Tar Forming Temperatures of American Coals.

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The material presented in this paper is the result of a series of investigations started in the laboratories of the University of Wisconsin and later continued at Purdue University. In form the paper is a brief of a part of a bulletin of the University of Wisconsin published by the author in 1914, with the addition of the results of the subsequent work.

The nature of the volatile matter in bituminous coal is attracting considerable attention at the present time. This is due not only to the enormous amount of coal annually used in the United States, but also to the important part volatile matter plays in determining how the coal must be handled in order to obtain the best results.

One of the most important and troublesome constituents of the volatile matter is tar, especially when the coal must be used in boiler furnaces or in power gas producers.

The investigations to be discussed in this paper had in view: (1) the determination of the temperature limits between which tars are distilled from the various classes of coal; (2) the temperature limits of the maximum rate of evolution of tars; (3) the relative quantities of tars distilled from the various general classes of coal: and (4) the lowest temperature at which one may be certain that the last trace of tar has been driven off from the coal.

Briefly stated, the results show that the temperature at which the first trace of tar appears will range from about 200°C. to about 385°C. usually falling quite near 300°. The maximum deposit will start at a temperature varying between 330° and 450°C. and will end between 430° and 530°C. The last trace of tar will appear between 530° and 680°C. The amount of tar produced seems to vary not so much with the amount of volatile matter in the coal as with the ratio of the carbon to the hydrogen as shown by the ultimate analysis of the coal.

When fresh coal is supplied to a furnace the volatile matter commences to distill off and if properly mixed with air and burned there is no heat loss. The tarry products do not give trouble in gas producers when the gas is burned hot in ovens or furnaces. If however, the gas is allowed to cool, these products condense and stop up the piping, and unless removed, will clog up the engine valves if used for power purposes. The removal of these tarry products not only involves special and expensive apparatus and the expenditure of power, but also results in a loss of the available heat from the gas.

The problem as here presented is the outgrowth of an attempt to adapt the suction gas producer to the use of bituminous fuel. The type of producer used is what is known as the re-circulating producer such as is represented by the Whitfield and Pintsch patents. In this type of producer an attempt is made to draw off the tarry vapors from the top of the fuel column and introduce them again into the fire at the very bottom of the producer. The finished gas is drawn from the central portion of the fuel column. This location must be chosen with at least three points in mind:

(1) It must be far enough down in the fuel column to be below the point at which the last trace of tar is driven off from the coal.

(2) It must not be any farther down than is necessary, or the loss due to the sensible heat in the gas will be excessive. This loss, in percentage of the total heat value of the coal, will equal approximately the number of hundreds of degrees F. at which the gas leaves the producer. Thus, if the gas leaves at 1,200°F., the loss will approximate 12 per cent. of the total heat value of the coal burned.

(3) The point of exit must be high enough above the bottom to allow ample opportunity for the CO_2 and H_2O resulting from the combustion of the distilled volatile matter to be reduced to free H_2 and CO.

To fulfill these several requirements, it is necessary to know exactly when each factor is operative. The depth of the incandescent zone that is necessary for a producer of a given size and capacity, and the precautions that are necessary to prevent a concentration of draft at any part of the producer, are fairly well known from practice. The most important item that is left for investigation is therefore to ascertain the exact temperature at which the last trace of tar is driven off from the coal.

An attempt was made to follow the temperature conditions met with in the gas producer, in these laboratory tests. This made it necessary to place the following list of requirements on the laboratory apparatus:

(1) The coal must be heated very slowly and at a uniform rate.

(2) The heat must be conducted from the outside to the center of

the body of coal by some good conductor, as the coal itself is a very poor conductor of heat and all particles in the body of coal must always be at a uniform temperature during the heating.

(3) The temperature of the coal must be accurately known at all times.

(4) The gases driven off from the coal must be swept out as soon as formed.

(5) The gases must be cooled down and continuously tested for tar.

(6) Any tar deposited in the pipes at a low temperature must not be allowed to re-distill at a higher temperature and then appear in the gas.

1. *The Furnace.* After considering the various possible means of heating the coal it was decided to use an electric resistance furnace. By this means the coal could be heated at any rate desired and the rate of heating could be controlled at all times, or the coal held at any desired temperature for any length of time. The furnace used is shown in cross section in Fig. 1 of the accompanying drawing, and was made as follows: A cylinder, (1), 3½" inside diameter and 20" long was made out of 16 B. & S. gage sheet iron, riveted at the seam. Around this was wound four thicknesses of wet asbestos paper (2). About 75 feet of 12 B. & S. gage nichrome resistance wire (3), was wound around this, four turns to the inch. The asbestos paper insulated the wire from the cylinder. Around this was wound more wet asbestos paper, to hold the wire in place, and the whole was covered by a layer of asbestos pipe covering (7), about 2" thick. The ends of the resistance wire were fastened to electric terminals on the furnace. The current passed through this furnace was taken from a 110 volt alternating current circuit, and was varied by means of a small water rheostat. The amount of current was measured by an ammeter in the circuit, as is shown in the sketch of the apparatus.

Six or seven amperes were required to bring the temperature up from 20° C. to 600° C. in four or five hours. Direct current would have been somewhat preferable had it been available, but the alternating current used did not jar the coil sufficiently to do any damage.

2. *The Coal Cartridge.* The cartridge in which the coal was placed to be heated was about 2½ " inside diameter by 6" long. It was made up as shown in Fig. 1. (4) is a 2½" short nipple, having 2½" couplings (5) screwed on to both ends. Into these couplings pipe plugs (6) were screwed, thus forming a closed cartridge. One plug was drilled and

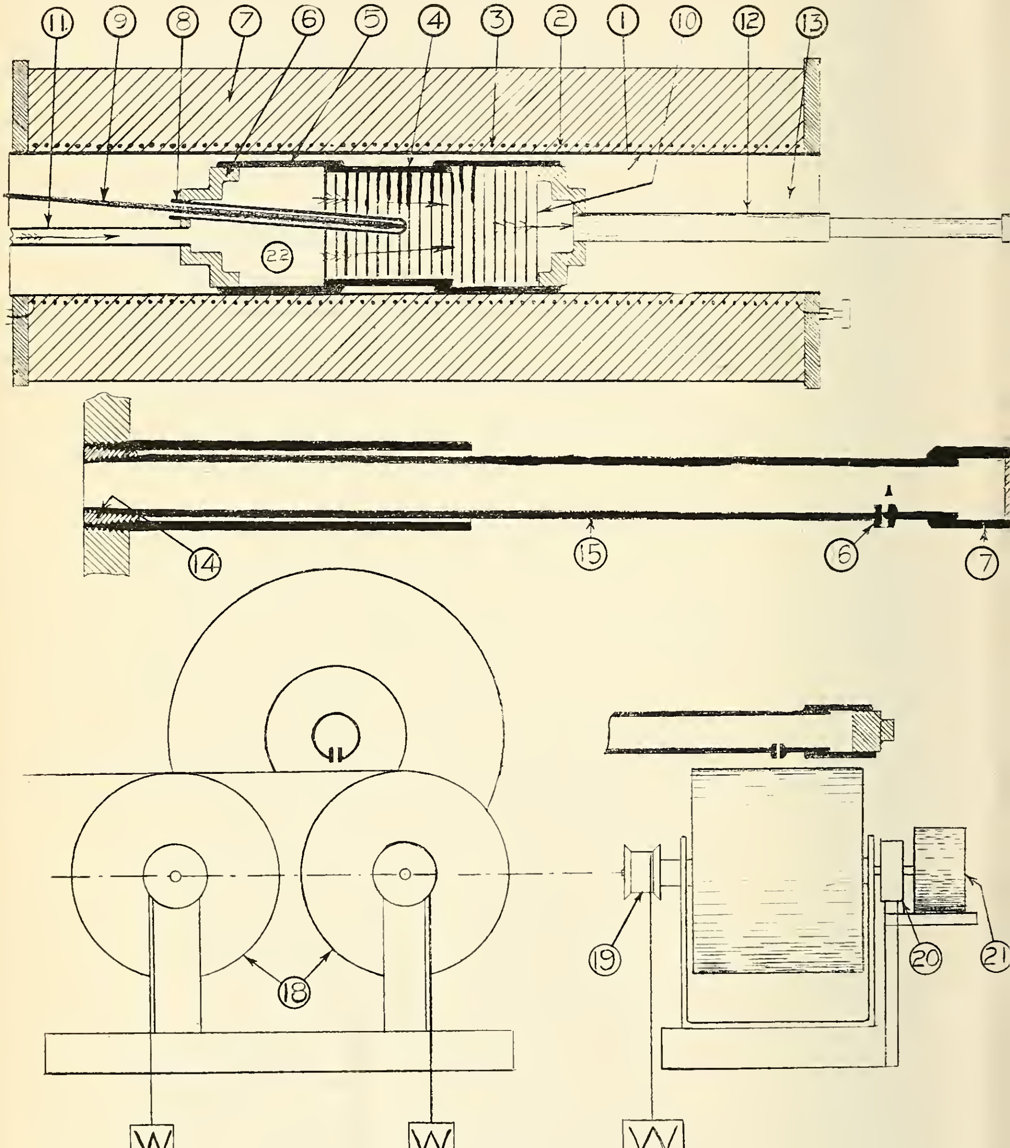


Fig. 1.

tapped for the $\frac{1}{2}''$ pipe (12), through which the gas from the coal could pass out. The other was drilled and tapped for a thermometer well (8) and $\frac{1}{4}''$ pipe (11). The body of coal heated each time was therefore $2\frac{1}{2}''$ in diameter, and it was necessary to have all the particles of coal in this mass at the same temperature. As coal is a very poor conductor of heat, it was decided to place iron disks (10) $\frac{1}{4}''$ apart throughout the entire length of the cartridge. These disks were large enough to touch the iron cartridge all around, thus taking on its temperature, and were drilled full of small holes to allow the gas to pass through them. As they were $\frac{1}{4}''$ apart, the heat had to be conducted through only $\frac{1}{8}''$ of coal. This fact, together with the very slow rate of heating employed, led us to expect the temperature throughout to be the same, within very close limits. The temperature was read at the very center of the coal body, by means of a thermo couple, the end of which extended down to and touched the end of the thermometer well (8).

3. *Means of measuring the temperature.* The thermo couples used were made of iron and nichrome wires welded together in an electric arc. The couples were used with a Brown millivolt meter, with a resistance of 85 ohms. It was carefully calibrated and checked at the time the experiments were completed. The couples were correct to within 10° C. throughout the range of temperatures here reported. The couples were left in place throughout each entire test, and the temperature readings made whenever desired.

4. *To keep the gases swept out as formed.* To sweep the gases out as they were formed gas free from tar was forced into the cartridge under pressure, through the $\frac{1}{4}''$ pipe (11), and allowed to pass out through (12) in a constant stream. The pressure of this gas inside the cartridge was measured by a mercury manometer, and was kept at about $2\frac{1}{2}''$ of mercury. This gas could not be allowed to contain any O_2, as it might then burn the coal or tar vapors at the higher temperatures, so air with the O_2 burned out was used. The arrangement of the apparatus as used is shown in Fig. 2. The air was burned in a small furnace made of a piece of 6″ pipe about 2′ 6″ long. This pipe had grates at the bottom and a coupling and plug at the top. The coupling was drilled and tapped $\frac{1}{2}''$ pipe size on one side, and connected to a large coil of $\frac{1}{2}''$ pipe which rested in a tank of cold water. The small furnace thus constructed was filled with an anthracite fire and the plug at the top put in. The air pump then pumped air through the furnace and cooling coil and compressed

it into the large air tank, where it was stored for use. By this means the supply of gas for a complete test could be stored up before the test itself was started. One more precaution had to be taken in using this gas, as it could not be allowed to affect the temperature of the coal as it passed through. To prevent this, a coil of pipe was placed over a gas flame and the gas passed through and heated up to the temperature of the coal, before it was allowed to enter. The temperature of the gas was measured by a thermo couple which extended into it through a tee in the pipe line. To make assurance doubly sure the end of the cartridge itself was filled with steel chips, as is shown at 22 in the sketch in Fig. I. The entering gas was thus forced to pass through a considerable volume of these chips before coming into contact with the coal. It was found difficult to heat the gas up to the highest temperature of the producer. This might tend to affect the seeming temperature at which the last traces of tar appear. The tendency of the gas would always be to be lower than that of the coal. For this reason the end of the thermocouple was placed in the coal at the end where the gas enters it, and therefore at its cooler end, in case there should be any difference at all. Thus the temperature reported as the one at which the last trace of tar appears is as accurate as it is possible to make it.

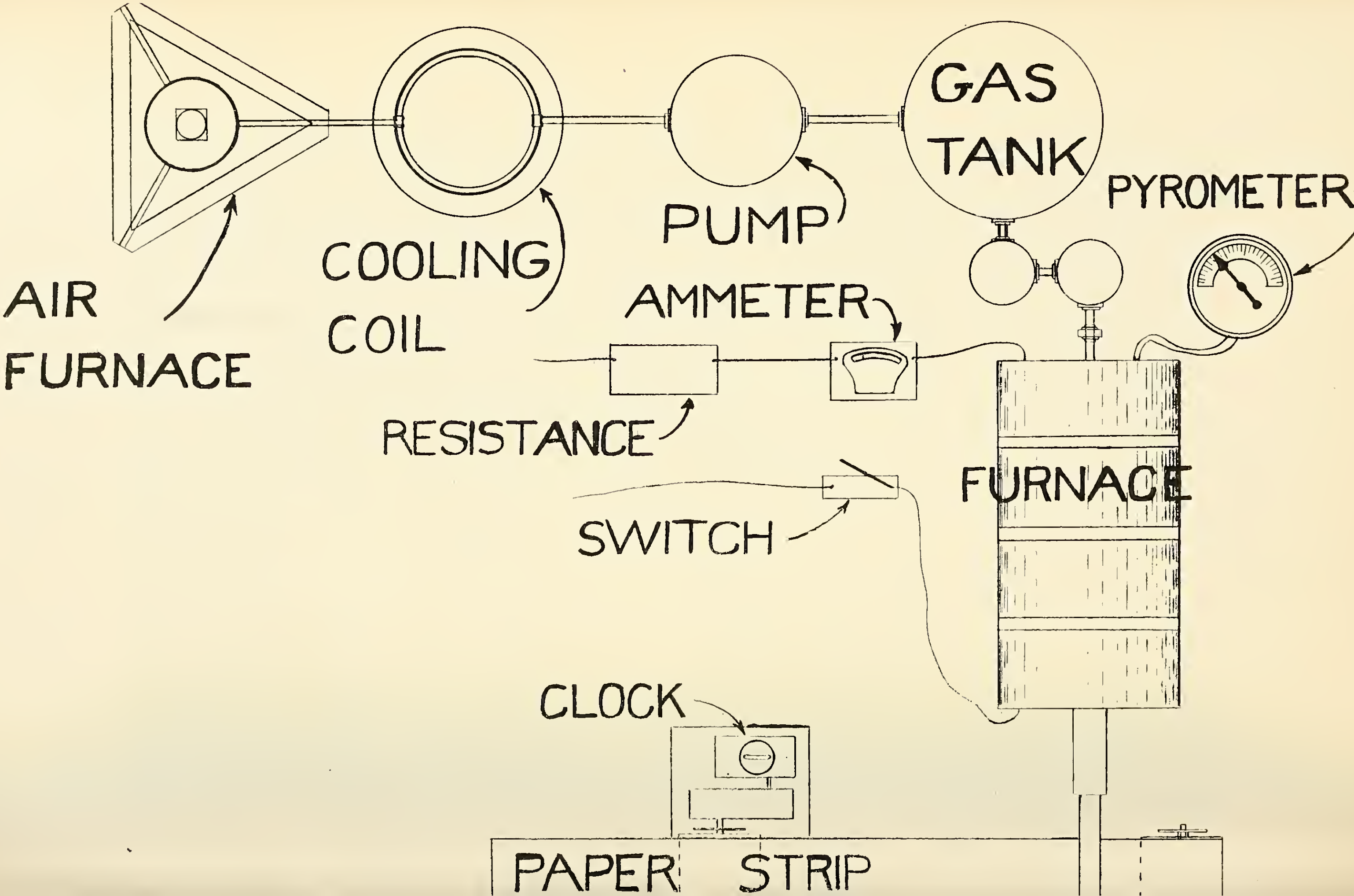
5. *To test the gases for tar.* The next problem was to find a means of subjecting the gases from the coal to a continuous test for tar. The most searching and satisfactory test known to the author, and the one used by the gas companies over the country, is to allow a small stream of the gas to strike a piece of white paper at a high velocity. If there is any trace of the tar at all in the gas, it soon leaves a spot on the paper. This test was adopted. To use it, the gas must be cooled down before it strikes the paper. This was accomplished by keeping a cloth filled with cold water constantly lying on pipes (12) and (18). It was desired to have the test continuous. The device used to accomplish this is shown in Figs. 1 and 2. The rollers (18) are about 10″ in diameter and are supported by steel rods through their centers which turn freely in iron supports at either side. On one end of each of these steel rods was placed a small wooden spool, around which was wound a cord, supporting weights W_1 or W_2. A long strip of cloth was wound around one of these rollers and its end started around the other. A piece of paper ribbon was wound on with the cloth. W_1 and W_2 tend to turn the rollers in opposite directions, thus keeping the cloth and paper strip tight. W_1 is enough heavier than

W_2 to cause both to turn, unless held back in some way. The key of an alarm clock (21) was fastened to a train of gears (20), and these in turn to the stem of roller (18), so that the rate of motion was held back to a speed governed by the running of the clock. In this case the speed was 30″ an hour. The rollers were set in such a way as to cause the paper to pass about ¼″ under the end of the orifice (16) in pipe (15). The strip of paper was marked at the beginning and end of the test, so that the exact time when any point on the paper was under the orifice could be determined. Thus a continuous record was kept of the amount of tar in the gas.

It might be well to state here that all of the tar is not taken out of the gas by this means. The tar particles in the cooled gas are very fine and light, and many of them are cushioned off from the paper, and never touch it to stick. Consequently the tar deposited on the paper does not represent all of the tar content of the coal. On the other hand, the slightest trace of tar in the gas will quickly black the paper, and the deposit is probably very nearly proportional to the entire tar content of the gas.

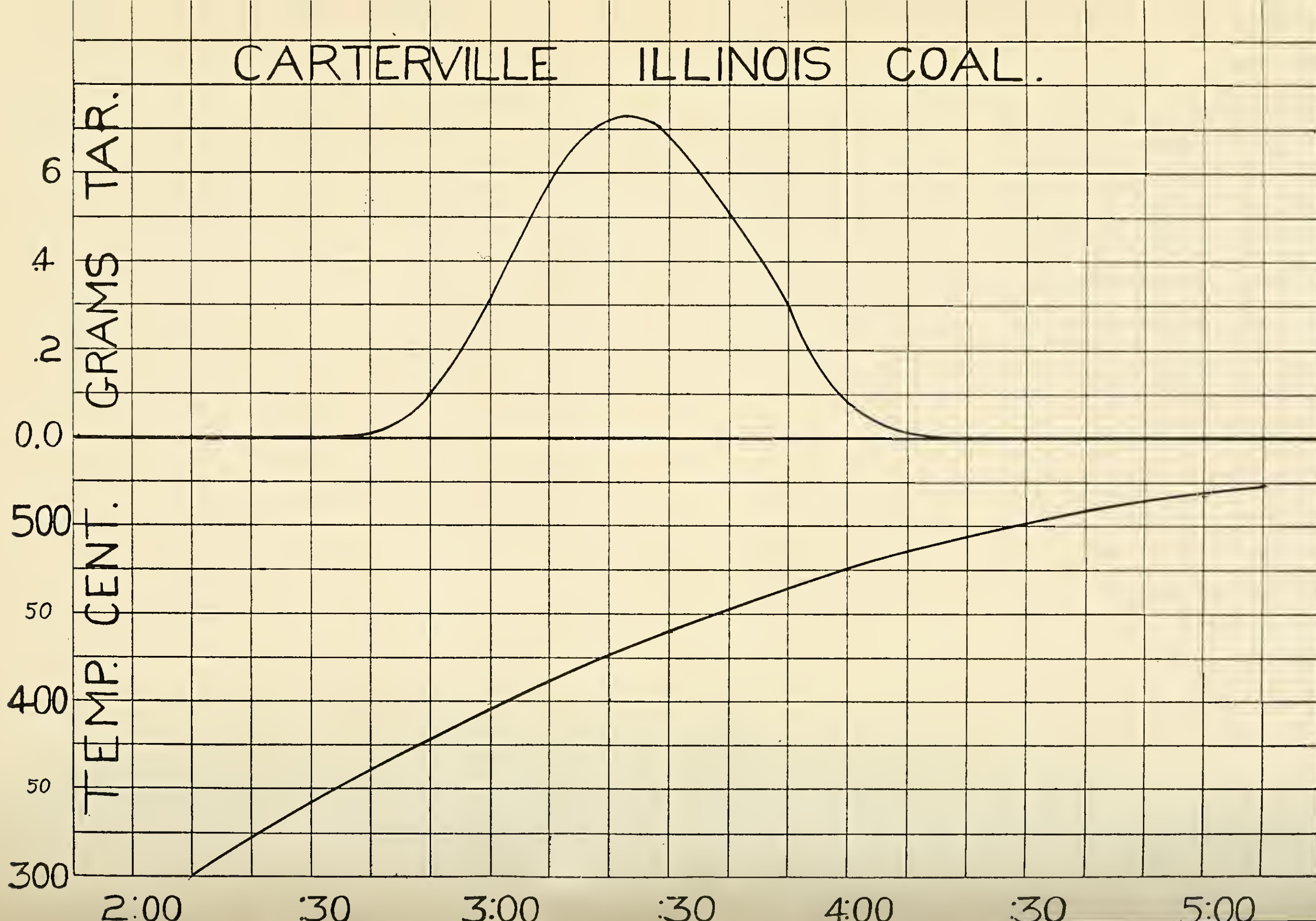
6. *To prevent re-distillation of tar once deposited in exit pipe.* The remaining problem was that of making sure that no tar could be deposited in pipe (15) at a low temperature and be later re-distilled. to show up on the paper at too high a temperature. To accomplish this a large number of duplicate pipes were made and carefully fitted into the threaded bushing (14). By changing these pipes (15) every five or ten minutes, the effect of such a tendency was quite completely eliminated.

The coals tested were chosen to represent the different American grades. They were first ground and screened over a mesh of 20 wires per inch and through one of 10 wires per inch. About 315 grams of coal will fill the cartridge, and it was put in in layers ¼″ thick between iron disks. The cartridge was then placed in the middle of the furnace, the thermo couple put in place, and the asbestos packed in against both ends, cutting off the radiation here, and causing the ends and middle, all to keep at the same temperature. A current of 6 amperes was then passed through the resistance wire of the furnace. While the latter was coming up to the temperature where the light oils start to come off, the thermo couples were connected up, the flame placed under the gas pre-heating coil, the gas from the storage tank turned on, the paper rolls connected up to the clock and the clock started. The pipes (15) were cleaned and prepared for immediate use, and the data sheet prepared. As soon as


GAS
TANK
PYROMETER
PUMP
COOLING
COIL
AIR
FURNACE
AMMETER
RESISTANCE
FURNACE
SWITCH
CLOCK
PAPER
STRIP

the thermo couple indicated a temperature close to that at which there was prospect of an oily deposit, the paper rolls were put in place, the paper marked and the test started. When the tar commenced to show up the temperature of the furnace was recorded and the pipe (15) changed every 10 minutes. As the temperature of the furnace rose to 300° C. the current was increased $\frac{1}{4}$ of an ampere, at 400° C $\frac{1}{2}$ of an ampere more, and at 500° C. $\frac{3}{4}$ of an ampere. This was done to take care of the increased radiation, and to keep the rise in temperature at a constant rate. When the paper ceased to show any signs of a tar deposit it was again marked and timed and the current shut off. The strip of paper was then cut up into lengths corresponding to 10 minute periods, and carefully weighed. As the weight of the paper per inch was very constant, the excess in weight over that of clean paper was in each case due to the tar. From this two curves could be drawn, with time plotted horizontally, while one had temperature centigrade and the other grams of tar plotted vertically. These curves when placed one right over the other, as here given in Fig 3, indicate the amount of tar coming off at each temperature. The points where the tar starts and stops can not be indicated by this curve, as the ends of the deposit are too thin to have appreciable weight. They are consequently separately noted elsewhere.

The first condensible gas to be driven off from the coal and appear on the paper record is water vapor. After the last of the water has disappeared there is quite a temperature range through which there is no deposit at all. Then the paper will begin to show a slight trace of oil. This will gradually increase in amount and give the paper the appearance of having been parafined. The deposit will then gradually assume a brownish color, as though engine oil were appearing. Later a temperature will be reached at which the deposit will increase very rapidly in amount, and will assume a distinctly tarlike appearance. The first tar to be deposited is usually very soft and sticky at room temperature. As the temperature rises the tar becomes steadily stiffer, until it is finally hard and brittle when cooled. The temperature range through which the maximum deposit occurs will vary from about 100° C., for some western coals, to 175° for some of the samples from the east. At the higher limit of this range the deposit becomes rapidly smaller in amount until it is too small to weigh, but the paper is still distinctly browned. This discoloration becomes less and less plain, until it finally disappears entirely. There is no definite temperature at which the first and the last trace of the tar appears, in the same sense that water has a boiling temperature. The first deposit is so indistinct that it is almost impossible to tell whether there is a deposit or not. The increase is also so very gradual that it is difficult to choose the temperature at which to report the first appearance of a deposit. This gradual increase will extend over a temperature range of from 50° to 150° C. before there will be a sufficient deposit of tar to feel sticky to the finger. The determination of the temperatures between which the maximum deposit occurs is likewise an arbitrary matter, and also the temperature at which the last trace of tar appears. Therefore the results as here reported must not be too literally interpreted. However they are a very careful estimate of the facts as they are and the highest temperature reported is one at which one may feel assured that the very last trace of tar has disappeared from the coal.



CARTERVILLE ILLINOIS COAL.
GRAMS TAR.
6
.4
.2
0.0
TEMP. CENT.
500
50
400
50
300
2:00
:30
3:00
:30
4:00
:30
5:00