

## Relative Activity of Transition Metal Catalysts in Coal Liquefaction

Diwakar Garg and Edwin N. Givens

Corporate Research & Development Department  
Air Products and Chemicals, Inc.  
P.O. Box 538, Allentown, PA 18105

### Abstract

The catalytic activity of transition metals for coal liquefaction was studied and compared. Impregnation of coal with transition metals significantly increased the production of oils and the conversion of asphaltenes and preasphaltenes in coal liquefaction. Overall conversion of coal increased marginally with transition metals. The production of hydrocarbon gases decreased slightly with metals. Iron impregnation was more active in preasphaltenes conversion than cobalt, nickel, and molybdenum; whereas the other metals were more active in asphaltenes conversion than iron. Hydrogen consumption decreased with the use of metals. The quality of generated solvent decreased with iron, whereas it increased with other metals. Significant synergism was observed between iron and molybdenum. Simultaneous impregnation of coal with iron and molybdenum significantly increased the conversion of coal, asphaltenes, and preasphaltenes, and the production of oils compared to individual metals. The mixture of iron and molybdenum also decreased the hydrocarbon gas production over iron and molybdenum alone. In addition, the quality of generated solvent was higher with iron and molybdenum mixture compared to iron alone.

### Introduction

Extensive research has been performed in the areas of catalytic and non-catalytic coal liquefaction. It is well known that in coal liquefaction, high-molecular weight compounds rupture thermally, producing unstable free radicals. These free radicals react with hydrogen donated by hydrogen donor species present in the process solvent to form stable species. Therefore, the presence of sufficient hydrogen donor compounds in the coal liquefaction reaction mixture is necessary to prevent the repolymerization of free radicals thereby aiding the production of lower-molecular-weight oils and asphaltenes. It has been speculated that mineral matter catalyzes the coal liquefaction reaction by enhancing the transfer of hydrogen from the gas to liquid phase thus maintaining the hydrogen donor capability of the process solvent.

The catalytic effect of mineral matter on hydrogenation of model compounds and coal has been investigated by a number of investigators.(1-12) Iron compounds which are abundant both in nature and as an article of commerce were studied extensively. The Germans found that adding iron sulfate and Bayermasse (iron oxide containing material obtained from aluminum manufacture) to feed slurry improved coal liquefaction.(13) Numerous researchers who have studied the catalytic activity of iron as either iron pyrite or pyrrhotite in liquefaction have reported improved results.(14-22)

Like iron, molybdenum and several other transition metal have been shown to catalyze coal liquefaction.(13,23,24,25,26) Since transition metals are both expensive and scarce, their application in liquefaction will depend greatly on their activity at low concentrations. Interestingly, several metals have been shown to be very active in coal liquefaction at very low concentrations.(13,25,26)

In the present paper, the activity of iron, molybdenum, cobalt, and nickel in catalyzing the liquefaction of coal is discussed. The catalytic activity will be related to the product distribution which will include hydrocarbon gas make, oil yield, asphaltene and preasphaltene yields, and degree of coal conversion. The effect of iron and molybdenum mixtures was also studied. All the data reported in this paper refer to results in a continuous 100 pounds per day coal process unit.

### Experimental Section

Materials. A low-ash, low-pyrite Eastern Kentucky Elkhorn #2 coal obtained from a mine in Letcher County was used in the study. The sample was treated in a coal preparation plant to reduce the ash and pyrite contents. This sample was purposely selected to minimize the influence of the coal ash and pyrite on the liquefaction. The coal sample was ground to 95% minus 200 mesh particles, dried in air and screened through a 150 mesh sieve prior to use. The detailed analysis of the screened coal is reported in Table 1.

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, 0.4% preasphaltenes, and 0.8% insoluble organic material (pyridine insolubles). The process solvent contained organic compounds boiling in the range of 550 to 850°F temperature.

Iron sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was received from Textile Chemical Company, Reading, Pennsylvania. The sample contained approximately 97% iron sulfate crystals and minor quantities of iron oxide, titanium dioxide and magnesium sulfate as impurities. Ammonium molybdate, nickel nitrate, and cobalt nitrate were reagent grade materials obtained from Fischer Scientific Company, Fair Lawn, New Jersey.

Metals Impregnation. A sample of coal was impregnated with 1% iron by adding a 10.0% ferrous sulfate solution in distilled water to ground coal. Three different samples of coal were impregnated with 0.02% molybdenum, nickel, and cobalt by mixing the samples with 0.5% ammonium molybdate, nickel nitrate and cobalt nitrate solutions, respectively. Since molybdenum, nickel, and cobalt are very expensive compared to iron, very low concentrations (200 ppm) of these metals based on coal were used. Another sample of coal was impregnated simultaneously with a mixture of 1 wt.% iron and 0.02 wt.% molybdenum based on coal. The impregnated coal samples were dried at 60°C for 72 hours and ground under nitrogen before use in liquefaction experiments.

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 ensured that solvent vaporization matched that of an actual coal liquefaction dissolver and that coal minerals did not accumulate.

Since there was no slurry preheater, all of the sensible heat was 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. (27)

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°F, 2,000 psig hydrogen pressure, 1,000 rpm stirrer speed, hydrogen feed rate equivalent to 5.5 wt. % of coal, and a superficial slurry space velocity of 1.5 inverse hours. The coal concentration in the feed was 30 wt.%.

At least 10 reactor volumes of the product were discarded prior to collecting a product sample. A complete sample consisted of one 8-oz product slurry, one 1-L 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 (asphaltene), (3) benzene-insoluble and pyridine-soluble material (preasphaltene), and (4) pyridine-insoluble material. The latter contains insoluble organic material (IOM) and mineral residue. The overall coal conversion is calculated as the fraction of organic material (moisture-ash-free coal) soluble in pyridine.

## Results and Discussion

Effect of Transition Metals - The impregnation of Elkhorn #2 coal with 1 wt.% iron had no effect on overall coal conversion but increased the production of oils from 12 to 25% (Table 3). The production of hydrocarbon gases decreased with iron; the decrease in the production of hydrocarbon gases is statistically significant at this level. The production of heteroatom gases changed marginally with iron impregnation. The preasphaltene concentration decreased from 44 to 36% with iron impregnation. Hydrogen consumption based on elemental hydrogen balance decreased from 0.6 to 0.4 percent with iron impregnation.

The hydrogen contents of the oil, asphaltene and preasphaltene fractions were lower with iron impregnation compared to the baseline run (Table 4). Apparently the dispersed iron system was not effective in hydrogenating the liquefaction products. This would be advantageous in that expensive hydrogen would not be wasted in hydrogenating SRC (asphaltenes and preasphaltenes), which would be used ultimately as a boiler fuel. The SRC sulfur content was unchanged with iron impregnation. Likewise, the sulfur contents in the various fractions were unaffected with iron (Table 4). Nitrogen content in the oil and asphaltene fractions decreased slightly, whereas it increased in the preasphaltene fraction. The oxygen content of oils decreased slightly, but it increased

significantly in the asphaltene and preasphaltene fractions with iron impregnation. No definite conclusion could be drawn concerning deoxygenation because oxygen content was determined by difference.

The hydrogen distribution in the solvent generated by coal liquefaction was determined by proton NMR to determine the changes in solvent quality by iron impregnation. The hydrogen donor capability of a solvent was measured in terms of the combined concentration of  $H_a$  and  $H_o$ . The higher the combined concentration of  $H_a$  and  $H_o$ , the better would be the quality of the process solvent. Data in Table 5<sup>o</sup> revealed that the hydrogen donor capability of the solvent generated with no catalyst and with iron was lower than that of the original process solvent. The aromatic hydrogen content of solvent increased with both no catalyst and with iron. However, the increase in aromatic hydrogen content was more dramatic with iron. The decrease in the quality of the solvent generated with iron was contrary to the speculation made by several researchers that mineral matter improved coal liquefaction by enhancing hydrogen transfer from gas to liquid. In terms of actual plant operation, a decrease in solvent quality means a decrease in the liquefaction performance. Therefore, the generated solvent has to be hydrogenated externally to increase its hydrogen donor capability and to maintain the liquefaction performance of the iron catalyst.

The impregnation of coal with 0.02 wt.% (200 ppm) cobalt and molybdenum increased the coal conversion slightly. The magnitude of the increase in coal conversion was very similar to that obtained with 1 wt.% iron (Table 3). The coal conversion, however, decreased with nickel impregnation. The production of oils increased significantly from 12 to 20-21% with cobalt, nickel, and molybdenum. The increase was slightly lower than that obtained with iron. The production of hydrocarbon gases was higher with cobalt, nickel and molybdenum than iron but still lower than the base-line run. Preasphaltenes conversion increased with cobalt, nickel, and molybdenum, but it was much lower than that noted with iron. Asphaltenes yield was slightly lower with cobalt, nickel, and molybdenum than iron; asphaltene concentration decreased from 21 to 18 with cobalt, nickel, and molybdenum, whereas it decreased to 19 percent with iron.

Hydrogen consumption based on elemental hydrogen balance was lower with cobalt, nickel and molybdenum compared to baseline run (Table 3). Lower hydrogen consumption was due to lower production of hydrocarbon gases and lower hydrogen contents in the asphaltene and preasphaltene fractions (Table 4). Like iron, other metals were also found to be ineffective in hydrogenating asphaltenes and preasphaltenes. Nitrogen and sulfur contents in various fractions were very similar with and without metals. The hydrogen contents of the oil fractions obtained with metals were similar to the base-line run except for nickel (Table 4).

The quality of solvent generated with cobalt, nickel and molybdenum was higher than that generated either with iron or without metals (Table 5). The concentration of  $H_{AR}$  decreased and that of  $H_a$  and  $H_o$  either increased or maintained with cobalt, nickel and molybdenum. The increase in the quality of generated solvent is an indicative of enhancement of hydrogen transfer from gas to liquid phase with cobalt, nickel and molybdenum catalysts.

The above discussion showed that the impregnation of Elkhorn #2 coal with metals significantly increased oils production, increased preasphaltene conversion and decreased hydrocarbon gas make. The metals, however, did not change SRC sulfur content.

Comparing the activity of iron to that of other metals, it was found that iron impregnation yielded higher oils production and preasphaltenes conversion than other metals. However, other metals were more active in asphaltene conversion than iron. The hydrogen content of generated solvent decreased with iron and nickel, whereas it was maintained with cobalt and molybdenum. The quality of generated solvent decreased with iron, but it increased with other metals.

Interaction of Metals in Coal Liquefaction - To utilize the selective activity of iron for the conversion of preasphaltenes and of other metals for the conversion of asphaltene, a sample of coal impregnated simultaneously with iron and molybdenum was liquefied. The conversion of both asphaltene and preasphaltenes increased with iron/molybdenum mixture compared to iron and molybdenum alone (Table 6). In addition, oils production increased significantly with the mixture compared to iron and molybdenum alone. Iron and molybdenum together not only increased oils production and asphaltene and preasphaltenes conversion but also significantly increased the overall coal conversion from 87 to 91%. The production of hydrocarbon gas was lower with mixture than either alone. The SRC sulfur content changed slightly, but the change was within the limits of experimental error. These increase in coal conversion, oils production and asphaltene and preasphaltenes conversion indicated a significant synergistic effect of the two metals.

Hydrogen consumption with the iron/molybdenum mixture was higher than molybdenum and iron alone (Table 6). The hydrogen content of the various fractions generated with iron/molybdenum mixture was very similar to that obtained with iron and molybdenum alone (Table 7). No significant differences were noted in the nitrogen and oxygen contents in the various fractions generated with iron and molybdenum alone or used together except for slightly lower nitrogen content noted in preasphaltene fraction obtained with iron/molybdenum mixture. The quality of solvent generated with iron/molybdenum mixture was higher than iron alone, but was lower than that obtained with molybdenum alone (Table 8).

The above discussion shows that a synergism exists between iron and molybdenum in the catalysis of coal liquefaction reaction. This synergism can be effectively utilized to increase the oils production and the conversion of asphaltene and preasphaltenes. Furthermore, the increase in oil production can be obtained without significantly increasing hydrogen consumption by taking advantage of synergistic effect. The combination of iron and molybdenum, however, is ineffective in reducing SRC sulfur content.

### Conclusion

The impregnation of coal with transition metals like iron, cobalt, nickel, and molybdenum increases the oils production by increasing the asphaltene and preasphaltene conversion. Metals impregnation also help in improving overall coal conversion except for nickel. The production of hydrocarbon gases decreases with metals. Likewise, hydrogen consumption decreases with metals. Iron is more active for the conversion of preasphaltenes and the production of oils than other metals, where s it is less active for the conversion of asphaltene.

These differences may partly be due to the use of higher concentration of iron than other metals. Since iron is rather inexpensive compared to other metals, it is economically feasible to use higher concentration. On the other hand, it is not economically feasible to use higher concentration (greater than 200 ppm) of other metals. Simultaneous impregnation of coal with iron and molybdenum shows significant synergism in coal liquefaction. The conversion of coal, asphaltenes, and preasphaltenes and the production of oils are much greater with iron/molybdenum mixture than either of them alone. The mixture also results in lower hydrocarbon gas make than iron and molybdenum alone. The mixture, however, is ineffective in reducing the SRC sulfur content.

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Table 1

Chemical Analysis of Elkhorn #2 Coal Sample

|                               | Weight % |
|-------------------------------|----------|
| Carbon                        | 77.84    |
| Hydrogen                      | 5.24     |
| Oxygen                        | 7.20     |
| Sulfur                        | 1.08     |
| Nitrogen                      | 1.75     |
| Moisture                      | 1.55     |
| Dry Ash                       | 6.29     |
| <u>Distribution of Sulfur</u> |          |
| Total                         | 1.08     |
| Sulfate                       | 0.04     |
| Pyrite                        | 0.25     |
| Organic                       | 0.79     |

Table 2

Analysis of SRC-II Heavy Distillate

| Element  | Weight % |
|----------|----------|
| Carbon   | 89.4     |
| Hydrogen | 7.2      |
| Oxygen   | 1.7      |
| Nitrogen | 1.1      |
| Sulfur   | 0.6      |

Table 3

Effect of Transition Metals on Coal Liquefaction

|  | None  | Iron                   | Cobalt | Nickel | Molybdenum |
|--|-------|------------------------|--------|--------|------------|
| Catalyst Metal Concentration, wt. % Coal | -     | 1.0                    | 0.02   | 0.02   | 0.02       |
| Feed Composition                         |       | 70% Solvent + 30% Coal |        |        |            |
| Temperature, °F                          | 825   | 825                    | 825    | 825    | 825        |
| Pressure, psig                           | 2,000 | 2,000                  | 2,000  | 2,000  | 2,000      |
| Hydrogen Flow Rate, MSCF/T               | 18.9  | 20.6                   | 23.8   | 23.8   | 23.7       |
| Reaction Time, Min.                      | 35    | 32.8                   | 36.7   | 37     | 36.5       |
| Product Distribution, wt. % MAF Coal     |       |                        |        |        |            |
| HC                                       | 5.2   | 3.5                    | 3.8    | 4.8    | 4.1        |
| CO, CO <sub>2</sub>                      | 0.7   | 0.6                    | 0.7    | 0.7    | 0.7        |
| H <sub>2</sub> S                         | 0.3   | 0.2                    | 0.4    | 0.6    | 0.6        |
| Oils                                     | 12.2  | 25.0                   | 21.5   | 20.0   | 21.7       |
| Asphaltenes                              | 21.2  | 19.1                   | 17.7   | 17.0   | 17.6       |
| Preasphaltenes                           | 44.2  | 35.8                   | 40.2   | 38.5   | 40.3       |
| I.O.M.                                   | 14.7  | 13.5                   | 14.3   | 16.5   | 13.7       |
| Water                                    | 1.5   | 2.3                    | 1.4    | 1.9    | 1.8        |
| Conversion                               | 85.3  | 86.5                   | 85.7   | 83.7   | 86.8       |
| Hydrogen Consumption, Wt. % MAF Coal     | 0.64  | 0.40                   | 0.39   | 0.33   | 0.40       |
| SRC Sulfur, %                            | 0.6   | 0.6                    | 0.6    | 0.5    | 0.6        |

Table 4

Distribution of Elements in Various Liquefaction Reaction Fractions

| Catalyst                      | None | Iron | Cobalt | Nickel | Molybdenum |
|-------------------------------|------|------|--------|--------|------------|
| Oil Fraction, wt. %           |      |      |        |        |            |
| C                             | 89.5 | 89.9 | 89.6   | 89.8   | 89.5       |
| H                             | 7.2  | 7.1  | 7.2    | 7.1    | 7.2        |
| O <sup>a</sup>                | 1.7  | 1.5  | 1.7    | 1.7    | 1.7        |
| N                             | 0.9  | 0.8  | 0.8    | 0.8    | 0.9        |
| S                             | 0.7  | 0.7  | 0.7    | 0.6    | 0.7        |
| Asphaltene Fraction, wt. %    |      |      |        |        |            |
| C                             | 85.9 | 85.6 | 85.6   | 85.0   | 85.3       |
| H                             | 6.3  | 6.0  | 5.8    | 5.9    | 5.9        |
| O <sup>a</sup>                | 4.8  | 5.5  | 5.7    | 6.2    | 6.0        |
| N                             | 2.4  | 2.4  | 2.3    | 2.4    | 2.2        |
| S                             | 0.6  | 0.5  | 0.6    | 0.5    | 0.6        |
| Preasphaltene Fraction, wt. % |      |      |        |        |            |
| C                             | 85.3 | 82.9 | 83.5   | 83.6   | 83.4       |
| H                             | 5.2  | 4.9  | 4.7    | 4.6    | 5.1        |
| O <sup>a</sup>                | 6.2  | 8.9  | 8.9    | 9.0    | 8.3        |
| N                             | 2.2  | 2.6  | 2.3    | 2.3    | 2.6        |
| S                             | 0.6  | 0.7  | 0.6    | 0.5    | 0.6        |

<sup>a</sup> Oxygen is determined by difference.

Table 5

Distribution of Protons in the Oil Fraction

| Catalyst              | Process Solvent | Generated Solvent |      |        |        |            |
|-----------------------|-----------------|-------------------|------|--------|--------|------------|
|                       |                 | None              | Iron | Cobalt | Nickel | Molybdenum |
| Total Hydrogen, wt. % | 7.2             | 7.2               | 7.1  | 7.2    | 7.1    | 7.1        |
| H <sub>AR</sub>       | 3.20            | 3.26              | 3.64 | 2.90   | 2.88   | 2.75       |
| H <sub>a</sub>        | 2.02            | 1.95              | 1.80 | 2.12   | 2.24   | 2.32       |
| H <sub>o</sub>        | 1.98            | 1.99              | 1.66 | 2.18   | 1.97   | 2.13       |

H<sub>AR</sub> = concentration of aromatic protons

H<sub>a</sub> = concentration of alpha protons defined as protons on carbon atoms immediately adjacent to an aromatic ring.

H<sub>o</sub> = concentration of beta and higher protons defined as those protons residing on two or more carbon atoms removed from an aromatic ring.

Table 6

Synergistic Effect in Coal Liquefaction

| Catalyst<br>Metal Concentration,<br>wt.% coal | Iron<br>1.0            | Molybdenum<br>0.02 | Iron + Molybdenum<br>1.0 iron + 0.02<br>molybdenum |
|---|------------------------|--------------------|--|
| Feed Composition                              | 70% Solvent + 30% Coal |                    |  |
| Temperature, °F                               | 825                    | 825                | 825  |
| Pressure, psig                                | 2,000                  | 2,000              | 2,000  |
| Hydrogen Flow Rate, MSCF/T                    | 20.6                   | 23.7               | 23.4   |
| Reaction Time, Min                            | 32.8                   | 36.5               | 37.2   |
| Product Distribution, wt.% MAF Coal           |                        |                    |  |
| HC  | 3.5                    | 4.1                | 3.1  |
| CO, CO <sub>2</sub>                           | 0.6                    | 0.7                | 0.7  |
| H <sub>2</sub> S                              | 0.2                    | 0.6                | 0.6  |
| Oils  | 25.0                   | 21.7               | 36.3   |
| Asphaltenes                                   | 19.1                   | 17.6               | 15.2   |
| Preasphaltenes                                | 35.8                   | 40.3               | 33.0   |
| I.O.M.  | 13.5                   | 13.7               | 9.3  |
| Water   | 2.3                    | 1.8                | 1.8  |
| Conversion                                    | 85.6                   | 86.8               | 90.7   |
| Hydrogen Consumption,<br>wt.% MAF Coal        | 0.4                    | 0.40               | 0.59   |
| SRC Sulfur, %                                 | 0.6                    | 0.6                | 0.7  |

Table 7

Distribution of Elements in Various Liquefaction Fractions

| Catalyst<br>Oil Fraction, % | Iron | Molybdenum | Iron • Molybdenum |
|-----------------------------|------|------------|-------------------|
| C                           | 89.9 | 89.5       | 89.8              |
| H                           | 7.1  | 7.2        | 7.2               |
| O <sup>a</sup>              | 1.5  | 1.7        | 1.6               |
| N                           | 0.8  | 0.9        | 0.8               |
| S                           | 0.7  | 0.7        | 0.6               |
| Asphaltene Fraction, %      |      |            |                   |
| C                           | 85.6 | 85.3       | 85.1              |
| H                           | 6.0  | 5.9        | 5.9               |
| O <sup>a</sup>              | 5.5  | 6.0        | 6.0               |
| N                           | 2.4  | 2.2        | 2.4               |
| S                           | 0.5  | 0.6        | 0.6               |
| Preasphaltene Fraction, %   |      |            |                   |
| C                           | 82.9 | 83.4       | 83.7              |
| H                           | 4.9  | 5.1        | 4.9               |
| O <sup>a</sup>              | 8.9  | 8.3        | 8.4               |
| N                           | 2.6  | 2.6        | 2.3               |
| S                           | 0.7  | 0.6        | 0.7               |

<sup>a</sup> Oxygen is determined by difference.

Table 8

Distribution of Protons in the Oil Fraction

| Catalyst<br>Total Hydrogen, wt.% | Iron | Molybdenum | Iron + Molybdenum |
|----------------------------------|------|------------|-------------------|
|                                  | 7.1  | 7.2        | 7.2               |
| H <sub>AR</sub>                  | 3.64 | 2.75       | 2.92              |
| H <sub>a</sub>                   | 1.80 | 2.32       | 2.15              |
| H <sub>o</sub>                   | 1.66 | 2.13       | 2.13              |

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