

MOISTURE REMOVAL FROM AND LIQUEFACTION OF BEULAH ZAP LIGNITE.

K. S. Vorres^{*}, D. Wertz^{**},
J. T. Joseph^{***}, and R. Fischer^{***}

^{*}Chemistry Div., Bldg. 211, Argonne National Lab., Argonne, IL 60439,

^{**}Dept. of Chemistry, Univ. So. Miss., Hattiesburg, MS, 39406,

^{***}Amoco Oil Co. R&D, Naperville, IL, 60566

Keywords: Drying, Liquefaction, Lignite

INTRODUCTION

Lignite reserves represent an important resource for the production of synthetic liquid fuels. The high reactivity of lignite would indicate a high throughput from a given process train. However the moisture content of this material has been a concern for efficient processing into liquid hydrocarbons. Furthermore, drying might introduce irreversible changes to the pore structure which would limit the rates of reaction.

This collaborative study has been undertaken to help understand the role of moisture in the liquefaction and also to understand the kinds of changes that take place in the coal particles during drying.

The physical structure of coal consists an organic matrix and inorganic matter containing an extensive network of pores. The pore network usually contains water. Mraw and Silbernagel (1) suggested that the amount of water present in as-mined coals provides a measure of pore volume. However, Kaji et al. (2) examined the water-holding capacity, specific surface area, and pore volume of 13 coals from various locations, ranging from lignite to anthracite, and found no correlation between the water-holding capacity and the pore volume. Assuming that the total coal oxygen is distributed uniformly through the coal and the functional-group oxygen increases with oxygen content, Kaji et al. found a linear relationship between the hydrophilic sites and the water-holding capacity of coal. The relationship between the total oxygen content of coal and the water-holding capacity may be fortuitous since oxygen-functional groups are not the only hydrophilic sites in coal (3). Moreover, the presence of minerals, especially smectite lattices, and various cations will also strongly influence the coal-water interactions.

Vorres et al. (4) and Vorres and Kolman (5) studied the kinetics of vacuum drying of coal to understand the complex coal-water interactions. From isothermal thermogravimetry analysis, i.e., the weight loss vs. time at fixed temperature, Vorres and his co-workers observed that the dehydration of Illinois No. 6 in the form of a block, -20 mesh, and -100 mesh, follows a desorption kinetics mechanism. Thus, they concluded that the rate controlling mechanism of dehydration is governed by the surface of coal. In addition, Vorres and his co-workers indicated that the particle size and the history of coal also affect the dehydration kinetics of coal. More recently, Abhari and Isaacs (6) used the thermogravimetric analysis (TGA) technique to explore the drying

kinetics of six coals from the Argonne coal-sample series. They used a bulk moisture/pore moisture model to explain the observed drying kinetics for the six coals, in which the order of kinetics, i.e., the order of dehydration showed a strong dependence on the rank of coal. These researchers assumed that water in coal is held by the physisorption process. This assumption is at variance with the temperature dependent NMR results (7) and the contention of Kaji et al. (2). Even more recently, Vorres et al reported the kinetics of drying of lignite in dry nitrogen. They observed a unimolecular mechanism, with a transition after the loss of about 85% of the water present in the original sample (8). The transition resulted in a lower rate with the unimolecular mechanism. Studies with the thermobalance and differential scanning calorimeter indicated the same mechanism and transition (8).

In this paper, we report our recent results on: the kinetics of water's desorption from Beulah-Zap lignite coal, as determined by thermogravimetric analysis (TGA); physical structure changes as observed with x-ray diffraction; and the effects on liquefaction due to drying.

EXPERIMENTAL

Isothermal Thermogravimetry

Coal drying was done with a Cahn model 121 thermobalance attached to an IBM PC/XT microcomputer. Vendor-supplied software was used to monitor the progress of individual runs, and convert data files to a form that could be further studied with Lotus 123.

The data were obtained as files of time, temperature and weight at 10 second intervals. Run times varied from 7-16 hours. Sample sizes varied from about 20-160 mg. Temperatures were varied between 20 and 80 C. The gas velocity past the sample was varied from 20 to 160 cc/min in the 25 mm diameter tube. The sample was placed in either a quartz or a platinum hemispherically-shaped pan. Sample included the two mesh sizes (-100 and -20) of the Argonne Premium Coal Samples and also one or two small pieces which came from lumps which were stored under nitrogen.

Samples were quickly transferred from ampoules which had been kept in constant humidity chambers with water at room temperature (293°K). In the thermobalance system a period of about 5 minutes was used to stabilize the system and initiate data acquisition. A condenser was made to replace the usual quartz envelope that surrounds the sample. An antifreeze solution was circulated from a constant temperature bath through the condenser to maintain constant temperature during the experiments. This was more stable than the furnace and provided very uniform temperature control during the experiments.

The gas atmosphere was cylinder nitrogen (99.99%) or "house" nitrogen from the evaporation of liquid nitrogen storage containers used without further purification and passed over the sample at rates of about 20-160 cc/min.

Data were initially analyzed by testing the weight loss as a function of time with 13 different kinetic expressions including geometrical, unimolecular, first and second order diffusion to establish a best fit (8). Regression analysis was used to obtain the kinetic constants. Lotus 123 was used for analysis of individual run data.

Round Robin Sample Preparation

In order to compare the results of drying with the help of several techniques a set of samples was prepared and distributed. A batch of twenty five grams of -100 mesh lignite was dried in a vacuum oven at room temperature. One batch was dried for 4 hours, and the other for 24 hours. The samples were brought to atmospheric pressure under nitrogen, quickly transferred to a nitrogen filled glove bag, and transferred to previously dried screw cap vials. The vials were further sealed with tape around the cap. These samples were distributed to the University of Southern Mississippi for x-ray diffraction studies and Amoco Oil Company for liquefaction studies and comparison with fresh lignite sample.

RESULTS AND DISCUSSION

Isothermal Thermoogravimetry

The data were normalized to one gram of starting sample weight. The best fit of the data were obtained with a unimolecular decay kinetic expression. Plots of \ln (water left) versus time gave a characteristic shape. The plot indicates a consistent slope for the initial 85% of the moisture loss of the coal. A transition then occurs. The rate is then reduced to about 0.5-0.1 of the earlier rate. Figure 1 shows a typical plot of \ln water left (mg/gm sample) as a function of time (10 second intervals).

The rates are similar for different particle sizes if the sample weight and gas velocity are held constant. Table 1 indicates the similarity in rates for 150 mg samples in the hemispherical quartz container. Activation energies are also given for each particle size.

Table 1. Rate Constants for First Segment
(mg water/gm sample/10 sec)

Temperature--> Size	20 C	40 C	80 C	E_a Kcal/mole
-100	.00009	.00024	.00099	8.2
-20	.00007	.00024	.00131	10.0
Block	.00010	.00023	.00085	7.3

The activation energy calculated from these data averages 8.5 Kcal/mole.

The rate is a function of the size of the sample and the gas velocity around the sample. The size of the sample affects the depth of the material through which the moisture must diffuse to escape. The normalized rates were inversely proportional to the sample size. The rate is directly proportional to the gas

velocity since the more rapidly moving stream is more effective in removing the water molecules or limiting the opportunity for rehydration.

The effect of temperature is measured through the activation energy from an Arrhenius plot. Figure 2 shows the data plotted for several sets of data representing three different constant gas velocities. The lines are almost parallel and indicate an average activation energy of 8.0 Kcal/mole. The higher gas velocities are able to more effectively remove water molecules and increase the rate of drying.

Varying the sample weight also varies the depth of the sample in the container. Figure 3 indicates the change in rates as the sample weight is changed at different temperatures. The rate in terms of mass of water lost per gram of sample in a given time is greater for the smaller, and therefore thinner samples. The probability of a water molecule recombining with the lignite rather than leave the sample diminishes as the diffusion path is shortened.

The use of vacuum to remove moisture was seen to be capable of much more rapid removal of water than a stream of dry nitrogen. The ratio of the rate coefficients is an order of magnitude greater, and would imply a rate advantage to this technique for engineering for rapid processing of pulverized fuel.

The initial removal of about 85% of the moisture and then a transition to a slower rate of water loss implies a structural rearrangement. It is believed that the pores of the particles are changed after this amount of water is lost in a manner that makes the further loss of water more difficult.

X-RAY DIFFRACTION STUDIES

The X-ray diffraction studies carried out at the University of Southern Mississippi shown in Figure 4 indicate that the physical structure of the coal (not the inorganic material) changes with the drying. Further the reduced "noise" level associated with the diffraction pattern on the recorder indicates that there is a greater regularity in the dried coal than the raw or partially dried material. Further studies of the diffraction data are underway to provide additional insight into the changes that have been observed. The figure indicates the diffractograms from: A. untreated lignite, B. partially dried lignite and C. dried lignite.

The peak at 22° is due to an internal standard that was added. The peak at 14° is due to the 002 plane of graphitic material associated with coal samples. Note that the peak shape for untreated lignite is reasonably symmetrical implying a distribution of spacings about an average value. The partially dried material has a distorted shape for the 002 peak indicating that the larger planar spacings are no longer present in the sample. In the dried sample the peak is again relatively symmetrical.

LIQUEFACTION STUDIES

The oil yield measurements have been carried at Amoco Oil Co. at the Naperville Research Center. Small samples were added to tetralin, and the material heated under hydrogen at 1000 psi to 400 C for four hours. The product gases were recovered and analyzed by gas chromatography. The liquid and residual material were extracted with a series of solvents to give oil, preasphaltene and asphaltene fraction amounts.

The studies indicated that the different coal samples did give different oil yields, as well as preasphaltene and asphaltene yields. The initial data indicate that the raw and partially dried samples gave higher preasphaltene and asphaltene yields than the dried material, with the highest yields for the partly dried sample. Conversely the oil yield was highest for the dried sample, lowest for the partly dried material and the starting material had an intermediate value. The data are given in Table 2. The total of the oil, preasphaltene and asphaltene was almost the same for all samples. The gas yield was the same for the two moist materials and higher than the dried material, suggesting a role for moisture in gas production. Hydrogen diminishes for dried coal, while carbon monoxide increases. Methane and higher hydrocarbons remain about the same for all levels of dryness, suggesting that they are released by some mechanism which is not dependent on moisture, i. e. they may simply be dissolved in the matrix. Carbon dioxide yield increased for the partly dried material and then decreased for the dry material suggesting two competing reactions.

Table 2. Initial Liquefaction Results from Lignite Samples

Coal	Raw	High Moisture	Low Moisture
Moisture:	32.2%	23.9%	0.3%
<u>Products, Wt%</u>			
OIL	24	21	31
ASPHALTENE	24	25	20
PRE-ASPHALTENE	11	13	7
UNCONVERTED	31	31	33
TOTAL GASES	10.5	10.5	8.5
<u>GAS BY TYPE:</u>			
hydrogen	0.209	0.196	0.156
carbon monoxide	0.238	0.276	0.340
methane	0.486	0.474	0.480
carbon dioxide	5.373	5.543	4.849
ethane	0.163	0.166	0.154
propane	0.056	0.055	0.054
propylene	0.011	0.011	0.009

CONCLUSIONS

The lignite drying kinetics follow a unimolecular rate law which is first order in the water in the sample. There are two segments in the dehydration kinetics plots, and each follows a unimolecular rate law. The first drying segment includes about 80-85% of the water loss. The second drying segment includes most of the remaining water and occurs at about half the rate of the first segment. The mechanism is unchanged over the range 20-80°C. The activation energy for the initial moisture loss is about 8 Kcal/mole. The water jacketed heating system provides superior temperature control. The rate of drying is sensitive to the gas velocity over the sample. The rate of drying is dependent on the sample size and the sample depth. Rates are generally similar for -20 and -100 mesh samples. The same mechanism is observed for differential scanning calorimetry measurements. X-ray powder diffraction measurements show structural changes during the drying process. Drying improves the oil yield from lignite samples as a result of hydrogenation.

ACKNOWLEDGMENTS

One of the authors (KSV) gratefully acknowledges the support of the U. S. Department of Energy, Pittsburgh Energy Technology Center for the part of the work dealing with the kinetics of drying.

REFERENCES

1. Mraw, S. C. and B. G. Silbernagel, Am. Inst. Physics Proceedings 70, 332 (1981).
2. Kaji, R., Y. Maranaka, K. Otsuka, and Y. Hishinuma, Fuel 65, 288 (1986).
3. Laskowski, J. S., Am. Chem. Soc. Preprints Fuel Chem. Div. 32 (1), 367 (1987).
4. Vorres, K. S., R. Kolman, and T. Griswold, Am. Chem. Soc. Preprints Fuel Chem. Div. 33 (2), 333 (1988).
5. Vorres, K. S. and R. Kolman, Am. Chem. Soc. Preprints Fuel Chem. Div. 33 (3), 7 (1988).
6. Abhari, R. and L. L. Isaacs, Energy & Fuels 4, 448 (1990).
7. Unsworth, J. F., C. S. Fowler, N. A. Heard, V. L. Weldon, and V. J. McBrierty, Fuel 67 1111 (1988).
8. Vorres, K. S., Molenda, D., Dang, Y. and Malhotra, V. M., Am. Chem. Soc. Preprints Fuel Chem. Div. 36 (1), 108 (1991).

Figure 1, Lignite Dried in N₂, 80 C

ND65, -100 mesh, 80 cc/min, 160 mg, rbb

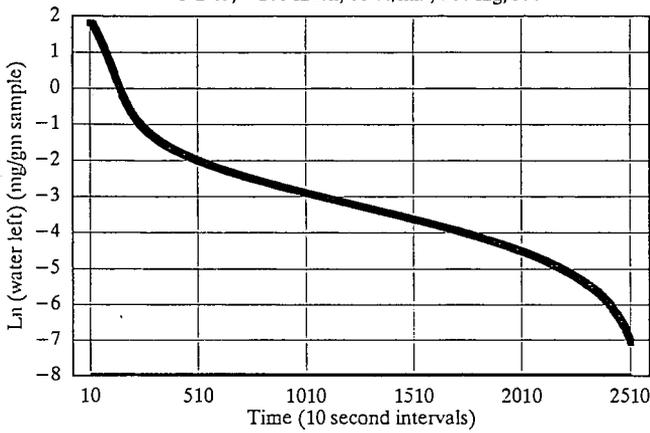


Figure 2, Arrhenius Plot, Lignite Dried in N₂

-20 mesh, 150 mg samples, 30,40, 60 C

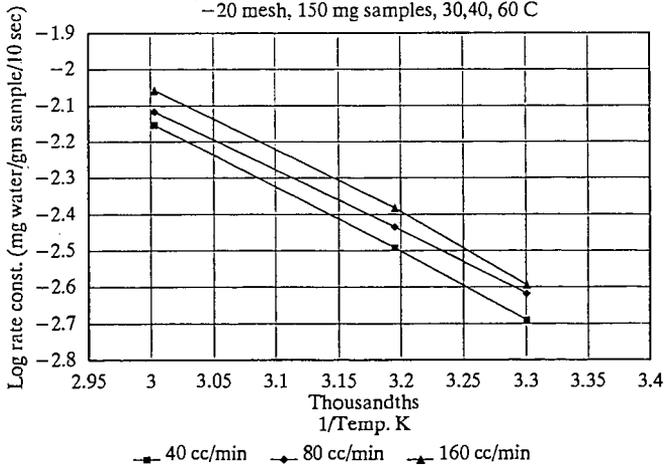


Fig. 3, Rates Change as Sample Weight Changes
75, 150 mg samples, 30,40, 60 C

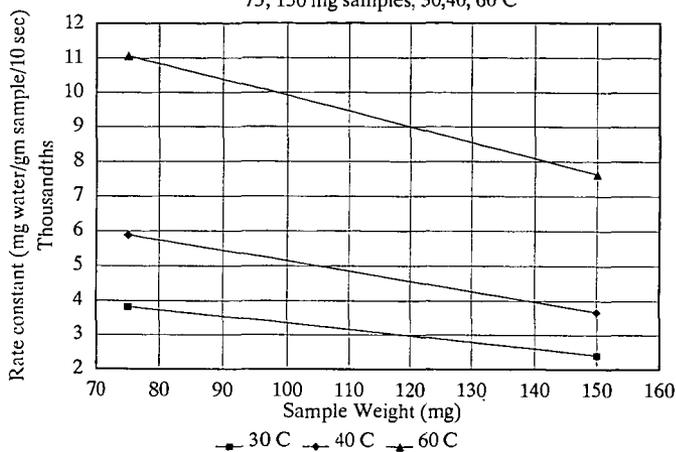
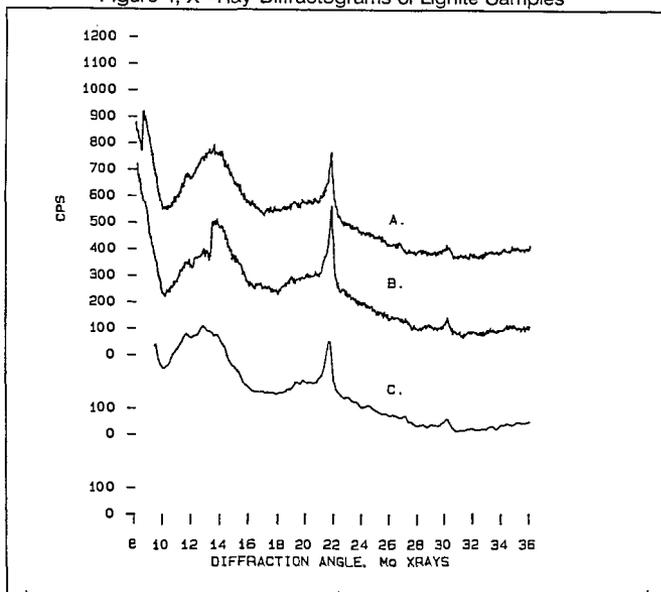


Figure 4, X-Ray Diffractograms of Lignite Samples



A = Raw lignite B = Partly dried C = Dried