

# Laboratory Study of the Self-Heating Tendency of Coals and Their Pyrolysis Chars

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Laboratory experiments were performed to examine the self-heating tendencies of bituminous coals and lignite as compared to chars prepared by their pyrolysis. The effects of oxygen, moisture, initial temperature, volatile matter content, and rank of coal were studied. The primary role of moisture was to supply an initial heat of adsorption which raised the temperature to a point where the oxidation reactions were self-sustaining. The pyrolysis chars were found to have no greater tendency toward self-heating than their parent coals, and in particular, the lignite char was found to be much more stable than the lignite from which it was prepared.

The tendency of coals and chars to spontaneously combust or self-heat is well-known. The self-heating is caused by exothermic reactions, primarily oxidation and the adsorption of water vapor (Nordon, 1979). The extent of the self-heating is determined by chemical kinetics and thermodynamics together with the transport phenomena governing the supply of reactants and the dissipation of generated heat. A temperature increase results when the local production of heat exceeds the heat loss by convection, diffusion, and conduction. Recent interest in this phenomenon stems from the interest of several utilities to pyrolyze coal destined for power plant consumption, obtain the volatilized liquid product, and use the resulting partly desulfurized char as inexpensive boiler fuel. The liquid product from pyrolysis would be upgraded into premium fuels that hopefully would more than defray the cost of the operation. Such a process would entail the storage of large amounts of char. One concern is that such chars might be more reactive and thus less stable toward self-heating in storage than the parent coals from which they were produced. To examine this problem, this work compared the self-heating tendency of a set of coals and their chars containing various amounts of volatile matter.

Basically, the factors involved in the self-heating of coal and char can be divided into two areas: the first being the properties of the coal or char and the second being the environment or storage conditions. The properties of the coal or char include chemical composition, rank, size of particles, volatile matter content, the extent of prior oxidation or weathering, and the percentage of equilibrium moisture saturation.

At low temperatures, oxidation reactions are slow and the heat produced by oxidation is small in comparison to the heat of adsorption of water vapor (Bhattacharyya, 1970, 1971). In addition to supplying a heat of adsorption, water vapor may also have a catalytic effect on certain oxidation reactions (Nordon et al., 1979). The susceptibility of coal to self-heating and spontaneous ignition has been observed to increase with decreasing rank, with lignite and subbituminous coals being more susceptible to self-heating than bituminous coals (Kuchta et al., 1980). It appears that pyrites may play a role in raising the tem-

perature to a critical point (75–85 °C) at which the oxidation rate is sufficiently high to support further spontaneous heating and eventual ignition at a higher temperature (Li and Parr, 1926). In one investigation in which oxidation rates were measured for chars prepared at different temperatures, Nordon et al. (1979) found that an 8-fold decrease in volatile matter content caused a 3- to 5-fold decrease in the oxidation rate.

In addition to coal properties, the storage conditions have a significant effect on the self-heating behavior of coals. As noted by Daw (1982), at some critical size there is a transition from a stable lower temperature storage condition to an elevated temperature condition, the exact behavior depending on transport and kinetic factors. Nordon (1979) has developed a finite-difference model which accounts for storage conditions and other boundary conditions in the self-heating of coal and char.

Various laboratory methods have been developed for studying the self-heating tendency of coals. Lawn et al. (1981) have described an experimental technique and a model whereby laboratory results can be extrapolated to predict field behavior. Among other methods are the nonadiabatic heating of coal using a programmed temperature (Schmeling et al., 1978), the adiabatic calorimeter (Kuchta et al., 1980), the isothermal measurement of heat generation rates (Bhattacharyya et al., 1971), the determination of minimum self-ignition temperature (Cameron and MacDowal, 1972), the crossing-point method (Sherman et al., 1941), and the adiabatic self-heating method (Shea and Hsu, 1972). The latter method was adopted for the work reported herein in that the relative self-heating tendency of a coal sample was determined by monitoring the temperature rise of the sample under a given set of laboratory conditions.

## Experimental Section

**Materials.** Analyses of the coals and of selected prepared chars used in this study are described in Table I. A description of the physical condition of the materials is given below: (1) Western Kentucky No. 9 coal (I), obtained from Tennessee Valley Authority (TVA), was in 1-in. (nominal) pieces when received. This coal was ground and

**Table I. Proximate and Ultimate Analysis of Coals and Chars Used in the Pyrolysis and Self-Heating Experiments<sup>a</sup>**

supplier/ preparer	TVA	TVA	Dallas Power & Light
location of mine or production	Western Ken- tucky	Western Ken- tucky	Texas
seam	No. 9 (I) <sup>b</sup>	No. 9 (II) <sup>c</sup>	
material	bituminous coal	bituminous coal	lignite
proximate analysis (dry basis)			
% volatile matter	39.9	35.0	47.0
% ash	7.1	18.6	13.5
% fixed carbon	53.0	46.4	39.5
BTU/lb			
dry	13 757	11 652	11 028
maf	14 804	14 313	12 745
ultimate analysis (dry basis)			
% carbon	75.8	64.5	64.8
% hydrogen	5.5	5.0	5.2
% nitrogen	1.6	1.4	1.1
% oxygen	7.0	5.4	14.1
% sulfur	3.0	5.1	1.3

supplier/ preparer	this work		
location of mine or production	Western Kentucky	Western Kentucky	Western Kentucky
seam	KY No. 9 (I)	KY No. 9 (II)	KY No. 9 (II)
material	char	char	char
proximate analysis (dry basis)			
% volatile matter	3.5	0.8	18.6
% ash	11.0	24.4	19.3
% fixed carbon	85.5	74.8	62.1
BTU/lb			
dry	12 694	11 016	11 476
maf	14 270	14 565	14 226
ultimate analysis (dry basis)			
% carbon	83.6	73.2	67.1
% hydrogen	1.0	1.1	4.2
% nitrogen	1.3	0.8	1.6
% sulfur	2.1	4.0	4.1
% oxygen	1.0	3.5	3.7

<sup>a</sup> The analyses were performed by TVA's Power Service Center Central Laboratory, Chattanooga, TN, using a Modified Blending Method to determine the volatile matter content. All analyses are in weight percent. <sup>b</sup> (I): Signifies first shipment of coal received from TVA. <sup>c</sup> (II): Signifies second shipment of coal received from TVA.

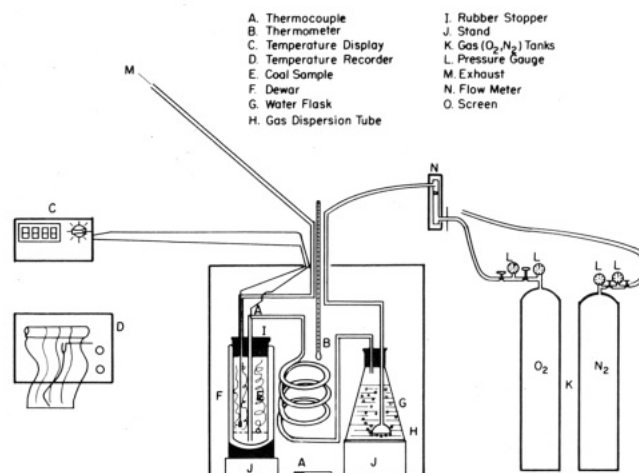
screened with a 3–14-mesh fraction being used in pyrolysis and self-heating experiments. A second shipment of Western Kentucky No. 9 (II) was received from TVA which had the following particle size distribution and was used as received.

Tyler mesh size	wt %
3–5	0.7
5–8	3.8
8–14	15.1
–14	80.4

(2) Texas lignite supplied by Dallas Power and Light Corp., Dallas, TX, was received wet and in nominally 1-in. pieces and was ground and screened to 3–14-mesh particle size before use.

(3) Chars, produced by pyrolysis in this work using Texas lignite and Kentucky coals, were ground to –3 mesh before use in the self-heating experiments.

**Equipment. Pyrolysis Apparatus.** A stainless steel pyrolysis vessel (10.8 cm i.d. and 29.8 cm tall) inserted in a Lindberg well furnace was used for pyrolyzing coal to

**Figure 1.** Schematic diagram of the self-heating apparatus.

produce chars of different volatile matter content. The pyrolysis vessel was equipped with a chromel–alumel thermocouple located 7 cm from the bottom and with an inlet and outlet for gas flow. Vapors generated from the pyrolysis experiments were trapped by a condenser external to the reaction vessel. A detailed diagram and heating rate profiles are given by Sahawneh (1982).

**Self-Heating Apparatus.** The self-heating apparatus shown in Figure 1 consisted of a double-wall Dewar (24 cm long, 6.8 cm i.d., 8.6 cm o.d. with 665-mL capacity) made of borosilicate glass located in a constant-temperature oven. Nitrogen or oxygen was fed through a disperser at the bottom of the Dewar after passing through a water-filled saturator as desired. The sample temperature was monitored by a thermocouple located 1.27 cm above the gas disperser; the inlet gas temperature was measured by a second thermocouple located in the inlet stream before entering the Dewar.

**Procedures. Pyrolysis.** Western Kentucky coals and Texas lignite were used to produce chars having various volatile matter contents. Each coal sample was prepared by drying at 110 °C in 25 in. of Hg vacuum for approximately 24 h until constant weight was achieved. Before pyrolysis, the sample sealed in the pyrolysis vessel was purged with nitrogen which was then typically shut off before pyrolysis was begun. The furnace temperature was set to the desired pyrolysis temperature (i.e., the highest temperature to be reached during pyrolysis). The sample temperature was monitored at timed intervals throughout the pyrolysis process.

**Self-Heating.** For the self-heating experiments, the coals and chars were ground and then dried for 24 h at 110 °C under 25 in. of Hg vacuum. Each coal or char sample tested had a volume of 500 cm<sup>3</sup> and a sample weight of approximately 400 g. A gas flow rate of 160 cm<sup>3</sup>/min at room temperature was used.

To perform a typical self-heating experiment, the oven was set to the desired starting temperature (65, 95, or 100 °C) and the sample was brought to constant temperature under a flow of dry nitrogen. To initiate a self-heating experiment, the saturator was filled with water and the flowing gas was typically changed to oxygen. At 65 °C, the relative humidity of the oxygen passing through the coal was measured and was found to be saturated with water. During the reaction, the sample temperature was continuously monitored. The oxygen flow was terminated for safety reasons if the sample temperature reached 350 °C. In the experiments where the sample temperature reached a maximum below 350 °C and then decreased, the experiment was not terminated until the sample temperature

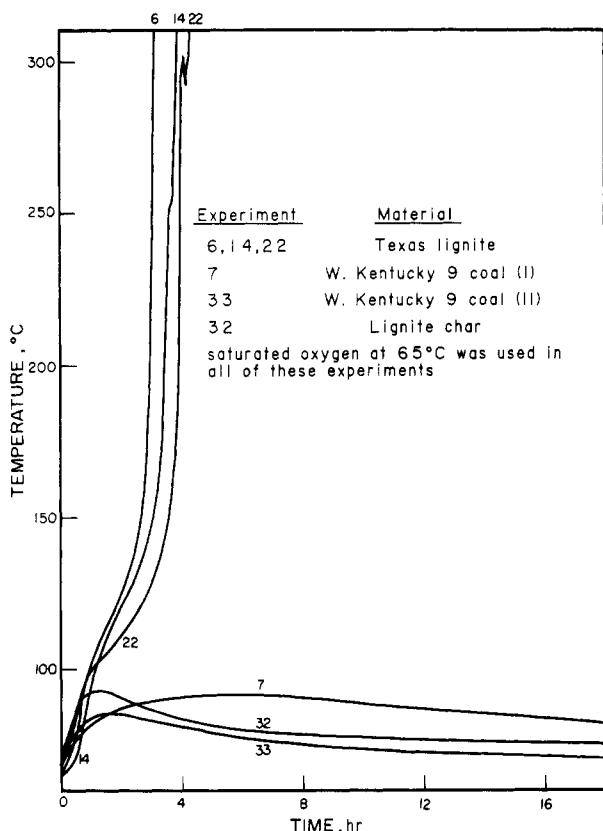


Figure 2. Comparison of the self-heating behavior of Texas lignite, lignite char, and Western Kentucky coals.

had decreased to within 10 °C of the starting temperature.

## Results and Discussion

**Pyrolysis Experiments.** Chars were prepared from lignite and bituminous coals at maximum temperatures ranging from 280 to 970 °C. Two lignite chars were produced at high temperatures, 970 and 930 °C, in which 92.1% and 91.5% of the volatile matter were removed, respectively. Pyrolysis of Western Kentucky No. 9 coal (I) removed between 4% and 86.5% of the volatile matter. Six carbonizations of Western Kentucky No. 9 coal (II) were performed in which the maximum temperature ranged from 395 to 965 °C, removing from 35.7% to 90.6% of the volatile matter.

**Self-Heating Experiments Using Texas Lignite, Lignite Char, Bituminous Coals, and Chars.** Typical results from the self-heating experiments are shown in Figure 2. All six of the self-heating experiments performed using Texas lignite at 65 °C with saturated oxygen showed a rapid and sustained increase in temperature. These experiments were terminated at 350 °C to prevent ignition. In general, as seen from Figure 2, the rate of temperature rise was rapid at the beginning of the experiment, slower in the middle, and very rapid near the end when the experiment was terminated. This type of curve with its characteristic inflection point is typical of curves derived from the classical theory of thermal explosions (Essenhig, 1981). Norden (1979) has discussed this theory in light of the self-treating of coals and chars and has noted that direct application of the thermal explosion theory without modification is not appropriate because several assumptions of the theory are violated. None of the Western Kentucky coals showed a maximum temperature increase (MTI) greater than 35 °C when tested at an initial temperature of 65 °C in saturated oxygen, indicating that the self-heating tendency of the Western Kentucky bituminous coal is considerably lower than that of the lignite.

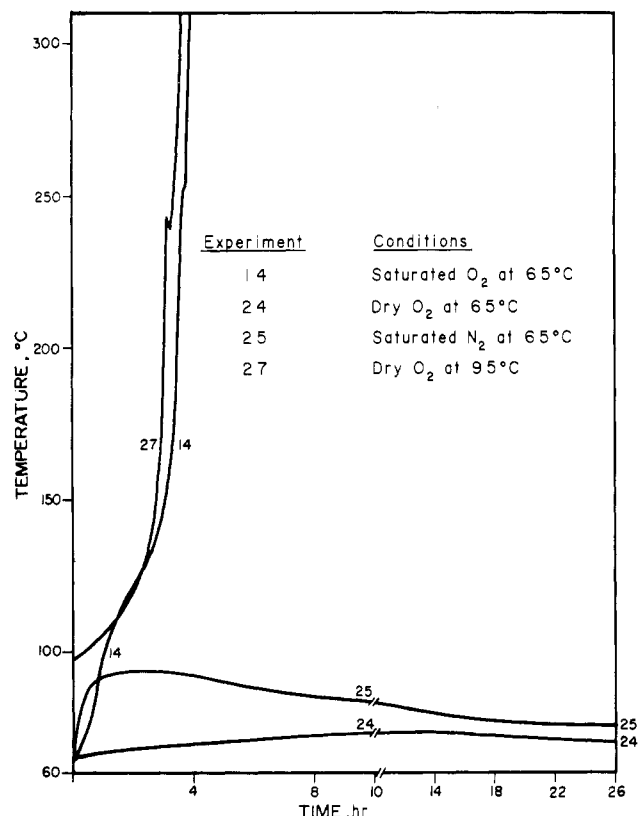


Figure 3. Self-heating behavior of Texas lignite under different experimental conditions.

In dramatic contrast to the self-heating behavior of Texas lignite, the chars produced from the lignite did not self-heat to any appreciable extent when tested at 65 °C. The MTI of lignite char in duplicate experiments was less than 30 °C as shown by experiment 32 in Figure 2.

Chars of various volatile matter contents produced from the bituminous coal were tested also for their tendency to self-heat. The self-heating curves of chars with amounts of volatile matter removed ranging from 22% to 86.5% were evaluated. The MTI ranged only from 12 to 26 °C, starting from an initial temperature of 65 °C in saturated oxygen. There appeared to be no definitive correlation between MTI and the volatile matter content of the chars. However, the chars produced from the bituminous coals appeared to be at least as stable toward self-heating as the parent coal itself in that they demonstrated similar behavior when tested at an initial temperature of 65 °C in saturated oxygen.

In an attempt to differentiate between the self-heating tendencies of the bituminous coals and their chars, the initial temperature of the test sample, i.e., the oven temperature, was increased from 65 to 100 °C. At this increased initial temperature level, several of the coal and char samples tested exhibited sustained temperature rises; however, several other apparently identical samples tested in a like manner gave an MTI of less than 30 °C. Thus, in contrast to the situation with the lignite and its char, the tests at 100 °C were not definitive in discriminating between the self-heating tendency of the bituminous coals and their chars.

**Effect of Reaction Conditions on the Self-Heating of Lignite.** In addition to the experiments performed by using saturated oxygen at 65 °C shown in Figure 2, three additional conditions as shown in Figure 3 were used to investigate the effects of moisture and oxygen on the self-heating of dried lignite. In the presence of dry oxygen at 65 °C, the temperature of the lignite increased by less

than 10 °C and then rapidly decreased as shown by experiment 24. When dry oxygen was used at 95 °C as shown by experiment 27, the lignite sample temperature rose rapidly and continuously until it was terminated at 350 °C. In saturated nitrogen at 65 °C, the temperature of the lignite rose 29 °C and then decreased toward the initial temperature as shown in experiment 25. Several observations can be made from these experiments. In the case of Texas lignite, an initial temperature increase of 29 °C is caused apparently by moisture adsorption at 65 °C, and this initial heat of adsorption increases the temperature to a point where the oxidation rate is then self-sustaining. These experiments should not be taken to infer that the only function of moisture is to release the initial heat of adsorption, as moisture may also have a catalyzing effect on certain oxidation reactions as pointed out by Nordon et al. (1979). Oxidation by dry oxygen at 65 °C was not sufficient to raise the temperature to the point of self-ignition under these conditions. However, at an initial temperature of 95 °C, the oxidation reactions were sufficiently rapid to be self-sustaining, even in the absence of moisture. Thus, in this case, the major role of water vapor appears to be to provide the initial heat of adsorption necessary to allow a critical temperature to be reached at which point the oxidation reaction becomes self-sustaining.

### Conclusion

The relative self-heating tendency of coals and chars can be examined conveniently in the laboratory by using testing equipment of the type described herein. The self-heating experiments performed on two ranks of coal in this study support the trend for the self-heating tendency to increase with decreasing rank. Texas lignite self-heated in saturated oxygen at 65 °C, showing a continual and sustained rise in temperature. In contrast, under the same conditions, the Kentucky bituminous coals did not self-heat to any appreciable extent, showing a maximum temperature increase of less than 35 °C, followed by a slow decrease toward the initial temperature of 65 °C.

The effect of water vapor on the self-heating phenomenon was readily evidenced by the experiment in which saturated nitrogen flowed through a lignite sample. The increase in temperature produced by the adsorption of water vapor was adequate to increase the temperature to where an oxidation reaction would be self-sustaining.

However, the effect of water vapor may not be restricted to providing the heat of adsorption alone as it may have other effects not discernible in this work, involving a catalysis of certain oxidation reactions. For lignite, the rate of oxidation with dry oxygen was self-igniting when begun at 95 °C, whereas it was not when begun at 65 °C. The heat of adsorption of water vapor approximately accounted for this 30 °C difference in temperature.

The chars produced by coal pyrolysis were in the case of lignite much more stable than the parent lignite itself. The low rank coal, lignite, self-heated continuously from 65 °C; however, the high-temperature char produced from lignite did not self-heat to a significant extent. Chars produced from Kentucky bituminous coal resembled the parent coals in their behavior and did not self-heat at 65 °C. Thus, based on this work, it appears that the storage stability of chars probably will be at least as good and, in the case of lignite, much better than the coals from which they are prepared.

### Acknowledgment

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### Literature Cited

- Bhattacharyya, K. K. *Prepr.—Div. Fuel Chem., Am. Chem. Soc.* **1970**, *14* (1), 59.  
 Bhattacharyya, K. K. *Fuel* **1971**, *50* (4), 367.  
 Cameron, A.; MacDowal, J. D. *J. Appl. Chem. Biotechnol.* **1972**, *22*, 1007.  
 Daw, C. S. "Self-Heating of Coal and Char: A Literature Review"; Oak Ridge National Laboratory: Oak Ridge, TN, June 1982; ORNL/TM-8273.  
 Essenhigh, Robert H. In "Chemistry of Coal Utilization"; Volume, Elliott, M. A., Ed.; Wiley: New York, 1981; 2nd Suppl. Vol, Chapter 19, pp 1287–1292.  
 Kuchta, J. M.; Rowe, V. R.; Burgess, D. S. *Rep. Invest.—U. S. Bur. Mines* **1980**, No. 8474.  
 Lawn, C. J.; Street, P. J.; Baum, M. M. "18th Symposium (International) on Combustion", The Combustion Institute: Pittsburgh, PA, 1981; p 731.  
 Li, S. H.; Parr, S. W. *Ind. Eng. Chem.* **1926**, *18*, 1299.  
 Nordon, P. *Fuel* **1979**, *58*, 456.  
 Nordon, P.; Young, B. C.; Bainbridge, N. W. *Fuel* **1979**, *58*, 443.  
 Sahawneh, Basem M. M.S. Thesis, Auburn University, Auburn, AL, 1982.  
 Schmeling, W. A.; King, J.; Schmidt-Collerus, J. J. *Adv. Chem. Ser.* **1978**, No. 170, 1.  
 Shea, F. L.; Hsu, H. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1972**, *11*, 184.  
 Sherman, R. A.; Pilcher, J. M.; Ostborg, H. N. *ASTM Bull.* **1941**, No. 112, 23.

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