

## EFFECT OF CATALYST DISTRIBUTION IN COAL LIQUEFACTION

Diwakar Garg and Edwin N. Givens  
Corporate Research and Development Department

Air Products and Chemicals, Inc.  
P.O. Box 538, Allentown, PA 18105

Effect of the mode of catalyst addition was studied for the liquefaction of Eastern Kentucky Elkhorn #2 coal in a continuously stirred tank reactor. Particulate addition of iron as pyrite significantly catalyzed the coal liquefaction reaction. Both coal conversion and oil yield increased on addition of pyrite to the feed slurry; oil production increased by more than a factor of two both at 825° and 850°F. Pyrite Concentration had negligible effect on product distribution, but the mode of catalyst addition had a big impact on coal liquefaction. Impregnation of coal with one weight percent iron gave a similar product distribution as obtained with addition of 3.5 weight percent iron in the form of particulate pyrite. Significantly lower hydrocarbon gas make and hydrogen consumption were noted with impregnation over particulate addition. SRC sulfur content was marginally higher with impregnation. Solvent hydrogen content increased with particulate addition whereas it decreased with impregnation.

### Introduction

The basic non-catalytic process for liquefaction of coal was developed by Bergius<sup>1</sup> in Germany circa 1912. In 1925 Brown-coal tar was catalytically hydrogenated for the first time with molybdenum oxide. This advance led to the development of the catalytic hydrogenation of coal.

A number of catalysts were studied and reported to give improved yield and product quality<sup>2</sup>. Adding two percent molybdenum on coal as ammonium molybdate substantially increased the liquefaction performance. Subsequent experiments showed that 0.05 percent molybdenum gave a yield equal to that obtained with two percent when the alkalinity of coal was reduced. Because molybdenum was expensive and in short supply in Germany, it was replaced by iron catalyst. The Germans found that adding iron as iron sulfate to the feed slurry improved the liquefaction of coal<sup>2</sup>. Bayermasse, an iron oxide-containing material obtained as by-product from aluminum manufacture was also shown to be active in coal liquefaction. In terms of iron content, twice as much Bayermasse as sulfate was needed to produce the same results in hydrogenation of coal. In certain cases the addition of sulfur to the system also improved the catalytic liquefaction effect of the iron<sup>2</sup>. The iron to sulfur ratio in the liquefaction residue suggested that iron sulfide (FeS) was the ultimate form of the iron. With the advent of x-ray diffraction technique the FeS was found to be in the form of pyrrhotite<sup>3</sup>,  $Fe_{1-x}S$ .

Wright and Severson reported that the addition of iron as contained in the residues from coal liquefaction increased the hydrogen transfer capacity of anthracene oil.<sup>4</sup> Seitzer<sup>5</sup> magnetically separated the iron sulfur compound from coal liquefaction residues and used it as a catalyst in subsequent liquefaction reactions. He found that the magnetically separated material had, per

weight of iron, about the same catalytic effect as ferrous sulfate. Furthermore, he found that the magnetically separated material catalyzed the addition of hydrogen to the dissolved coal.

Moroni and Fischer<sup>6</sup>, who reviewed many papers in the area of coal mineral catalysis, concluded that pyrite was active in coal conversion. Neither the addition of the coal liquefaction residue nor the magnetically separated residue delineated whether pyrrhotite had better catalytic activity than pyrite. A significant amount of work has been done more recently to determine the true catalytic activity of pyrite and pyrrhotite. A detailed summary of literature on pyrite and pyrrhotite catalysis has been made by Garg and Givens.<sup>7</sup>

The distribution of catalyst in the coal appears to be a critical factor in coal conversion. The method of applying the catalyst to the coal affects the catalyst distribution. For example, iron sulfate was shown to be much more effective when impregnated than when mixed mechanically.<sup>2,8</sup> Although prolonged mixing improved the effectiveness of the catalyst, the improvement was less than gained by impregnation. The method of impregnation is also quite important as was shown in one case in which an attempt to impregnate coal in-situ during hydrogenation gave poor results.<sup>8</sup>

A reduction in particle size of the pyrite, reported to play an important role in catalyzing the coal liquefaction reaction, improved the catalytic activity of the pyrite.<sup>9</sup> Significantly more oil production was reported with the use of finely divided pyrite<sup>10</sup> than with hand ground pyrite.<sup>11</sup>

The contact between catalyst and coal can be increased either by adding finely divided catalyst (two to three micron size) or impregnating it on coal using a water soluble compound like iron sulfate or dispersing it at the molecular level in the reaction mixture by using thermally unstable organic compounds like iron naphthenate. In the present paper data are presented which show the catalytic activity of pyrite and impregnated iron sulfate in coal liquefaction. The effect of simple particulate addition of pyrite is compared to catalyst impregnation. The catalytic activity for the coal conversion reactions are related to the product distribution including hydrocarbon gas make, oil, asphaltene and preasphaltene yields, and degree of coal conversion. All of the data reported in this paper refer to results in a continuous 100 pounds per day coal process unit.

## Experimental

**Materials:** Elkhorn #2 was a washed sample taken from a preparation plant in Floyd County, Kentucky. The coal sample was ground to 95% minus 200 mesh particles and dried in air. The coal was screened through a 150 mesh sieve prior to use. The detailed analysis of the screened coal is reported in Table 1.

A 550-850°F cut of SRC-II heavy distillate supplied by The Pittsburg and Midway Coal Mining Company was used as a process solvent. The chemical analysis of the process solvent is shown in Table 2. The solvent contained 93.8% pentane-soluble oils, 5.0% asphaltenes and 0.4% preasphaltenes.

The pyrite sample was received from an operating mine in southwestern Pennsylvania. The sample was dried at 110°C in nitrogen and then ground to 99.9% minus 325 U.S. mesh size in the presence of liquid nitrogen. The chemical analysis of the pyrite is given in Table 3. The sample was comprised of 75%

pyrite, 5% carbonaceous organic material and 20% magnetite, quartz, and other inorganic materials. The BET surface area of the pyrite was 1.0 m<sup>2</sup>/g and the material was relatively non-porous.

Iron sulfate (FeSO<sub>4</sub> · 7H<sub>2</sub>O) was received from Textile Chemical Company, Reading, Pennsylvania. The chemical analysis of the iron sulfate is given in Table 4. The sample contained approximately 97% iron sulfate crystals.

**Equipment:** Process studies were done in a continuous 100 pound/day coal liquefaction unit equipped with a continuous stirred autoclave. The use of a stirred tank reactor insured that solvent vaporization matched that of an actual SRC-1 dissolver and that coal minerals did not accumulate. Since there was no slurry preheater, all of the sensible heat had to be provided by resistance heaters on the reactor. Because of this high heat flux, the reactor wall was about 27°F hotter than the bulk slurry. Multiple thermocouples revealed that the slurry temperature inside the reactor varied by only 9°F from top to bottom. A detailed description of the reactor is presented elsewhere.<sup>12</sup>

The products were quenched to 320°F before flowing to a gas/liquid separator that was operated at system pressure. The slurry was throttled into the product receiver while the product gases were cooled to recover the product water and organic condensate. The product gases were then analyzed by an on-line gas chromatograph.

**Procedure:** Coal liquefaction runs were performed at 825 and 850°F, 2000 psig hydrogen pressure, 1000 rpm stirrer speed, hydrogen feed rate equivalent to 5.5 wt.% of the coal and a superficial slurry space velocity of 1.5 inverse hours. The coal concentration in the feed was 30 wt.%. Iron sulfate was impregnated on the coal by dissolving it in water and mixing it with coal. Impregnated coal sample was dried in nitrogen and ground to minus 200 mesh prior to use. The concentration of impregnated iron was 1.0 wt.% on the basis of coal. The concentration of pyrite was varied from 2.5 to 10 wt.% of feed slurry.

At least 10 reactor volumes of the product were discarded prior to collecting a product sample. A complete sample consisted of one 8-oz. sample of product slurry, one 1-liter sample of product slurry as back-up sample, a light condensate sample and a product gas sample.

The product slurry from the continuous reactor was solvent separated into four fractions: (1) pentane-soluble material (oil), (2) pentane-insoluble and benzene-soluble material (asphaltenes), (3) benzene-insoluble and pyridine-soluble material (preasphaltenes), and (4) pyridine-insoluble material. The latter contains insoluble organic material (IOM) and mineral residue. A detailed procedure for performing this separation will be reported elsewhere. The overall coal conversion is calculated as the fraction of organic material (moisture-ash-free coal) soluble in pyridine.

## Results and Discussions

Effect of Pyrite on Coal Liquefaction - At 825 and 850°F, addition of pyrite increased the coal conversion from ~85 to ~92% (Table 5). The production of hydrocarbon gases, CO + CO<sub>2</sub>, and water, marginally increased with pyrite. Oil production increased by more than a factor of two; 12 to 28% and from 8 to 27%

on addition of pyrite at 825 and 850°F, respectively. Production of preasphaltenes decreased and asphaltenes remained apparently unchanged. The additional converted coal and preasphaltenes with pyrite ended up in the oil fraction. Hydrogen consumption increased from 0.64 to 1.68% and from 0.53 to 2.41% on addition of pyrite at 825 and 850°F, respectively. Also, an additional amount of 0.5% hydrogen was consumed in reducing the added pyrite. X-ray diffraction analysis of coal liquefaction residue showed a complete conversion of pyrite to pyrrhotite. SRC sulfur content remained the same. Oil hydrogen content unchanged in the absence of pyrite but increased in its presence.

In summary, the addition of pyrite to coal during liquefaction improved conversion of coal and preasphaltenes, increased production of oil and hydrocarbon gases, promoted rehydrogenation of the process solvent and increased consumption of hydrogen. Increasing reaction temperature in the presence of pyrite increased conversion of preasphaltenes and increased production of hydrocarbon gases and hydrogen consumption. The conversion of coal and production of oil and asphaltenes marginally decreased with increasing temperature.

Effect of Pyrite Concentration on Coal Liquefaction - Conversion of coal and production of hydrocarbon gases remained the same upon increasing the pyrite concentration from 2.5 to 10 wt. percent. (Table 6, Figures 1 and 2). The production of CO + CO<sub>2</sub>, water and oil shown in Table 6 and Figures 2 and 3 increased slightly as pyrite concentration increased. Asphaltenes remained the same and preasphaltenes decreased with increasing concentration of pyrite (Figure 4). Hydrogen consumption increased significantly as the pyrite concentration increased as shown in Table 6 and Figure 5. SRC sulfur content plotted in Figure 6 also marginally increased. Finally, increasing the concentration of pyrite from 2.5 to 10 wt.% of feed slurry had no significant effect on liquefaction of Elkhorn #2 coal.

Effect of Iron Impregnation on Coal Liquefaction - Conversion of coal was not significantly affected by impregnation at both 825 and 850°F. The production of hydrocarbon gases decreased considerably with iron impregnation while oil production increased by over a factor of two at both temperatures (Table 7). Asphaltene yield was unchanged but preasphaltene yield decreased considerably with iron impregnation. X-ray diffraction analysis of coal liquefaction residue showed a complete conversion of iron sulfate to pyrrhotite. Hydrogen consumption and SRC sulfur content were not significantly affected by iron impregnation. Oil hydrogen content was maintained without any additive but decreased with iron impregnation at both 825 and 850°F. Finally, iron impregnation significantly reduced the hydrocarbon gases and preasphaltenes production and increased the oil production.

Comparison of Iron Impregnated Versus Particulate Addition - The liquefaction of coal impregnated with one wt.% iron based on coal is compared with addition of 3.5 wt% particulate iron in the form of pyrite to coal-oil slurry. Conversion of coal was slightly lower with iron impregnation compared to pyrite addition. Iron impregnation gave significantly lower hydrocarbon gases production and hydrogen consumption (Table 8, Figures 7 and 8). Oil, asphaltenes and preasphaltenes production with iron impregnation were comparable to that obtained by pyrite addition. SRC sulfur content was marginally higher with iron impregnation. Oil hydrogen content was improved with pyrite, whereas it decreased with iron impregnation.

The above data emphasize the importance of the method of catalyst distribution in coal liquefaction. The effectiveness of a metal catalyst can be enhanced significantly by increasing the intimate contact between catalyst and coal. The mode of catalyst distribution therefore determines the amount of catalyst required for the reaction.

### Conclusion

Addition of pyrite significantly catalyzes the coal liquefaction reaction. It improves coal conversion, increases oil and gases production, increases hydrogen consumption and rehydrogenates the process solvent. Changing the concentration of pyrite does not significantly alter the coal liquefaction reaction. Mode of catalyst addition is very important in coal liquefaction. The activity of a catalyst depends on the level of intimate contact of catalyst with coal. Therefore, the concentration of the metal catalyst can be greatly reduced without affecting product distribution by insuring efficient contact between catalyst and coal. The reduction in catalyst loading will eventually increase the overall throughput of the plant, drastically reduce the load in the solid-liquid separation unit, and improve the overall process economics.

### References

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**TABLE 1**  
**CHEMICAL ANALYSIS OF COAL SAMPLE**

	ELKHORN #2 WEIGHT %
<b>ULTIMATE ANALYSIS (AS RECEIVED)</b>	
CARBON	77.84
HYDROGEN	5.24
OXYGEN	7.20
SULFUR	1.08
NITROGEN	1.75
<b>PROXIMATE ANALYSIS (AS RECEIVED)</b>	
ASH	6.29
MOISTURE	1.55
<b>DISTRIBUTION OF SULFUR</b>	
TOTAL SULFUR	1.08
SULFATE SULFUR	0.04
PYRITE SULFUR	0.25
ORGANIC SULFUR	0.79

**TABLE 3**  
**ANALYSIS OF PYRITE**

	WEIGHT %
CARBON	4.48
HYDROGEN	0.34
NITROGEN	0.61
SULFUR	41.34
OXYGEN	5.97
IRON	42.30
OTHER IMPURITIES (BY DIFFERENCE)	4.96
TOTAL	100.00

SURFACE AREA = 1.0 m<sup>2</sup>/g

**TABLE 4**  
**ANALYSIS OF IRON SULFATE**

	WEIGHT %
FERROUS SULFATE, FeSO <sub>4</sub>	53.78
IRON, Fe <sub>2</sub> O <sub>3</sub>	0.06
TITANIUM, TiO <sub>2</sub>	0.33
MAGNESIUM SULFATE, MgSO <sub>4</sub>	1.80
COPPER	0.0004
LEAD	0.0005
WATER OF CRYSTALLIZATION	42.28
TOTAL	99.25

**TABLE 2**  
**ANALYSIS OF HEAVY DISTILLATE**

ELEMENT	WEIGHT %
CARBON	89.44
HYDROGEN	7.21
OXYGEN	1.70
NITROGEN	1.10
SULFUR	0.55
NUMBER AVERAGE MOLECULAR WEIGHT	222

TABLE 5  
LIQUEFACTION OF COAL IN THE PRESENCE AND ABSENCE OF PYRITE

FEED COMPOSITION	70% SOLVENT + 30% COAL		60% SOLVENT + 30% COAL + 10% PYRITE	
	Fe CONC., WT. % COAL	TEMP., °F	Fe CONC., WT. % COAL	TEMP., °F
TEMP., °F	825	850	825	850
PRESSURE, PSIG	2000	2000	2000	2000
RESIDENCE TIME, MIN.	35	39	37	39
HYDROGEN TREAT RATE, MSCF/T	18.9	23.0	19.9	22.5
PRODUCT DISTRIBUTION, WT. % MAF COAL				
HC	5.2	7.0	5.7	10.6
CO, CO <sub>2</sub>	0.7	0.6	0.9	1.2
H <sub>2</sub> S	0.3	0.3	0.0	0.0
OIL	12.2	8.3	28.2	27.0
ASPHALTENES	21.2	21.6	24.3	22.3
PREASPHALTENES	44.2	43.4	29.6	25.6
I.O.M.	14.7	15.7	8.1	9.3
WATER	1.5	3.1	3.2	4.0
CONVERSION, % MAF	85.3	84.3	91.9	90.7
HYDROGEN CONSUMPTION, * WT. % MAF	0.64	0.53	1.68	2.41
OIL HYDROGEN CONTENT, WT. %				
START	7.2	7.2	7.2	7.2
FINISH	7.2	7.2	7.5	7.5
SRC SULFUR, %	0.61	0.55	0.60	0.57

\*HYDROGEN CONSUMPTION DOES NOT INCLUDE THE HYDROGEN REQUIRED FOR REDUCING FeS<sub>2</sub> TO FeS

TABLE 7  
EFFECT OF IRON IMPREGNATION ON COAL LIQUEFACTION

FEED COMPOSITION	70% SOLVENT + 30% COAL		70% SOLVENT + 30% COAL	
	Fe CONC., WT. % COAL	TEMP., °F	Fe CONC., WT. % COAL	TEMP., °F
TEMP., °F	825	850	825	850
PRESSURE, PSIG	2000	2000	2000	2000
RESIDENCE TIME, MIN.	35	37	33	41
HYDROGEN TREAT RATE, MSCF/T	18.9	19.9	20.6	27.3
PRODUCT DISTRIBUTION, WT. % MAF COAL				
HC	5.2	7.0	3.5	4.4
CO, CO <sub>2</sub>	0.7	0.6	0.6	0.5
H <sub>2</sub> S	0.3	0.3	0.2	0.2
OIL	12.2	8.3	25.0	30.3
ASPHALTENES	21.2	21.6	19.1	20.8
PREASPHALTENES	44.2	43.4	35.8	27.5
I.O.M.	14.7	15.7	13.5	13.1
WATER	1.5	3.1	2.3	3.2
CONVERSION, % MAF	85.3	84.3	86.5	86.9
HYDROGEN CONSUMPTION, * WT. % MAF	0.64	0.53	0.40	0.60
OIL HYDROGEN CONTENT, WT. %				
START	7.2	7.2	7.2	7.2
FINISH	7.2	7.2	7.1	7.0
SRC SULFUR, %	0.61	0.55	0.61	0.57

TABLE 8  
IRON IMPREGNATION VERSUS PARTICULAR ADDITION

FEED COMPOSITION	PYRITE		IMPREGNATION	
	Fe CONC., WT. % COAL	TEMP., °F	Fe CONC., WT. % COAL	TEMP., °F
TEMP., °F	850	100	850	100
PRESSURE, PSIG	2000	3000	2000	4100
RESIDENCE TIME, MIN.	35	38	38	41
HYDROGEN TREAT RATE, MSCF/T	24.2	27.3	24.2	27.3
PRODUCT DISTRIBUTION, WT. % MAF COAL				
HC	10.2	10.6	10.2	4.4
CO, CO <sub>2</sub>	0.9	0.9	0.9	0.5
H <sub>2</sub> S	0.3	0.3	0.2	0.2
OIL	25.6	24.3	25.6	30.3
ASPHALTENES	22.3	18.6	22.3	20.8
PREASPHALTENES	28.2	32.3	28.2	27.5
I.O.M.	14.7	15.7	13.5	13.1
WATER	3.2	3.5	3.2	3.2
CONVERSION, % MAF	90.7	89.6	90.7	86.9
HYDROGEN CONSUMPTION, * WT. % MAF	1.75	1.81	1.75	0.80
OIL HYDROGEN CONTENT, WT. %				
START	7.2	7.2	7.2	7.2
FINISH	7.3	7.5	7.3	7.0
SRC SULFUR, %	0.49	0.51	0.49	0.57

\*HYDROGEN CONSUMPTION DOES NOT INCLUDE THE HYDROGEN REQUIRED FOR REDUCING FeS<sub>2</sub> TO FeS

TABLE 6  
EFFECT OF PYRITE CONCENTRATION ON COAL LIQUEFACTION

FEED COMPOSITION	70% SOLVENT + 30% COAL		60% SOLVENT + 30% COAL + 10% PYRITE	
	Fe CONC., WT. % COAL	TEMP., °F	Fe CONC., WT. % COAL	TEMP., °F
TEMP., °F	850	850	850	850
PRESSURE, PSIG	2000	2000	2000	2000
RESIDENCE TIME, MIN.	35	39	37	39
HYDROGEN TREAT RATE, MSCF/T	24.2	22.2	22.5	22.5
PRODUCT DISTRIBUTION, WT. % MAF COAL				
HC	10.2	9.9	10.6	10.6
CO, CO <sub>2</sub>	0.9	0.9	1.0	1.2
OIL	25.6	24.3	27.0	27.0
ASPHALTENES	22.3	18.6	22.3	22.3
PREASPHALTENES	28.2	32.3	28.2	25.6
I.O.M.	14.7	15.7	8.1	9.3
WATER	3.2	3.5	4.0	4.0
CONVERSION, % MAF	90.7	89.6	90.7	90.7
HYDROGEN CONSUMPTION, * WT. % MAF	1.75	1.81	2.41	2.41
OIL HYDROGEN CONTENT, WT. %				
START	7.2	7.2	7.2	7.2
FINISH	7.3	7.5	7.5	7.5
SRC SULFUR, %	0.49	0.51	0.57	0.57

\*HYDROGEN CONSUMPTION DOES NOT INCLUDE THE HYDROGEN REQUIRED FOR REDUCING FeS<sub>2</sub> TO FeS

Figure 1  
Variation in the Conversion of Coal  
With the Concentration of Pyrite

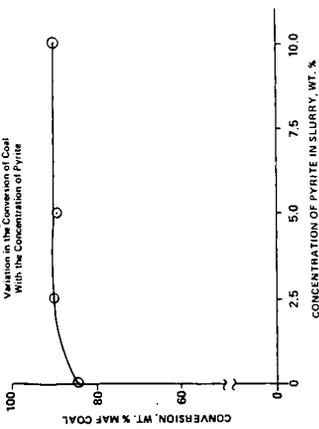


Figure 2  
Variation in the Production of Gases and Water  
With the Concentration of Pyrite

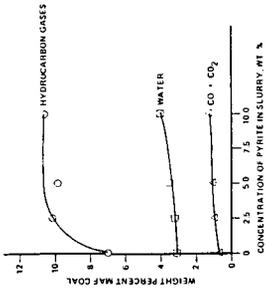


Figure 3  
Variation in the Production of Oils  
With the Concentration of Pyrite

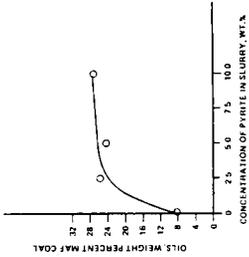


Figure 4  
Variation in the Production of Asphaltenes and Preasphaltenes  
With the Concentration of Pyrite

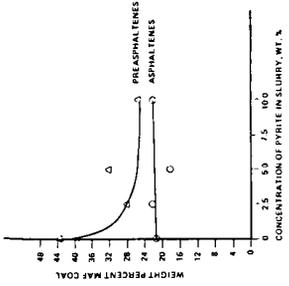


Figure 5  
Variation of Hydrogen Consumption With the  
Concentration of Pyrite

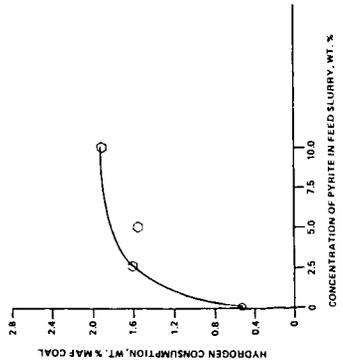


Figure 6  
Variation of SRC Sulfur Content With the Concentration  
of Pyrite

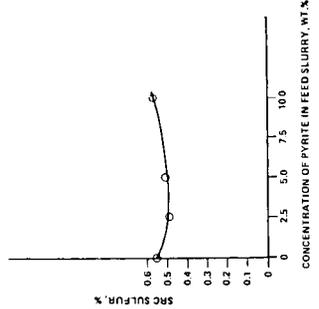


Figure 7  
Iron Impregnation Versus  
Particulate Addition

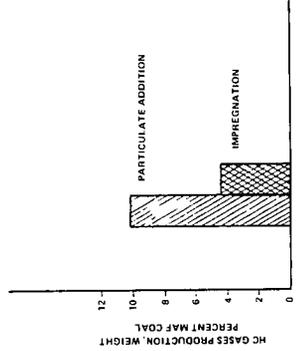


Figure 8  
Iron Impregnation Versus  
Particulate Addition

