

THE COMPARISON OF A LIGNITE CHAR, SUBBITUMINOUS COAL CHAR, AND A BITUMINOUS COAL CHAR USED IN THE REACTION WITH STEAM TO PRODUCE HYDROGEN.

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ABSTRACT

The use of coal as a carbon source in the char-steam reaction to produce hydrogen gas over the temperature range 700°-800°C (973-1073 K) at atmospheric pressure has been studied in detail. Velva lignite has properties which give its char superior reactivity over those of the other coals tested. Catalysis with alkali carbonates enhanced the reactivity of Velva char substantially, whereas demineralization reduced the reactivity to a relatively constant value over the temperature range studied by removing inorganic material and altering the surface characteristics of the coal. Char produced from a Wyodak subbituminous coal and River King bituminous coal were much less reactive than Velva in the absence of catalyst but responded positively to the addition of alkali carbonates. Upon demineralization, these coals also showed reduced reactivity and altered surface features. This paper discusses the results of the experiments in terms of the reactivity data, SEM photos and elemental mapping, organic properties as determined from <sup>13</sup>C NMR and ESCA spectroscopy, and inorganic content of the substrates.

INTRODUCTION

The bench-scale production of hydrogen at atmospheric pressure and moderate temperatures (700°-800°C) from the uncatalyzed and catalyzed reaction of low-rank coal char and steam has been studied extensively at the University of North Dakota Energy and Mineral Research Center (UNDEMRC). The gasification process focuses on utilizing the gasification and the water-gas shift reactions at these conditions to optimize hydrogen production. The limiting step in the process at these conditions is the char-steam reaction (1).

Although the low-rank coals that have been tested exhibit somewhat different reactivities from one another, they are generally more reactive than those of higher rank.(2) The reasons for the differences in reactivity within a rank remain controversial. However, surface area as it relates to turnover number, and the presence of specific catalytic inorganic materials, are certain to play a role in enhancing or retarding reaction rate. Similarly, the decrease in reactivity with increasing rank may be the result of one or both of these, along with the increasing aromatic nature of the coal. This study examined some of the similarities and differences in the chemical properties between representatives of the three ranks, that is, lignite, subbituminous and bituminous coals.

The selection of test coals for this study was based on previous gasification performance as determined from the char reactivity data base at UNDEMRC. One of the test coals that was known to gasify readily was a lignite from the Velva, North Dakota, coal mine. This coal has been extensively studied at UNDEMRC as a feedstock for the hydrogen production process. These studies indicate that this coal is an excellent candidate for use in the gasification process and is

currently being used as a basis for comparing other candidate coals. The subbituminous coal selected was likewise a much-studied Wyodak coal from Wyoming. Although Wyodak reacts more slowly in the bench-scale tests than the Velva lignite, its reactivity is greatly enhanced when the reaction is catalyzed by an alkali catalyst. The bituminous coal was the unwashed high-ash Illinois #6 coal.

## EXPERIMENTAL

The reactions between the coal chars and steam were studied with two different Thermogravimetric Analysis (TGA) systems. The kinetic study of weight change of carbon with time for the char-steam reaction was carried out on a DuPont 951 Thermogravimetric Analyzer (TGA) interfaced with a DuPont 1090 Thermal Analyzer.

Approximately 30 mg samples of -100 x +140 mesh as-received or demineralized coal, or as-received coal containing  $K_2CO_3$  catalyst, were devolatilized under argon flowing at 160 cc/min. The resulting char was then reacted with steam ( $p_{H_2O}=0.1$ ) for a period not exceeding 180 minutes. Weight, time, and temperature data were recorded for the duration of the experiment. Total gas (product gas plus carrier gas) samples were collected over the duration of the run and were analyzed by gas chromatography (GC).

Selected experiments were duplicated on an UNDEMRC-built large TGA (1) so that large gas samples could be collected, ensuring a more accurate gas analysis. Reactivity parameters, (k), were calculated at each of three temperatures (T) and Arrhenius plots of  $\ln k$  vs  $1/T$  were constructed for calculating energy of activation ( $E_a$ ) and frequency factor, (A), as previously described.(3)

Char analyzed by spectroscopic techniques was prepared as in the char-steam reaction experiments, but was cooled to room temperature under argon. These samples were analyzed by Electron Spectroscopy for Chemical Analysis (ESCA) and 50 MHz solid  $^{13}C$  Nuclear Magnetic Resonance Spectrometry (NMR). The NMR technique used on the samples was an adaptation of the Bloch Decay technique in which no cross-polarization with hydrogen and no proton decoupling was used (4). Instead, the  $^{13}C$  spins were polarized directly rather than from rapidly relaxing hydrogen nuclei, thus removing the question of the quantitative nature of cross-polarization in hydrogen deficient species.(5) All spectra were obtained using the same pulsing parameters and TOSS was used to eliminate spinning sidebands. Samples of each char were examined by Scanning Electron Microscopy (SEM) to determine surface elemental distribution and to obtain photographs of the char surface. The field was scanned and representative particles were photographed and mapped to determine the elemental distribution.

## RESULTS AND DISCUSSION

There are several significant similarities and differences between the coals used in this study. Two of the basic differences in the coals used in this study were their rank and their geographical origins. The Velva lignite is a northern Great Plains lignite from a mine near Velva, North Dakota. The Wyodak subbituminous coal was from the Green River Basin in Wyoming. The Illinois #6 was a bituminous coal obtained from the River King mine in southern Illinois.

Proximate and ultimate analyses of the three coals are listed in

Table 1. The Velva lignite sample was higher in moisture and ash content than the Wyodak sample. The River King bituminous was lower in moisture but much higher in mineral matter than either of the other two. The three coals have equal quantities of MAF volatile matter and of fixed carbon by weight.

TABLE 1  
PROXIMATE AND ULTIMATE ANALYSES

| Proximate Analyses          | <u>Velva</u> | <u>Wyodak</u> | <u>River King</u> |
|-----------------------------|--------------|---------------|-------------------|
| Moisture %                  | 29.3         | 13.7          | 5.8               |
| Ash, wt % mf                | 13.5         | 8.1           | 35.8              |
| Volatile Matter, wt % mf    | 39.3         | 42.7          | 29.2              |
| Volatile Matter, wt % maf   | 45.4         | 46.4          | 45.6              |
| Fixed Carbon, wt % mf       | 47.2         | 49.3          | 35.0              |
| Fixed Carbon, wt % maf      | 54.6         | 53.6          | 54.4              |
| Heating Value, Btu/lb AR    | 7185         | 8057          | 9477              |
| Ultimate Analyses, mf, wt % |              |               |                   |
| Hydrogen                    | 3.84         | 4.76          | 2.61              |
| Carbon                      | 59.93        | 66.64         | 44.81             |
| Nitrogen                    | 0.94         | 0.91          | 0.40              |
| Sulfur                      | 0.53         | 0.51          | 5.16              |
| Oxygen (Diff)               | 21.26        | 19.10         | 6.56              |

A third difference was in the reactivities of the coal chars in uncatalyzed char-steam reactions as illustrated by Figure 1. The Wyodak subbituminous coal char reacted more slowly than the lignite char but the slowest reaction was that involving the River King char. The reactions of all three chars were enhanced by the presence of alkali catalyst. The River King char reacted the slowest of the three, and therefore the uncatalyzed and catalyzed reaction of that char were only followed through < 25% carbon conversion.

The reactivities of the test coals, the coals containing  $K_2CO_3$  catalyst, and the demineralized coals are shown in Table 2. Note that the bituminous coal char and the demineralized coal chars reacted with steam very slowly at all three temperatures resulting in the termination of each experiment before 50% conversion could be accomplished. The Velva lignite char had reactivities that were 1.5-2 times those of the other coals at each temperature. Catalysis of the reaction at the lower two temperatures increased the reactivity of the Wyodak to values exceeding those of the Velva coal char. However, at 800°C, the reactivity of the Velva was increased to 2.5 times that of the Wyodak. The reactivity of the River King is greater over the first 0-15 wt % carbon conversion than over the remainder of the conversion as shown in Figure 1. This is attributed to the higher state of oxidation on the char surface particle compared to the subsurface layers, making the surface carbon functionalities more hydrophilic than those beneath the surface. The reactivity of the River King char is lower than that of the other two coal chars even when comparing its highest k value (15% carbon conversion) with 50% carbon conversion for each of the other two. In addition, of the forms tested for this River King, none was greatly responsive to changes in temperatures within the studied temperature range.

TABLE 2.

CHAR-STEAM REACTIVITIES FOR THREE COALS AT 700°, 750°, and 800°C.

|                    | Velva                        | Coal<br>Wyodak | River King |
|--------------------|------------------------------|----------------|------------|
| Conversion, wt % C | 50                           | 50*            | 15         |
| Temperature (°C)   | <u>k</u>                     | <u>k</u>       | <u>k</u>   |
| 700                | 1.35                         | 0.84           | 1.10       |
| 750                | 2.10                         | 0.94           | 1.23       |
| 800                | 3.56                         | 2.23           | 1.52       |
|                    | <u>Coal w/ 10 wt % K2CO3</u> |                |            |
| 700                | 4.06                         | 9.87           | 5.00       |
| 750                | 8.17                         | 11.13          | 5.81       |
| 800                | 34.81                        | 13.07          | 8.41       |
|                    | <u>Demineralized Coal</u>    |                |            |
| 700                | 1.06                         | 1.51           | 1.49       |
| 750                | 1.40                         | 3.25           | 3.06       |
| 800                | 1.15                         | 8.33           | 3.13       |

\* k calculated for 10% conversion of demineralized Wyodak char carbon.

The inherent inorganic contents of the ash for the three test coals are shown in Table 3. The aluminum, silicon, and iron concentration of the River King was much higher than in the other two coals. The potassium concentration was also higher in the bituminous coal than in the other two but apparently not in sufficient quantity to enhance the rate of reaction to a level near those of the lower rank coals. The sodium and calcium concentrations, two other elements known to be good catalysts, were much higher in the lower rank coals than in the River King. An effect related to a change in total inorganic content was noted. It was observed that on demineralizing the River King coal, the char reactivity was enhanced over that of the raw coal. Demineralization of the other two test coals left their chars less reactive than the those of the parent coal.

TABLE 3.

RESULTS OF ASH ANALYSES BY XRFA OF THREE COALS IN MOLES OF ELEMENT PER 10000 GRAMS OF COAL.

| ELEMENT    | VELVA | WYODAK | RIVER KING |
|------------|-------|--------|------------|
| Aluminum   | 3.02  | 2.38   | 10.81      |
| Silicon    | 3.43  | 3.95   | 26.77      |
| Sodium     | 1.06  | 0.27   | 0.00       |
| Potassium  | 0.04  | 0.05   | 1.49       |
| Calcium    | 8.32  | 3.38   | 2.34       |
| Magnesium  | 2.87  | 1.20   | 1.16       |
| Iron       | 0.94  | 0.70   | 9.43       |
| Titanium   | 0.14  | 0.13   | 0.38       |
| Phosphorus | 0.10  | 0.14   | 0.04       |
| Sulfur     | 1.41  | 1.02   | 1.64       |

The SEM photographs in Figure 2 show the surface effect that results from charring the test coals containing  $K_2CO_3$  catalyst. The ragged, irregular surface and lack of apparent pores in the uncatalyzed char was in contrast to the rounded, nodular surface on the alkali catalyzed char. The degree to which the surface of the coal changed on charring with the addition of catalyst differed among the coals. The Velva char surface was remarkably porous and contained uniform, evenly spaced nodules of approximately  $0.05 \mu m \times 0.10 \mu m$  in size. The nodules on the surface of the catalyzed Wyodak and River King coal chars were rounded and numerous but not uniform in either size or distribution. The demineralized Wyodak and River King chars had a good deal of surface relief in the form of a few nodules and concavities whereas the surface of the demineralized Velva was relatively smooth. The differences in the surface relief appear to parallel the differences in reactivity and is probably due to changes in available active sites. SEM mapping of the surface for inorganic element distribution showed that the inorganic matter was not distributed uniformly over the surface of the chars except for the potassium. The uniform distribution of the potassium in even the low moisture coals imply a fluid dissemination of the catalyst.

Carbon-13 Nuclear Magnetic Resonance ( $^{13}C$  NMR) spectra of chars prepared at temperatures of  $750^\circ C$  shown in Figure 3 indicated the loss of most of the aliphatic carbon on charring. Aromatic carbonyl groups were present in the demineralized Velva and Wyodak chars whereas they appeared to be absent in the other chars. Integration of the demineralized Velva char spectrum indicated the presence of more aliphatic carbon than in the raw Velva char. The opposite was observed for the Wyodak chars, in which the raw Wyodak char had more aliphatic carbon than its demineralized counterpart. The aliphatic content of the two River King chars did not differ significantly.

Table 4 shows the ratio of carbon to the other elements found by ESCA on the surface of the char particles. The carbon-to-oxygen ratio of the lignite was about the same on the surface of the raw char as it was on the demineralized char. However, the ratio increased by factors of 5 and 3 on the demineralized chars over the raw chars of Wyodak and River King, respectively. In the latter two cases, the demineralization appears to remove oxygen along with the mineral matter and/or remove C-O functionalities leaving less

TABLE 4.

SURFACE ATOMIC RATIOS AS DETERMINED BY ESCA, IN ATOMS C PER ATOM Y

| Atomic Ratio | VELVA |     |      | WYODAK |      | RIVER KING |      |
|--------------|-------|-----|------|--------|------|------------|------|
|              | Raw   | Dem | Dem* | Raw    | Dem  | Raw        | Dem  |
| C/O          | 4.1   | 4.8 | 16.6 | 6.1    | 30.7 | 8.5        | 22.7 |
| C/N          | 107   | 134 | 60.7 | 132    | 136  | 68.5       | ND   |
| C/Na         | 747   | 403 | 456  | 159    | ND   | 411        | 466  |
| C/Si         | 16.6  | 403 | 152  | 56.6   | 951  | 30.4       | ND   |
| C/S          | 372   | 806 | 456  | 397    | 476  | 117        | 93.1 |
| C/Ca         | 374   | ND  | ND   | 33.0   | 951  | 822        | 466  |
| C/Al         | 83.0  | 806 | 182  | 41.7   | 476  | 31.6       | 103  |
| C/Fe         | ND    | ND  | ND   | 793    | 951  | 822        | 466  |

\* 90 minute sputter  
 ND = Not Detected

reactive carbon functionalities on the surface of the particles. The change in inherent catalyst materials, sodium (Na), calcium (Ca), and iron (Fe), between raw coal char and demineralized coal char from the same coal differed for each of the coals. No pattern that would indicate a particular catalytic effect was observed for any of the three. Likewise silicon (Si), nitrogen (N), and sulfur (S) changes showed little correlation to the effect of demineralization that would facilitate a conclusion.

#### CONCLUSIONS.

All three coals responded to the addition of the  $K_2CO_3$  catalyst in the char-steam reaction. Reactivity of the Velva char increased by factors of three to ten at a given temperature with the addition of the catalyst. However, the Wyodak char responded with greater increases in reactivity at the lower two temperatures upon catalyst addition, increasing reactivity six to ten times. The addition of catalyst to the River King char increased the reactivity by a factor of ~5 but the char reactivity was affected very little by temperature over the temperature range studied. Demineralization of the coals reduced the reactivity of the Velva char but increased the reactivity of the River King over that of their respective raw coal chars. Scanning electron microscopy showed that the char surface is affected by both demineralization and catalyst addition to the raw coal. Larger than expected aromatic carbonyl peaks were obtained in the  $^{13}C$  NMR spectra of demineralized Velva and Wyodak chars:

#### REFERENCES

1. Timpe, R.C., R.E. Sears, and G.G. Montgomery, ACS Div. Fuel Preprints, 32, No. 4, 1, (1987).
2. Takarada, T., Y. Tamai, and A. Tomita, Fuel, 64, 1438, (1985).
3. Timpe, R.C., S.A. Farnum, S.J. Galegher, J.G. Hendrikson, M.M. Fegley, ACS Div. Fuel Preprints, 30, No. 4, 481, (1985).
4. Axelson, D.E., Solid State Nuclear Magnetic Resonance of Fossil Fuels, Chapters 2-3, Multiscience Pub. Ltd., Canada, (1985).
5. Botto, R.E., R. Wilson, and R.E. Winans, Energy and Fuels, 1, 173-181, (1987).

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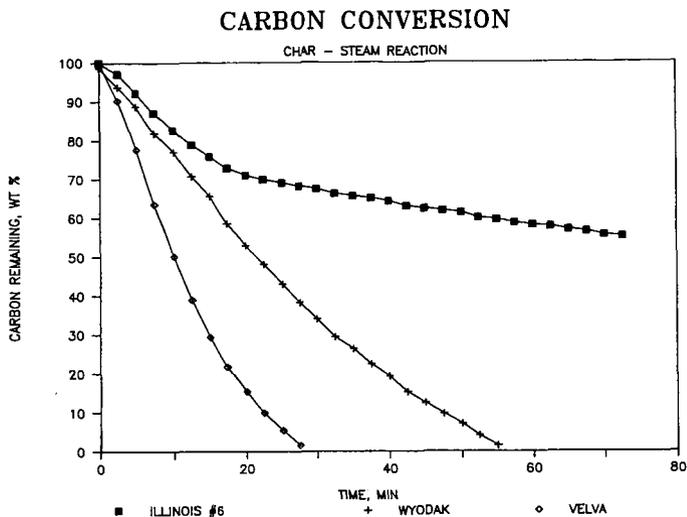


Figure 1. Conversion of Velva lignite, Wyodak subbituminous, and Illinois #6 char carbon on reacting with steam at 750°C.

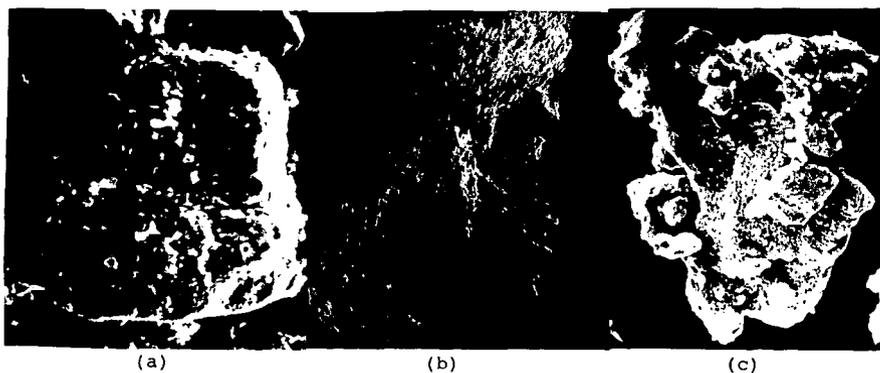
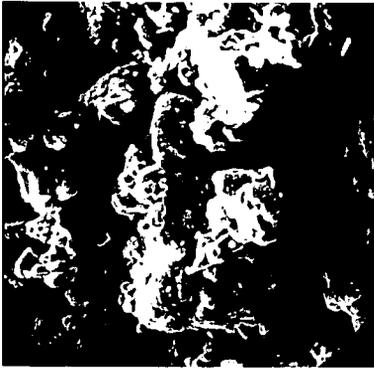
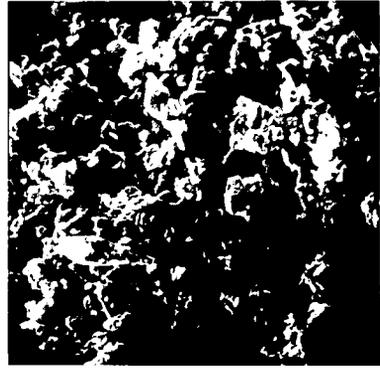


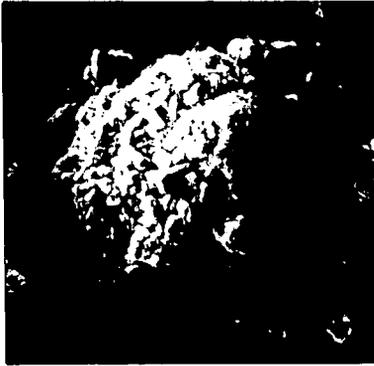
Figure 2. SEM photos of chars of the raw (a, d, g) and demineralized (b, e, h) coals and chars of each coal with 10 wt %  $K_2CO_3$  added (c, f, i). The photos shown are of chars of Velva lignite (a, b, c), Wyodak subbituminous (d, e, f), and Illinois #6 bituminous (g, h, i) coals.



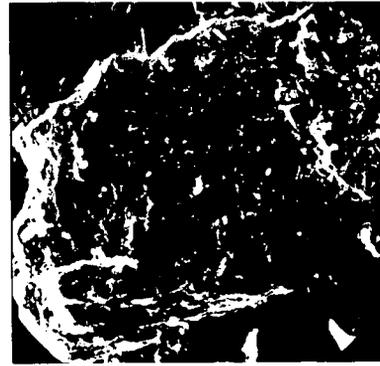
(f)



(g)



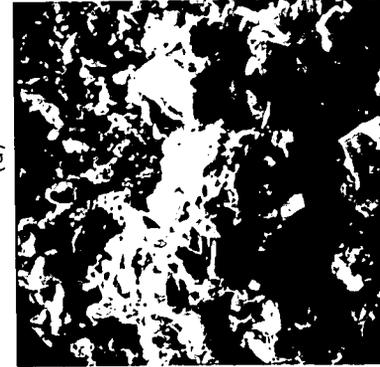
(e)



(h)



(d)



(i)

Figure 2 (continued).

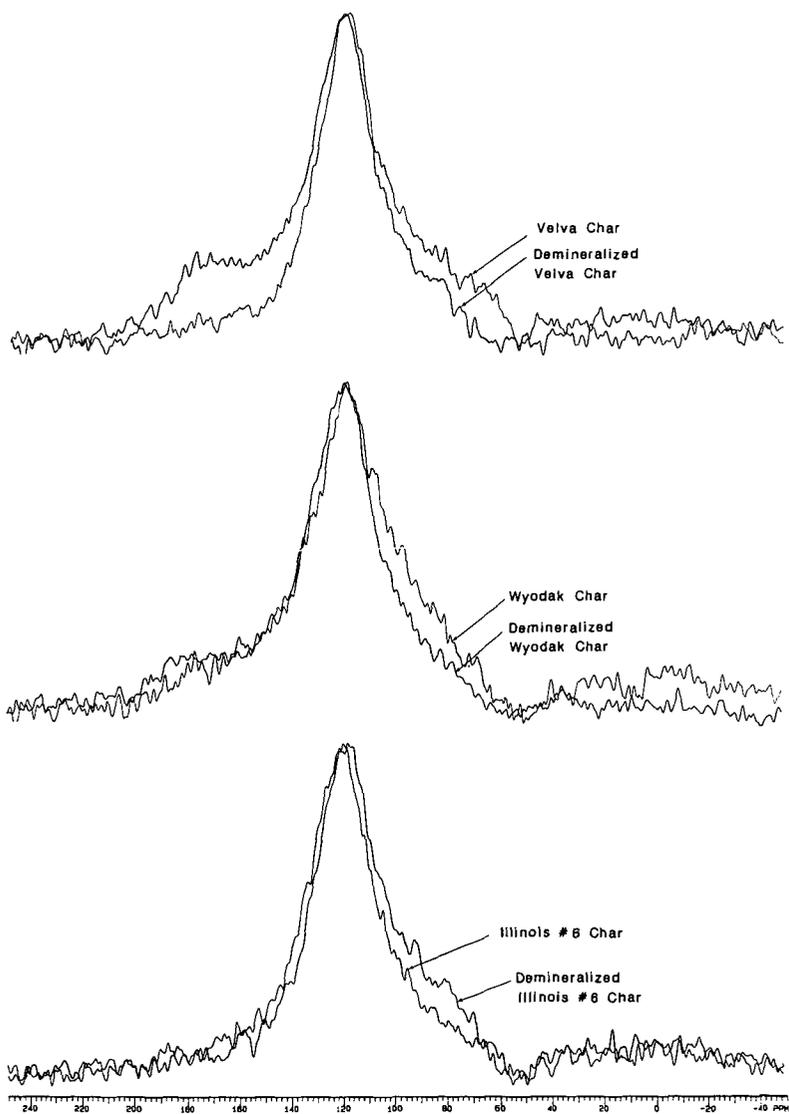


Figure 3. Solid  $^{13}\text{C}$  NMR spectra of chars from raw and demineralized Velva lignite, Wyodak subbituminous, and Illinois #6 bituminous coals.