

ILLINOIS COAL AS A SOURCE OF SMOKELESS FUEL

S. W. PARR, UNIVERSITY OF ILLINOIS

Until recent years the topic of coke and its production carried with it in America substantially no accessory thought or idea except the simple one of metallurgy, and to all intents and purposes coke in its original significance meant pig iron. Indeed, in a general way we measured our coke production in terms of pig iron, pound for pound. A ton of coke meant a ton of iron, or a ton of iron meant a ton of coke.

Recently, however, we have had somewhat rudely thrust upon us a number of related subjects such as tar and toluene, dyes and drugs, synthetics without number, some with notable and some with ignoble propensities, and then still more recently fuels—fuels of the fuel oil type, fuels of the motor spirit type and perhaps, most interesting of all, fuels of the gas type, in which there is neither ash nor clinker, neither smoke nor soot, until, possibly because the wish is father to the thought, we imagine we can catch occasional visions of fuel gas as the predominating feature, and drugs and dyes and tars and even coke itself as merely by-products in the process of gas manufacture. It is a fascinating program and indeed one not without a very considerable amount of logical environment. So if there is reason in it with the premises fairly grounded in scientific fact, we may perchance be headed for "Spotless Town" without our really knowing it. Evidence toward this end may be somewhat scant or lacking or even possibly of a negative sort. If, perchance, there is any virtue in the old saying that it is darkest just before daylight, then a cursory glance at window sills and curtains and draperies will justify us in thinking that from the standpoint of the old adage at least, the daylight must be pretty close at hand. However, of a somewhat more positive character we may note that the American Gas Association has a standing committee on the Complete Gasification of Coal, and

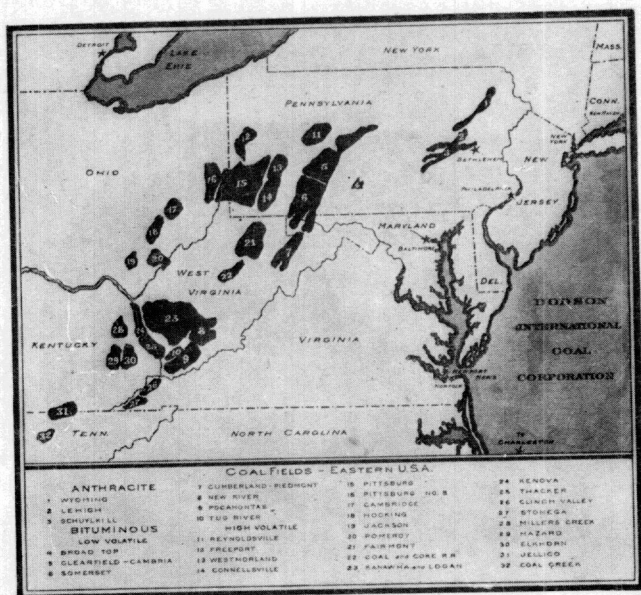


FIG. 1. Distribution of Coal in Eastern United States.

in France, Rene Masse proposes* that fuel in the gaseous form only be allowed, and that the use of solid fuel in any form whatsoever be prohibited. The argument for such a regulation moreover is not based as might be supposed upon artistic or sanitary considerations, but is advocated strictly as a conservation measure, to extend the life of the coal resources of France. Again, Samuel Wellington of England says** "From the analysis of thermal efficiencies given, there is every attraction for the consideration of the claims of gas as a profitable process in the conservation of coal for whatever purpose it is required."

Indeed, we are even now approaching a state of mind where it may be considered in place to revive the frequently quoted paragraph from an address by Sir William Siemens, delivered in 1881, wherein he says:

"I am bold enough to go so far as to say that raw coal should not be used as a fuel for any purpose whatsoever, and that the first step toward the judicious and economic production of heat is the gas retort or gas producer, in which coal is converted either entirely into gas or into gas and coke."

But whatever the ultimate goal of accomplishment, it is very self-evident that coke is one and the most important of the way-stations. We will do well, therefore, to give more than passing attention to that topic. What is coke? Where does it come from? How is it made? Now we will find at the outset that we cannot go far toward an answer to any of these questions without raising the same question with regard to coal, namely, What is coal?—Where does it come from?—How is it made? We at once begin to see something of the magnitude of the task set before us. Only a few of the more salient points, of course, can be touched upon within the limits of a single discussion of this sort, and then only for the purpose of maintaining a certain sequence upon which a better understanding of the final results may be based.

**Chemie Indust.*, 1918, p. 665.

***London Gas World*, 1919, p. 405.

WHAT IS COKING COAL?

Coals of the eastern United States tend to run somewhat in parallel lines, the most easterly being anthracites, then a much longer line of semi-bituminous coals, and then a longer line of bituminous coals parallel in the main to the semi-bituminous fields, extending southward into Kentucky and westward into Ohio.

But the farther west we go the less we hear about coking activities, the great Connellsville region, for example, in southwestern Pennsylvania being the peak of the curve as we go west.

When we take into our vision the coal fields of the entire United States, we note from the standpoint of coking proclivities that the farther west we go the less credit is given the coals for the purpose of coke making. This is entirely consistent with our technical literature which relegates all these coals to the non-coking class which have a hydrogen-oxygen ratio of 60 per cent or less. The ultimate verdict vitally affects the vast coal fields of the mid-continental region as well as not a few extensive areas in Colorado and Utah, and in the great Canadian Northwest.

This is a rather serious matter for these regions, if it truthfully represents the situation. According to the map, showing the coal areas of the United States, one is impressed with the relative extent of the deposits, especially in comparison with the areas furnishing the coking coals of the eastern United States. Moreover, we were forcibly reminded during the war of the economic waste involved in long freight hauls that could be avoided. One steel works alone near Chicago producing less than $\frac{1}{8}$ of the iron of that district uses a train load of coke per day. This would mean, let us say, three trains coming and three trains going, or six trains under constant movement to keep up that one supply. It is 460 miles from Pittsburgh to Chicago. It is, say, 100 miles from some of the principal Illinois fields to Chicago.

It should be stated at the outset that reference is here made to Illinois coals as a type rather than a product

having geographical limitations. It is to be so considered in this discussion, and as a matter of fact the characteristics as to high oxygen and non-coking character according to present standards would cover also the deposits in Indiana, western Kentucky and the coals of all the states west of the Mississippi from Iowa to Oklahoma.

The importance of determining the really correct status for these high oxygen coals is further emphasized when we note the relative coal reserves of some of the principal producing regions. Colorado would seem to lead the list. But so much is inaccessible owing to the great depth of the deposits below the surface, that for purposes of this discussion, the Colorado reserves might for the present at least be set aside or given a lower place in the list. It would appear then that Illinois leads even West Virginia and Pennsylvania in the matter of potential quantity. The coal in this region is readily accessible, is mined with comparative ease and is contiguous to great industrial centers. Its relative value as an asset to the resources of the state is a matter of great importance. Similar statements would apply equally to the adjoining states where the same coal measures are met with.

So far as ordinary everyday purposes are concerned, it can be shown by reference to a chart on production that aside from the particular adaptation to coke making, these coals are entirely on an equal plane with the coals of either West Virginia or Pennsylvania. For example—suppose we cut off from Pennsylvania the coal output which is mined for the purpose of cokemaking. The remaining tonnage will very well represent the relative rank of the several states with respect to their coal output for general industrial purposes. The annual output of coal for coking purposes is in round numbers about 65,000,000 tons. If we subtract that entire tonnage from the Pennsylvania yield of bituminous coal, the remaining 100,000,000 tons or less just about equals the annual Illinois output.

So much for the lay of the land. Now what is coal anyway?

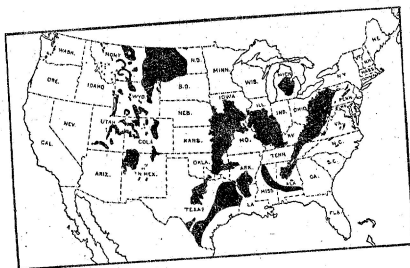


FIG. 2
Known Coal Areas of the United States.

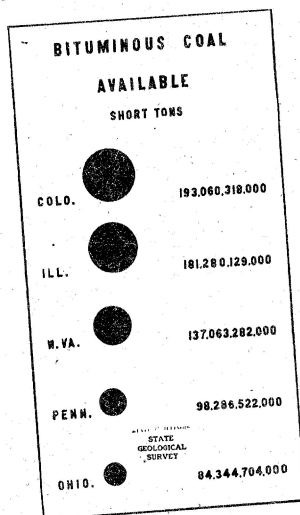


FIG. 3
Relative Coal Resources
of Five States.

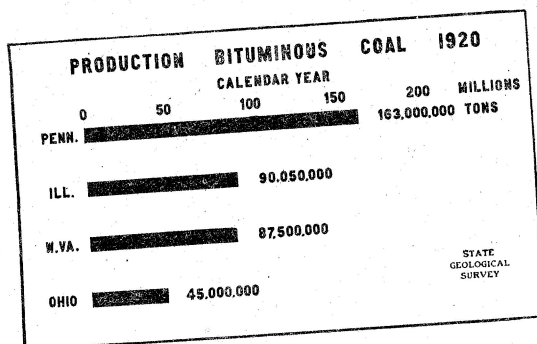


FIG. 4
Coal Production of Four States for 1920.

COMPOSITION OF COALS

This question was first installed, so to speak, in the chemical laboratory at the University of Illinois in 1902, and it is no exaggeration to say that today in this year of grace, 1921-22, it is more installed than ever. The slight hitch which occurred 20 years ago in the curve for the output of anthracite means that for the major part of that year the country at large was deprived of its smokeless fuel, and dire necessity was the mother of the practice of burning bituminous coal. Hence, the question, "What is coal?"

We have already seen that geographically the Illinois fields are about midway between the deposits of the East and the West. In a general way this is true also geologically. The fact is still further emphasized when we look at the coals chemically. In this chart, we have average

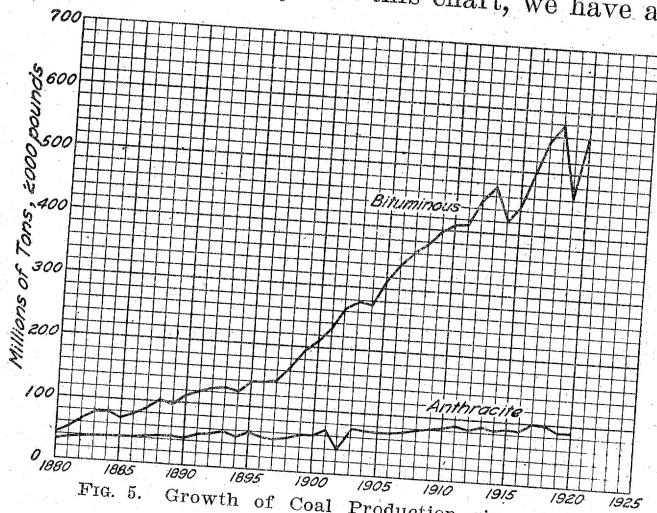


Fig. 5. Growth of Coal Production since 1880.

analyses showing the composition of three types, a low volatile Eastern bituminous coal, an Illinois coal and a lignite. For our purpose in this discussion it is desired to call attention to one characteristic difference only, that is the shaded portion. This represents the residual oxygen or "hydroxy" compounds which remain from the initial organic material after all the vicissitudes of decay and geological alteration have taken place.

The chart is interesting because it illustrates at least the chemical method ordinarily employed for determining whether a given coal would coke or not. For example, if the ratio of hydrogen to oxygen is 1:1 or even $\frac{3}{4}$:1 or 75 per cent of the oxygen percentage, then the coal is considered to be in the coking class. But if the ratio of hydrogen to oxygen is, let us say, 0.6:1, that is 60 per cent or less, then the coal is classed as non-coking. When one insists on a definition of these terms from those who make use of them, their answer really amounts to this: "A non-coking coal is one which is not being coked." They do not say it is one that cannot be coked, hence, fortunately the door is left open for the foolish to venture in.

For a better emphasis upon this oxygen factor, to be discussed presently, let us make a new set of ratios from these charted values,—a ratio of the inert or oxygen compounds to the volatile combustible residue, not because we wish to introduce a new ratio as a coking index, but simply as emphasizing from another angle the oxygen content of these coals. Such ratios would then appear as follows:

- (1) 4:14, or approximately..... 30%
- (2) 14:21, or approximately..... 60%
- (3) 21:20, or approximately.....100%

From the standpoint of the usual classification, those coals which pass beyond a ratio between the oxygen compounds and the hydrocarbons or volatile combustible of 1:2 or 50%, bring us into the class of non-coking coals.

It will be evident at once that we have here no explanation whatever as to the reason for coking or non-coking properties. The use or status to be given to analytical results of this sort is that of a definition only. It is a definition moreover which is not even empirical in its derivation. The most that can be said of it is that its basis is that of a coincidence—and any case which might arise to break the coincidence would vitiate the value of the definition.

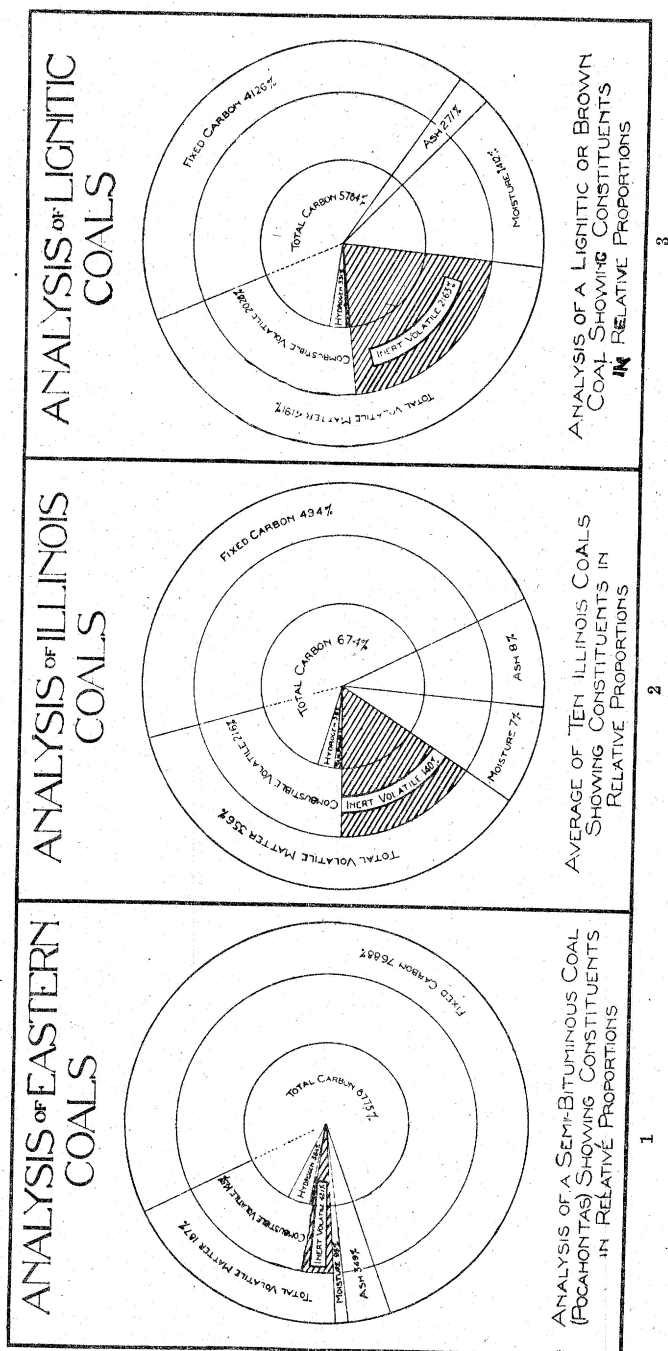


Fig. 6. Analysis of Typical Coals.

This brings us directly to the question as to what is involved in carbonization—and by carbonization is meant not simply the destructive distillation of organic matter but the production at the same time of a strong dense coherent mass, capable of being handled and suited for use in either domestic or industrial appliances. Are there any underlying principles which play a fundamentally important part in the production of coke? In other words, is there a theory of carbonization applicable in a general way to coals of all types, the recognition or observance of which would enable us to attain the utmost limit of possibility in the matter of coke formation?

Let us review some of the existing theories. In the old beehive oven the coal having a depth on the floor of the oven of about 3 ft. was decomposed by the heat of the burning gases which were discharged from the coal into the upper part of the chamber. As the decomposition proceeded downward, the gaseous products of decompositions were obliged to pass upward through the highly heated layers, thus undergoing secondary decomposition. The carbon deposited on the surface of the coke in this process of decomposition gave a silvery lustre and was believed to play a part in the formation of the cell structure of the product.

Now, this is hardly to be credited with the designation of a theory. It is doubtless a description of some things that take place upon or around the coke after it is formed. It is distinctly silent as to what is going on down in the coal mass at the zone of active decomposition. The fact of the matter is that the coals worked upon in this fashion were for the most part from the Connellsville region, and would be entirely indifferent as to what theory was proposed for their coking property. They would coke just as well under one theory as another or under no theory whatever.

EFFECT OF OXYGEN ON COKING

We come next to a study of coals resulting from the use of solvents which separate the coal without decomposition into two portions, one of which has distinctly non-

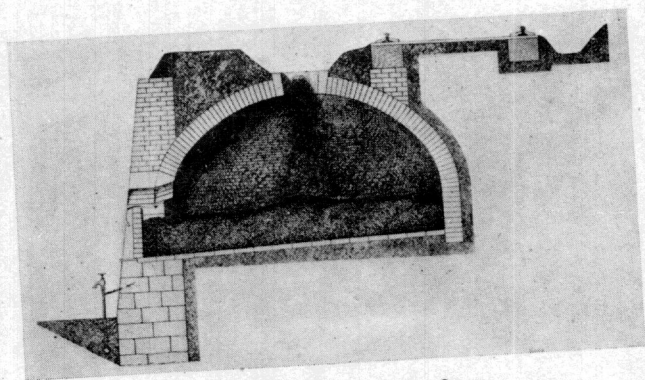


FIG. 7. Beehive Coking Oven.

coking and the other has distinctly coking properties. We have here the first real forward step in the study of the carbonization. The results obtained by these methods were well summarized by the late Professor Vivian Lewes in his Cantor lectures delivered in London in 1911. He called the non-soluble, that is the non-coking substance, the degradation product of cellulose or cellulosic residue, and soluble, or coking substance, he called resinic material. In the light of present-day studies, these names are not happily chosen, but that fact does not interfere with the value of the method itself. A continuation of this line of investigation is being very ably carried on by Professor Bone of London and by Professor Wheeler of the University of Sheffield.

In our own laboratory at the University of Illinois, it continues to be the most prolific source of information and furnishes the most numerous avenues of approach to the fundamental characteristics of these two type substances. It is along these lines, moreover, that we have made the most encouraging progress in our studies as to the underlying principles involved in the carbonization of coal.

It will be altogether impossible to go into a detailed discussion of the facts which have been developed, not only because there are so many of them, but also because there are so many which are in process of development and have not yet reached full maturity, and the plucking of immature fruit of this sort is not conducive to mental health and tranquility.

A few points, however, will give a general idea of what has been accomplished.

In the chart here shown, we have an illustration of the two type substances, the larger amount being the insoluble residue or non-coking substance and the smaller portion being the so-called resinic or coking material. The amount in each sample will give also a general idea of the relative proportion of these two substances as found in Illinois coals.

Now from the discussions that have thus far been presented in the literature, it would appear that the soluble material at the right, Fig. 8, is looked upon as

the active coking constituent and that the insoluble material or cellulosic residue is inert, and when it does not predominate in too great an amount over the soluble material, a good coke results. In this view of the theory of coke formation, the active coking material, the soluble or so-called resinic bodies, plays the part of a binder to the non-coking portion.

This theory would seem to have substantial confirmation by so simple an experiment as the following: Suppose we take a sample of the original coal of the type here used and coke the unaltered material in a crucible according to the ordinary procedure for the determination of volatile matter. We shall obtain a sample of normal coke such as this particular coal may be expected to produce. If now we take these type substances as illustrated in Fig. 8 and reassemble the non-soluble or cellulosic residue with the proper proportion of the coking substance, we shall have after the carbonizing process again a sample of coke which can in no way be distinguished from the first or normal sample. Hence the demonstration of the simple binding function of the resinic material would seem to be established.

But suppose now we proceed a few steps farther. We know that freshly mined coal has a tremendous avidity for oxygen and that if we permit a finely ground sample of Illinois coal to become fully saturated with that element all tendency on the part of the coal to produce coke is lost. Let us, therefore, saturate a portion of each of these subdivisions with oxygen and recombine them in their proper proportions, and for comparison, to make the circle complete, we will retain the sample already made in which both subdivisions were in the fresh or unoxidized condition. In Fig. 8 we have illustrated on the left, one sample of coke which has resulted from a recombination of the fresh or unoxidized portions in their correct ratios, and at the right we have a sample of coke resulting from a recombination in correct proportions of an oxidized resinic substance with a fresh or unoxidized residue. Note especially that the resulting coke is indistinguishable from the normal sample at the left in the

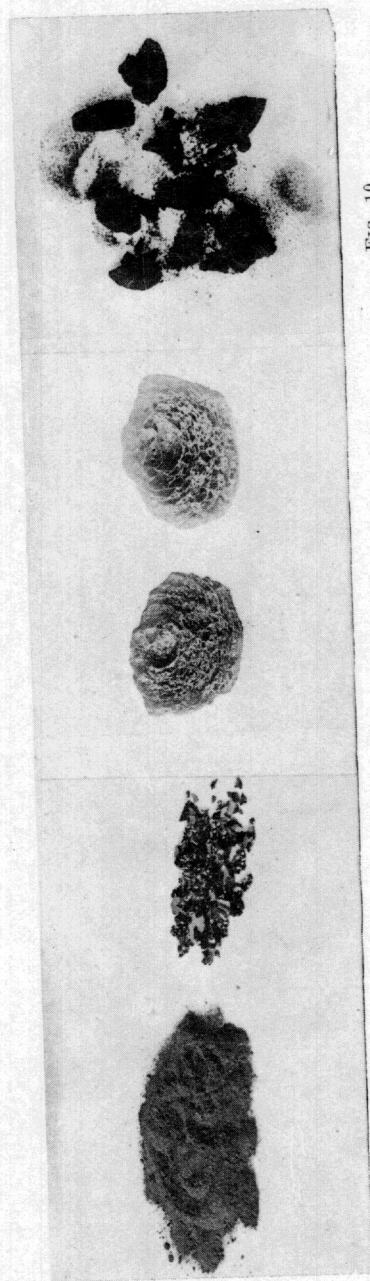


FIG. 8. Coal separated by solution into non-coking and coking constituents. FIG. 9. Samples of coke from original coal and reassembled constituents, the binding substance having been oxidized before combining. FIG. 10. Effect of oxidizing the non-coking residue on coking property of coal.

figure. This result is quite the opposite from what would be expected. If a coal which has been completely oxidized will not coke, and if the resinic matter carries the coking principle, then complete saturation of the resinic portion with oxygen should destroy its coking or bonding property. But it does not, the resulting sample being indistinguishable from the standard made for comparison.

Now we will reverse the process, saturating the non-coking cellulosic residue with oxygen and leaving the resinic material in the fresh unoxidized state. Upon recombining and carbonizing, we have the result as shown in Fig. 10. Here the coking property has been completely destroyed.

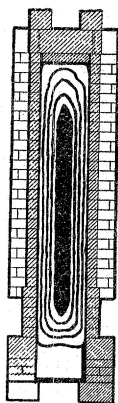


FIG. 11. Progressive Coking Lines in By-Product Oven.

Evidently our theory of the coking process will have to go farther back than the simple idea of a binding material, to a study of the factors that enter into the properties of both constituents and the conditions that affect their modification on the one hand or their preservation and indeed their accentuation on the other. Here it would seem from this illustration that we have worked out an answer to the question how not to make coke instead of the question "How is it made?" On the contrary, it may very well happen that the most direct information as to how to do a thing may come from positive evidence as to how it should not be done.

By way of illustration taken from some of our experiments: Here is a high volatile eastern coal with excellent coking properties. It has in its normal condition a hydrogen-oxygen ratio of 73 per cent. Now by saturating with oxygen under suitable conditions whereby it has taken up approximately 50 times its volume of oxygen, it has a hydrogen to oxygen ratio of 33 per cent, and has dropped out of the coking class absolutely as we would expect. By suitable procedure, however, and recognition of the part that the cellulosic residue may play in the carbonization process, it is possible to produce a normal coke even from this highly oxygenated sample which, as we have seen, was reduced in its H:O ratio from 73 to a percentage of 33.

LOW TEMPERATURE CARBONIZATION

Space will not permit of details in connection with the behavior and control of these factors. One point of fundamental importance and interest must suffice. It relates to the property of all coals in general and high oxygen coals in particular of decomposing with the evolution of heat. The interactions involved, therefore,

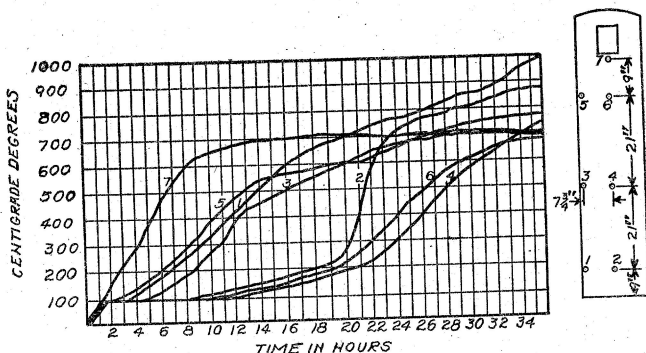


Fig. 12. Progress of Temperature Changes in By-Product Oven.

which it is essential to control, are exothermic in character. This fact should be coupled with another important one, namely, the control of these interacting substances can best be carried out under low temperature conditions of carbonization, that is, at temperatures below approximately 750 deg. C. (1382 deg. F.).

Fortunately for our purpose this fact of exothermicity and of carbonization are not only compatible with each other, but we believe are essential to the successful accomplishment of the prime purpose we seek, namely, the carbonization of high oxygen coals.

In attempting to maintain low temperature conditions, the first problem with which one is confronted is the physical impossibility of conveying heat into the center of a non-conducting mass without maintaining at the exterior a high heat head for the purpose of driving the heat forward through the insulating layers of coke that are continually in the process of formation. Some idea of the actual conditions involved may be seen from Fig. 12 here presented. The diagram at the right is a cross-section of a by-product oven with points indicated where temperatures within the coking mass were taken. It will be seen that in an extended 35-hr. coking period, the temperatures at the center of the mass did not reach the stage of decomposition, say 250 deg. C. (482 deg. F.) until after 20 hr. The obtaining of heat transmission, therefore, by simple process of conductivity is at once seen to be impracticable if low temperature conditions throughout the mass are to be maintained. It is at this point that we have attempted to use the exothermic reactions involved in the carbonization process. These exothermic reactions are directly due to the oxygen compounds of the raw coal. By reference again to the chart, Fig. 6, showing the makeup of an Illinois coal, we can at once see the possibility of a very considerable amount of heat available from this source. The high oxygen content therefore becomes an asset instead of evidence of a nullifying influence in the process of carbonization. The direct measurement of this exothermic heat has been one of the most interesting as well as one of the most elusive features of the problems involved. If time permitted it would be worth while to illustrate the methods of measurement employed. It will doubtless be better at this point to follow out the sequence of the process wherein use is made of the exothermic heat and how it is made available.

Let us assume, by way of illustration, that in the case of an average Illinois coal, we have an amount of this potential heat equal to 4 per cent of the total heat of the coal, or approximately 500 B.t.u. per pound. Now, if we can drop a mass of coal into a retort whose walls are heated to 750 deg. C. (1382 deg. F.) and start off the exothermic reactions in such a manner that they will become autogenous, they will, of course, pass beyond the outer zone of heat furnished from the walls of the oven and proceed to the center of the mass regardless of either the heat head at the surface or the insulating property of the mass.

In the illustration here shown, these conditions have been secured. Note particularly that a narrow zone at the outer rim shows a coke formation which has been due to the direct application of heat from the walls of the retort. Beyond this zone and thus soon out of reach of the exterior heat, the reactions became autogenous and quickly penetrate to the center. Naturally also we would expect that in order to travel alone, they must have at least slight surplus of heat at every stage of progress inward, which would thus be cumulative in effect and to the end of the process would show a higher temperature at the center of the mass than at any other point. This correctly represents the uniform condition at the termination of an experiment. Incidentally, it is interesting to note not only the texture and cell structure peculiar to the carbonization that occurs under these conditions, but also that the sample at the left is from an Illinois coal with the high oxygen value as already shown in the chart, while the sample at the right is from a high volatile eastern coal which would at once be placed among the coking coals because of its low oxygen content. The texture, strength, density, etc., of the two examples seem to be very much alike.

The question will at once arise in your minds as to why this effect is not secured in the regular byproduct coke oven. The wall temperature starts the coal at even a higher stage, say 1000 deg. C. (1832 deg. F.), while we are using from 700 to 800 deg. at the start. Why do not the exothermic reactions occur and travel autog-

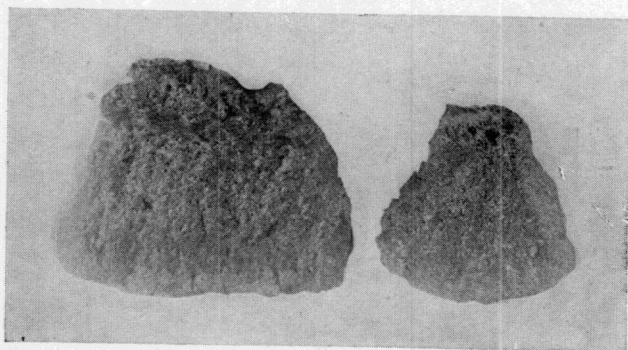


FIG. 13. Samples of Coke from Illinois Coal at Left and Eastern Coal at Right.

enously to the center in the usual method of procedure? A brief bit of figuring will answer the query. Let us recall that we are assuming a source of heat of this sort equal to 500 B.t.u. per pound. Now if we start out with a mass of coal at 30 deg. C., or say 100 deg. F., and plan to raise the temperature of the mass to 800 deg. C., or 1500 deg. F., we must provide heat enough to raise the mass through 1400 deg. F. Roughly, the specific heat of coal is 50 per cent that of water, hence it will require 700 B.t.u. to do the work of raising the temperature of the mass without taking into account the latent heat of vaporization for the water present. But we have to our credit only 500 B.t.u.; hence, no matter how good a start we give to the reactions, they will cease to operate as soon as we pass beyond the zone of external heat where that effect is lost by reason of poor conductivity. As we say when attempting to start a fire with green or wet wood, "the fire goes out."

On the other hand, if we raise beforehand the temperature of the mass to say 300 deg. C., or 600 deg. F., slightly below the point of active decomposition, the work remaining to be done is now that of raising the temperature of the mass through only 800 deg. F., or in terms of heat units, we require only 400 B. t. u. Since we assume 500 B.t.u. at our disposal and expend only 400, we have a slight margin to our credit which accounts for our cumulative effect and higher temperature in the center at the close of the process.

This, therefore, in a general way sets forth what we believe to be the essential factors that must be taken into account in the coking of high oxygen coals.

A summarized view would indicate that the theory of carbonization needs to be rewritten or revised in such a manner as to cover the case of high oxygen as well as low oxygen coals. That when the factors are thus understood and their influence properly controlled, the so-called non-coking coals may be brought into the coking class, and that the low temperature condition is the one which lends itself most readily to the carrying out of the carbonization process. Perhaps the most important of all is the utilization of the exothermic property

whereby the slow effect by conductivity is replaced by the relatively quick procedure of preheating the coal, thus securing autogenous chemical reaction throughout the mass.

For the present at least we are content to leave the ultimate goal of fuel gas and stop at the coke stage, especially in view of the fact that the coke produced in this manner comes into the class of smokeless fuels with combustion characteristics quite comparable to the anthracite or semi-anthracite type.