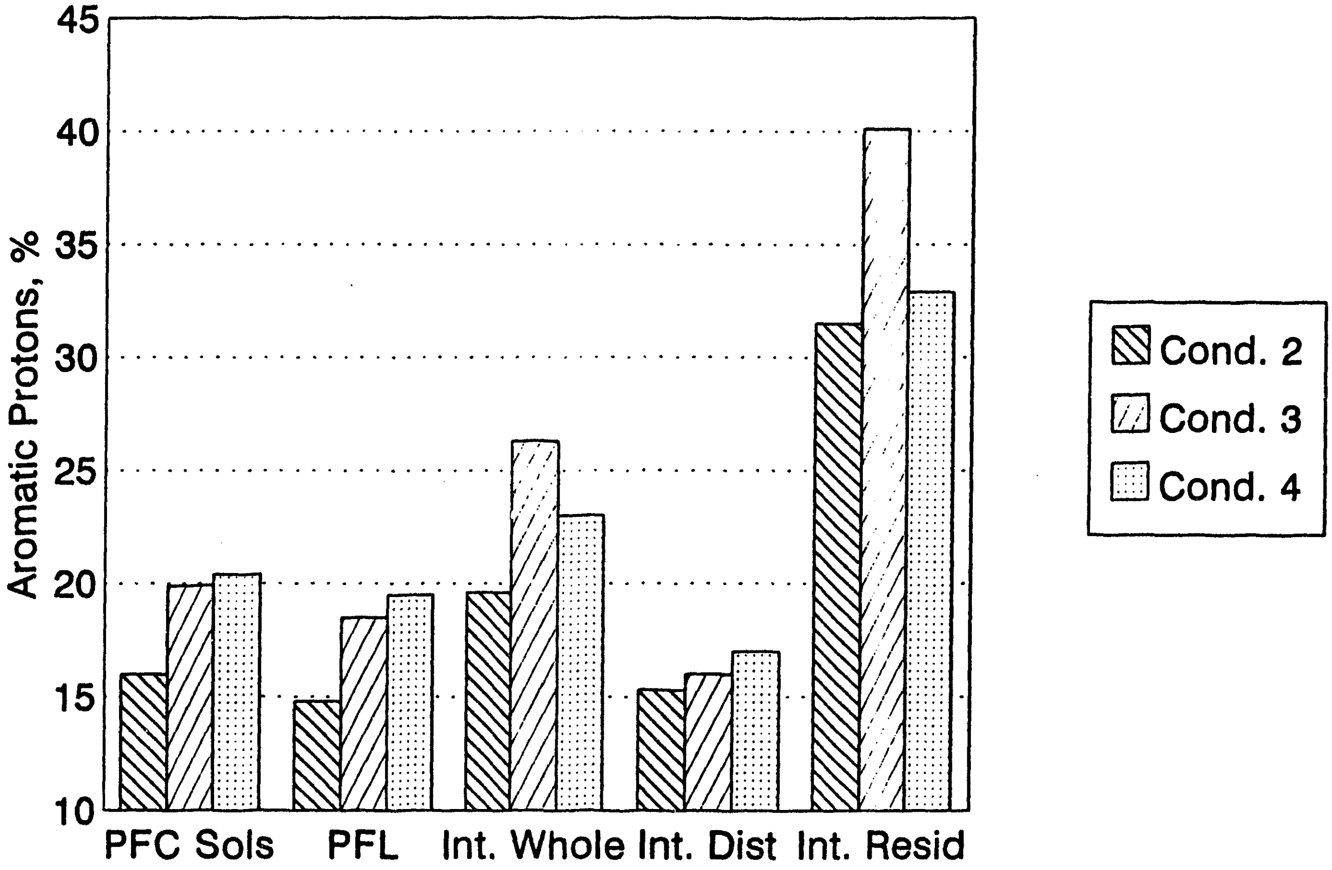


Figure 6. Proton Aromaticity.

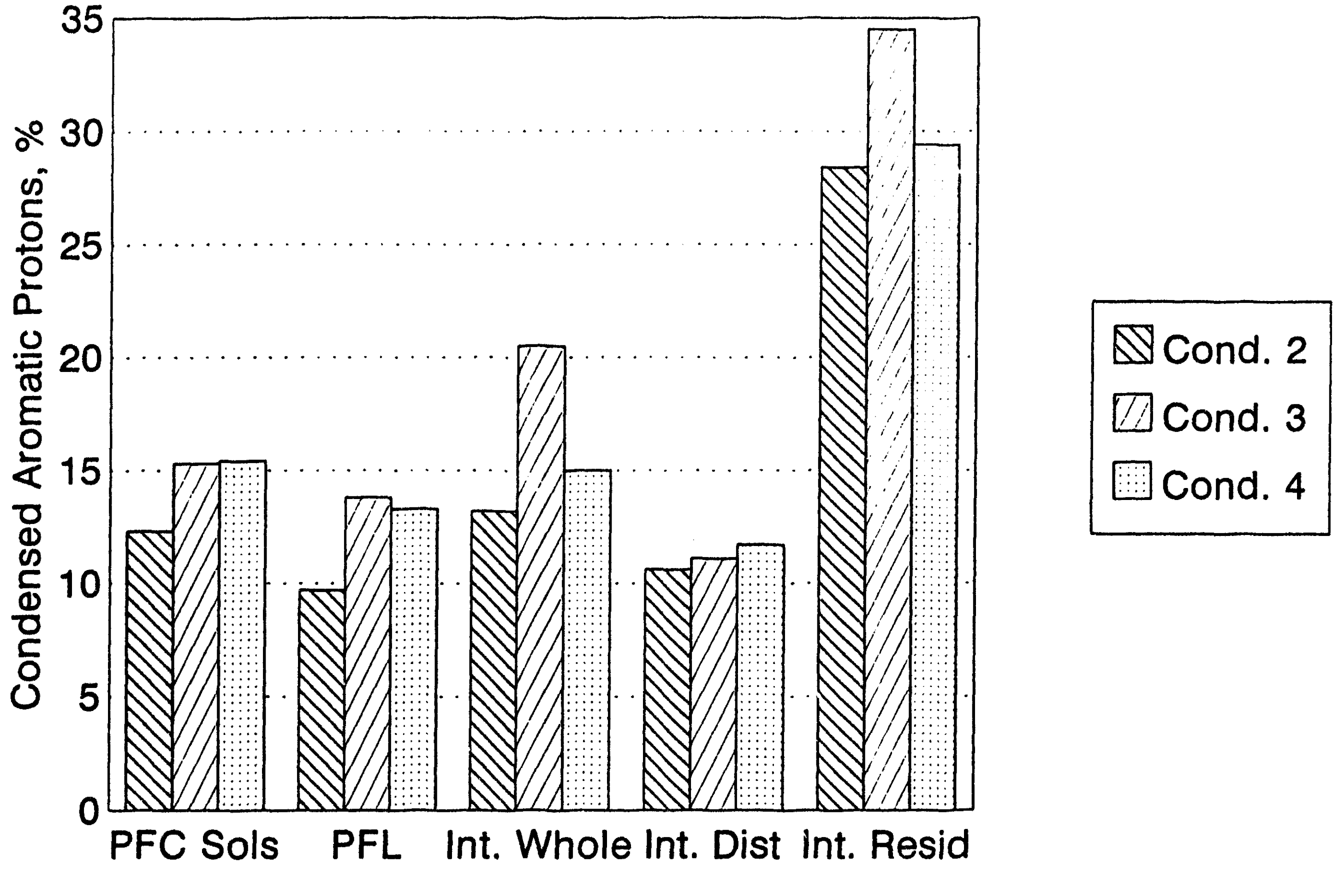


Figure 7. Condensed Aromatic Protons.

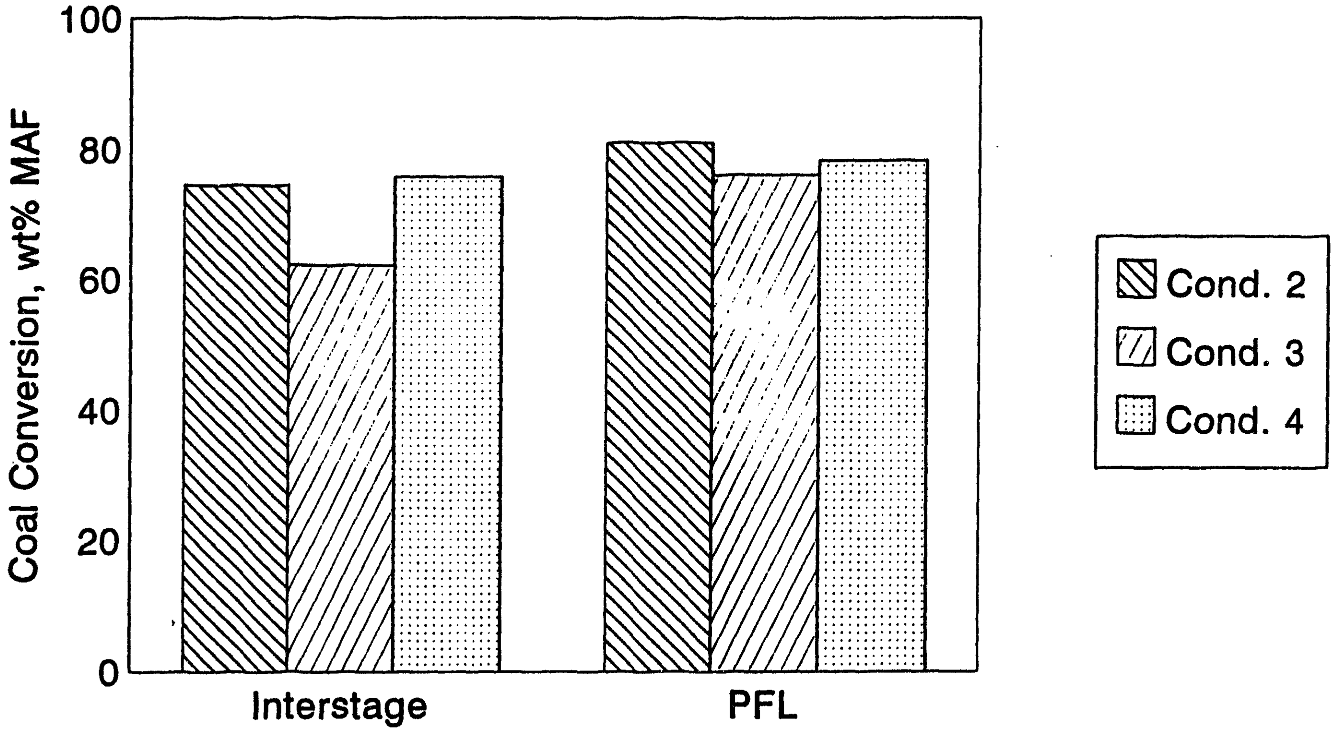


Figure 8. Solvent Quality Microautoclave Tests (9 g solvent, 6 g Old Ben Mine Coal, 30 min, 750 °F).

The Effect of Dispersed Catalysts on First Stage Coal Liquefaction

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ABSTRACT

The use of unsupported iron catalysts for first-stage coal liquefaction has been the focus of recent studies at the Pittsburgh Energy Technology Center (PETC). A highly dispersed pyrrhotite catalyst produced from coal impregnated with FeOOH has been developed. This highly dispersed catalyst has been shown to be effective for first-stage coal liquefaction in studies at PETC and elsewhere.[1-6] It has been reported that the preparation and activation sequence of the FeOOH both play an important role in developing a highly active form of pyrrhotite.[1,2] The focus of the effort in the past year has been to employ the catalyst for use with subbituminous coals, to determine the effect of varying the time component of the activation sequence, and to conduct studies to develop a more fundamental understanding of the activity of the catalyst.

The impregnation procedure using FeOOH was successfully used with a subbituminous coal. In continuous-unit tests, the optimum activation temperature for an Fe-impregnated subbituminous coal was found to be higher than the optimum activation temperature for an Fe-impregnated bituminous coal (275°C). Reducing the slurry residence time in the activation reactor by one half (from 20 minutes to 10 minutes) did not lower the observed activity of the catalyst. In fact, conversions and distillate yields appeared to be slightly higher at the shorter residence time in the activation reactor. In microautoclave tests, the overall coal conversions were similar with a highly active iron catalyst derived from impregnated FeOOH as with ammonium heptamolybdate; however, molybdenum catalysts have a higher hydrogenation activity than iron. Also, to be compatible with the use of powdered catalysts under development at PETC and elsewhere, a procedure was developed to deliver a consistent concentration of particulate catalyst with the coal-oil slurry in the continuous unit.

To improve the efficiency of a process utilizing FeOOH precipitated on coal, a series of tests was made to determine the minimum amount of coal that needs to be impregnated with FeOOH. This minimum occurs between 10 wt% and 20 wt% of total coal. The effect of processing variables such as catalyst concentration, pressure, and solvent to coal ratio were also investigated.

INTRODUCTION

Recent PETC research has emphasized development of a disposable catalyst option based

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on the use of highly dispersed FeOOH impregnated on coal. It was shown that significant liquefaction activity results at moderate iron concentrations by careful control of the impregnation step and optimization of preliquefaction stage conditions. High first-stage conversions of bituminous coal (Illinois No. 6) were obtained employing Fe concentrations of only 2500 ppm based on coal.[1-3] It was shown that this approach could be applied to the liquefaction of Black Thunder subbituminous coal with appropriate modifications of the coal impregnation procedure and activation conditions.[4,5] As reported,[4,5] 5000 ppm Fe impregnated onto Black Thunder coal resulted in coal conversions approaching those observed with 1500 ppm Mo (as ammonium heptamolybdate). Some differences were observed in the application of the iron impregnation procedure between the two coals.[5,7,8] Some of these differences include optimal water to coal ratio, optimal ammonium hydroxide requirement for precipitation, preferred activation conditions, and the minimum Fe concentration needed. The iron impregnation procedure has been scaled up and the impregnated coal was tested at HRI.[6,9] Successful bench-scale tests were conducted by HRI in the 50 lb/day 2-stage liquefaction unit that demonstrated the effectiveness of using highly dispersed, fine-particle catalyst systems including iron and molybdenum.

The immediate objective of this project is to assess the potential of recent PETC dispersed catalyst technology developments for incorporation into advanced liquefaction configurations. Areas of investigation include (1) continued optimization of conditions (i.e., activation time and temperature and fraction of coal impregnated with catalyst precursor) for use of dispersed catalysts for liquefaction of bituminous and subbituminous coals, (2) alternate dispersed catalyst options, (3) continuous testing of emerging catalyst technologies under development at PETC and elsewhere and (4) implications of process conditions on the use of dispersed catalysts (i.e., catalyst concentration, reactor pressure, solvent quality, and solvent to coal ratio). The ultimate goal is to facilitate the integration of dispersed catalyst technology into more economical process schemes.

EXPERIMENTAL

Experiments were conducted with -200 mesh Illinois No. 6 (Burning Star No. 2) coal and Black Thunder mine coal (Wyodak Anderson seam, Campbell County, Wyoming). The coal was slurried with second-stage vacuum-tower overhead (V-1074) from Run 262 of the Wilsonville Advanced Coal Liquefaction Test Facility. This heavy distillate was generated while operating in a close-coupled integrated two-stage liquefaction mode.[10] Properties of the coals are summarized in Table 1. Properties of the solvent are summarized in Table 2.

The molybdenum catalyst precursor used was ammonium heptamolybdate (AHM) obtained from Fisher Scientific Co. Typically, the AHM was added as a 12 wt% aqueous solution to the feed slurry. A high-surface-area MoS_2 catalyst was prepared in a 1-L semi-batch autoclave charged with AHM and tetralin and heated to 425°C for 30 minutes under a constant flow of $97\%H_2/3\%H_2S$ at 2500 psig.[11-13] The resultant MoS_2 was recovered by tetrahydrofuran (THF) washing of the product on a 0.45-micron filter. The product contained 51 wt% MoS_2 (identified by elemental analysis and XRD); the remaining 49 wt% was carbon. The BET surface area of the total material was 261 m^2/g.[13]

Hydrated iron oxide (FeOOH) was dispersed onto the feed coal by an incipient wetness procedure.[1] Approximately 40 g of 2.5 wt% $Fe(NO_3)_3$ in distilled/deionized water was used to wet each 50 g batch of coal. The resultant paste was rapidly added to an ammonium hydroxide solution containing 2.6% NH_3. A high-surface-area, powdered FeOOH was precipitated on the coal. The resultant aqueous coal suspension was pressure filtered with a 0.45 micron filter. The iron-impregnated coal was vacuum dried at 40°C for 16 hours. Iron-impregnated coal samples were analyzed for ash and moisture to account for the added Fe and changes in moisture content as a result of the preparation.

Catalyst precursors were screened by microautoclave tests in a 40-mL tubular microautoclave.[3] Initial comparisons of the activity of catalyst precursors were made based on solubility analysis of the products. Experiments were conducted by adding 3.3 g of coal to the reactor with 6.6 g of PANASOL, a mixture of alkylated naphthalenes obtained from Crowley Chemical Co. Elemental sulfur was added to the reactor in many cases to sulfide the catalyst precursors.

Semi-batch (batch slurry, flow-through gas) tests were performed in a 1-L stirred-tank reactor to obtain more definitive product yield and conversion information and sufficient product for additional characterization. The feed charge consisted of 400 g of slurry that typically consisted of a 2:1 ratio of V-1074 solvent to coal.[3] Catalysts, if any, were activated *in situ* during heatup under a flow rate of 4 SCFH of $97\%H_2/3\%H_2S$ at 2,500 psig.

Continuous mode catalytic coal liquefaction experiments were conducted in a computer-controlled 1-L bench-scale unit.[3] Provision is included for injection of an aqueous catalyst stream into the feed slurry immediately prior to the reactor. The unit is a once-through system without recycle. A typical feed charge consisted of a coal/solvent mixture with a coal concentration of 30 wt% at an overall slurry feed rate of 200-480 g/h. The system was run at each condition for at least 30 hours prior to the collection of samples. The products were characterized in terms of gas yield and composition, solubility in heptane and THF, and 850°F distillation.

RESULTS AND DISCUSSION

Activation Studies

It had been reported previously that the iron catalyst precursor (FeOOH dispersed onto coal) requires a preliquefaction stage at temperatures between 275°C and 300°C for use in continuous systems[2,3]. It is likely that any small-particle, highly dispersed iron catalyst precursor may require an activation stage to develop maximum activity. Earlier results had indicated that the primary function of this stage is catalyst activation and not coal conversion.[3]

The residence time used in the activation stage of earlier continuous 1-L tests at PETC was 20 minutes. This time was determined by the maximum flowrate and preactivation reactor volume. Since this step could have a significant impact on the economics of a larger scale operation, studies were conducted to determine whether shorter activation times would be sufficient. This seemed possible because microautoclave studies had indicated that highly dispersed FeOOH adsorbed on a carbonaceous surface can be converted to a finely divided form of pyrrhotite at temperatures between 275 and 300°C within 5 minutes. A series of tests was conducted with FeOOH-impregnated Black Thunder coal to determine the effect of reducing the residence time to 10 minutes by reducing the preactivation volume by one half. The results of these tests, as well as earlier tests with a 20-minute activation-reactor residence time, are summarized in Figure 1. There appears to be no effect of reducing the activation reactor residence time to 10 minutes. The residence time can probably be reduced even further; a typical preheater in a larger-scale continuous unit may be sufficient to activate the catalyst. Future tests will be conducted to investigate the extent to which the activation reactor residence time can be further reduced.

Tests were made to determine if the optimum activation temperature was affected by reducing the residence time. The results indicate that, for Black Thunder, the optimum activation temperature is still within the 275°C to 300°C temperature range.

Spiking (Fraction of Coal Impregnated) Studies

One of the least attractive features of the current FeOOH-impregnation approach is the need to treat the total feed coal. One way of improving the potential economics of this approach is to impregnate the iron catalyst precursor on a fraction of the coal feed. This fraction could then be added to the remainder of the coal (spiked) in the reaction sequence.

Tests were conducted to investigate the effect of impregnating the FeOOH precursor on fractions of Illinois No. 6 coal. These tests were conducted at constant overall iron concentrations of 5000 ppm Fe based on total maf feed coal, that is, the smaller the fraction of impregnated coal used, the higher the concentration of Fe on these fractions. The results, summarized in Figure 2, indicate that there appears to be a minimum quantity of impregnated coal, between 10 wt% and 20 wt%, necessary to achieve optimum catalytic effect (0 wt% impregnated refers to a case in which 5000 ppm powdered FeOOH was physically mixed with the coal). For Illinois No. 6 coal, this limit was shown to correlate with the fraction of accessible polar groups on the outside surface of the coal.[11] Figure 3 presents the effect of impregnating fractions of Black Thunder coal with FeOOH. The results are similar to the Illinois No. 6 results. However, the minimum amount of impregnated coal that can be used to give optimum catalytic effect seems to be slightly higher than for Illinois No. 6. One of the problems in preparing coals for spiking may be that the FeOOH is not effectively dispersed onto the coal surface. To maintain a constant overall concentration of Fe, higher concentrations of Fe are needed for the smaller fractions of coal loaded (e.g., the required Fe loading is 5 wt% if only 10 wt% of the coal is to be impregnated to maintain an Fe concentration of 5000 ppm based on total coal). At these higher concentrations, the FeOOH may not effectively interact with the coal surface. Further studies are planned to determine if the coal surface can be modified so that more polar groups are available on the surface to allow higher concentrations of Fe to be used.

Alternate Catalyst Precursors

Recent large-scale integrated tests have indicated the potential of using dispersed molybdenum catalysts in the first stage of a two-stage coal liquefaction operation.[9] An important practical consideration for the economic use of dispersed molybdenum catalysts is to minimize the amount of molybdenum required. Typically, Mo has been shown to be effective in concentration ranges from 100 ppm to several thousand ppm Mo. A series of semi-batch and continuous liquefaction tests were made to investigate the effect of reducing the concentration of Mo from 1000 to 100 ppm, based on coal. The Mo was added as an aqueous solution of ammonium heptamolybdate. The results, summarized in Figures 4 and 4a, indicate that relatively small losses in coal conversions were observed with reduction of the concentration to 100 ppm. Concentrations lower than 100 ppm Mo will be studied to fully define the concentration effect.

A practical and economical method of adding a dispersed catalyst is to use a pre-activated powder. This would eliminate the use of aqueous media and an activation stage. To test this approach, a highly dispersed form of MoS_2 that is capable of being added to the feed slurry as a dry powder without the requirement of an *in situ* activation step was prepared from AHM in tetralin. The procedure used to produce this material was described above. A similar approach has been described elsewhere.[14] The recovered MoS_2 (identified by XRD) was very well dispersed with a high surface area, 261 m^2/g. Approximately 49% of the recovered material was carbonaceous. The carbon was identified by X-ray photoelectron spectroscopy as being micro-graphitic in structure.

Microautoclave studies with DECS-6 Blind Canyon coal indicated that this form of MoS_2 added as a powder was as active as an impregnated form of AHM. No significant differences in coal conversions to heptane soluble (48.0% and 47.5% for the impregnated AHM and powdered MoS_2, respectively) or THF soluble (91.0% and 90.4%) products were observed. To date, attempts to extend this procedure to the iron system have not yielded a form of iron with a dispersion approaching that of the MoS_2.

An important consideration for using powdered forms of catalyst precursors is the delivery of a consistent concentration of catalyst to the feed slurry. For batch operations, the problem may be trivial and essentially requires that proper weights of catalytic materials are added to the reactor and properly mixed. However, in continuous units, the problem is not as straightforward. The powder typically consists of a very finely divided material that is not soluble in any component of the feed slurry. In earlier tests on the continuous unit system at PETC, simply adding the powdered material directly to the feed tank resulted in large variations of catalyst concentration in the feed slurry (up to 100%). This indicated incomplete mixing in the feed tank. To overcome this problem, a procedure was developed in which the powdered precursor was premixed with a fraction of the solvent and this premixed material was then added to the feed tank. The result was that the concentration of catalyst delivered to the reactor had a standard deviation of less than 5% for 20 samples taken over a 5-hour period. This procedure will provide greater confidence in continuous unit testing of powdered forms of catalyst precursors being developed at PETC and elsewhere.

Effect of Processing Conditions

An important variable in the projected economics of coal liquefaction processing schemes is the reaction pressure. Tests were undertaken to investigate the effect of reducing the total reactor pressure. The approach undertaken in this effort is to determine if an appropriate combination of solvent quality with dispersed catalysts could lead to significant reductions in the required pressure in the initial stages of coal liquefaction.

An initial series of tests to investigate the effect of pressure was conducted in the microautoclave reactors with PANASOL as the vehicle. The effect of reducing the cold charge pressure from 1000 psig to 100 psig (using a high surface area MoS_2 catalyst that does not require activation) is shown in Figure 5. The major loss in conversion occurs below a cold charge pressure of 750 psig. Not surprisingly, if a 50:50 mixture of tetralin and PANASOL was used, no effect of pressure was observed.

The effect of pressure is currently being tested in the 1-L semi-batch reactor. The effect of reducing the pressure (at temperature) from 2500 psig to 1000 psig is being studied using V-1074 as the solvent and AHM as the catalyst precursor. The results of these tests are summarized in Figure 6. The conversion of $850^{\circ}F^{+}$ material decreases as pressure is reduced. However, the catalyst precursors used in the 1-L tests required activation, whereas the catalyst used in the microautoclave tests did not require activation. Further tests are planned to investigate the effect of pressure in the 1-L unit both with respect to catalyst activity (with a preactivated catalyst) and with respect to catalyst activation.

Solvent to Coal Ratio Studies

An important effort underway in the coal liquefaction program is to improve the process throughput by reducing the solvent to coal ratio. Reduction of solvent to coal ratio can have significant impacts on coal liquefaction behavior. One effect is the operational difficulty associated with utilizing feed streams that are higher in solids content. There is also the possibility that reduction in solvent to coal ratio would affect the overall coal conversions. HRI has shown that a bench-scale continuous coal liquefaction system can be operated at solvent to coal ratios approaching 0.8 to 1. The effect on coal conversions was previously tested at PETC and the earlier results had shown that with molybdenum catalysts the solvent to coal ratio could be reduced significantly and overall coal conversions could still be maintained.

The effect of solvent to coal ratio on the liquefaction of Black Thunder subbituminous coal was reinvestigated in semi-batch tests with impregnated-FeOOH and AHM catalyst precursors as well as no added catalyst. The results from these tests are summarized in Table 3 and indicate that the coal conversions are not affected by reduction of solvent to coal ratio from 2:1 to 1:1.

CONCLUSIONS

The impregnation procedure using FeOOH was successfully used with a subbituminous coal. In continuous unit tests, the optimum activation temperature for Fe-impregnated subbituminous coal was found to be higher than the optimum activation temperature for an Fe-impregnated bituminous coal (275°C). Reducing the slurry residence time in the activation reactor by one half (from 20 minutes to 10 minutes) did not lower the observed activity of the catalyst. In fact, conversions and distillate yields appeared to be slightly higher at the shorter residence time in the activation reactor. In microautoclave tests, the overall coal conversions were similar with a highly active iron catalyst derived from impregnated FeOOH as with ammonium heptamolybdate; however, molybdenum catalysts have a higher hydrogenation activity than iron. Also, to be compatible with the use of powdered catalysts under development at PETC and elsewhere, a procedure was developed to deliver a consistent concentration of particulate catalyst with the coal-oil slurry in the continuous unit.

To improve the efficiency of a process utilizing FeOOH precipitated on coal, a series of tests was made to determine the minimum amount of coal that needs to be impregnated with FeOOH. This minimum occurs between 10 wt% and 20 wt% of total coal.

The effect of processing variables such as catalyst concentration, pressure, and solvent to coal ratio were also investigated. Molybdenum catalysts were shown to be effective at concentrations as low as 100 ppm based on coal. The effect of pressure reductions appears to be more pronounced in 1-L semi-batch reactions than microautoclave reactions. This may be due to differences in catalyst activation in the two systems. The catalyst in the microautoclave did not require activation, whereas the precursor used in the 1-L reactor did require *in situ* activation. There was no observed effect on coal conversion with a reduction of solvent to coal ratio from 2:1 to 1:1.

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