

Presented Before the Division of Fuel Chemistry
American Chemical Society
Chicago, Ill., August 30 - September 4, 1964

THE USE OF THE MICROSAMPLE STRIP FURNACE IN COAL RESEARCH

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INTRODUCTION

The pyrolysis and carbonization behavior of coal has been studied intensively since the industrial revolution. Many techniques have been developed, but most require relatively large quantities of material; they are time-consuming and expensive to perform. The Microsample Strip Furnace described in this paper uses only a few milligrams of material and evaluations can be carried out in a matter of minutes. Techniques have been developed to study coking behavior on heating, weight loss on heating, the nature of the product evolved during the heating sequence, and ash distribution and properties.

These techniques generally yield qualitative information. The observations assist in the interpretation of the phenomena involved, and serve as a guide in setting up more quantitatively precise experiments. Qualitative differences in pyrolysis behavior can readily be observed and problems such as sample heterogeneity readily detected.

APPARATUS

The Microsample Strip Furnace (or often called simply a hot-stage microscope) has been described in previous publications¹. The model available at Princeton (Figure 1) is similar except that manual temperature controls are employed. Essentially, the unit consists of an enclosed microstrip furnace and swing-out, stereoscopic, variable power microscope. The microscope is fitted with a vertical illuminator, so that an optical pyrometer can be used to

¹A. R. Conroy and J. A. Robertson, "Controlled Atmosphere Hot Stage for Microscopic Observations of Glass Melting Phenomena. Part I," The Glass Industry, 44, 76-9, 139-43 (1963).

measure the temperature of the hot strip. The furnace consists of a strip of platinum, molybdenum or other refractory metal held between two water-cooled electrodes. Power for resistance heating is supplied by a 4-volt, 100 ampere step-down transformer. The temperature can be raised slowly by manually adjusting the autotransformers or quickly by presetting the autotransformers and then snapping the switch on. The furnace assembly is covered with an envelope consisting of a piece of three-inch Pyrex pipe to the top of which is sealed a plane piece of optical quartz. The sample is viewed through the quartz plate, and since a long working distance objective is used at 7-30 X total magnification, cooling of the microscope is not required. The enclosed area can be flushed with any gas desired. This gas is introduced so as to sweep across the quartz window and thus prevent fogging by condensibles.

The temperatures that can be reached depend mainly on the resistivity and thickness of the strip material. We used 3-5 mil thick, 8 mm wide platinum or molybdenum in this study. The maximum temperature obtainable is limited by the melting point of the material, 3190°F for platinum and 4750°F for molybdenum.

PRELIMINARY OBSERVATIONS

Microscopically, coal is a heterogeneous composite of macerals. It is desirable to make a preliminary microscopic observation to determine the minimum particle size which is representative of the material under study. If the heterogeneity is large with respect to the size of the particle preferred for microscopic study, then the various components can be separated and studied individually. The final conclusions are then weighted accordingly. Or, a composite of fine particles can be studied as representative of the total composition. If the heterogeneity is of fine structure, so that individual particles of the desired size are representative, the sample can be considered as homogeneous for the tests described. The latter was the case in the coals used in this study.

The individual behavior of the various macerals on heating can be observed, if desired, by heating a thin section, in which the macerals have been identified, in direct contact with the strip. The thin section must be carefully cleaned to remove the cement used in its preparation. Also, the cement-solvent system chosen must not modify the section.

Slow oxidation of the coal particle in air often brings out the structural discontinuities which are difficult to see in the untreated particle. This oxidation can be carried all the way to the final ash skeleton, showing the distribution of ash-forming minerals.

A few minutes spent in this preliminary examination will permit the selection of more meaningful samples for subsequent studies, and will provide a better understanding of the phenomena to be observed later.

CARBONIZATION OF COAL

Different ranks of coal show great differences in behavior under fixed heating conditions, and coals of the same rank show different behaviors if heating rates or atmospheres are varied. For example, it can be readily seen that a lignite which undergoes excessive particulate shrinkage, through loss of gas only, can be processed in equipment that would be completely unable to handle a coking coal. Observations of this nature before designing of laboratory or pilot set-ups reduce later problems. The time required for such observations is minimal.

Observations made before designing laboratory equipment should be followed by periodic examination of intermediates and products prepared in laboratory, pilot and shake-down plant runs. Often a product characteristic not apparent, except by microscopic study, can indicate needed process changes. The anomaly can often be duplicated under the microscope and the remedy checked for effectiveness before being applied on a larger scale.

Experiments in which heating rate was varied have been especially informative. The hot stage offers a much wider range of available heating rates than most pyrolysis equipment and so allows one to determine what might happen beyond the limits of the larger equipment. This is illustrated in experiments involving shock heating of various coals.

A small piece of coal, about 1-2 mg, was placed on the strip and shock heated to about 1000°C by snapping the switch with the transformers preset for 1000°C. Coking coal, such as Federal melts, exudes tars and vapors which condense on the glass vessel, and forms a coke button. A non-coking subbituminous coal such as Elkol does not melt, but puffs out into a porous structure with the loss of light vapors (Figure 2). A simple test for coking is to heat two particles of coal in contact with each other. Coking coals will fuse while non-coking coals will not. The strength of the bond after cooling can be easily estimated by probing with a needle while observing through the microscope.

WEIGHT LOSS

It had been thought that the observed volume changes could be used to estimate the percentage of coal volatilized. However, because of density and porosity changes in the char, this was not

possible. It was therefore decided to attempt a semi-quantitative approach by weighing a coal particle before and after exposure on the hot stage. It was found that, with care, particles of coal weighing one to three milligrams could be handled. Weighing was performed on a microbalance sensitive to 10.000001 gm (1 microgram).

Considerable technique development was necessary to reduce the experimental scatter found initially. Direct handling of coal particles with forceps proved impractical as the chars tended to be too friable. Microcrucibles about 2 mm on the edge were folded from platinum foil or gauze. The tared crucibles were then used to contain the coal. Besides increasing reproducibility, this system allowed the evaluation of fine-grind particles on the hot stage. However, the metal of the crucible did not make perfect contact with the metal strip, even though the strip was bent to the shape of the crucible and the latter was held as by a spring. Also, the total weight of metal that had to be heated was about doubled. As a result, the maximum temperature obtainable was reduced from 3200°F to 2200°F.

Heat transfer to the sample was from the heated strip only. Thus, heat flow was essentially unidirectional, with the bottom heated first. This phenomenon could be clearly observed in coking coals, where liquefaction and coking occurred in waves starting from the heat source.

The time to reach set temperature was estimated from the current pulse observed on an ammeter. When the switch was closed, the current rose quickly to a high value. As the metal strip heated, its resistance increased, decreasing the current. It was presumed that, when the current had decreased from the peak value to a steady state, the strip had reached temperature equilibrium. The effect of crucible and coal on time to steady state could be observed. It was estimated that it took 1.5 to 2.5 seconds to reach a temperature of 1830°F.

Weight-loss curves for several coals are presented in Figures 3-7. All curves reflect increased volatilization with increasing temperature. Further, the amount volatilized is often greater than that obtained in the ASTM volatile-matter test. The amounts volatilized at 1742°F are compared in Table I. In Figure 4 the number beside each point represents the number of experiments averaged to obtain it.

These findings are similar to those of Loison and Chauvin².

²R. Loison and R. Chauvin, "Rapid Pyrolysis of Coal," Cerchar, Cheltenham International Coal Science Conference, 1963.

Since volatilizations by shock heating are for the most part greater than those obtained by the ASTM technique, the heating rate must be responsible for the increase. At the time the results were obtained, the possibility that error inherent in the technique was responsible for all the variation was considered. Now this can be discounted because of other data obtained in Project COED which supports the conclusion concerning the dependence of volatilization on the heating rate³. However, the data obtained here gave us the confidence that increased volatilization could be obtained, and therefore guided the experiments which quantitatively proved this finding.

TAR AND LIQUOR YIELD

In order to estimate more quantitatively the amount of tar and liquor formed, a measured amount of coal was placed in a melting-point capillary tube. The hot strip was bent into a loop to hold the coal-containing end of the capillary. On shock heating, it was found that the vapors exuded and condensed in the upper regions of the capillary with the heavier material condensing nearer the coal. The nature of the exudate, whether tar, liquid, or gas, could be easily observed through the microscope and its condensation behavior followed. As shown in Figure 8, coking coal such as Federal tended to have more heavy tar, while the product from non-coking coals such as subbituminous Elkolare lighter and more mobile. A semi-quantitative comparison of yield can be made by measuring the lengths of capillary containing the various fractions.

The capillary tube technique has been found to be particularly useful in the rapid screening of unknown coals. By using a standard fill (0.5 cm) of a sized coal (40-60 mesh), an unknown coal can be compared with known standards with regard to water content, melting (coking) behavior, volume change on heating, tar evolution, tar character (light or heavy) and sometimes gas evolution (made visible by entrained tar). The entire observation takes about five minutes and requires only a few milligrams of sample.

ASH DISTRIBUTION AND PROPERTIES

Considerable information can be gained by observing the burning of a single particle of coal under the microscope. If desired, the oxidation can be carried out slowly, avoiding visible flames thus making possible the observation of the slow removal of carbon from the ash skeleton; or the combustion can be forced to determine its

³J. F. Jones, M. R. Schmid, R. T. Eddinger, Chem. Eng. Prog. 10, No. 6, 1964.

influence. By regulating the oxygen content of the atmosphere, the rate of oxidation can be controlled and the influence of temperature isolated.

When a coal particle is slowly oxidized, the ash-producing minerals are left at their original sites and a skeleton structure is retained. The original minerals may be converted to oxidized forms, e.g., pyrite converted to hematite, but in the absence of liquifaction, the converted minerals remain distributed in space about the same as their predecessors. This allows the observer to decide if beneficiation techniques would be useful in upgrading the coal and to what degree of size reduction the coal must be ground before separation could be expected.

After the ash structure has been studied, the temperature can be raised and the ash melting characteristics observed. The ash melting point or melting range can be easily measured and the reaction or fluxing of ash components noted. The behavior of the ash on heating gives clues as to problems that might be encountered in commercial use of the coal, such as clinker formation, fluxing of fire brick, or fly-ash control.

CONCLUSIONS

The techniques just described show that the hot-stage microscope can be a very useful tool in coal research. It can be used for qualitative observation of coal-structure carbonization behavior, and ash characteristics. Semi-quantitative results can be obtained, providing reasonable guide lines for scale-up work.

ACKNOWLEDGEMENT

The authors thank FMC Corporation for permission to publish this paper. Part of this work was supported by the Office of Coal Research through the United States Government Contract 14-01-0001-235 (Project COED).

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TABLE I

Comparison of Volatilization at 1742°F (950°C), Dry Basis

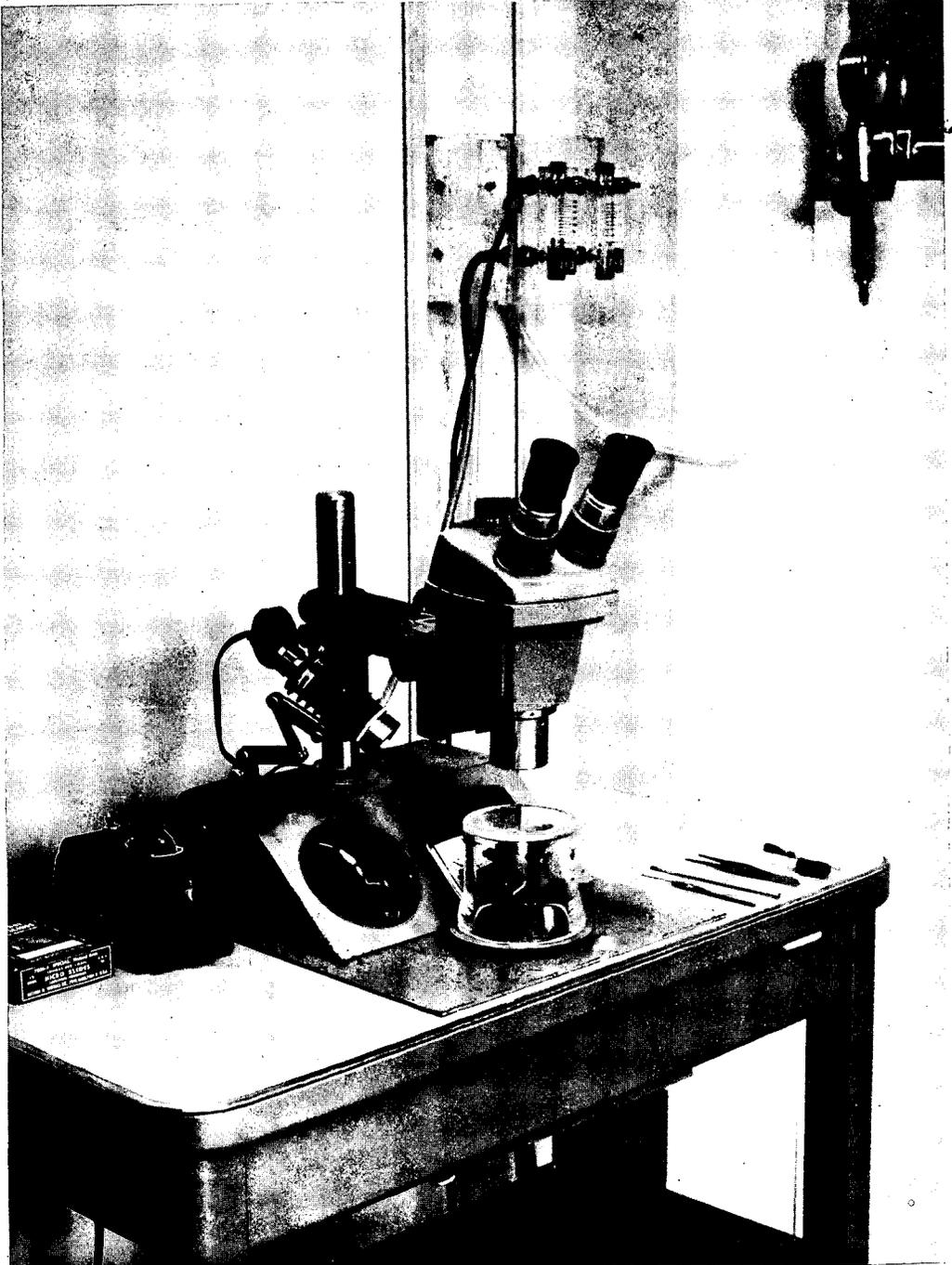
	<u>ASTM Procedure</u>	<u>Hot Stage</u>	<u>Percentage Increase</u>
Elkol ¹	40.7	48	17
Federal ²	37.7	49	30
Kopperston No. 2 ²	31.6	36	14
Colver ²	25.3	19	neg. -25
Orient No. 3 ²	44	41	neg. -7

¹Kemmerer Coal Company, Frontier, Wyoming

²Eastern Associated Coal Corp., Pittsburgh, Pa.

³Freeman Coal Mining Corp., Chicago, Illinois

Figure 1



Microsample Strip Furnace with Microscope
Note glass envelope covering the electrode posts.

Figure 2



A. Federal Coal before shock heating



B. Federal Coal after shock heating. Residue formed from a tarry liquid which solidified.



C. Elkol Coal after shock heating. Material cracked open to release gases.

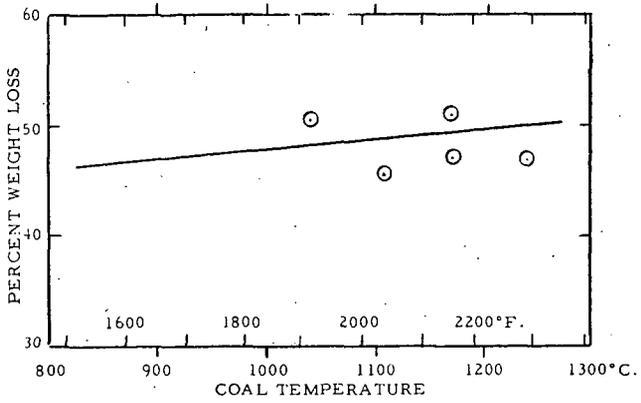
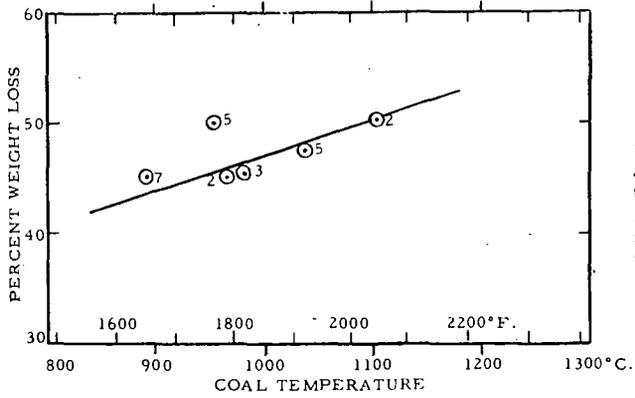


FIGURE 3

Weight Loss of Elkol Coal on Hot Stage



Points are average of tests, (number indicates how many tests were made).

FIGURE 4

Weight Loss of Federal Coal on Hot Stage

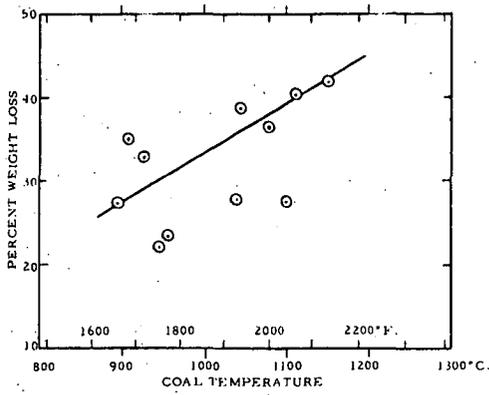


FIGURE 5

Weight Loss of Kopperston No. 2 Coal on Hot Stage

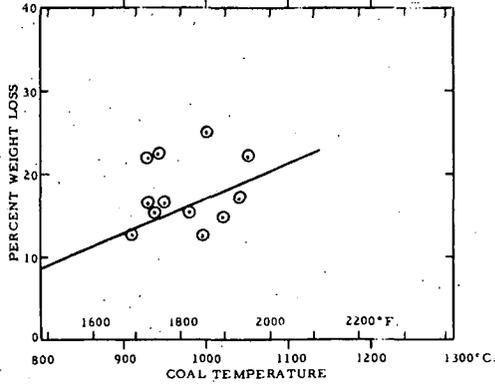


FIGURE 6

Weight Loss of Colver Coal on Hot Stage

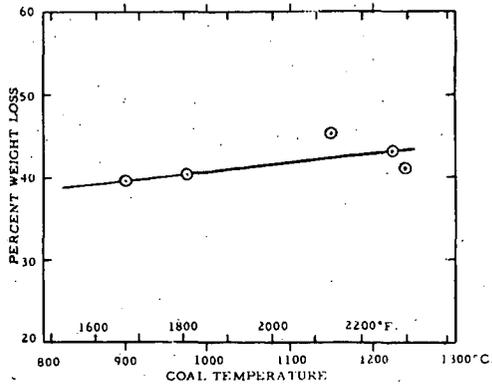
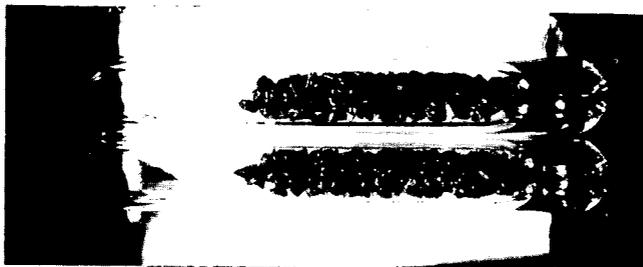


FIGURE 7

Weight Loss of Orient No. 3 Coal on Hot Stage

Figure 8



A. Before shock heating.
Federal on right,
Elkol on left.



B. After shock heating.
Federal has given more
of a heavier tar than
Elkol.

Figure 9



Elkol coal after mild oxidation. Ash is uniformly distributed throughout particle.