

## USE OF CATION-EXCHANGE TO PRODUCE HIGHLY DISPERSED IRON CATALYSTS IN LOW RANK COALS

M. Mehdi Taghiei, F. E. Huggins, B. Ganguly, and G. P. Huffman  
IMMR/CFCLS, University of Kentucky, Lexington, KY, 40506.

### Abstract

A significant enhancement of both liquefaction yields and desirable products from two lignites has been achieved by incorporating iron in the lignites by an ion-exchange process. At 5-8% iron content, total conversions approached 88% and oil yields were about 45% compared to 62% total conversion and 33% oil yield for the raw coal. The effect of catalyst loading on cation-exchanged lignites was studied to determine the concentration that results in the optimum oil yield.  $^{57}\text{Fe}$  Mössbauer and XAFS spectroscopies were used to characterize the catalyst structure and size distribution in the iron cation-exchanged lignites before and after liquefaction. The results indicate that the added iron is initially present in bimodal form, with most present as highly dispersed goethite ( $\alpha\text{-FeOOH}$ ) particles, 50-100Å in diameter, but with a significant fraction (about 30%) of the iron in particles less than 30Å in diameter, which may represent molecularly dispersed ferric ions at the ion-exchange (carboxyl) sites. With sufficient sulfur present in the system, the iron is rapidly transformed to pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) during liquefaction.

### Introduction

A number of studies<sup>1-3</sup> have been conducted on the activity of various iron-based catalysts during liquefaction of coals of different rank. Recent research<sup>4</sup> has shown that sulfated iron catalysts can significantly enhance the conversion yield of high-rank coals. However, for lower rank coals, the improvement in conversion yield through the addition of similar sulfated catalysts has not yet been achieved. The oxygen contents of low-rank coals such as lignites are significantly higher than those of high-rank coals, and as a result, oil yields from liquefaction of low-rank coals tend to be low due to  $\text{CO}_2$  formation. A considerable portion of this oxygen derives from carboxyl groups and other oxygen functional groups. In low-rank coals, most of the exchangeable cations are associated with carboxyl groups, and a number of studies<sup>5,6</sup> have shown that the behavior of lignites in coal conversion processes is greatly affected by the amount and type of exchangeable cations present.

The results of this study indicate that iron ion-exchanged into the low-rank coals constitutes a catalyst in a state of dispersion ranging from molecular ions to particles a few nanometers in diameter. Superparamagnetic modeling of Mössbauer spectra<sup>7</sup> indicates that the iron particle size in a high-iron loaded lignite has a bimodal character, with the majority of the particle sizes ranging from 50 to 115Å in goethite form, but with a significant fraction (about 30%) less than 30Å, which may derive from ferric cations in ion-exchange sites bound to the oxygen anions of carboxyl groups. The direct coal liquefaction (DCL) total conversion and oil yields of the iron ion-exchanged Beulah and Hugel lignites used in this work were enhanced significantly compared to the raw lignites.

## Experimental

The two lignites used in this study are Beulah (obtained from Dept. of Energy Coal Sample, DECS-11) and Hagel (obtained from Pen. State Office of Coal, PSOC-1482) from the Fort Union region in North Dakota. The original iron contents of these lignites are less than 0.5 percent. The ion-exchange experiments were carried out in a 10 liter fermenter using a freshly made 0.05M aqueous solution of ferric acetate at a controlled pH of about 2.8 and a constant temperature of 60°C. The iron contents of the Beulah and Hagel lignites after the ion-exchange process were 7.8% and 5.33%, respectively. The efficiency of lower loadings (~1 wt%) of iron in the ion-exchanged lignites during liquefaction was also investigated.

### Liquefaction Experiments:

Two sets of coal liquefaction experiments were conducted. The first set of experiments was carried out with tubing bombs in a fluidized sand bath. This set of experiments was designed to investigate the effect of iron catalysts on the total yield and product distribution in the liquefaction process. The tubing reactor was first charged with a slurry mixture of lignite and tetralin in a 1:2 ratio in the presence of dimethyl disulfide (DMDS) as a sulfur donor, and pressurized to 800 psi (cold) with hydrogen. Control liquefaction experiments, using slurry mixtures of the same lignite samples with a 30Å iron oxide and with no catalyst, were run under the same conditions to compare the catalytic effects of an ultrafine particle iron oxide with those obtained for the ion-exchange catalyst. The products were separated into THF insoluble organic materials (IOM), THF soluble, toluene insoluble (preasphaltene), toluene soluble, pentane insoluble (asphaltene), and pentane soluble (oil and gas) fractions. The soluble product percentage yields were calculated on a dry, ash-free (daf) basis as follows:

$$\text{Percentage soluble products} = \frac{\text{total soluble products}}{\text{daf lignite}} \times 100$$

Pentane solubles were determined by subtracting the sum of asphaltenes, preasphaltenes and the IOM residue from the weight of the starting lignite. The results were reproducible within ±2%.

The second set of experiments was designed to generate larger samples for the detailed characterization of the chemical structure and reactions of the added iron. The apparatus used to prepare the samples for these experiments was an one liter autoclave. This autoclave was connected at the top to a vessel for holding the sample prior to heating. At the bottom, four nitrogen-purged sampling lines were attached to the outlet valve of the autoclave to collect the liquefaction products directly from the autoclave without exposure to air. Liquefaction experiments in the autoclave were performed at 385°C and 400°C under 1500 psi of hydrogen pressure (cold) in the presence of excess tetralin (tetralin:coal 3:1) and dimethyl disulfide (DMDS) as a sulfur donating species.

### Mössbauer and XAFS Spectroscopies:

Mössbauer spectra for the as-received, demineralized, and ion-exchanged lignite samples were obtained using a conventional constant-acceleration-type Mössbauer spectrometer<sup>8</sup>. The samples were run at several temperatures to determine the size distribution. Calculation of the particle size distribution is described in detail elsewhere<sup>7</sup>. XAFS measurements were performed at beam line X-19A at the National Synchrotron Light Source in Brookhaven National Laboratory. Iron K-edge XAFS spectra of the samples were obtained in transmission mode using a Si(111) double crystal monochromator.

### Results and Discussion

The effect of iron concentration on liquefaction yields of Beulah and Hagel coal is shown in Figure 1. It can be seen that the asphaltene and oil conversion yields increased significantly for both ion-exchanged lignites compared to the raw coals. The preasphaltene yields, however, tend to decrease as a result of catalyst addition to the lignite. We have also compared the results obtained using a physically added 30Å iron oxyhydroxide catalyst to those obtained using cation-exchanged iron at approximately the same concentrations. The 30Å iron oxyhydroxide catalyst was provided by Mach I Inc., and its interesting structural properties are discussed in several forthcoming publications<sup>9,10</sup>. It is evident from Figure 1 that the ion-exchanged iron is a more active catalyst than the 30Å iron oxide.

Mössbauer and XAFS spectroscopies were used to characterize the structure of the cation-exchanged iron both before and after DCL. The characterization of iron-based DCL catalysts by Mössbauer and XAFS spectroscopies has been discussed in detail elsewhere<sup>11</sup>. The Mössbauer spectra of the Beulah and Hagel lignites containing cation-exchanged iron are shown in Figures 2 and 3, respectively. The spectra are fit with one or several magnetic components and quadrupole doublets (peak positions denoted by bar diagrams), and a superparamagnetic relaxation component (dashed curve). As discussed by Ganguly et al.<sup>7</sup>, at a given temperature, particles with diameter less than some critical value will give rise to a quadrupole doublet, particles with a diameter greater than some larger critical value will exhibit a six-peak magnetic hyperfine spectrum, and particles with diameters between these two values will give rise to superparamagnetic spectra. Approximate size distributions can be determined by measuring the percentages of these three components as a function of temperature and the size distribution determined in this manner for the cation-exchanged Hagel lignite with 5.33% Fe is shown in Figure 4. It is seen that the size distribution is bimodal, with approximately 70% of the particles in the 50-100Å size range, and 30% having diameters less than 30Å. Much of the iron in the latter size category may in fact be ferric iron that is molecularly dispersed and bonded to oxygen anions of the carboxyl groups in the lignite, whereas, the larger particles result from hydrolysis of either iron acetate or ion-exchanged iron to form goethite. The low-iron cation-exchanged coals exhibit similar Mössbauer spectra, but a detailed study of the temperature dependence of the superparamagnetic relaxation spectra has not yet been completed. Nevertheless, it is evident that most of the iron in these samples is contained in iron oxyhydroxide particles less than 100Å in diameter, and a significant percentage of the iron is present in the less than 30Å diameter size category.

Both the x-ray absorption near edge structure (XANES) and the radial structure function (RSF) derived from the iron K-edge XAFS spectra of the iron loaded lignites exhibit significant size related effects. Typical results are shown in Figure 5. The XANES of the Hagel lignite sample is compared to that of bulk goethite in Figure 5a, while the corresponding RSF are compared in Figure 5b. It is seen that the XANES of the iron loaded Hagel lignite sample and goethite are quite similar, with the exception of an increase in the intensity of the small pre-edge peak. This occurs because the surface iron atoms of ultrafine ferric oxide particles are no longer in centrosymmetric octahedral coordination, but in reduced coordination number sites, which cause the intensity of the pre-edge ( $1s \rightarrow 3d$ ) transition to increase. The RSF of the Hagel lignite sample and goethite exhibit similar peaks, but the peaks corresponding to the iron shell are decreased in amplitude for the iron in the lignite, consistent with a small particle size<sup>11</sup>.

Further studies are in progress (i) to determine the structure and size distribution of the cation-exchanged iron as a function of concentration, both before and after liquefaction, (ii) to investigate the use of the cation-exchange process for preparation of small particle metal oxides containing Mo, Co, Al, Ni, etc., and (iii) to evaluate the potential of these ion-exchange catalysts for lignite liquefaction.

#### Acknowledgement

This research was supported by the U.S. Department of Energy through DoE contract No. DE-FC22-90-PC90029 as part of the research program of the Consortium for Fossil Fuel Liquefaction Science.

#### References:

- 1- Herrick, D. E.; Tierney, J. W.; Wender, I.; Huffman, G. P.; Huggins, F. E. *Energy & Fuels* **1991**, *4*, 231.
- 2- Tanabe, K.; Yamaguchi, T.; Hattori, H.; Sanada, Y.; Yokoyama, S. *Fuel Proc. Technol.* **1984**, *8*, 117.
- 3- Cook, P.S.; Cashion, J. D. *Fuel* **1987**, *66*, 661.
- 4- Pradhan, V. R.; Tierney, J. W.; Wender, I.; Huffman, G. P. *Energy & Fuels* **1991**, *5*, 497.
- 5- Matsumoto, S.; Walker Jr., P. L. *Carbon* **1986**, *25*, 277.
- 6- Linares-Solano, A.; Hippo, E. J.; Walker Jr., P. L. *Fuel* **1986**, *65*, 776.
- 7- Ganguly, B.; Huggins, F. E.; Rao, K. R. P. M.; Huffman, G. P. *J. Catalysis*, **submitted**.
- 8- Huffman, G. P. *Chemtech.* **1980**, *10*, 504.
- 9- Ganguly, B.; Huggins, F. E.; Feng, Z.; Huffman, G. P. *Phys. Rev.*, **submitted**.
- 10- Zhao, J.; Huggins, F. E.; Feng, Z.; Lu, F.; Shah, N.; Huffman, G. P., *J. Catalysis*, **submitted**.
- 11- Huffman, G. P.; Ganguly, B.; Zhao, J.; Rao, K. R. P. M.; Shah, N.; Feng, Z.; Huggins, F. E.; Taghiei, M. M.; Lu, F.; Wender, I.; Pradhan, V. R.; Tierney, J. W.; Seehra, M. S.; Ibrahim, M. M.; Shabtai, J. S.; Eyring, E. M., *Energy & Fuels* **1992**, in press.

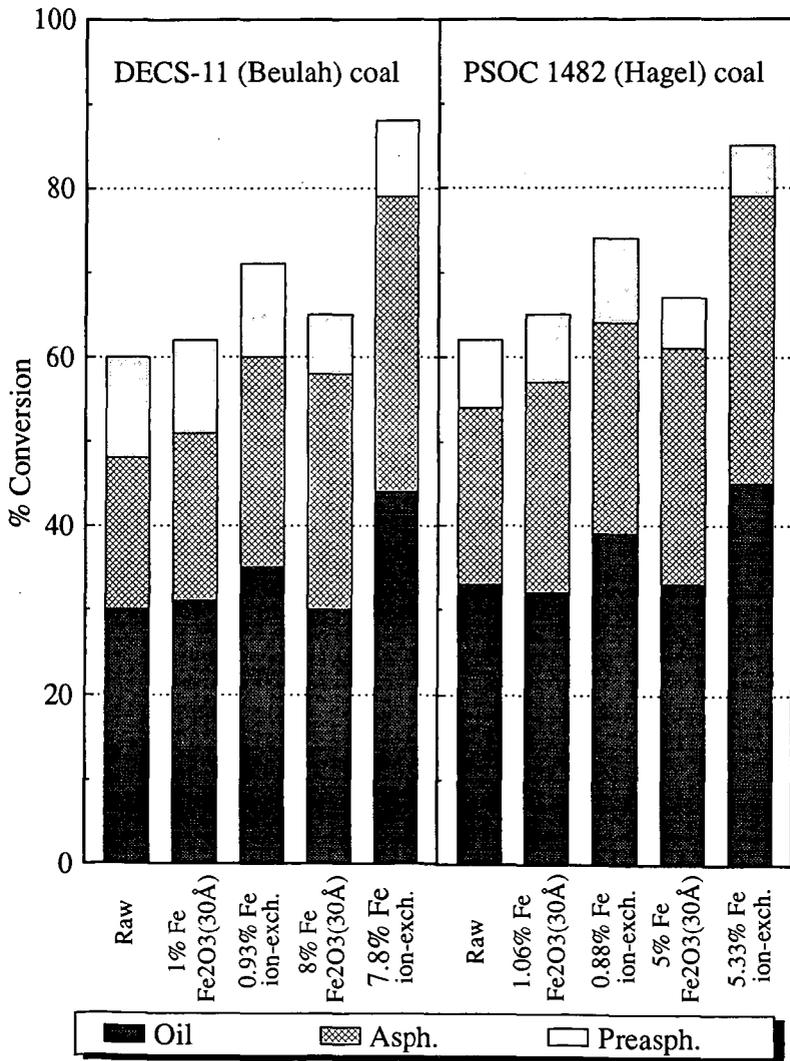


Figure 1. Comparison of liquefaction product yield for Beulah and Hagel lignites

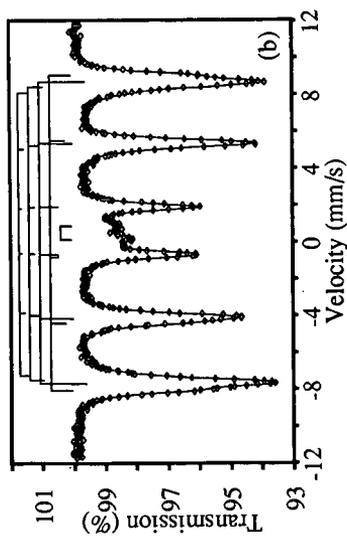
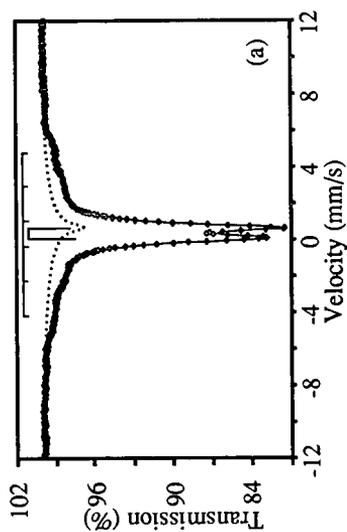


Figure 2. Mössbauer spectra of ion-exchanged Beulah lignite with 7.8% iron, (a) at room temperature, (b) at 12K.

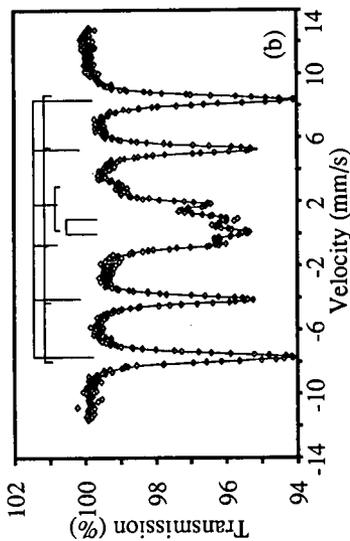
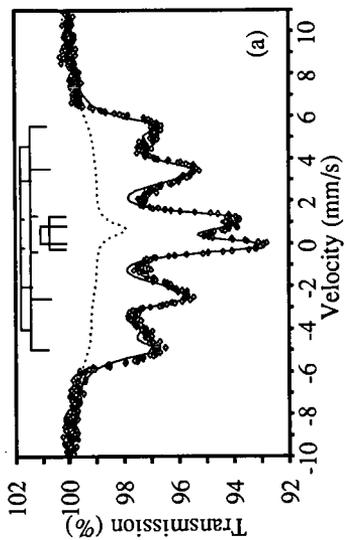


Figure 3. Mössbauer spectra of ion-exchanged Hagel lignite with 5.33% iron, (a) at room temperature, (b) at 12K.

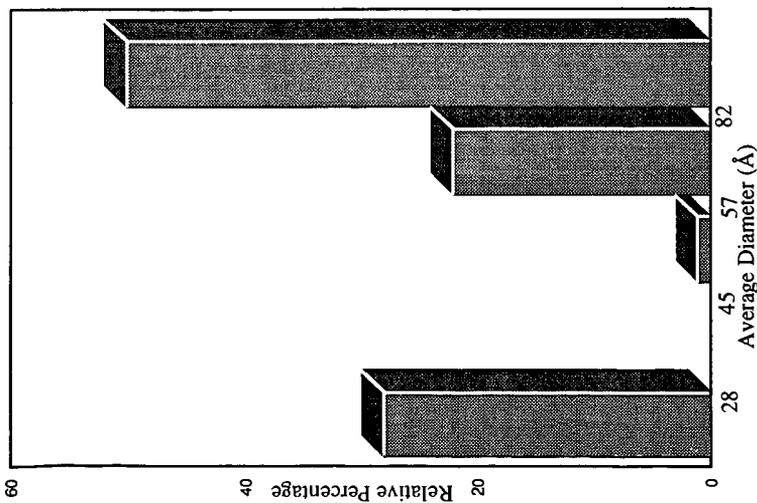


Figure 4. Size distribution of iron species in Hagel lignite containing 5.33 wt% iron.

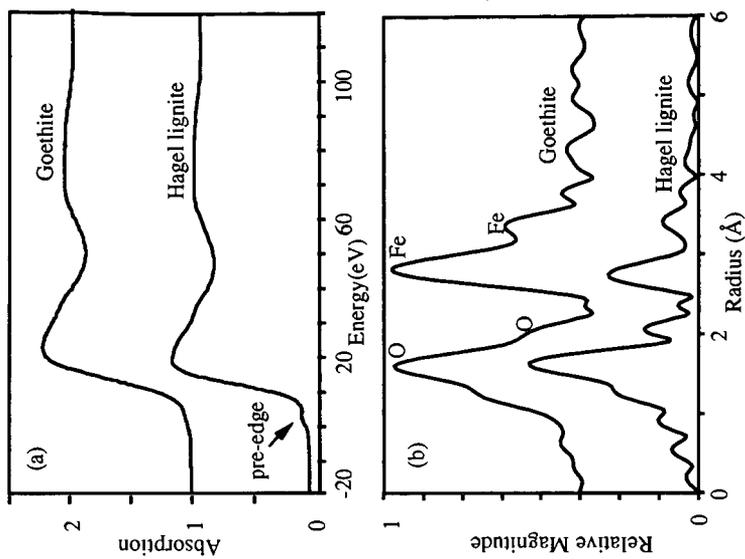


Figure 5. Comparison of iron K-edge (a) XANES, and (b) RSF of bulk goethite and iron loaded Hagel lignite.