A Study of the Influence of Wall Temperatures on the Rate of Travel of the Fusion Zone in Coke Ovens,

by

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MASTER OF SCIENCE

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Certification by the Department of Chemical Engineering,

Approved by:

Director Buffalo Station, School of Chemical Engineering Practice.
June 4, 1925.

Professor A. L. Merrill,
Secretary of the Faculty,
Massachusetts Institute of Technology.

Dear Sir:

I submit herewith a thesis entitled "A Study of the Influence of Wall Temperatures on the Rate of Travel of the Fusion Zone in Coke Ovens" in partial fulfillment of the requirements for the degree of Master of Science.

Respectfully submitted,
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I. PRELIMINARY DISCUSSION.

Object.

The purpose of this study was to observe the influence of wall temperatures on the rate of travel of the fusion zone in coke ovens. In view of the fact that there are so many variables to deal with in the operation of the commercial size oven, it was decided to construct a small coke-oven in which these variables could be controlled or made the same in the various runs.

Abstract.

The fusion zone in the oven was followed by both the temperature and pressure methods. The temperatures across the charge were measured by thermocouples inserted from the top of the oven and was entirely satisfactory; the method of locating the fusion zone by the increase in gas pressure was used with only slight success.

The results showed that the rate of coking depends directly upon the wall temperature used, only a slight increase in temperature being necessary to greatly increase the rate of coking.

Runs were made at combustion-space temperatures of 1600°F and 1800°F, and wall temperatures of 1400°F and 1600°F, approximately.

An experimental oven, (16' x 18' x 36' inside dimensions) having steel plates for sides, top and bottom, was constructed. A combustion space was built on either side in which a mixture of coke-oven gas and preheated air
was burned.

Introduction.

Up to the present time many investigations have been made on coke ovens and coke oven practice both in this country and in Europe. Much valuable work on effects of operating conditions on the final products has been secured, but almost no data of any value is to be found on the conditions existing within the coke oven. The reason for this lack of data is not due to the fact that no attempts have been made to collect it, but rather to difficulties that arise in the process of getting the results. Many variables enter into the coking of coal, and in the past the investigations have been made on full size ovens, where control of all conditions is impossible to secure.

The distillation of coal in closed retorts, externally heated, depends upon the following factors:

1. The size of the coal particles.
2. The moisture content of the coal.
3. The actual temperature of the heating walls.
4. The volume of the charge relative to the volatile content of the coal.
5. The time during which the charge is heated.
6. The pressure under which the distillation takes place.

Or in other words, these factors may be combined into three, namely: time, temperature and pressure. Under any given conditions of temperature and pressure,
it is the rate at which the heat penetrates the coal particles that determines the coking time.

The distillation of coal is an exothermic reaction, approximately 350 B.T.U. per pound of coal being liberated. This figure varies widely, however, depending on the character of the coal. If coal could be brought to the proper carbonizing temperature, and so well insulated that no heat would be lost, the coking would proceed from the heat of reaction. It is obviously impossible to do this as the gases evolved carry off the heat, as sensible heat, faster than it is formed. Thus the heat given up by the reaction is but a small part of the total heat involved, and it can be neglected.

Carbonization process.

There are three general stages in the carbonization of coal in a closed retort:

First, there is a preliminary decomposition which begins as soon as the coal has acquired a certain fairly definite temperature, which temperature remains practically constant in the fusion zone. This reaction is an endothermic one.

Second, the products from this first stage, which consist mainly of the higher members of the aliphatic series, undergo a molecular simplification,- compounds of less than three atoms of carbon resulting. This stage, taking place within the coal particles, is also an endo-
thermic reaction, depending on the absorption of heat to maintain it.

Third, the gaseous vapors, from the second stage, escaping from the coal particles, are acted on by the radiant and conducted heat from the walls and charge proper, and undergo complicated reactions. The lower members of the aliphatic series (CH₄, C₂H₆) break away, leaving the residues which unite into more complex cyclic hydrocarbons. These cyclic compounds, under the combined influence of heat and time, decompose with the formation of hydrogen, carbon and still higher ring compounds.

A typical coke-oven gas analysis is:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illu. (C₂H₄)</td>
<td>2.95%</td>
</tr>
<tr>
<td>CO</td>
<td>6.25%</td>
</tr>
<tr>
<td>H₂</td>
<td>43.55%</td>
</tr>
<tr>
<td>CH₄</td>
<td>33.45%</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>2.15%</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.20%</td>
</tr>
<tr>
<td>O₂</td>
<td>0.85%</td>
</tr>
<tr>
<td>N₂</td>
<td>8.60%</td>
</tr>
</tbody>
</table>

Coking Process.

The coals used for gas making come under the general head of long flame coking coals, whose composition is about as follows:

Volatile matter--- 34% to 40%.
Ash-- less than 12%
Sulphur-- less than 1.2%.
When a fresh charge of coal is introduced into a hot retort, the first effect is an immediate reduction of the temperature of the inner surface of the retort as the heat is absorbed by the cold charge. The temperature of the charge is acquired by means of radiation and by conduction from the hot walls. Experiments have shown that heat penetrates through the charge four or five times as fast by conduction as by radiation.\textsuperscript{1} From this it would seem that it would be advisable to completely fill the oven.

With the first rise of temperature, some gas is evolved with a sudden rush, and free moisture is driven off, much of which condenses in the cool central portion of the charge, as is shown by the fact that the temperature of the center of the charge remains at about 200°F for approximately two-thirds of the coking period.\textsuperscript{3}

As the temperature rises, the coal begins to fuse, beginning the distillation proper. Numerous workers have investigated this temperature, and it is believed today that an isothermal temperature of about 725°F is maintained in the fusion zone.\textsuperscript{4,5} During this period of fusion, the coal is pasty and semi-liquid. There is a very large and rapid evolution of gas, the major part of the volatile constituents of the coal are distilled, leaving the coke structure.

The relative rate of carbonization toward the center of the charge, or the average coking velocity, is
1.0 to 1.2 inches per hour in the modern by-product coke-ovens of the Koppers or Semet Solvay type. In the new Kopper's ovens 13 3/4 inches wide, a coking time of ten hours has been attained, thus showing a coking velocity of 1.375 inches per hour. A rate any faster than this gives coke of a very much poorer quality.

The fusion temperature of 725° is reached by the combined effects of radiation and conduction and also from the heat transferred by the hot vapors as they pass up through the charge, the heat given up by the hot gases amounting to about one-half of the total amount of heat necessary to reach this temperature.

The larger the coal size, the longer will be the period of coking, the other conditions remaining the same.

The presence of moisture in the coal is shown by the lower initial temperature obtained, but this has no particular effect as it is nearly all driven off before the carbon has reached a high enough temperature to react with it. A small amount of it reacts, however, with the hot carbon at the oven walls, and an increase in moisture content of the coal gives a somewhat higher percentage of CO₂ in the gas liberated.

The higher the temperature of the heating walls, the faster will be the coking rate. Experiments have shown that an increase in pressure extends the coking time very much, whereas if a suction is used, the period is shortened.
II. EXPERIMENTAL WORK.

Description of Apparatus.

The oven was built with 1/2 inch steel plates for the sides and 3/4 inch plate for the top and bottom. These were fastened to angle irons driven a foot into the ground, the inside dimensions of the oven, or the coking space, being 16 inches by 18 inches by 36 inches. On either side of the oven a 5 inch combustion space was built out of fire brick, one course of brick being laid against the steel plate and two courses laid for the outer wall of the flue, fire clay mortar being used.

Along the top of both flues was laid a horizontal one inch air pipe and right below this a one inch gas pipe. Both of these lines had 1/4 inch holes drilled along one side (1 1/2 inches apart). These holes were directed so that the air supply would cut across the path of the gas, the flame striking the wall about one-third of the way down the side.

The entrance to the stack was at the bottom of the flue and at one end, there being a separate stack for both sides. The stacks were of brick up to the top of the oven, on top of which was a seven foot length of ordinary stove pipe. This afforded more than enough draft, and a damper had to be inserted to reduce the pull on the combustion space.

The incoming air line, (both sides being alike),
was run into the stack at the top level of the oven, then into the combustion space and along the bottom, a return bend bringing the line back again to the stack and up to the entrance level, from where it led to the distributing pipe over the gas line. By this means a fairly high pre-heated air was delivered and mixed with the gas. Crushed firebrick was spread over the air pipes in the bottom of the flue to keep the flames from melting them.

The gas burners were constructed with the gas entering at the middle through a tee and being sent to both ends. This method necessitated the removal of part of the top and side of the flue for renewal of the burner tubes, so that difficulty was removed by inserting a single pipe for the gas burner, the tee being outside the oven.

For measuring the wall temperatures, three vit罗斯il tubes were inserted through the combustion space from the outside. These tubes were open on both ends, and were right against the steel plate side. Care should be taken to prevent cooling of the oven and flues, which cracks the tubes. Chromel-alumel couples were used for the lower temperatures, and iron-constantan couples for the higher temperatures. These were in contact with the walls for the wall temperatures, and were about six inches out from the wall for the combustion space temperature.

The top was made up of a 3/4 inch plate with two five-inch diameter holes for charging in the coal;
a two-inch diameter hole for the gas outlet pipe; and a rectangular opening six-inches wide across the top at a 60° angle with the side.

The coal was stored in two conical hoppers suspended over the charging holes, the hoppers being fitted with hinged traps for quick emptying of the coal. During the run, the charging holes were covered with iron plates, sealed with luting material.

The gas from the oven was led out through a 2 1/2 inch pipe, fitted with a tee for draining of tar and water during the test, and for securing gas samples.

The rectangular opening in the top was covered with a 1/2 inch plate, in which twelve holes were drilled and tapped 1 1/2 inches apart on a 60° angle, in one row for the thermocouples, and in a second parallel row, twelve holes for pressure tubes for fusion zone location. The couples were held in one-inch extra heavy tubes, welded on the end which was inserted into the charge. These tubes were kept at the proper location and distance by having guiding tubes attached to, and extending about four-inches above the plate. The pressure tubes were 1/8 inch tubes, which like the thermocouple tubes, were forced down to the middle of the charge.

The ends of the oven were closed by bricks four inches thick, set in with mortar.

After the oven was heated up slowly for several
days to avoid cracking of the brickwork, the outside was painted with the following mixture to close small cracks:

1 part of silica clay.
2 parts of fire clay.
1 handful of coarse salt.
1 quart molasses for 12-quart bucket of mixture.

Water to make mixture to consistency of paint.

Method of Procedure.

Before a run was started, the walls and combustion spaces were brought up to the desired temperature. When this temperature was constant, the coal was emptied from one of the hoppers and leveled through a hole in one end. The other hopper was then added, and leveled. The coal used for all runs came from the same storage pile, and was the same as used in the Koppers ovens at this time at the Bethlehem Steel Company, Lackawanna plant. Approximately 450 pounds were used for each run.

After both hoppers were empty, the charging holes were quickly covered and the couple tubes, couples and pressure tubes were inserted and connected up. The couples were connected through two nine-point switches to a Hoskins millivoltmeter. The pressure tubes (the 1/8 inch iron tubes leading to the top and one end of the oven) were connected to small bottles serving as traps for the tar, etc. and then were all connected to the top of manometer tubes
which were all connected at the bottom to a manifold attached to a reservoir for adjusting the zero-reading. By this means the pressure gradient across the oven could be easily followed.

Readings on the wall and top couples were started at once after the charging, and the pressure tube readings were taken as the gas pressure developed inside the oven.

The runs were continued till the temperature across the top was very nearly the same, as shown by all couples.

III. RESULTS.

The results of Run Number 2 are given in graphical form in plots Numbers 1 and 2 immediately following.

Additional data and the results of gas samples taken during the run are given in the appendix.
Isotherms of Coking Rate

Data by:
- Sweitzer
- Holden
- Carpenter

Buffalo Station - MIT SCFP
Dec. 1923

Temperature of Run 2100°F
(Flue Temperature)

Plot #4

Time in Hours from Start

Distance from Left Wall - Inches.
Isotherms of Coking Rate

Undergraduate Thesis by:
- Beadle
- Meyers
- Rubens

“Mechanism of High Temperature Coal Carbonization”

Buffalo Station - M.I.T. S.C.E.P.
June 1923

Temperature of Run 2400°F (Flue Temperature)

Plot # 5

Distance from Left Wall - Inches.
Temperature Gradients in Coke Oven.

Flue Temperature - 1800°F.

Oven Width - Inches.
Fig XLV
Temperature Gradients Across Oven

20 Hours after Start

Plot # 7.

2100°F.
Temperature Gradients in Coke Oven
Flue Temp ~ 2520°F

Plot #8

Oven Width ~ Inches

Curve No. | Heat from Start
----------|------------------
1         | 6
2         | 8
3         | 10
4         | 12
5         | 13
Plot #9.

Flue Temperature and Rate of Heating at Oven Center.
IV. DISCUSSION OF RESULTS.

The fusion zone in a coke-oven can be located by two different methods: the pressure method, and the temperature method. The pressure method, as described on Pages 10 and 11, has the disadvantage that the tubes extending into the charge become plugged up with tar, necessitating frequent cleaning. This method was not successful on these runs, so the temperature method was relied upon.

The fusion temperature of coal ranges from 550°F to 750°F, depending upon the kind of coal used. Twelve chromel-alumel couples were inserted across the top of the oven, readings being taken at regular intervals. By this method, the condition of the charge was followed throughout the run.

If plots Number 1 and 2, of Run 2 (time-temperature curves), are compared to similar curves from data by Von Hilgenstock,- Sweitzer, Holden and Carpenter,- Beadle, Meyers and Rubens, and others, they would appear at first sight to be dissimilar. But if on these two plots, the curves below 700° are covered up, the remainder of the curves will resemble the curves of other workers. The Run Number 2 was made at a comparatively low temperature, (flue temperature 1800°F, wall temperature 1600°F). The work of Sweitzer, Holden and Carpenter was made at 2100°F, while that of Beadle, Meyers and Rubens was made at 2500°,
both of these temperatures being flue temperatures.

If the temperature is high, an outer layer is formed at once against the walls, this layer being a thick, sticky mass of semi-plastic coal, across which there is a high temperature drop. This insulating or protecting layer is formed around 600°-650°F, and in the higher temperature runs, by forming early, protects the center of the charge and keeps it cool.

By long, low temperature heating, on the other hand, the resins, which are the bonding materials, are destroyed, and a coking coal can be made non-coking by such treatment.

In the Run Number 2, the temperature was not high enough for this fusion zone to form at once, and as a result, the whole mass of the charge came up to the temperature of about 700° at the same rate, which condition makes this run appear unlike other runs.

If the isotherms are compared of the three runs of 1800°, 2100°, and 2500°, (Plots 3, 4 and 5), it will be seen that in run Number 2 (plot 3), the charge was around the fusion temperature of 725° for about 8 hours; in the 2100° run (plot 4) for about 2 hours; and in the 2500° run (plot 5) for less than an hour.

In plots 7 and 8, of the temperature gradients, the presence of the fusion zone is shown clearly for the higher temperature runs by the sharp drop in temperature, especially in the earlier hours of the runs. Plot 6.
However, lacks these sharp temperature changes, showing the gradual formation of the fusion zone.

By employing a high wall temperature, a poor coal can be coked in a narrow oven, as is shown in the operation of the Roberts and Koppers types, which use a wall temperature of approximately 2500°F. This temperature allows the formation of the insulating layer and there is no opportunity to drive off the resins of the coal.

From plot 9, comparing the rate of heating of the oven center and flue temperatures, it will be seen that there is a critical temperature for the formation of a well defined fusion zone. It was intended to study this temperature location, but with the experimental oven as built, the temperature could not be secured. That the difference in temperature is not very great for widely varying coking rates is shown by the fact that in the Semet Solvay 18 1/2 inch oven, the temperature is only reduced from 2500°F to 2300°F to change from 17-hour coke to 24-hour coke.
V. CONCLUSIONS.

1. Flue temperature of the oven directly influences the rate of coking.

2. Small changes in temperature cause a big difference in rate of coking.

3. There is a critical temperature at which there is a well defined fusion zone, above which temperature good metallurgical coke and poor gas results, and below which poor coke but better gas is produced.

4. This critical temperature marks the division between high and low temperature carbonization.
VI. RECOMMENDATIONS.

It is recommended that improvements be made in the design of the oven and further work be done, using higher temperatures.

The combustion spaces should be enlarged as there is a sufficient amount of coke-oven gas available, but with present conditions, the flues are not large enough to permit enough gas to be burned to attain temperatures much above 1800°F.

The burner design should be changed in order to permit of easier replacement. Some method for maintaining a constant amount of gas being burned, should also be installed.
VII. APPENDIX.

Data.

Distances of couples from left wall:

Couple No. 1--- 1.125 inches.

' ' No. 2--- 2.375 ''
' ' No. 3--- 3.625 ''
' ' No. 4--- 4.875 ''
' ' No. 5--- 6.125 ''
' ' No. 6--- 7.375 ''
' ' No. 7--- 8.625 ''
' ' No. 8--- 9.875 ''
' ' No. 9--- 11.125 ''
' ' No.10--- 12.375 ''
' ' No.11--- 13.625 ''
' ' No.12--- 14.875 ''
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<td>6.5%</td>
<td>8.0%</td>
<td>8.9%</td>
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<tr>
<td>Illu.</td>
<td>0.3</td>
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<td>1.1</td>
<td>1.5</td>
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<tr>
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<td>0.6</td>
<td>1.6</td>
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<tr>
<td>CO</td>
<td>1.6</td>
<td>3.0</td>
<td>3.0</td>
<td>2.9</td>
</tr>
<tr>
<td>CH₄</td>
<td>10.1</td>
<td>30.7</td>
<td>12.2</td>
<td>15.6</td>
</tr>
<tr>
<td>H₂</td>
<td>10.9</td>
<td>12.9</td>
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<td>10.1</td>
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<tr>
<td>N₂</td>
<td>68.5</td>
<td>43.9</td>
<td>61.6</td>
<td>60.4</td>
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<tr>
<td></td>
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<thead>
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<td>5/21/25</td>
<td>5/22/25</td>
</tr>
<tr>
<td>CO₂</td>
<td>7.7</td>
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<td>5.0</td>
</tr>
<tr>
<td>Illu.</td>
<td>1.5</td>
<td>1.2</td>
<td>0.2</td>
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<td>O₂</td>
<td>1.2</td>
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<td>7.2</td>
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<tr>
<td>CO</td>
<td>3.7</td>
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<td>1.5</td>
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<tr>
<td>CH₄</td>
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<td>7.5</td>
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<td>H₂</td>
<td>11.4</td>
<td>10.1</td>
<td>25.7</td>
</tr>
<tr>
<td>N₂</td>
<td>55.8</td>
<td>59.7</td>
<td>52.9</td>
</tr>
<tr>
<td></td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
</tr>
</tbody>
</table>
Average Analysis for entire run:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>7.93%</td>
</tr>
<tr>
<td>Illu.</td>
<td>1.10%</td>
</tr>
<tr>
<td>O₂</td>
<td>2.38%</td>
</tr>
<tr>
<td>CO</td>
<td>2.46%</td>
</tr>
<tr>
<td>CH₄</td>
<td>14.33%</td>
</tr>
<tr>
<td>H₂</td>
<td>11.86%</td>
</tr>
<tr>
<td>N₂</td>
<td>59.94%</td>
</tr>
</tbody>
</table>

100.0%

The difference between this analysis and the analysis of a typical coke-oven gas is due to the fact that the oven was operating under a suction, and air was being drawn into the oven through the thermocouple and pressure tube holes in the top of the oven.
BIBLIOGRAPHY.

2. Foxwell, G.E. "The Path of Travel of the Gases in the Coke Oven". 1921.