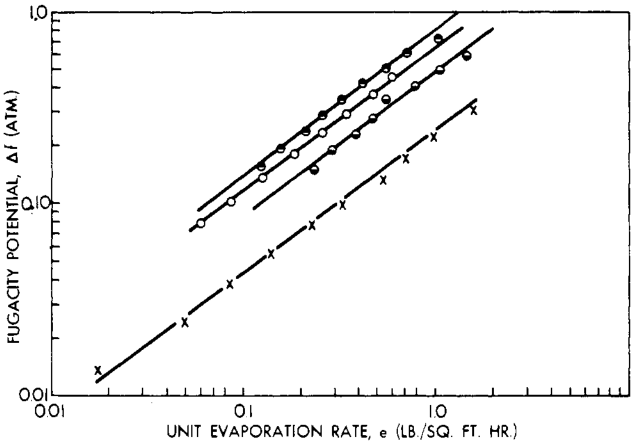

Figure 4. Dependence of vaporization rate on fugacity potential

defining the process of heat transfer from a horizontal plate facing downward (7).

The unit vaporization rate is plotted against fugacity potential for each liquid in Figure 4 and the data can be well correlated by the following equation:

$$e = C \cdot \Delta f^{1.32} \tag{9}$$

where the value of C varies from liquid to liquid.

Liquid	C
Water	6.58
Carbon tetrachloride	2.96
Ethyl alcohol	1.80
Benzene	1.33

It is anticipated that continuation of this part of the investigation under sub- and superatmospheric pressure will provide valuable information, from which more general relations can be derived.

NOMENCLATURE

Cp = heat capacity at constant pressure, B.t.u. per °F.
D = diffusion coefficient, sq. feet per hour
d = characteristic dimension, feet
e = unit vaporization rate, $\frac{\text{lb.}}{\text{hr. sq. ft.}}$
f = fugacity, atm.
g = acceleration due to gravity, ft./sec.^{2}
h = heat transfer coefficient, B.t.u./hr. sq. ft. °F.
k = thermal conductivity, B.t.u./ft. °F./ft.

kg = mass transfer coefficient, lb. moles/hr., sq. ft. atm.
P = total pressure, atm.
pf = film pressure factor, atm.
R = gas constant, atm. cu. ft./(lb. mole.) OR
t = temperature, °F.
u = convective velocity, feet per second
μ = viscosity of air film, lb./ft. hr.
ρ = density of air film, $\frac{\text{lb.}}{\text{cu. ft.}}$
θ = reciprocal average temperature, $\frac{1}{°\text{F.}}$
Δf = fugacity potential of vapor, atm.
Δm = temperature difference between interface and bulk air, °F.
ϕ = unique function defined by Equations 1 and 2

Dimensionless Groups

$$\frac{Cp \cdot \mu}{k} = \text{Prandtl number}$$

$$\frac{\mu}{\rho D} = \text{Schmidt number}$$

$$\frac{g \cdot \theta \cdot \Delta m \cdot d^3 \cdot \rho^2}{\mu^2} = \text{Grashof number}$$

$$\frac{g \cdot d^3 \cdot \rho^2 \cdot \frac{\rho_\infty}{\rho s} - 1}{\mu^2} = \text{Grashof number for mass transfer}$$

$$\frac{hd}{k} = \text{Nusselt number}$$

$$\frac{kg \cdot R \cdot T \cdot pf \cdot d}{D \cdot P} = \text{Nusselt number for mass transfer}$$

$$\frac{du\rho}{\mu} = \text{Reynolds number}$$

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Upper Explosive Limits of Cumene

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In common with most other hydrocarbons, cumene forms explosive mixtures with air. These explosive mixtures are limited or rendered nonexplosive in three ways: by diluting with air until the mixture is too lean to explode (lower limit), by diluting with fuel until the mixture is too rich to explode (upper limit), and by diluting with an inert substance until there is insufficient oxygen to explode.

Previously, only a small amount of information was available concerning the explosive limits of cumene (*1–3*), and this information pertained only to the limit as a function of the oxygen-nitrogen-cumene ratio at atmospheric pressure. However, it is impossible to predict the effect of

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[1] Deceased, March 30, 1956.

pressure or temperature changes upon explosive limits. Consequently, the present investigation was undertaken to determine the explosive limits of dry and wet cumene under various conditions of temperature, pressure, and oxygen content.

To carry on this work, it was necessary to design and construct equipment capable of furnishing a desired gaseous mixture at elevated pressures and of determining whether this mixture was explosive. Previous investigators, notably those of the United States Bureau of Mines, (*4, 5*), have studied the various factors affecting the limits of flammability. The most important factors are: method of ignition, direction of flame propagation, dimensions of the reaction vessel, humidity, pressure, temperature, and turbulence. In the present work, the first three factors were held constant and the last four were investigated.

APPARATUS

An apparatus, incorporating the findings and recommendations of the Bureau of Mines and designed to give maximum range to the explosive mixtures, was constructed. As finally developed, the apparatus consisted essentially of five parts:

1. A gas feed system by which various mixtures of two gases could be introduced into the system from compressed gas cylinders.
2. A saturator bomb in which the gas stream was saturated with the vapor of the test liquid or liquids.
3. A combustion chamber in which the gas vapor was ignited by a spark and flammability was measured.
4. A condenser system for condensing and collecting the vapor from the gas streams.
5. A constant pressure control regulator and a wet-test meter for maintaining the pressure and measuring the volume of gas flowing through the system. A schematic diagram of this flow system is given in Figure 1.

The gas feed system consisted of a cylinder of high pressure nitrogen and a cylinder of high pressure air, each connected to a common tee. Valves in each line permitted variations in the flow of the two gases, supplying various mixtures. The mixed gases were passed through a small orifice (a needle valve) to provide further mixing. Gages were available to measure the pressure drop across this valve. In practice, this pressure drop varied from 100 to 400 pounds per square inch gage. Before the mixed compressed gas passed into the system, a small amount was continuously analyzed by a Pauling oxygen analyzer.

The high pressure gas mixture then passed through a double valve system into the saturator bomb. The gas was piped to the bottom of the bomb, where it passed through a fritted steel plate and bubbled up through the test liquid. The temperature of this liquid was maintained by an electric heater, wound around the bomb. The temperature of the liquid was measured by three thermocouples located at various distances from the bottom of the saturator. Additional temperature readings were made of the bomb casing by attached thermocouples. The pressure and temperature of this saturator determined the mole per cent of the liquid in the outgoing vapor.

From the saturator, the vapor passed through heated lines into the combustion chamber. This vessel was also a pressure bomb, 2.5 inches in diameter and 32 inches long, heated to a temperature 10°F. above the saturator temperature to prevent condensation. Connected to this bomb were a drain valve, a rupture disk, a maximum pressure indicating gage, and an inlet valve. About 8 inches above the bottom, a spark plug was inserted in an opening in the side of the vessel. The two electrodes of the spark plug were connected by a small piece of platinum wire (B. & S. gage No. 36). A small amount of gun cotton was also wound around one of the electrodes. The electrical connection to the spark plug was regulated from inside the control room. Eighteen inches above the spark plug well there was another opening in which was inserted a plug holding a collodion strip. If this strip of collodion was burned during an experiment, the test mixture was considered explosive. The temperature of the vapors in the combustion chamber was measured by a thermocouple located in the central thermowell. This same thermocouple measured the temperature rise occurring during an explosion.

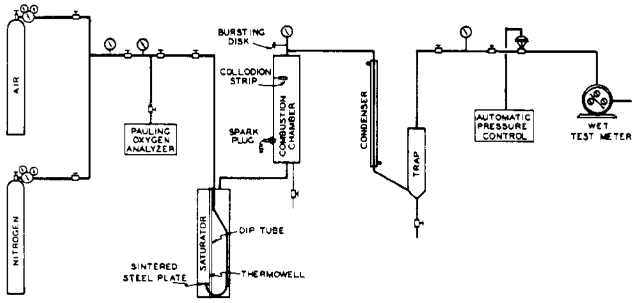

Figure 1. Schematic diagram of explosive limits apparatus

After leaving the combustion chamber, the vapor passed through a 4-foot water-cooled condenser, where the vaporized liquid was condensed and collected in a trap. An outlet needle valve on this trap permitted emptying, even during a run or when operating under high pressure.

From the condenser section the gas stream passed through another double-valve system into the control room where there was an automatically controlled constant pressure valve. This valve maintained the system at any desired pressure up to 150 pounds per square inch gage. The exit gas from this valve was at atmospheric pressure and was measured by a wet-test meter. The escape gases were then vented to the atmosphere. Before venting, this gas could be analyzed for oxygen content if desired.

All the controls necessary for regulating the apparatus during an experiment were located in a control room. The rest of the apparatus was located within a concrete high pressure cell. Thus, it was not necessary for the operator to be near the bombs during high pressure and ignition. A system of mirrors permitted the operator to view the outside pressure gages from the safety of the control room.

EXPERIMENTAL PROCEDURE

The saturator bomb was charged with 2000 to 3000 ml. of test liquid, which consisted of cumene or cumene and water. Phenol, 0.05 weight % of cumene, was added to prevent oxidation. While this material was coming up to temperature, a fresh spark plug and collodion strip were inserted in the combustion chamber. The apparatus was then pressurized with the test gas which was allowed to flow through the system until a dynamic equilibrium was reached. At equilibrium conditions, the combustion chamber was swept out with six times its volume of test mixture.

After the sweepout time, the test mixture was analyzed by measuring the amount of liquid collected in the trap while a certain volume of gas passed through the apparatus. This analysis was compared with that predicted from the temperature and pressure of the saturator. When these two values agreed, the saturator, firing chamber, and condenser were isolated and the spark plug was activated.

Explosions were indicated by a temperature and pressure rise. However, the final criterion was the condition of the collodion strip placed near the top of the chamber. A test was considered an explosion if the collodion strip was

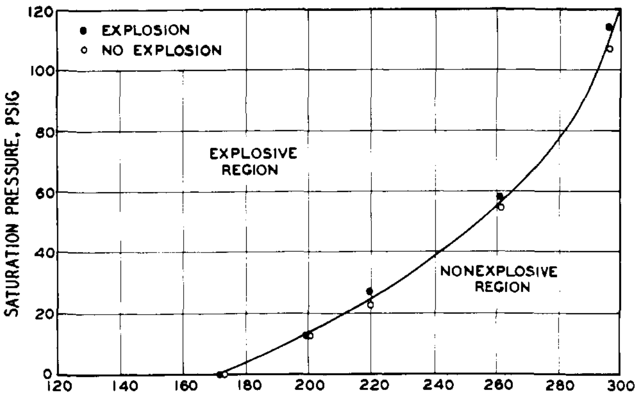

Figure 2. Effect of temperature and pressure upon upper explosive limits of cumene and air

completely burned, on the limit if it was partly burned, and a nonexplosion if it was intact. The following experimental data were collected on each run:

Temperature of saturator contents (three points)
Temperature of inside of combustion chamber
Pressure
Rate of gas flow at atmospheric pressure
Oxygen content of entrance and exit gases
Milliliters of liquid collected from condenser trap
Cubic feet of gas passed while liquid samples were collected
Pressure rise (if any)
Temperature rise (if any)
Condition of collodion strip after ignition

DISCUSSION OF RESULTS

Calibration Runs. Before work on the cumene systems, was begun, the results obtainable by the present apparatus were compared with those obtained from other apparatus, by determining the upper explosive limits of air-benzene at normal pressure and of air-propane at high pressure. Thus, it was found that, at atmospheric pressure, the upper limit of benzene mixtures occurred at 7.3 mole % of benzene. This compares favorably with the accepted value of 7.1 mole % of benzene (*5*). At 100 pounds per square inch gage, the upper limit of propane mixtures occurred between 22.0 and 23.7 mole % of propane, whereas the Bureau of Mines (*6*) value is 25.0 mole % of propane.

Cumene-Air System. Initially, the effect of pressure upon the upper explosive limits of the cumene-air system was studied. Figure 2 is a plot of the bracketing values at several temperatures and pressures. The apparatus furnished saturated mixtures only; therefore, in this graph the temperatures and pressures are those of the saturator bomb. The area to the left of the curve in Figure 2 is the region of explosive mixtures, as determined by saturation pressure and temperature. This region extends until a lower limit (excess oxygen) is reached at a lower temperature. However, this lower limit was not investigated in the present study. At atmospheric pressure and saturation temperatures above 174°F., the vapor is too rich in cumene to explode; at 100 pounds per square inch gage, the saturation temperature necessary to obtain a fuel-rich, nonexplosive mixture is 295°F. These values correspond to mixtures containing 8.8% of cumene-91.2% of air at atmospheric pressure and 10.8% of cumene-89.2% of air at 100 pounds per square inch gage. Several intermediate values were also obtained and are indicated in Figure 2.

These results can also be expressed as the amount of saturation pressure necessary to obtain an explosive mixture at a given saturation temperature. Thus, at 200°F. a pressure of 12.5 pounds per square inch gage is necessary to obtain an explosive mixture; whereas, at 298°F. a pressure in excess of 108 pounds per square inch gage is necessary. In all cases, the values given are valid only for saturated vapor mixtures.

Cumene-Air-Water System. These dry cumene experiments gave an upper explosive limit value at various pressures as a base curve for further work. However, as water narrows the explosive limits of many hydrocarbons, a study to determine the effect of water upon the upper explosive limits of cumene was undertaken. Because of the design of the equipment, only mixtures saturated with both water and cumene were obtainable.

Figure 3 is a plot of the bracketing values at several temperatures and pressures. As usual, water lowered the upper explosive limit of cumene-air mixtures from the values obtained with dry cumene and air. For example, at atmospheric pressure a saturation temperature above 174°F. is necessary to render a dry cumene-air mixture nonexplosive; with wet cumene mixtures, a temperature of only 140°F. or above is necessary to give a nonexplosive mixture.

Again, increased pressure raised the upper explosive limit. For example, at atmospheric pressure, the limiting mixture contained 3.9% of cumene; but, at 70 pounds per square inch gage, the value increased to 5.7% of cumene. Expressed in terms of saturation temperature and pressure, a wet vapor mixture below 140°F. will explode at atmospheric pressure, whereas at 214°F. a pressure in excess of 50 pounds per square inch gage is necessary to form an explosive mixture. Thus, the presence of water increases the safety of the cumene oxidation by narrowing the region of explosive mixtures.

Ignition under Flow Conditions. Because turbulence affects the flammability of a gaseous mixture, comparative runs were made on a static and dynamic system. It was found that, at 238°F. and 85 pounds per square inch gage and with the air flowing at the linear rate of 0.1 foot per second through the combustion chamber, a mixture consisting of 5.8% of cumene, 28.4% of water, and 65.8% of air would explode, although mixtures of the same composition were nonexplosive under static conditions. The temperature and pressure rise indicated that this mixture was very close to the dynamic upper limit. However, this experiment does indicate that the upper explosive limits are increased slightly by flow.

Diminished Oxygen Systems. The foregoing work on explosive limits of cumene-air systems indicated a need to know more about the effect of oxygen on the explosive limits of cumene. Consequently, determinations were made of the explosive limits of both dry and wet cumene under conditions of diminished oxygen content. In this manner, three component diagrams (Figures 4 and 5) of the explosive region were obtained both at atmospheric pressure and at 80 pounds per square inch gage.

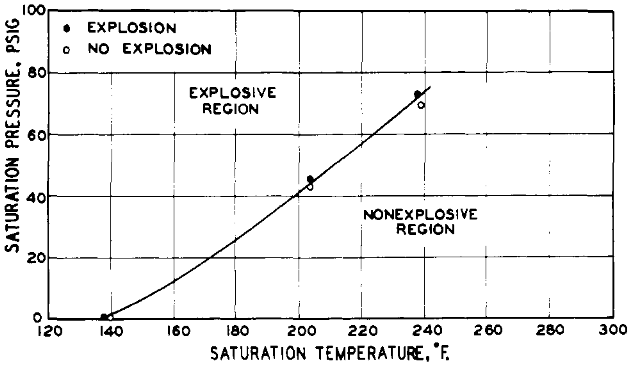

Figure 3. Effect of temperature and pressure upon upper explosive limits of cumene, air, and water

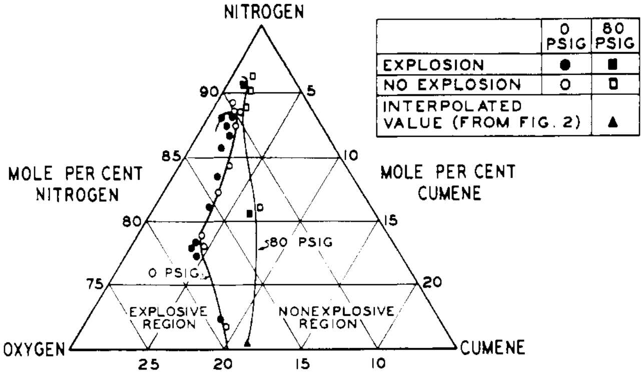

Figure 4. Explosive limits of dry cumene-oxygen-nitrogen

The curves in Figures 4 and 5 are upper limit curves only, except for the one at 80 pounds per square inch gage in the wet system. In this case enough data were collected to plot the entire explosive area, bounded by both the upper and lower limit curves. In the remaining cases, the upper limit curve was carried only to the turning point as shown. Presumably the lower limit boundary is a straight line parallel to the left-hand edge of the triangular diagrams and of the same cumene concentration as the turning point. However, this region was not examined.

Figure 4 is a ternary diagram of the explosive limits of the system cumene-air-nitrogen. The inner curve is the upper limit of the explosive region at atmospheric pressure. The sharp break in this curve at about 4.0% of cumene is surprising and may be due to a difference in the nature of the oxidation reaction above and below this point. At atmospheric pressure, dry gaseous mixtures containing less than 10% oxygen are no longer explosive, regardless of the cumene concentration.

The outer curve of Figure 4 is the upper limit of the explosive region at 80 pounds per square inch gage. As expected, the explosive area at high pressure is greater than the explosive area at atmospheric pressure. The minimum oxygen required for combustion at 80 pounds per square inch gage was only 8.5%.

Figure 5 is a ternary diagram of the explosive limits of the system cumene-oxygen-nitrogen-water at the same two pressures. In these cases the two inert substances (nitrogen and water) are plotted as one component, although only the nitrogen is independent. The molar amount of water is directly proportional to the molar amount of cumene. Because of this, Figure 5 is valid only for systems saturated with both water and cumene at a given temperature and pressure.

The inner curve is the upper limit of the explosive region at atmospheric pressure. The area within the outer curve is the explosive region at 80 pounds per square inch gage. These two curves clearly illustrate the widening of the explosive limits that takes place with an increase in pressure. The over-all explosive area of these wet mixtures is somewhat less than that of the dry mixtures (Figure 4).

At atmospheric pressure, the minimum amount of oxygen necessary for combustion is 11.5%, whereas only 9.4% is required at 80 pounds per square inch gage. These minimum oxygen values are somewhat higher than those of the dry mixtures. Thus, moisture tends to decrease the explosive area by lowering the upper limit and increasing the minimum oxygen necessary to affect combustion.

Because the data used to construct the ternary diagrams were obtained at constant pressure, changes in saturation temperature were necessary to vary the amount of cumene. Thus, the points of the curve were obtained at different temperatures. These temperatures varied from 96° to 172°F. in the dry case and from 94° to 142°F. in the wet case.

Temperature and Pressure Rise. In addition to other data, the pressure rise and the temperature rise developed during an explosion of the cumene mixtures were measured. Because most experiments were conducted near the limits, only moderate temperature and pressure rises were observed. Pressure rises of 2 to 20 pounds per square inch gage were common; however, in one case a pressure of 260 pounds per square inch gage was reached from an initial pressure of 115 pounds per square inch gage. In most cases, the temperature rise was from 0 to 5°F.; although, in the case mentioned above, a 30°F. rise was noted. The amounts of the temperature and pressure rise are probably related to the size and shape of the combustion chamber and are not absolute values for the mixture concentration.

PROBABLE ERRORS

In addition to the regular errors of mechanical inaccuracy (pressure and temperature readings), unique errors associated with this work include the use of a closed system, temperature of the combustion chamber, and the cumene employed.

The explosion tests were all conducted in an enclosed system. Thus, a pressure was built up within the apparatus during each positive experiment. In those near limiting cases where partial burning would occur, the pressure built up by this burning may have been sufficient to cause complete burning; hence, the mixture would be reported explosive. This error may lead to slightly wider limits than would be obtained with an open or a no-pressure rise system.

Another factor affecting the explodability of mixtures is the temperature of the combustion chamber. Because this was kept 10°F. hotter than the saturator, the test mixture was always ignited at a temperature somewhat greater than that used to vaporize the liquid. This heat may also cause widening of the limits, because some near-limiting mixtures at saturation temperature burn at the elevated temperature of the combustion chamber. However, in the temperature region investigated, this effect appears to be slight (*7*, *8*).

Dow commercial grade cumene was used in making these determinations. This hydrocarbon analyzed 93.3% of cumene by freezing point. The presence of slightly more volatile impurities, such as ethylbenzene, may have lowered the upper explosive limits somewhat, because more hydrocarbon would be present in the vapor than was calculated for any given temperature.

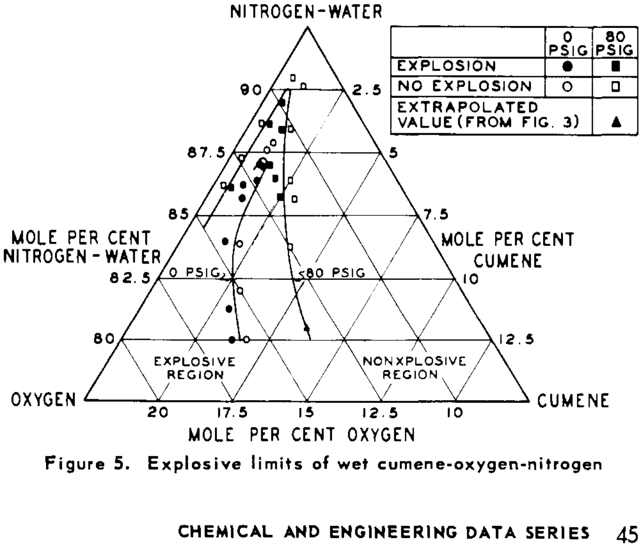

Figure 5. Explosive limits of wet cumene-oxygen-nitrogen

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.

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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 he 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.