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DRYING OF BEULAH-ZAP LIGNITE AND WYODAK SUBBITUMINOUS COAL

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ABSTRACT

Beulah-Zap lignite and Wyodak-Anderson (-100 and -20 mesh from the Argonne Premium Coal Sample Program) were dried in nitrogen under various conditions of temperature (20-80°C), gas flow rates (20-160 cc/min), and sample sizes (20-160 mg). An equation relating the initial drying rate in the unimolecular mechanism was developed to relate the drying rate and these three variables over the initial 80-85% of the moisture loss for the lignite. The behavior of the Wyodak-Anderson subbituminous coal is very similar to that of the lignite. The nitrogen BET surface area of the subbituminous sample is much larger than the lignite.

INTRODUCTION

Economical production of synthetic coal liquids suitable for transportation fuels is a continuing goal of a number of coal conversion programs. The vast reserves of low rank coals in the western part of the U. S. provide a plentiful supply of input for potential processes. The low rank coals generally possess a high reactivity in many chemical reactions which also make them attractive feedstocks. One of the major detractors, however, is the high moisture content associated with many of these fuels, ranging up to 40%. An economical means of removing the moisture without sacrificing the reactivity or oil yields would be desirable.

A number of studies have been carried out on the drying behavior of coals from a fundamental viewpoint (1,2,3,4,5). The drying behavior has been found (1,2,3,4) to follow a unimolecular mechanism in a flow of dry gas (nitrogen or carbon dioxide) over a range of temperatures, gas flow rates and sample sizes). The mechanism proceeds through two stages. The initial stage accounts for about 80-85% of the moisture loss, while the second accounts for all but about 1% of the rest of the loss.

EXPERIMENTAL

Coal drying was done with a modified Cahn model 121 thermobalance or thermo-gravimetric analyzer (TGA) 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 7-23 hours. Sample sizes typically started at about 80 mg, but varied from

20-165 mg. Runs were typically isothermal, with temperatures selected from 20 to 80°C. The gas velocity moving upward past the sample was typically 80 cc/min (but ranged from 20 to 160) in the 25 mm diameter tube. The thermobalance was modified so that all of the gas flow passed around the sample, rather than partly through the weighing mechanism. The sample was placed in a quartz flat bottom bucket about 10 mm internal diameter. The samples were the -100 mesh Argonne Premium Coal Samples: Beulah-Zap lignite and Wyodak-Anderson subbituminous (6).

Samples were quickly transferred from ampoules which had been kept in constant humidity chambers with water at room temperature (20°C or 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 and furnace that surrounds the sample. Water was circulated from a constant temperature bath through the condenser to maintain constant temperature during the experiments. This was more stable than the original furnace and provided uniform temperature control during the experiments.

The atmosphere for the nitrogen gas runs was cylinder nitrogen (99.99%) or "house" nitrogen from the evaporation of liquid nitrogen storage containers used without further purification.

Data were analyzed on a separate microcomputer as reported earlier (1-4). Regression analysis was used to obtain the kinetic constants in terms of mg of water lost/gm sample per 10 second time interval. Lotus 123 was used for analysis of individual run data. In some runs, approximations to a first and second derivative of the rate expressions were made in Lotus 123 by averaging over a number of the 10 second time intervals before and after the point of interest. These derivatives were plotted with the rate data to aid in identifying the beginning of the transitions from an initial phase of drying to a second, slower phase. The initial drying kinetic data from a run at a temperature different from room temperature were collected over a time in which the sample was reaching the temperature of the system. These runs indicated that the initial rate increased for about 10-30 minutes until a constant value for the first phase was reached. Figure 1 indicates typical weight changes over the duration of a run for the Beulah Zap lignite and the Wyodak-Anderson subbituminous samples. Note that the lignite has a higher initial moisture content and therefore can lose more water.

Surface area measurements were carried out to complement the drying kinetic runs. The surface area was assumed to be important in that it determines the amount of exposure to the gaseous phase. The greater the surface area the greater the overall reaction rate will be, assuming a similar reactivity per unit of surface and comparable access to exterior and interior surface.

The Quantasorb Jr. instrument was used for nitrogen BET (Brunauer-Emmett-Teller) measurements of the surface. A series of values were obtained on samples which were prepared by drying in the vacuum oven at a range of temperatures as well as a set of nitrogen dried samples, prepared both in the vacuum oven with a flow of nitrogen at atmospheric pressure, and also the products

of some of the thermobalance runs. The typical run gives the data from the desorption cycle. Samples of nitrogen in helium (10, 20 and 30% nitrogen) were allowed to interact with the surface of the sample. Adsorption was carried out at liquid nitrogen temperatures. The amount of adsorbed nitrogen was determined by calibration of a thermal conductivity bridge.

RESULTS AND DISCUSSION

A typical run indicates a rapid initial moisture loss, followed by significantly reduced rates. A plot of the logarithm of the water left as a function of time gives two straight line segments followed by a downward slope for the loss of the last 1%. See Figure 2 for typical lignite and subbituminous coal runs. The first line segment has been correlated with the loss of "freezable" water, while the latter has been associated with "non-freezable" water as identified by Mraw and co-workers (7,8). The rate constants for the initial rate loss can be correlated with an Arrhenius plot to give an activation energy for the initial stage of water loss, but the second stage could not be correlated. A multiple regression analysis of the initial rate with the values of the absolute temperature, gas flow and sample weight was carried out with the data from 51 runs made with -100 mesh material in dry nitrogen. For an equation of the form:

Log Initial Rate (mg water left/gm sample/10 second interval)= c_1 * Temperature (K) + c_2 * Gas flow (cc/min) + c_3 * Sample Weight (mg) + c_4

The best fit was given for:
$$c_1 = .0248 \qquad c_2 = .00376$$
$$c_3 = -.00528 \qquad c_4 = -3.295$$

with an R^2 value of .867. These values cover experiments in the range of 20-80°C, 20-160 cc/min gas flow and 20-169 mg sample weight.

A smaller series of runs (6) made with the -100 mesh Wyodak subbituminous sample at gas flow rates of 80 cc/min were analyzed with multiple regression. The best fit over the range of 20-60°C and weight of 40-80 mg were given by:

log k_1 (initial rate in mg water left/gm sample /10 second interval) = .0242 * Temperature (K) -.00673 * Sample weight (mg) - 9.315. The R^2 value = .983. There is a similarity in the coefficients for the temperature and the weight for the two coals. The similarity in the two curves in Figure 2 would also indicate this.

The surface area measurement data are given in Table 1.

Table 1, Surface Area Measurements

Run #	Drying Method	Temp. °C.	Surface area m²/gm
ND173	Nitrogen	22	1.993

RM-59-1	Vacuum	22	3.221	
RM-59-1	Vacuum	22	2.889	reproducibility check
RM-68-2	Vacuum	22	2.969	repro. different sample
ND175	Nitrogen	40	1.811	
RM-67-1	Vacuum	40	2.141	
ND177	Nitrogen	60	1.887	
ND178	Nitrogen	70	1.286	Questionable value
RM-62-1	Nitrogen	110	1.819	
RM-63-1	Vacuum	110	1.768	
RM-65-1	Nitrogen	150	1.865	
RM-65-1	Vacuum	150	1.900	
RM-66-1	Vacuum	150	1.764	repeat above after

heating overnight in N2 at 150°C.

For comparison a run was made using Wyodak subbituminous coal:
RM-68-1   Vacuum   25   10.61
Clearly the subbituminous coal has a much larger surface area, reflecting a greater order in the coal particles, and better developed pore structure.

CONCLUSIONS

Generalizations on Lignite Drying

1. A complete understanding of the rate of lignite drying must include the effects of a number of variables. Some of these are inherent in the material itself, others depend on the processing given to the material, and still others have to do with mass transfer effects.

2. The rate of drying is affected by the temperature, gas flow, sample thickness and history. For the experiments conducted in this study the rate of drying from the 10 mm diameter container can be expressed by:

Log rate = .0248 * Temp. (K) + .00376 * gas flow (cc/min) - .00528 sample wt (mg) - 3.295.

3. There is a unimolecular mechanism for the initial 60-85% of the weight loss. A transition occurs to a slower mechanism until about 1% of the water remains.

4. There are at least two kinds of water present in the low rank coals. The terms "freezable" and "non-freezable" have been applied to these. The kinetic data support this concept, and extend the perception to exchange between the two forms. The initial water loss corresponds to "freezable" water, while the later loss corresponds to "non-freezable" water.

Generalizations on Subbituminous Drying

1. The behavior of subbituminous coal on drying is very similar to that of lignite.

2. The mechanism of drying is a unimolecular process. There is a transition after about 80% of moisture loss to a slower unimolecular process.

3. The rate of drying is affected by the temperature, sample thickness or weight and history. For the experiments conducted in this study the rate of drying from the 10 mm diameter container can be expressed by:

Log rate = .0242 * Temp. (K) - .00673 sample wt (mg) - 9.315.

4. The subbituminous coal has a larger nitrogen BET surface area, but the rate of drying is not enhanced by this larger area.

ACKNOWLEDGMENTS

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Fig. 1: Wyodak and Beulah−Zap Dried in N2, 40 C.
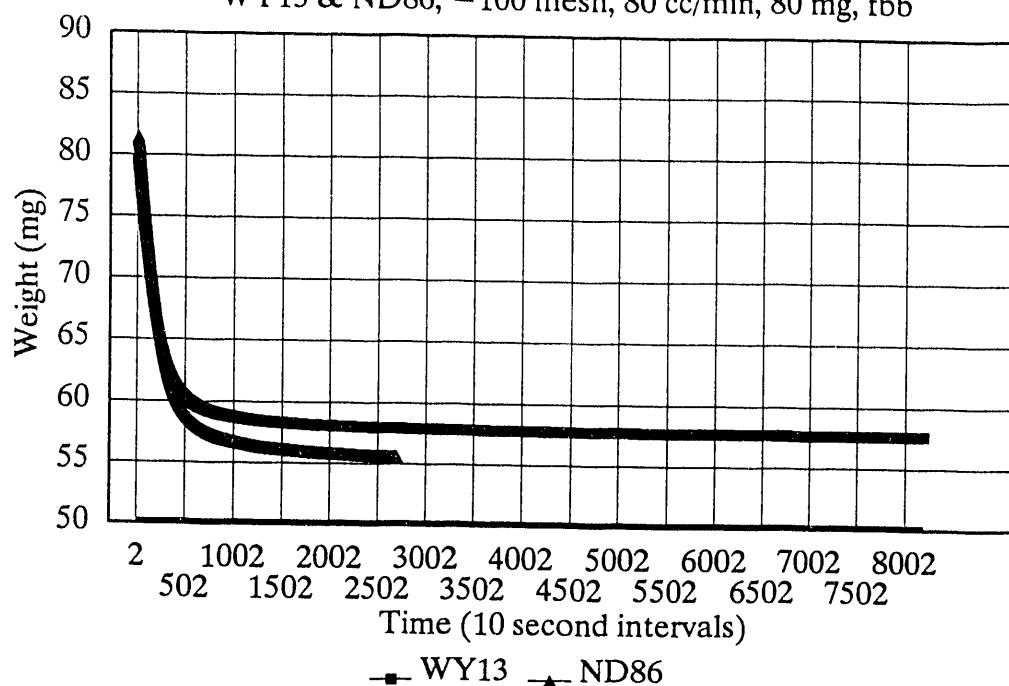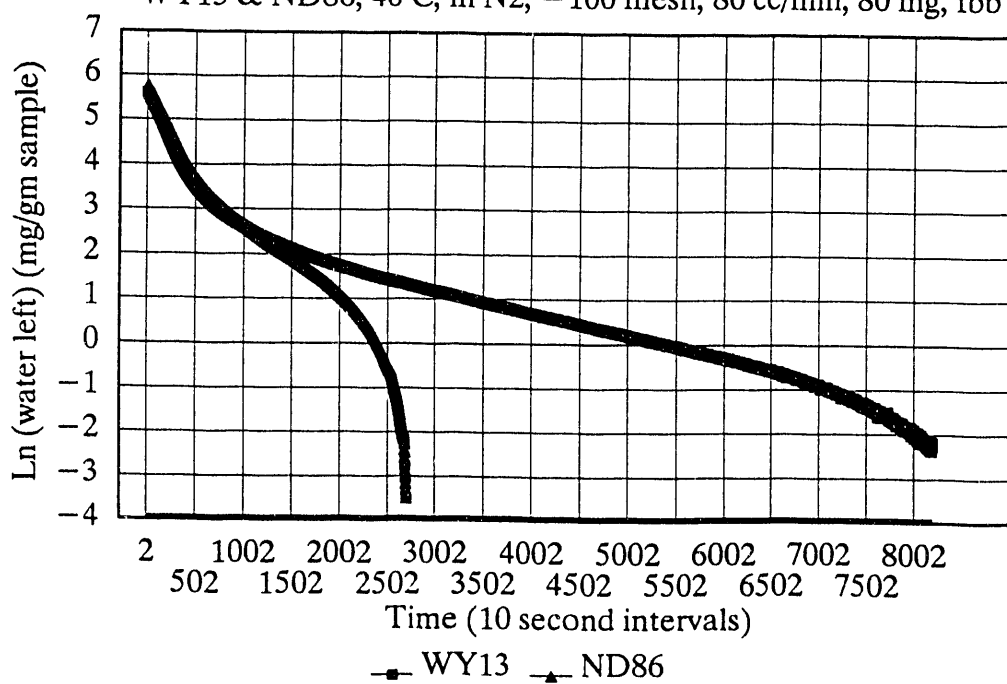### WY13 & ND86, −100 mesh, 80 cc/min, 80 mg, fbb

Fig. 1: Wyodak and Beulah−Zap Dried in N2, 40 C. WY13 & ND86, −100 mesh, 80 cc/min, 80 mg, fbb

Weight (mg) vs. Time (10 second intervals)

─■─ WY13   ─▲─ ND86

Fig. 2 Wyodak & Beulah−Zap Dried in N2, 40 C.
WY13 & ND86, 40 C, in N2, −100 mesh, 80 cc/min, 80 mg, fbb

Fig. 2 Wyodak & Beulah−Zap Dried in N2, 40 C. WY13 & ND86, 40 C, in N2, −100 mesh, 80 cc/min, 80 mg, fbb

Ln (water left) (mg/gm sample) vs. Time (10 second intervals)

─■─ WY13   ─▲─ ND86

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