The over-all net effect of the errors examined in the preceding paragraphs is believed to be small and on the conservative side.

CONCLUSIONS

The primary purpose of the present investigation, the definition of safe operating conditions for the air oxidation of cumene, was realized. By the use of the apparatus described, it was possible to find the explosive limits of various cumene-air and cumeme-air-water mixtures at elevated pressures. An increase in pressure caused a widening of the upper limits for both systems studied. Water caused a decrease in the upper explosive limit.

The data accumulated are of fundamental interest in the field of hydrocarbon flammability.

LITERATURE CITED

(1) Armstrong, G. P., Bewley, T., Turck, K. H. W. (to Hercules Powder Co.). U.S. Patent **2,619,510** (Nov. 25, 1952).
(2) Armstrong, G. P., Bewley, T., Turck, K. H. W. (to Distillers Co., Ltd.), Brit. Patent **653,761** (May 23, 1951).
(3) *Ibid.*, **699,047** (Oct. 28, 1953).
(4) Coward, H. F., Jones, G. W., U.S. Bur. Mines, Bull. **503**, 1–10 (1952).
(5) Jones, G. W., U.S. Bur. Mines, Rept. Invest. **3787** (1944).
(6) Kennedy, R. E., Spolan, I., Scott, G. S., *Ibid.*, **4812** (1951).
(7) O'Neal, Cleveland, Jr., Natl. Advisory Comm. Aeronaut. Tech. Note **3446**, 28 (April 1955).
(8) Zabetakis, M. G., Scott, G. S., Jones, G. W., *Ind. Eng. Chem.* **43**, 2120 (1951).

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Sorption of Water Vapor by Thermally Treated Lignite at Different Relative Humidities

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The mechanism of the coalification process, by which wood products are transformed through the various coal ranks, has received attention from numerous investigators. Generally, it is believed that the woody material advances in rank by a slow chemical process consisting in part of dehydration and decarboxylation, occurring over geological ages.

One avenue of approach to basic coalification mechanism and an understanding of fundamental coal structure has been a study of the forms and occurrence of moisture associated with the coal substance. Gauger (2) recognized that water was recoverable from coal from five sources, including:

1. Decomposition of organic molecules
2. Surface-adsorbed water
3. Capillary-condensed water
4. Dissolved water
5. Water of hydration of inorganic constituents of coal

Moisture included in types 2, 3, and 4 has been studied by water vapor sorption-desorption tests as applied particularly to lower rank fuels, which are considered to have some gellike properties. Lavine (*10*) summarized previous work and presented data on the dehydration-hydration of wood and natural lignite. Larian and others (*9*) extended the initial investigation by testing peat and brown coal, and promulgated the possible classification of North American fuels in terms of pore size as determined by the sorption studies. Gordon, Lavine, and Harrington (*3*) studied the effect of temperature and pressure on sorption of water vapor by lignite. Sorption studies of three basic types of natural lignite—woody, earthy, and peaty—were reported by Tasker (*15*) of the Ontario (Canada) Research Foundation for multiple desorption-sorption cycles wherein slightly different sorption characteristics were noted for each type.

Several investigators, among them Klein (*6*) and more recently Terres (*16*), showed that thermal treatment above the temperature required to initiate decarboxylation in addition to removal of the normally considered moisture resulted in artificial coalification or an accelerated metamorphism which advances somewhat the rank of the solid fuel treated. Kube (*8*) exposed samples of North Dakota lignite which had been thermally treated at various temperatures to 950° F. in an atmosphere saturated with water vapor at room temperature, and reported that differences in resorption of water vapor existed, depending upon the treating temperature.

Interest in the fundamental properties of North Dakota lignite has continued at a high level because of the large reserves (some 350 billion tons) of this low rank fuel (*1*). These deposits represent a major untapped power and chemical source in the United States.

The present report represents a portion of this continuing interest and extends the fundamental water vapor sorption-desorption tests to thermally treated lignite representing lignites originally obtained from a wide area covering the North Dakota deposit and its extension into Canada.

The major objectives of this investigation were to determine:

1. The influence of thermal treatment and type of lignite on sorption of water vapor by lignite.
2. The approximate increase in coalification caused by thermal treatment at temperatures sufficiently high to initiate decarboxylation of the colloidal lignitic substance.

Table I. Ultimate Analysis, Moisture Content, and Heating Value of Six Natural Lignites[a]

Lignite	Bienfait	Zap	Beulah	Dickinson	Custer	Baukol-Noonan
Ultimate analysis, %						
Hydrogen	6.9	6.3	6.5	7.0	7.1	6.8
Carbon	43.0	40.3	39.9	37.4	39.3	42.0
Nitrogen	0.8	0.6	0.6	0.5	0.7	0.8
Oxygen	43.8	44.0	43.1	47.7	48.0	43.0
Sulfur	0.4	1.1	1.2	1.4	0.4	0.4
Ash	5.1	7.7	8.7	6.0	4.5	7.0
Moisture, %	35.8	35.6	35.8	41.0	40.2	35.6
Gross heating value, B.t.u./lb.	7220	6720	6660	6370	6670	7100

[a] (p. 11, Table 1, *12*).

3. The influence of thermal treatment on heat requirements for vaporization of residual moisture.
4. The influence of type of atmosphere on water retention in lignite.

LIGNITES TESTED

The source of lignite and treatment after mining affect its physical and chemical properties. Consequently, a detailed history is presented for the samples used in these experiments.

All lignites used were originally obtained by strip mining in western North Dakota and southeastern Saskatchewan, Canada. These selected mines cover the major lignite producing areas in this region, and, as shown in Figure 1, extend from Bienfait, Saskatchewan, in the north to Dickinson in Stark County, North Dakota, in the south. Geologically speaking, the lignites are from the Fort Union formation, and are of Paleocene age. Ultimate analyses of the various natural lignites as well as moisture content are given in Table I. Variations in composition are caused primarily by differences in moisture and ash content. Moisture contents as determined by the xylene method ranged from 35.6% for the Baukol-Noonan lignite to 41.0% for the Dickinson lignite. These moistures represent as received percentage; bed moisture would be somewhat higher.

HEAT TREATMENT

The stoker-sized lignite, as received, was stored in sealed drums until thermally treated in the absence of air in a rotary metal drum retort of approximately 10-pound lignite capacity at the Bureau of Mines Lignite Experimental Station (*12*).

Nominal treating temperature was 700° F., as measured near the center of the retort. Heating was continued until moisture and gas evolution were considered negligible. The processing was not the same as normal drying, in so far as moisture, as determined by the xylene method, remained in the solid residue until a treatment temperature of about 400° F. was reached.

At 700° F. decarboxylation of the lignitic substance was appreciable; from 39 to 45 cu. feet of gas, chiefly carbon dioxide, was recovered per 100 pounds of natural lignite. Ultimate analyses of the solid residue from the thermal treatment are given in Table II. Differences in carbon and oxygen contents of these residues may be attributed to variations in ash content. On an ash-free basis, maximum differences in carbon concentration were less than 2 percentage units. Oxygen-carbon ratios were from 0.16 to 0.19, further indicating uniformity of the ultimate composition of the carbonized residue.

EXPERIMENTAL PROCEDURE

The experimental procedure is modified from the static method described by Lavine (*10*), which is believed to be better adapted to this work than the dynamic method used by Pearson (*14*). The present investigation differed from Lavine's in that the cycle of hydration-dehydration was followed, rather than the dehydration-hydration. The basic cycle was repeated three times, to determine if the characteristic hysteresis curve for the gellike natural lignite was retained in the thermally treated lignite.

SAMPLE PREPARATION

Representative samples were obtained by splitting the char (residue) from the treatment in the rotary-drum retort. These samples were crushed to – 1/8 inch with minimum handling and stored in waxed, screw-cap sealed bottles until prepared for the sorption tests.

The – 1/8-inch thermally treated lignite was removed from the sealed jars and pulverized in a Braun pulverizer, using three passes with progressive reduction in plate spacing between passes. The 80- to 100-mesh fraction was screened out between passes and placed in sealed glass sample jars. In all steps, care was taken to ensure minimum handling time, in order to limit exposure to the atmosphere. Pulverization in the disk mill was advantageous over pulverization by hand in a mortar as done by Lavine (*10*), in that less time was required (reduced exposure time) and more 80- to 100-mesh fraction could be obtained from the same initial weight of material.

Most of the fines produced during pulverization by hand were unsuitable, being less than 100 mesh.

HYDRATION AND DEHYDRATION PROCEDURE

The procedure used for the present tests is as follows: Approximately 1 gram of the thermally treated lignite was placed in a stoppered weighing bottle, and weighed on an analytical balance to 0.1 mg. Ten samples of each of the six lignites—Bienfait, Zap, Beulah, Dickinson, Custer, and Baukol-Noonan—were thus prepared and placed over concentrated sulfuric acid in a desiccator for 6 to 8 weeks at 104° F. (40° C.). The weight after this stabilization period was taken as the base or standard weight for future

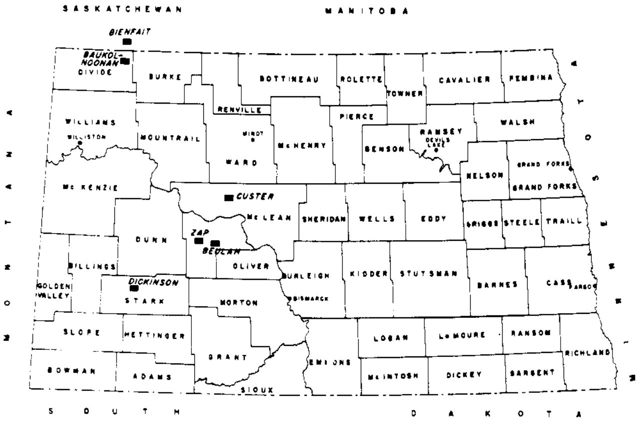

Figure 1. Source of lignites tested (13)

Table II. Ultimate Analysis and Heating Value of Solid Residue from Six Lignites Processed at 700° F.[a]

Lignite	Bienfait	Zap	Beulah	Dickinson	Custer	Baukol-Noonan
Ultimate analysis, %						
Hydrogen	4.0	3.6	3.5	3.7	4.0	3.9
Carbon	71.8	67.7	67.3	68.4	72.3	70.1
Nitrogen	1.4	1.1	1.1	1.0	1.3	1.4
Oxygen	13.4	11.1	11.1	11.0	13.5	12.2
Sulfur	0.6	1.6	1.7	1.7	0.5	0.7
Ash	8.8	14.9	15.3	14.2	8.4	11.7
Gross heating value, B.t.u./lb.	12,470	11,590	11,500	11,740	12,370	12,120

[a](Appendix 1, Table 12, *12*).

tests. Each lignite was then placed in a desiccator over a sulfuric acid solution of measured concentration having a known vapor pressure. Concentration of solutions ranged from 0 (distilled water, relative humidity 100%) to about 69% by weight of sulfuric acid (relative humidity about 6.3%). Plots were made of the specific gravity of sulfuric acid *vs.* concentration with solution temperature as parameter, and of concentration *vs.* water vapor pressure (*5*) to facilitate determination of acid concentration. Solutions of precalculated composition were prepared and the concentration was checked with a calibrated hydrometer. The samples were kept in the desiccator at 104°F. for 6 to 8 weeks, and reweighed. The weight gain over the base weight (corrected) was taken as the moisture gain. Moisture contents were then calculated on the basis of the "dry" or standard weight. The samples were again placed over concentrated sulfuric acid (specific gravity 1.84) for 6 to 8 weeks for dehydration and the cycle was repeated for a total of three complete cycles.

TEST EQUIPMENT

A constant temperature cabinet approximately 4 x 4 x 8 feet (inside dimensions) was constructed from insulating board. Heating was accomplished with a 2000-watt electric heater. A Brown Model 077 electric temperature controller with a Balco resistance bulb having a sensitivity of 0.1°F. was used to maintain the selected temperature of 104°F. To prevent local temperature variation, air was circulated with a continuous-operating revolving fan. A traverse of the area in which samples were exposed with a movable thermometer showed that a uniform temperature was maintained. Samples in weighing bottles were placed, one for each type of lignite tested, in 8-inch desiccators sealed with special high temperature grease. All samples were weighed with a Chain-o-matic analytical balance.

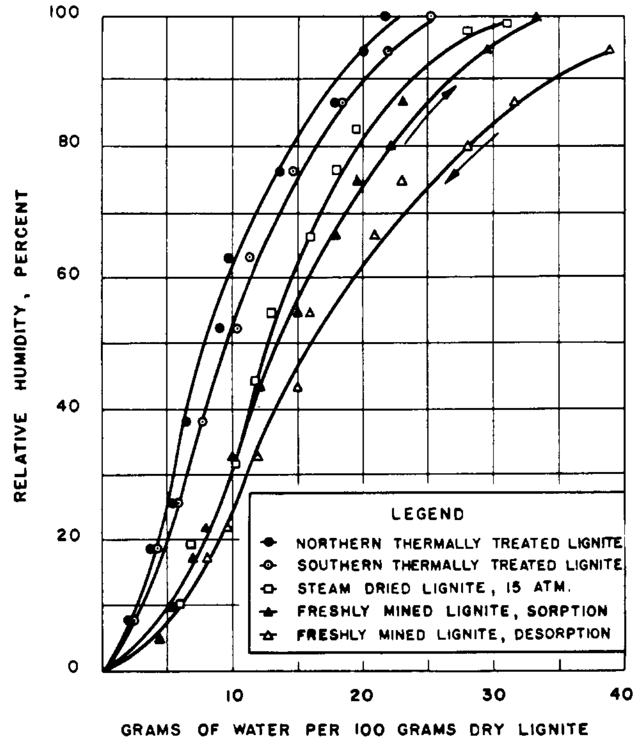

Figure 2. Relative humidity-water content curves for lignites at 104° F. (40° C.)

DISCUSSION OF RESULTS

Influence of Thermal Treatment and Type of Lignite on Water-Vapor Sorption. Of major interest in the present test series is the effect of thermal treatment on the ability of lignite to regain moisture from atmospheres of various relative humidities. Sorption data for the six different thermally treated lignites would allow comparison between lignites throughout the lignite deposit area.

Average data on moisture content for three sorption cycles on lignite previously thermally treated at 700°F., as determined in this investigation, are compared in Figure 2 with moisture contents of freshly mined lignites (desorption and sorption) from Lavine (*10*) and steam-dried lignite from Gordon (*3*).

The three thermally treated lignites from the northern part of the North Dakota-Southern Canada deposit (Bienfait, Baukol-Noonan, and Custer) exhibited nearly the same moisture retention, which was less at the same relative humidity than that of the three thermally treated lignites from the southern part (Zap, Beulah, and Dickinson). Thus a distinction was made between northern and southern lignites, and separate average curves were plotted. However, the distinction is slight. The conclusion that the commercial lignites in the entire field are rather uniform is supported by the uniformity of moisture and ash-free analysis, and of tar and gas yields upon thermal treatment (*12*).

A typical, somewhat S-shaped sorption curve was obtained when the water content of the thermally treated lignite was plotted as a function of the relative humidity (Figure 2). Differences between the moisture contents of the thermally treated lignites at the same relative humidity were less than those between the thermally treated and freshly mined or steam-dried lignite, as indicated by the curves in Figure 2.

The slope of the sorption curves for the thermally treated lignites was greater than that for freshly mined or steam-dried lignite, indicating that the vapor pressure increases more rapidly with water content than for the steam-dried or freshly mined lignite. Consequently, less moisture is present in thermally dried lignite. The effect of higher temperature level during initial dehydration is to decrease the ability of the lignite mass to assimilate water vapor. Tests at near 100% humidity have pointed out that the moisture regain decreased with level of treatment temperature, at least until a level of 950°F. (*8*).

It is believed that this decrease in ability to regain moisture is due not entirely to the presence of permanent or noncondensable gases in the capillaries formerly filled with water, which prevents the resorption of moisture, but mainly to changes in the lignite substance induced by the thermal treatment. This is evidenced by the fact that more moisture is retained by the steam-dried lignite, which was treated at approximately 390°F. (15 atm.), and still more by the lignite dehydrated at 104°F. (sorption curve for freshly mined lignite). Experiments at the Ontario Research Foundation (*15*) showed that successive dehydrations at room temperature lowered the ability of the lignite mass to regain moisture. Further evidence in the present case is that drying at increasing temperatures lessens the width of the hysteresis loop, which is still present at 104°F. but not noticeable for the steam-dried lignite or the lignite thermally treated at 700°F. The lignites thermally treated at 700°F. were taken through three complete sorption-desorption cycles without hysteresis in moisture retention.

At a relative humidity of 50%, which is approximately the average humidity occurring in the state of North Dakota, a moisture content of 8 to 9% is indicated in Figure 2 for the lignite dried at 700°F. and about 13 to 17% for the lignite dehydrated over sulfuric acid at room temperature. This effect of higher drying temperature is interesting because it has been assumed since the work by Lavine (*10*), that drying of lignite to less than 15% moisture was not practical, as the hygroscopic dried lignite would gain moisture to about 15% during transit or storage. Consequently, a lower moisture content may be practical, if a relatively high temperature is reached during initial dehydration.

Effect of Thermal Treatment on Coalification. From the vapor-pressure maintained over the sulfuric acid solutions and the apparent equilibrium moisture content of the lignite, the pore radii of the capillaries in the lignite mass may be estimated by the Thompson equation and the pore size-moisture retention relationship used to indicate the approximate rank of the coal (*9*).

Pore size *vs.* moisture retention for peat, brown coal, freshly mined lignite, and the lignite thermally treated at 700°F. is compared in Figure 3. Data for peat, brown coal, and freshly mined lignite were taken from Lavine (*10*), and data for the thermally treated lignite from the average results of the six lignites tested in the present investigation. Taking 50% of the moisture retained for a comparison standard as done by Lavine, it is found that this amount of bound water is held in capillaries less than 7.4 mμ in peat (Minnesota), 3.7 mμ in freshly mined North Dakota lignite, 2.5 mμ in thermally treated lignite, and 1.8 mμ in German brown coal. Study of the curve for the freshly mined and thermally treated lignite indicates that thermal treatment results in appreciable destruction of larger capillaries and to a lesser extent has diminished the number of smaller capillaries—i.e., most of the bound water is held in capillaries of intermediate size as compared to that of the freshly mined lignite. The over-all effect has been to decrease the apparent average size of the capillaries available for holding moisture.

Because of the relationship in descending pore size at 50% moisture retained (peat, lignite, brown coal), it had been proposed that pore size as determined from sorption studies be used for classification of North American solid fuels (*9*). However, such a basis is apparently not suitable for all fuel ranks. Other investigators (*16*) have described the effects of thermal treatment at relatively high temperatures as artificial coalification. On the basis of smaller average pore size, the thermally treated lignite may be considered to be metamorphosed to slightly higher rank than the fresh lignite, but still not so high as the brown coal reported by Lavine. However, consideration of the ratios of oxygen to carbon and net heating value to gross heating value for the thermally treated lignite indicates that a rank between subbituminous and bituminous has been achieved (*11*), which is a greater extent of coalification than indicated from pore size studies. The rank of brown coal in classification by pore size is not logical when compared to more standard classification, as the rank is indicated higher than the thermally treated lignite. The reason for this discrepancy is not known, but the brown coal may not have been a typical freshly mined coal. Its detailed history is not available.

Heat of Vaporization of Moisture from Thermally Treated Lignite. Latent heat of vaporization of moisture from the thermally treated lignite may be estimated from sorption data at 68°F. (20°C.) and 104°F. (40°C.), using the Clapeyron-Clausius equation as was done by Lavine for the freshly mined lignite (*10*). Assumptions used for this calculation are that water vapor obeys the ideal gas laws; that latent heat of vaporization is constant over the temperature range; and that the heat of vaporization is independent of lignite type. These assumptions are apparently valid for freshly mined lignite.

As in the case of the freshly mined lignite, the heat of vaporization was greater at lower moisture contents for the thermally treated lignite, but the numerical value for heats of vaporization at the same moisture contents were much higher for the thermally treated lignite. Heats of vaporization ranged from 1470 B.t.u. per pound at a moisture content of 20 grams water per 100 grams of dry lignite to 1900 B.t.u. per pound at 10 grams of water per 100 grams of dry lignite, with an average of 1660 B.t.u. per pound. Lavine's data (*10*) showed the heat of vaporization over the same moisture content to be 1080 to 1160 B.t.u. per pound, with an average of 1120 for the freshly mined lignite. The same calculations for water vaporizing from a plane surface gave a latent heat of vaporization of 1050 B.t.u. per pound.

The large increase in heat required to vaporize moisture from the thermally treated lignite, amounting to on the average about 80% more than that required for vaporization from a plane surface, indicates that the moisture is tenaciously held, and that the mechanism of retention may be changed. The increase is greater than that expected from consideration of departure from a plane vaporization surface. It should be reasonable to assume that the nature of the water me-

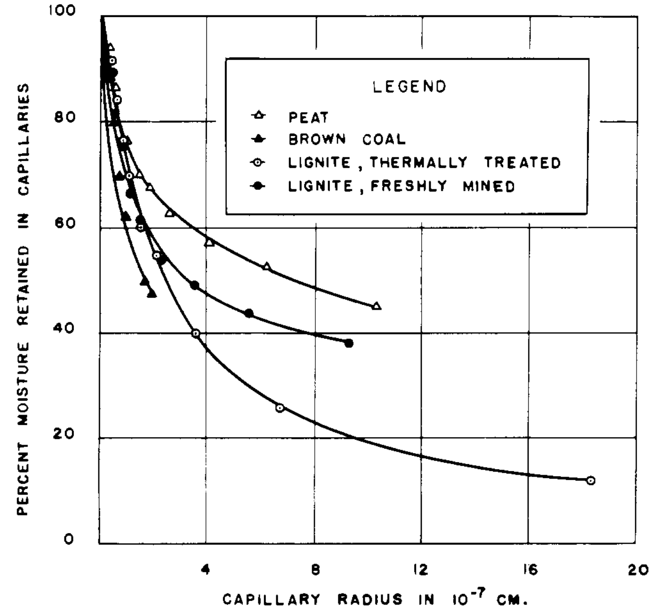

Figure 3. Moisture-pore size relationship at 104°F. (40°C.)

niscus for both thermally treated and freshly mined lignite is similar for the same moisture contents. However, the increase in average latent heat requirements for vaporization in the freshly mined lignite is only 7% greater than that from a plane surface. Thus, the moisture in the thermally treated lignite may be considered more tightly retained than in the natural lignite. Perhaps the more weakly held water in the natural lignite is associated with the gel structure of the lignite, which is evidently destroyed during thermal treatment at relatively high temperatures, as indicated by loss of hysteresis in the sorption curves.

Water retained by the gellike structure should follow closely the usual sorption laws for gels, and the heat of vaporization should not differ considerably from that calculated from a plane surface. This checks well for the freshly mined lignite, as the latent heat of vaporization from the freshly mined lignite is within 7% of that from a plane surface, but does not hold for the thermally treated lignite. Kreulen (*7*) in recent work distinguishes between a strongly assimilated moisture associated with the inner surface of lignite and weakly assimilated water associated with the gellike structure of the lignite. The strongly assimilated moisture did not follow the usual sorption laws nor did the calculated heat of vaporization correspond to that usually obtained for water, similar to the behavior noted in this investigation.

Influence of Type of Atmosphere on Water Retention. Dehydration over pure sulfuric acid for 6 to 8 weeks does not remove all moisture. The quantity of moisture remaining after the establishment of an "apparent" or "practical" equilibrium weight is problematical, and only a relative value for the moisture content of the lignite may be obtained. As there is disagreement over what is actually measured as "moisture" (*4*), especially with low rank fuels, the present method is believed adequate for the purposes of this investigation, which is essentially comparison of water retention at definite humidities. In addition, similarity of methods allowed comparison with the work of previous investigators at the University of North Dakota.

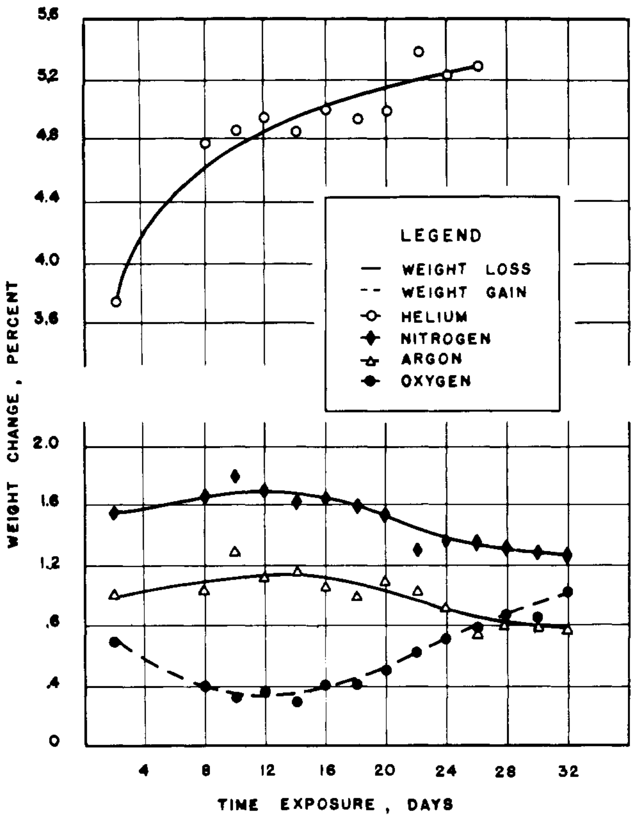

Figure 4. Weight change of thermally treated lignite dependent upon atmosphere at 104° F. (40° C.)

In preliminary tests, the thermally treated lignite was found to increase in weight over pure sulfuric acid after an initial loss. The initial loss was due to removal of moisture unavoidably gained during handling, storage, and pulverization of the samples. The weight increase, about 0.4% of the base weight, was constant after two 6- to 8-week periods in desiccators, allowing prediction of weight gain for subsequent cycles over pure acid. Consequently, a correction factor could be calculated for each lignite to be subtracted from the gross weight after each 6- to 8-week test period to give the "corrected" base weight. Repeated tests indicated that the correction was valid, in that weight gains at relatively low humidities could be predicted and reproduced. Without the correction, a standard weight could not be maintained. At high humidities, the correction factor was not as important, as it was a small fraction of the total weight gain.

Because of the thermal treatment in the rotary drum retort, the lignite had become activated sufficiently to sorb oxygen under the test conditions. Previous work with natural lignite dehydrated over sulfuric acid has shown that no sorption of other than water vapor occurred even after standing for periods up to 3 years (*15*). To check on oxygen sorption, a series of tests was performed with essentially a dry oxygen atmosphere over the lignite samples. Average results of a duplicate series on "dry" Custer lignite, run at 104° F., are presented in Figure 4. In the oxygen atmosphere over pure sulfuric acid, the weight of sample increased uniformly after a stabilization period of 15 days, with no apparent decline in rate of increase after 17 additional days' exposure. Thus, it is believed that oxygen retention by the thermally treated lignite is responsible for the weight increase noted over concentrated sulfuric acid in air-filled desiccators.

Tests in different inert gas atmospheres showed that varying percentages of moisture may be removed, depending upon the atmosphere. Results of a duplicate series of tests with dry Custer lignite over concentrated sulfuric acid in atmospheres of helium, nitrogen, and argon are compared in Figure 4. As expected, a net weight loss occurred in the inert gas atmospheres. Weight loss in the inert gas atmospheres was inversely dependent upon the molecular weight of the gas, the greatest loss occurring in the first day. Moisture loss in the helium atmosphere was much greater than in either the nitrogen or argon atmosphere, being about three times that in nitrogen and five times that in argon. The increased loss in moisture in helium is greater than expected and may be related to modification in sorption centers or retaining properties of the water in the capillaries. Similar results were observed in thermal drying of natural lignite in inert gas streams (*4*).

In nitrogen or argon atmospheres, little difference in weight was noted after the initial exposure period. Actually a slight gain occurred after about 20-day exposure, due perhaps to exposure to air during handling. The 6- to 8-week exposure in the actual test series would be sufficiently protracted to ensure a close approach to equilibrium conditions.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Brant, R., U. S. Geol. Survey, Circ. **226** (1953).
(2) Gauger, A. W., *Am. Inst. Mining Met. Engrs. Trans.* **101**, 148 (1932).
(3) Gordon, M., Lavine, I., Harrington, L., *Ind. Eng. Chem.* **24**, 928 (1932).
(4) Hoeppner, J., Fowkes, W., McMurtrie, R., Bur. Mines, Rept. Invest. **5215** (1956).
(5) "International Critical Tables," Vols. 1 and 2, McGraw-Hill, New York, 1933.
(6) Klein, H., *Braunkohle* **29**, 1 (1930).
(7) Kreulen, D., *Brennstoff-Chem.* **36** (17/18), 266 (1955).
(8) Kube, W., *Proc. N. Dakota Acad. Sci.* **6**, 83 (1952).
(9) Larian, M., Lavine, I., Mann, C., Gauger, A., *Ind. Eng. Chem.* **22**, 1231 (1930).
(10) Lavine, I., Gauger, W., *Ibid.*, **22**, 1226 (1930).
(11) Oppelt, W., *Proc. N. Dakota Acad. Sci.*, **6**, 36 (1952).
(12) Oppelt, W., Golob, E., Cooney, J., Kube, W., Bur. Mines, Mineral Research Invest., Prelim. Rept. **99** (1954).
(13) Oppelt, W. H., Kube, W. R., Chetvick, M. H., Kamps, T. W., Golob, E. F., Bur. Mines, Rept. Invest. **5164** (1955).
(14) Pearson, R., master's thesis (unpublished), University of North Dakota, 1950.
(15) Tasker, C., Ontario Research Foundation, Div. of Chem. Research Lignite, No. **23** (1933).
(16) Terres, E., *Brennstoff-Chem.* **33**, 1 (1952).

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Thermal Properties of Soybean Oil Meal

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Annual production of soybeans in the United States exceeds 350,000,000 bushels a year (*7*), probably about one half (*6*) the world total. Within the United States soybeans are grown widely in the Middle West. Cultivation of soybeans is a major effort in the corn belt states; over 20,000,000 acres (*5*) are devoted to this crop in that region, almost all harvested for the beans.

Two major raw materials arise from the soybean: oil and meal. Food products, principally margarine and shortening, utilize about 80% of the oil; the remainder is used in soap, paint and varnish, and miscellaneous nonfood products. Soybean meal is consumed for the most part as feed for livestock (about 90%), smaller amounts being used for soybean flour, plywood glue, and paper coatings, and in various industrial protein-containing materials.

Soybean oil meal is defined as the ground residue which remains after the oil is removed from the soybean, regardless of the process of extraction. Livestock feed is the primary market, except for a small outlet for industrial uses. Accepted specifications for soybean oil meal obtained by the two standard methods of processing, expelling and solvent extraction, are (*1*): for meal from either source, carbohydrates and fiber 7% (maximum), nitrogen-free extract 27% (minimum), and moisture 12.5% (maximum).

Minimum percentages of protein and fat differ, depending on the source of the meal. For hydraulic and expeller meals these are 41.0 and 3.5 and for extracted meals 44.0 and 0.5, respectively.

Following oil extraction the soybean meal is processed for solvent removal and to improve its nutritional properties. This usually involves raising the temperature of the meal by adding thermal energy through the walls of a container, by direct steam injection, or both.

Data useful in the design of apparatus used to process particulate materials are not overabundant. This is particularly true for materials which are biological in origin and hence susceptible to alteration upon exposure to air, moderate temperatures, or both. Typical of such material is soybean oil meal.

The objective of this work was to determine experimentally the thermal properties of a typical soybean oil meal, including thermal conductivity, thermal diffusivity, and heat capacity.

PROPERTIES OF MEAL, EXPERIMENTAL APPARATUS, AND PROCEDURE

Table I lists some of the physical and chemical properties of the soybean oil meal used in these studies. The meal was extracted in conventional Hansa-Meuhle type extractors using Skellysolve B as the solvent. Following the oil extraction the solvent was removed by heat and by direct steam injection at about 200°F. Solvent removal was considered complete. Residual oil content was found to be 0.7 to 0.8%, as shown in Table I.

Table I. Properties of Soybean Oil Meal after Solvent Removal

Size	Will pass 48 mesh
Oil content, %	0.7–0.8
Moisture content, %	13.2
Total protein, %	51.55 (dry stock basis)
Water-soluble protein, %	39.57 of total protein[a] (dry stock basis)
Variety of bean	Lincoln (probably)

[a] Determined by tentative procedure recommended by Soy Flour Association, revision of Dec. 10, 1946.

This meal may be further processed before being sold. It is frequently packaged in metal cans prior to final treatment. Meal which was canned but had not received its final (heat) treatment was supplied by the A. E. Staley Manufacturing Co., Decatur, Ill.

Thermal conductivity was obtained by using the concentric cylinder technique with a material of known conductivity as the reference. (Figure 1). Concentric copper tubes were arranged as indicated, with provisions for producing an atmosphere of saturated steam within the innermost tube. Two small iron-constantan thermocouples were located at points about diametrically opposite each other on each tube at the mid-point of the vertical sections.

The reference material used was Grade 6 Spheron carbon black furnished by Godfrey L. Cabot, Inc., Boston, Mass. At a mean temperature of 118°F. and a bulk density of 20.2

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