

## EFFECT OF ACTIVATION CONDITIONS ON DISPERSED IRON CATALYSTS IN COAL LIQUEFACTION

Cugini, A.V., Utz, B.R., Krastman, D., and Hickey, R.F.  
U. S. Department of Energy, Pittsburgh Energy Technology Center  
P.O. Box 10940, Pittsburgh, PA 15236

and  
Balsone, V.  
Gilbert Commonwealth, Inc., Library, PA 15129

### INTRODUCTION

Ongoing research at PETC has focused on improved means of developing high surface area, well dispersed slurry catalyst options for direct coal liquefaction applications.<sup>(1)</sup> Compared to supported hydroliquefaction catalysts now being employed, such catalysts can exhibit superior characteristics for use in a coal dissolution reactor, particularly with respect to loss of activity and contact with reactants during the early stages of coal liquefaction. If properly dispersed and activated, molybdenum is sufficiently active to be employed for coal liquefaction at low concentrations (<0.1 wt% based on coal). However, owing to the difficulty of recovering expensive transition elements such as molybdenum after use, iron has continued to be of interest as the basis of an economical and disposable catalyst for coal liquefaction.

The catalytic activity obtained by direct introduction of iron into the feed slurry in the form of readily available minerals such as oxides or sulfide (pyrite) concentrates is generally low. Such approaches are typically ineffective unless relatively high concentrations (several wt% based on coal) of iron are added.<sup>(2-4)</sup> Among the factors usually contributing to the low activity are poor initial dispersion and low surface area of the added iron phase, and a tendency for aggregation and loss of surface area (sintering) of the catalytically active iron sulfide (pyrrhotite) phase under coal liquefaction conditions.<sup>(5)</sup>

A variety of methods have been employed to increase the initial dispersion of iron in coal liquefaction systems. Catalyst precursors have been introduced by physically mixing very small particles into the feed slurry, deposition from aqueous solutions, addition in oil soluble forms, and impregnation of the feed coal by water soluble compounds.<sup>(6-12)</sup> Exploratory studies using such approaches have provided evidence for increased activity with reduction of iron particle size, the need for available sulfur donating species if non-sulfide precursors are used, and the inhibiting effect of coal on the agglomeration and growth of small particles of some iron catalyst precursors under liquefaction conditions. The studies also suggest that iron may be an effective liquefaction catalyst at concentrations well below 1 wt% of the feed coal by utilizing the proper precursors, introduction techniques, and activation conditions.

Based upon a review of past research and initial screening tests, an approach combining both coal impregnation and precipitation techniques to generate a highly active dispersed iron catalyst has shown considerable promise in liquefaction tests at PETC.<sup>(13)</sup> In effect, the carbonaceous matrix of the coal is being used as a support not only to disperse added iron but also to help sustain the initial high dispersion achieved subsequent to activation. Effort to date has been primarily directed toward a hydrated iron oxide (FeOOH) precursor, since sub-micron oxide particles are readily formed under the proper conditions.<sup>(14)</sup> The approach being pursued appears to be of rather general applicability in coal liquefaction, utilizes no expensive reagents, minimizes the iron requirement, and is capable of being adapted for use on a larger processing scale.

## EXPERIMENTAL

### Feedstocks

Experiments were conducted with -200 mesh Illinois No. 6 (Burning Star No. 2) coal obtained from the Consolidation Coal Company. Analyses of the ground coal are given in Table 1.

Second stage heavy distillate from recent operations in a close-coupled integrated two-stage liquefaction mode at the Wilsonville Advanced Coal Liquefaction Test Facility was used as the liquefaction vehicle.<sup>(15)</sup> The bituminous coal was slurried with second stage vacuum tower overheads (V-1074) from Run 257 (Illinois No. 6 coal). Properties of the vehicle are summarized in Table 2.

### Catalyst Precursors

For use in experiments testing the effect of physically mixing catalyst precursors into the feed slurry, FeOOH was prepared by precipitation from a ferric nitrate solution (200 g/L) with sufficient ammonium hydroxide to provide a three-fold excess of  $\text{NH}_4^+$  to Fe. A sample of  $\text{Fe}_2\text{O}_3$ , with a nominal particle size of one micron, was used as obtained from Spang and Company, Butler, PA. A pyrite concentrate was used that originated from the Robena coal preparation facility of the U.S. Steel (now USX) Corporation. All other chemicals and reagents were ACS grade.

Two molybdenum catalyst precursors were tested to establish a basis for comparison with the iron catalysts. These precursors were ammonium heptamolybdate (AHM) and ammonium tetrathiomolybdate (ATTM). The use of these precursors to form a dispersed  $\text{MoS}_2$  catalyst at liquefaction conditions has been documented. (1,16 and 17)

FeOOH was also dispersed onto the feed coals by an incipient wetness impregnation/precipitation approach. A solution of 1 g of ferric nitrate,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  dissolved in 40 g of distilled water was used to wet 50 g of the ground bituminous coal to incipient wetness. The wet paste was added rapidly to a solution containing 20 g of ammonium hydroxide (29%  $\text{NH}_3$ ) and 200 g of distilled water. Pressure-filtration of the aqueous coal suspension through a 0.45 micron filter resulted in a clear filtrate. The iron loaded coal was vacuum dried at 40°C.

X-Ray diffraction studies were conducted with a Rigaku computer-controlled diffractometer equipped with a long fine-focus Cu X-ray tube, a receiving graphite monochromator to provide monochromatic  $\text{Cu-K}_\alpha$  radiation, and a scintillation detector.

### Liquefaction Tests

Catalyst screening tests were conducted in 40-mL microreactors for 1 hour at 425°C using a 10g total charge of 2:1 vehicle (tetralin) to coal ratio. In tests comparing the effect of an added source of sulfur to ensure sulfiding of the iron, 0.1 g of  $\text{CS}_2$  was added to the charge. Heat-up rates of 2-3 minutes were obtained by immersing the microreactor in a fluidized sand bath preheated to 425°C. Coal conversion was calculated from the solubility of the coal-derived products in methylene chloride and in heptane determined by a pressure filtration technique, based on weight of insoluble residue.<sup>(18)</sup>

Semi-batch (batch slurry, flow through gas) tests were performed in a 1-L stirred-tank reactor system to obtain more definitive product yield and conversion information and sufficient product for additional characterization. The feed charge consisted of 500 g of 30 wt% coal slurry. Reactions were run at 425°C for 1 hour under 2500 psig of  $\text{H}_2/3\% \text{H}_2\text{S}$ . The gas feed rate was 4 SCFH. A 100 g aliquot of the reactor product was subjected to a single-stage vacuum distillation to approximate the 650°F, 650°F-950°F, and 950°F+ content. The 650°F- fraction was separated by

distillation at a pressure of 50 torr to a vapor temperature of 462°F. The product distillation was taken to a pressure of 5 torr and vapor temperature of 610°F to approximate the 950°F+ yield. A second 100 g aliquot of the reactor product was used to determine solubility yields following the general product workup scheme outlined in Figure 1. The product gas composition was determined by on-line gas chromatography monitoring and by the analysis of gas burette samples.

Further tests were performed in a computer-controlled 1-L bench-scale continuous liquefaction unit. A schematic of the unit is shown in Figure 2. For experiments with iron, an intermediate stage was added to assist in activating the catalyst precursor. The residence time in this intermediate stage was approximately 20 minutes. Continuous operations were carried out with a 30 wt% coal slurry, reactor temperature of 435°C, 2500 psig H<sub>2</sub>/3%H<sub>2</sub>S, and 1-h residence time. The gas flow rate was 4 SCFH; the slurry feed rate was 240 g/h. The product workup scheme in Figure 1 was followed.

#### Activation Studies:

The 40 mL microautoclave reactor was used to investigate the effect of activation temperature on the transition of FeOOH to pyrrhotite. In these experiments, FeOOH was impregnated onto carbon black rather than coal to eliminate the interferences caused by the indigenous pyrite in the coal. The carbon black was Raven 22 Powder obtained from Columbian Chemicals Co. The iron loaded carbon black and tetralin were rapidly heated (under H<sub>2</sub> in the presence of CS<sub>2</sub>) to temperatures of 100°C, 150°C, 200°C, 250°C, 300°C, 350°C, and 400°C and held at temperature for 5 minutes. The products were mixed with THF and filtered through a 0.45-micron filter paper. The filter cake, containing the iron loaded carbon, was recovered and analyzed by X-Ray diffraction.

## RESULTS AND DISCUSSION

### Catalyst Screening Experiments

A series of microautoclave screening experiments was initially conducted with Illinois No. 6 coal and a variety of iron additives. Results with no added iron, several iron oxide preparations, and AHM are compared in Figure 3. Coal conversions to heptane and methylene chloride solubles were similar in the presence of 5000 ppm iron as 1-micron particles of iron oxide or in the presence of H<sub>2</sub>S (from addition of 0.1 wt% CS<sub>2</sub>) with no added iron. Although not shown, introduction of 5000 ppm iron in the form of powdered coal-derived pyrite or dilute solutions of ferrous sulfate, or ferrous ammonium sulfate gave results comparable to physically mixing the powdered iron oxide into the tetralin/coal charge. Tests with powdered FeOOH gave some improvement in coal conversions. These conversions were further enhanced by addition of a sulfiding agent. The highest catalytic activity was developed after dispersion of the FeOOH precursor on the coal surface by an incipient wetness impregnation/precipitation procedure. Coal conversions with 2500 ppm iron added by this procedure were comparable to those obtained by addition of 1500 ppm molybdenum as a dilute solution of AHM. The screening studies indicate that the presence of hydrogen sulfide (or another sulfur source) is required to transform the FeOOH precursor into its most active form.

The general trends in liquefaction activity of the iron oxides in Figure 3 are consistent with expectations based on particle size considerations. The initially high metal dispersion that may be attained by solution impregnation can be largely lost in the subsequent drying procedure. The PETC procedure minimizes this problem by rapidly precipitating and fixing the precursor onto the coal surface in an insoluble form before drying. It is important that the coal surfaces only be wetted to incipient wetness during the impregnation step prior to precipitation. A procedure in which the coal is suspended in the impregnating solution and then treated with base to

deposit FeOOH on the coal has been described by Mukherjee and coworkers.<sup>(8)</sup> As shown in Figure 4, results obtained by this approach are only marginally better than those obtained by physically mixing the FeOOH precursor into the coal/solvent feed.

### Liquefaction Tests

Semi-batch stirred autoclave tests were conducted with Illinois No. 6 coal. Conversions at 425°C to soluble and distillate products obtained with the impregnated FeOOH, AHM, and no added catalyst are compared in Figure 5. Yield structures for 2500 ppm added iron (as impregnated FeOOH) and 1500 ppm molybdenum (as aqueous AHM) are presented in Table 3. The yield structure for the two cases appears to be similar. However, for the particular liquefaction conditions and active metal concentrations chosen, a higher total distillate yield was obtained from the iron catalyst. Elemental analysis of the distillation product fractions indicated little difference between the products from using FeOOH or AHM as the catalyst precursors.

The transitions involved in the generation of pyrrhotite from impregnated FeOOH were studied in a series of microautoclave experiments. The results are given in Table 4. These results indicate that a transition from amorphous to crystalline form occurs between 300°C and 350°C, after which crystalline pyrrhotite is observed. It is likely that pyrrhotite is present at temperatures below 350°C. The pyrrhotite present below 350°C must be smaller than 100 Å, since it was not detectable by X-Ray diffraction. Consequently, it may be expected that pyrrhotite formed prior to 350°C would exhibit a higher liquefaction activity than the pyrrhotite formed at 350°C.

A continuous unit evaluation of the impregnated iron catalyst was made with Illinois No. 6 coal. Table 5 compares product yields in this test using FeOOH and an activation temperature of 275°C with those obtained in a continuous unit test using dispersed molybdenum, added as aqueous ammonium tetrathiomolybdate (ATTM), as the catalyst. Under these liquefaction conditions, the observed conversions with iron are comparable to the observed conversions with molybdenum.

The effect of varying the intermediate temperature was investigated in a series of continuous liquefaction tests. Table 6 summarizes the results. The highest levels of conversion and smoothest operation were observed at 275°C. At 350°C, coal conversions were lower than at 275°C and operation of the unit was more difficult; minor plugging problems were observed. Below an activation temperature of 275°C the FeOOH may not have been fully sulfided (converted to pyrrhotite) and, therefore, did not exhibit the same catalytic activity as the pyrrhotite formed at 275°C. The decrease in coal conversion and more difficult unit operation at the higher activation temperature suggest that the pyrrhotite formed at 350°C was catalytically less active than at 275°C. This may be due to formation of the pyrrhotite having a larger crystallite size at 350°C than at 275°C. However, the results could also be attributed to thermal soaking differences between 275°C and 350°C. However, in earlier studies with the molybdenum system<sup>(17)</sup>, it was reported that the effect of thermal soaking was not observed. It has not been established that 275°C represents the optimal intermediate temperature; 275°C is an activation temperature that results in higher coal conversions using the dispersed iron catalyst than activation temperatures that are significantly different. Further studies of the effect of the activation temperature and residence time are being made.

Owing to differences in surface properties, functionality, and liquefaction characteristics between bituminous and subbituminous coals, it cannot be assumed that the exact iron catalyst precursor dispersion and activation conditions that are optimal for a bituminous coal are directly transferable to the case of a subbituminous coal. Preliminary semi-batch studies suggest that higher concentrations of an added sulfiding agent are required to fully activate the iron catalyst on low-sulfur bituminous coals. The optimal catalyst activation temperature in continuous operations may also be different for subbituminous coals. Extension of the current iron dispersion and activation approach to a subbituminous coal is currently under investigation.

### SUMMARY

A procedure for dispersing a finely divided form of iron on coal has been developed that yields a highly active catalyst for direct coal liquefaction applications. Feed coal is impregnated with  $\text{Fe}^{3+}$  by an incipient wetness procedure. Subsequently, the high dispersion and interaction with the coal surfaces is maintained by conversion of the added iron to an insoluble hydrated iron oxide ( $\text{FeOOH}$ ). Proper activation of this dispersed hydrated iron oxide under typical liquefaction conditions is shown to result in an effective disposable catalyst for the conversion of coal. In batch or semi-batch operations proper activation can be achieved during heat-up of the reactants. In continuous operations, an activation reactor stage is required.

Using iron concentrations as low as 2500 ppm (based on coal), batch liquefaction tests were conducted with Illinois No. 6 coal slurried with solvents from the Wilsonville Advanced Coal Liquefaction Test Facility. Conversions of the coal to distillate and soluble products at 425°C under 2500 psig of  $\text{H}_2/3\% \text{H}_2\text{S}$  for 1-h compared favorably with conversions under the same conditions using 1500 ppm of molybdenum added as ammonium heptamolybdate (AHM).

Bench-scale continuous-unit tests to better define the activation sequence of the iron catalyst in continuous operations were conducted with Illinois No. 6 coal. At an activation temperature of 275°C (and activation residence time of 0.33 hour) and a final reactor temperature of 435°C and residence time of 1 hour, the conversions observed with the impregnated  $\text{FeOOH}$  catalyst precursor were again similar to the conversions observed using added Mo. Significantly varying the activation temperature from 275°C results in poorer liquid yields and unit performance. Below 275°C sulfiding of the  $\text{FeOOH}$  precursor may be a problem; above 275°C the growth of pyrrhotite crystals may be detrimental to the liquefaction activity of the iron.

### ACKNOWLEDGEMENTS

The authors would like to thank Sidney S. Pollack and Elizabeth A. Frommell for their assistance in the X-ray diffraction study.

### DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

## REFERENCES

1. Lett, R.G., Cugini, A.V., Utz, B.R., Krastman, D., Cillo, D.L., and Jin, G.T. Dispersed Catalyst Approaches in Coal Liquefaction and Coprocessing. Proceedings 6th Korea - U.S.A. Joint Workshop on Coal Utilization Technology, 91-106. Seoul, Korea, October 17-18, 1989.
2. Mazzocco, N.J., Klunder, E.B., and Krastman, D. Study of Catalytic Effects of Mineral Matter Level on Coal. DOE/PETC/TR-81/1.
3. Garg, D., and Givens, E.N. Pyrite Catalysis in Coal Liquefaction. Ind. Eng. Chem. Process Des. Dev., 1982, 21, 113-117.
4. Paranjape, A.S., and Rhodes, D.E. Use of Iron Oxide and Hydrogen Sulfide to Improve Integrated Two-Stage Coal Liquefaction. Proceedings DOE Direct Coal Liquefaction Contractors' Review Meeting, 34-59. Albuquerque, NM, October 17-18, 1984.
5. Stohl, F.V. The Effects of Iron Sulfide Surface Area Variations on Coal Liquefaction. Fuel, 1983, 62, 122-126.
6. Andres, M., Charcosset, H., Chicke, P., Davignon, L., Djega-Mariadassou, G., Joly, J.-P., and Pregermain, S. Catalysis of Coal Hydroliquefaction by Synthetic Iron Catalysts. Fuel, 1982, 62, 69-72.
7. Djega-Mariadassou, G., Besson, M., Brodzki, D., Charcosset, H., Huu, T.V., and Varland, J. Evaluation of Highly Dispersed Catalysts During Hydroliquefaction of Coal. Fuel Processing Technology, 1986, 12, 143-153.
8. Mitra, J.R., Chowdhury, P.B., and Mukherjee, D.K. A Comparative Study on Deposited and Mixed Iron Oxide Catalysts for Hydrogenation of Coal. Fuel Processing Technology, 1984, 8, 283-291.
9. Anderson, R.R., and Bockrath, B.C. Effect of Sulfur on Coal Liquefaction in the Presence of Dispersed Iron or Molybdenum Catalysts. Fuel, 1984, 63, 329-333.
10. Watanabe, Y., Yamada, O., Fujita, K., Yoshinobu, T., and Suzuki, T. Coal Liquefaction Using Iron Complexes as Catalysts. Fuel, 1984, 63, 752-755.
11. Weller, S., and Pelipetz, M.G., Coal Hydrogenation Catalysts Studies of Catalyst Distribution. Ind. Eng. Chem., 1951, 43, 1243-1246.
12. Garg, D. and Givens, E.N. Effect of Catalyst Distribution in Coal Liquefaction. Fuel Processing Technology, 1983, 7, 59-70.
13. Utz, B.R., and Cugini, A.V. Method for Dispersing Catalyst Onto Particulate Material. Patent Application Filed.
14. Naono, H., and Nakai, K. Thermal Decomposition of  $\alpha$ -FeOOH Fine Particles. J. Colloid and Interface Sci., 1989, 128, 146-156.
15. Wesnor, J.D., Pinkston, T.E., Moore, D.L. Recent Progress at the Advanced Coal Liquefaction Facility in the Direct Liquefaction of Coal. Proceedings DOE Direct Liquefaction Contractors' Review Meeting, 23-42. Pittsburgh, PA, October 2-4, 1989.
16. Utz, B.R., Cugini, A.V., and Frommell, E.A., Dispersed-Phase Catalysis in Coal Liquefaction. Novel Materials in Heterogeneous Catalysis, ACS Symposium Series No. 437, 289-299 (1989).

17. Derbyshire, F.J., Catalysis in Coal Liquefaction: New Directions for Research, IEACR/08, IEA Coal Research, London (1988).
18. Utz, B.R., Appell, H.R., and Blaustein, B.D. Solubility Characterization of Coal-Derived Products Using Pressure Filtration. Fuel, 1984, 63, 1671-1676.

**Table 1. Analyses of Illinois No. 6 (Burning Star).**

<b>Proximate Analysis, (As Received)</b>	<b>wt%</b>
Moisture	4.2
Volatile Matter	36.9
Fixed Carbon	48.2
Ash	10.7
<b>Ultimate Analyses, (Moisture Free)</b>	<b>wt%</b>
Carbon	70.2
Hydrogen	4.8
Nitrogen	0.9
Sulfur	3.1
Oxygen (Difference)	9.9
Ash	11.1
<b>Sulfur Forms</b>	<b>wt%</b>
Sulfatic	0.03
Pyritic	1.2
Organic	1.9

**Table 2. Properties of V-1074 oil.**

<u>Ultimate Analysis</u>	<u>wt%</u>
Carbon	89.1
Hydrogen	9.8
Oxygen (Direct)	0.9
Nitrogen	0.4
Sulfur	0.04
Ash	<0.1
850°F (Vol%)	65
Heptane Insols, wt%	0.2
M <sub>n</sub> (daltons)	360 <sup>a</sup>
H <sup>*</sup> <sub>ar</sub>	0.15
f <sub>a</sub>	0.43

<sup>a</sup>VPO, tetrahydrofuran, 40°C

**Table 3.** Product yields from liquefaction of 30 wt% Illinois No. 6 coal and 70 wt% V-1074 in a semi-batch mode non-catalytically, with added iron (FeOOH) and added molybdenum (AHM). (Semi-batch 1-L autoclave; Reactor Temp. = 425°C, Time at Temperature = 1 hour, Pressure = 2500 psig, 97% $H_2$ /3% $H_2S$ ; Fe conc. = 2500 ppm, Mo. conc. = 1500 ppm, Gas Feed Rate = 4 SCFH.)

**Yield Structure (Ash Free Basis), Wt%**

<u>Component</u>	<u>Non-Catalytic</u>	<u>FeOOH</u>	<u>AHM</u>
C <sub>1</sub> -C <sub>4</sub>	3.2	3.0	2.3
C <sub>5</sub> -950°F	71.8	82.9	81.5
950°F+ Solubles	10.0	6.2	8.6
Heptane Insolubles	15.3	8.3	8.6
Non-Hydrocarbon Gases	1.0	1.0	1.0
Hydrogen	(1.3)	(1.6)	(2.0)

**Table 4.** Microautoclave Iron Activation Studies Using Carbon Black and Tetralin 1000 psig  $H_2$  Cold Pressure with Added  $CS_2$  Using 2500 ppm Iron as Hydrated Iron Oxide on Carbon

<u>Final Reactor Temperature °C</u>	<u>Dominant Iron Phase by X-Ray Diffraction</u>	<u>Pyrrhotite Area Under Curve</u>	<u>Estimated Crystallite Size</u>
100	Amorphous		
150	Amorphous		
200	Amorphous		
250	Amorphous		
300	Amorphous		
350	Pyrrhotite	87	400Å
400	Pyrrhotite	158	400Å

**Table 5.** Product yields from liquefaction of 30 wt% Illinois No. 6 coal and 70 wt% V-1074 in a continuous mode with added iron (FeOOH) and added molybdenum (ATM). (Continuous 1-L autoclave; Reactor Temp. = 435°C, Pressure = 2500 psig, 97% $H_2$ /3% $H_2S$ ; Fe conc. = 2500 ppm, Mo conc. = 1000 ppm, Gas Feed Rate = 4 SCFH; Slurry Feed Rate = 240 g/h.

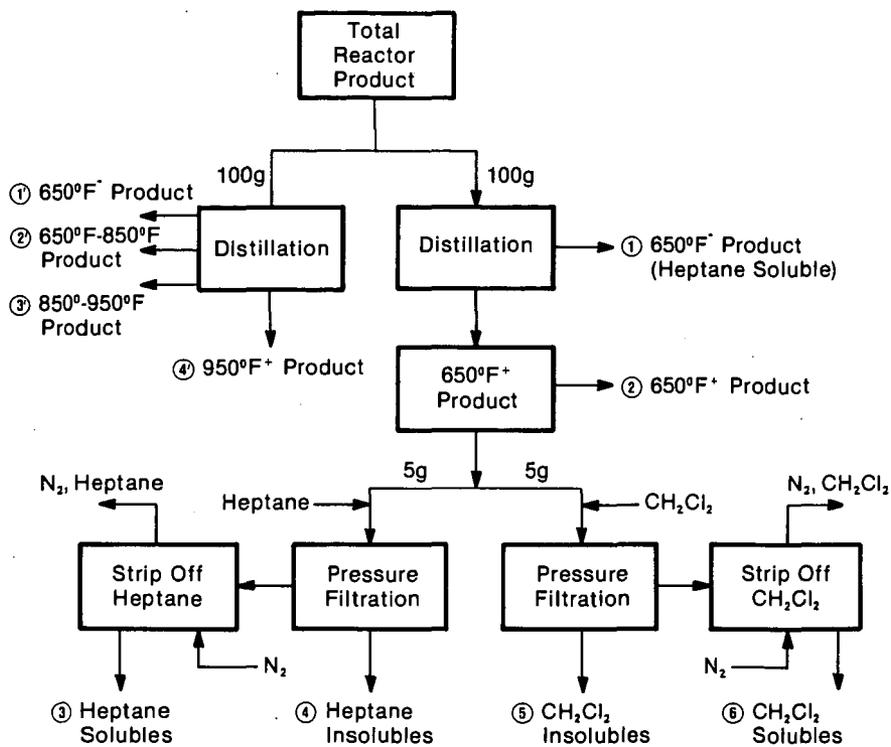
**Yield Structure (Ash Free Basis), Wt%**

<u>Component</u>	<u>FeOOH</u>	<u>ATM</u>
C <sub>1</sub> -C <sub>4</sub>	3.4	3.2
C <sub>5</sub> -950°F	82.7	83.5
950°F <sup>+</sup>	15.0	14.5
Non-Hydrocarbon Gases	1.4	1.4
Hydrogen	(2.5)	(2.6)

**Table 6.** Continuous Unit Iron Activation Studies Using Illinois No. 6 Coal and Wilsonville Recycle Solvent (30 wt% Coal in Solvent), 2500 psig (3%  $H_2S$  in  $H_2$ ) Using 2500 ppm Iron as Hydrated Iron Oxide on Coal

**Total Product**

<u>Reactor #1</u> <u>Temp. °C</u>	<u>Reactor #2</u> <u>Temp. °C</u>	<u>%</u> <u>950°F+</u> <u>in Total</u> <u>Product</u>	<u>%</u> <u>Methylene</u> <u>Chloride</u> <u>Insolubles</u>	<u>%</u> <u>Heptane</u> <u>Insolubles</u>	<u>Comments</u>
150	435	***	***	***	Plugged - after 12 hours
275	435	15	7.6	14.2	Smooth Operation - 32 hours
350	435	22	12.4	20.6	Rough Operation - 32 hours
50	435	***	***	***	Plugged - after 2 hours
275	435	16	6.4	13.0	Smooth Operation - 72 hours Normal Shutdown



**FIGURE 1. PRODUCT WORKUP SCHEME FOR 1-LITER SEMI-BATCH AND CONTINUOUS UNIT OPERATIONS.**

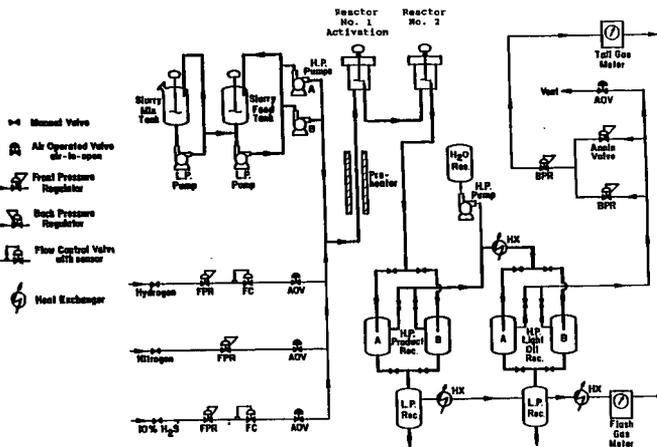


Figure 2. Bench-scale continuous unit configuration.

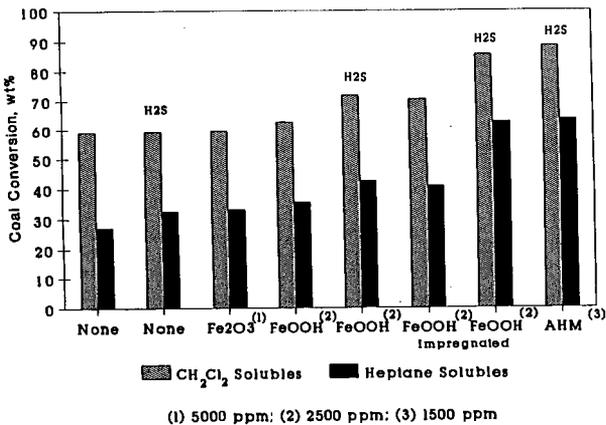
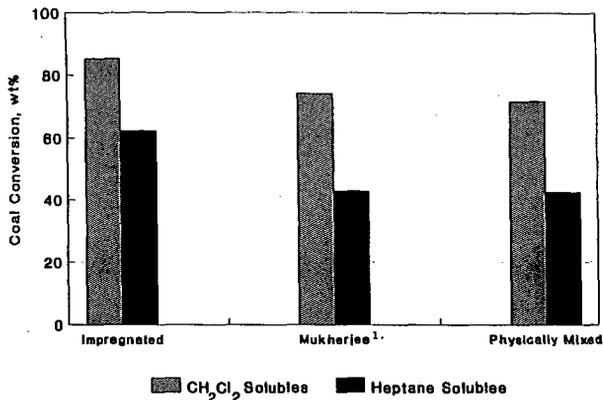
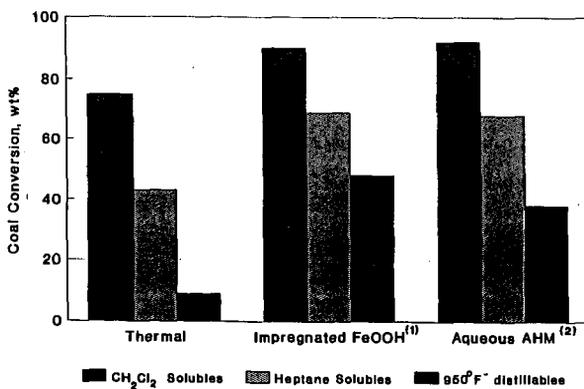


Figure 3. Effect of catalysts on coal conversion. (Microautoclave runs; 425°C, 1h, 2500 psig H<sub>2</sub>, 2:1 tetralin:Illinois No. 6 coal)



1. Coal/Catalyst mixture prepared according to procedure outlined in reference 8.

**Figure 4.** Effect of impregnation on coal conversion. (Microautoclave runs; 425°C, 1h, 2500 psig H<sub>2</sub>, 0.1 g CS<sub>2</sub>, 2:1 tetralin:Illinois No. 6 coal)



(1) 2500 ppm; (2) 1500 ppm

**Figure 5.** Effect of catalysts on coal conversion. (1-L semi-batch experiments; 425°C, 1h, 2500 psig, 97% H<sub>2</sub>/3% H<sub>2</sub>S at 4 SCFH)