

## Recent Progress in the Use of Disposable Catalysts for Coal Liquefaction

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### 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 and 7)</sup> Fundamental 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.

### EXPERIMENTAL

Experiments were conducted with -200 mesh Illinois No. 6 (Burning Star No. 2) coal obtained from the Consolidation Coal Company. 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 solvent.<sup>(8)</sup> The bituminous coal was slurried with second-stage vacuum tower overheads (V-1074) from Run 257 (that used Illinois No. 6 coal). Properties of the coal and solvent have been summarized in earlier papers.<sup>(1 and 9)</sup>

Molybdenum catalyst precursors were tested to establish a basis for comparison with the iron catalysts. The precursors used

were ammonium heptamolybdate (AHM) and ammonium tetrathiomolybdate (ATTM).

Hydrated iron oxide (FeOOH) was 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.

Semi-batch (batch slurry, flow through gas) tests were performed in a 1-L stirred-tank reactor system to obtain product yield and conversion information and to provide sufficient product for additional characterization. The semi-batch operation has been discussed in earlier papers.<sup>(1 and 9)</sup>

Further tests were performed in a computer-controlled 1-L bench-scale continuous liquefaction unit. A schematic of the unit has been presented in earlier papers.<sup>(1 and 9)</sup> 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  $\text{H}_2/3\% \text{H}_2\text{S}$ , and 1 h residence time. The gas flow rate was 5 SCFH; the slurry feed rate was 240 g/h.

A 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  $\text{H}_2$  in the presence of  $\text{CS}_2$ ) 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  $\mu\text{m}$  filter paper. The filter cake, containing the iron loaded carbon, was recovered and analyzed by X-Ray diffraction.

#### RESULTS AND DISCUSSION

Conversions of Illinois No. 6 Coal at 425°C to soluble and distillate products in semi-batch stirred autoclave tests with the impregnated FeOOH, AHM, or no added catalyst are compared in Figure 1. The 950°F distillate 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 liquefaction using either FeOOH or AHM as 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 1. These results indicate that a transition from amorphous (or sub-crystalline) to crystalline form occurs between 300°C and 350°C, after which crystalline pyrrhotite is observed. It is possible 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.

Evaluation of the impregnated iron catalyst was made with

Illinois No. 6 coal in the continuous unit. Table 2 compares product yields in this test using FeOOH and a temperature of 275°C in the activation reactor with those obtained in a continuous unit test using dispersed molybdenum, added as aqueous ammonium tetrathiomolybdate (ATTM), as the catalyst. Under these liquefaction conditions, at approximately double the catalyst concentration, the activity of the iron is comparable to the activity of the molybdenum.

The effect of varying the intermediate (activation) temperature was investigated in a series of continuous liquefaction tests. Table 3 summarizes the results. The highest levels of conversion and smoothest operation were observed with catalyst activation between 250°C and 300°C. At 350°C, coal conversions were lower, operation of the unit was more difficult, and minor plugging problems were observed. Below an activation temperature of 250°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 decreased 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 200°C and 350°C. Thermal tests (with no catalyst) were conducted using an intermediate temperature of 275°C. The results of the thermal tests are also summarized in Table 3. Thermal operations appear to be sensitive to the initial state of the test. The thermal data reported in Table 3 refer to two cases in which the unit had been operating well prior to beginning the thermal test. In a separate case in which the unit was operating at low conversions prior to the thermal test, plugging was observed. Further studies of the effect of the activation temperature and time on thermal and catalytic operations are planned. However, the results to date indicate that the activation stage functions both to activate the catalyst and to provide a thermal pretreating benefit. Further studies are planned to evaluate the effect of activation for both thermal and catalytic systems.

Work is now in progress to adapt the iron impregnation/FeOOH precipitation procedure to the liquefaction of subbituminous coals. Optimum conditions for the loading and activation of the iron are expected to be somewhat coal dependent. However, initially the preparation procedure for Illinois No. 6 coal has been applied without modification to Usibelli (Alaska) subbituminous coal. In the preparation step, during filtration of the ammonium hydroxide from the Usibelli iron impregnated coal, a brownish tinted filtrate was obtained rather than clear filtrate as observed with the bituminous coal. This appears to arise from the extraction of a small amount of polar organic material from the subbituminous coal; this filtrate is being further characterized. Semi-batch catalytic and non-catalytic liquefaction tests were conducted with Usibelli coal and second stage heavy distillate (V-1072) from Wilsonville Run 258 with Black Thunder subbituminous coal. The results of these tests, conducted under 2500 psig of 3% H<sub>2</sub>S/H<sub>2</sub>, indicate that catalytic activity is observed with the FeOOH impregnated subbituminous coal. A similar conclusion was drawn from semi-batch coprocessing tests with the Usibelli coal and Cold Lake petroleum resid. Optimization of the iron activation conditions requires

operation in a continuous mode. Initial slurry pumping problems rendered unsuccessful initial attempts to conduct the continuous mode liquefaction experiments in our small bench scale units with a Usibelli coal/V-1072 slurry. The problem has been diagnosed as arising from the use of a relatively coarse grind feed coal (about 60 mesh) with the V-1072 solvent which is lighter than the bituminous coal-derived solvent used in other tests as shown in Table 4. Further semi-batch and continuous tests of the subbituminous coal are planned.

#### SUMMARY AND CONCLUSIONS

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. The feed coal is impregnated with ferric iron by incipient wetness treatment. Subsequently, the high dispersion and interaction with the coal surfaces is maintained by conversion of the added iron to insoluble FeOOH. Proper activation of the dispersed FeOOH 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.

Continuous-unit bench-scale tests to better define the activation sequence of the iron catalyst were conducted with Illinois No. 6 coal. At an activation temperature between 250°C and 300°C (and activation residence time of 20 min.), a final reactor temperature of 435°C, and residence time of 1 h, the conversions observed with the impregnated FeOOH catalyst precursor were again similar to the conversions observed using added Mo. Significantly varying the activation temperature from the optimal temperature range resulted in poorer liquid yields and unit performance. The degree to which the effect of pretreater temperature can be attributed to catalytic effects and to thermal soaking effects is uncertain, but it appears that both effects may contribute.

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#### 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.

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**Table 1.** Microautoclave Iron Activation Studies Using Carbon Black and Tetralin 1000 psig H<sub>2</sub> Cold Pressure with Added CS<sub>2</sub> Using 2500 ppm Iron as Hydrated Iron Oxide on Carbon

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

**Table 2.** Product Yields from liquefaction of 30 wt% Illinois No. 6 coal and 70 wt% V-1074 in a continuous mode with added iron (FeOOH) or added molybdenum (ATM). (Continuous 1-L autoclave; Reactor Temp. = 435°C, Pressure = 2500 psig, 97% H<sub>2</sub>/3% H<sub>2</sub>S; Fe conc. = 2500 ppm, Mo conc. = 1000 ppm, Gas Feed Rate = 5 SCFH; Slurry Feed Rate = 240 g/h.)

Product Distribution (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*	15.0	14.5
Non-Hydrocarbon Gases	1.4	1.6
Hydrogen	(2.5)	(2.0)

**Table 3.** Continuous Operation - Activation Temperature Series (Continuous 1-L autoclave; Reactor Temp. = 435°C, Pressure = 2500 psig, 97% H<sub>2</sub>/3% H<sub>2</sub>S; Fe conc. = 2500 ppm, Gas Feed Rate = 5 SCFH; Slurry Feed Rate = 240 g/h.)

<u>Activation</u> <u>Temperature, °C</u>	<u>Catalyst</u>	<u>Product</u> <u>Quality</u>	<u>Conversion to</u> <u>250°F, %</u>	<u>Comments</u>
150	Iron	Poor	***	Plugged
275	Iron	Good	55	Smooth Operation
350	Iron	Viscous	30	Rough Operation
50	Iron	Poor	***	Plugged
275	Iron	Good	52	Smooth Operation
250	Iron	Good	54	Smooth Operation
300	Iron	Good	59	Smooth Operation
275	None		41	

**Table 4. Vehicle Solvents Used in Continuous Liquefaction Tests**

<b>Ultimate Analysis, wt%</b>	<b>Wilsonville V-1072<sup>1</sup></b>	<b>Wilsonville V-1074<sup>2</sup></b>
Carbon	89.0	89.1
Hydrogen	9.3	9.8
Oxygen(Direct)	1.1	0.9
Nitrogen	0.7	0.4
Sulfur	0.07	0.4
Ash	<0.1	<0.1
<b>850°F (Vol%)</b>	<b>86</b>	<b>65</b>
Heptane Insols, wt%	0.5	0.2
$M_n$	<b>280<sup>3</sup></b>	<b>360<sup>3</sup></b>
$H_{ar}^*$	0.19	0.15
$f_a$	0.61	0.43

1. Black Thunder subbituminous coal used in Wilsonville test.
2. Illinois No. 6 bituminous coal used in Wilsonville test.
3. VPO, THF, 40°C.

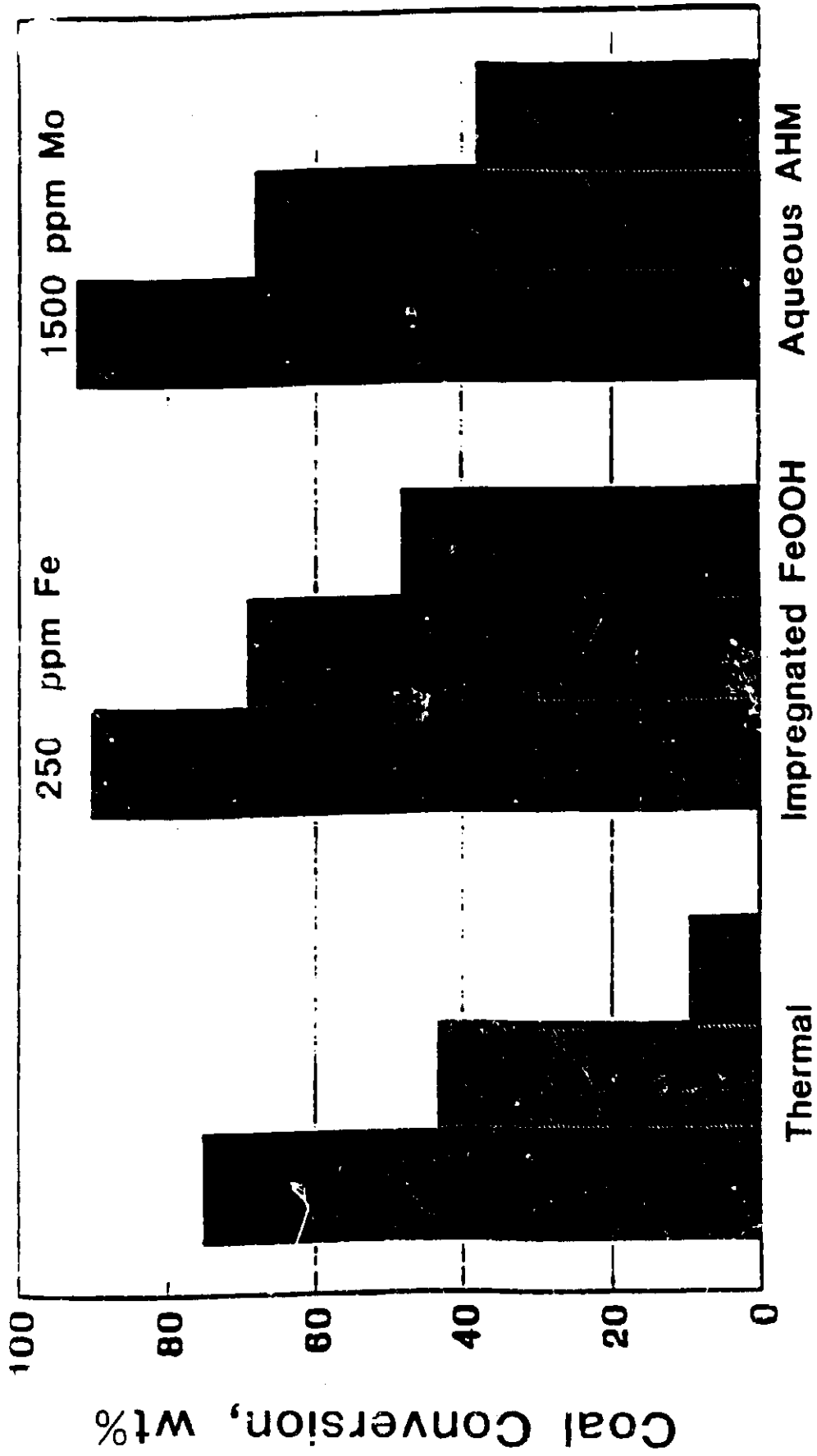


Figure 1. Effect of Catalysts on Coal Conversion. (1-L Semi-Batch Experiments; 425°C, 1h, 2500 psig, 97%H<sub>2</sub>/3%H<sub>2</sub>S at 4 SCFH).