A STUDY OF THE EFFECT OF HEAT ON NATURAL GAS

by

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INTRODUCTION

During the course of a study of the effect of heat on natural gas, it was decided to investigate the effect of time of contact of the gas in the reaction chamber. The variation in the composition of the product with varying yields and the ratio of light oils to tar was determined. Further, the effect of various catalysts was also studied.

In general it has been found that at any given temperature, there is an optimum velocity above or below which the yield decreases. Further, at constant velocity, there is an optimum temperature above or below which the yield decreases. The formation of carbon increases with increasing temperature and decreasing velocity. Of the catalysts used, metals, with the exception of copper, produced large quantities of carbon and hydrogen. Using clay as a catalyst, little carbon was formed and larger yields of light oils and tar were obtained.

REVIEW OF LITERATURE

Dalton and Henry (1) found that methane, when subjected to the continued action of an electric spark decomposed into carbon and hydrogen. Marchand (2) showed that products other than carbon and hydrogen could be obtained upon properly heating the paraffin hydrocarbons and
that the resolution of a hydrocarbon into its elements could not in general be considered the immediate result of a simple chemical change. The observations of Buff and Hoffman (3) supported the view of Marchand.

The first systematic study of the effect of heat on hydrocarbons was made by Berthelot (4). He contended, as did some earlier investigators, that a hydrocarbon never decomposed directly into its elements, but that the primary change always involves a polymerization to form denser hydrocarbons, which in turn undergo a series of similar changes until carbon finally appears as the product. The formation of acetylene was considered the chief factor in the formation of other hydrocarbons.

Bone and Weeler (5) found that methane was quite stable under 700 degrees C. and that the decomposition was a surface phenomenon at temperatures below 1200 degrees C. Bone and Coward (6) showed that the importance of acetylene in the formation of other hydrocarbons from methane was overestimated by Berthelot. They made quantitative determinations of the yields of various hydrocarbons obtained and gave special attention to the time factor.

Thermodynamic calculations made by Contelo (7) showed that the decomposition of methane into carbon and hydrogen should be almost complete at 700 degrees C. From an initial system of methane, ethane or ethylene, at temperatures above
400 degrees C., Cantelo concluded that the final equilibrium would be a system of methane, carbon, and hydrogen. Schwab and Pietsch (8) used a platinum wire coated with calcium oxide and barium fluoride. Only the molecules striking the wire were decomposed. Fischer and Trapsch (9) used a porcelain reaction tube and a gas rate of 70 liters per hour. A total quantity of 280 liters of gas produced 6.5 grams of oil, 1.6 grams of tar and a small quantity of carbon.

Vysoky (10) passed natural gas containing 94.5 per cent CH₄ through a quartz reaction tube. The results were as follows:

1. Benzene began to form at 800-850 degrees C.
2. The gases were exposed to the high temperature for 68 and 38 seconds; the yield of benzene and toluene remained the same for temperatures above 1000 degrees but became halved at 950 degrees C.
3. Oxygen was added to the gas before entering the reaction tube causing a reduction in the yield of benzene.
4. An oxygen and methane mixture was passed through the same reaction tube into which a copper wire coil was placed close to the inner wall. No benzene or toluene was detected over a temperature range of 650 to 1000 degrees C.
5. The copper coil was replaced by a silver coil but this had no catalytic effect on the reaction.
6. Copper oxide was placed in the reaction tube but it had no tendency to form light oils.

Smith (11) found that methane when subjected to a temperature of 1800 to 2200 degrees F. breaks up or "cracks." At slightly lower temperatures, the parts reunite but to form new products as they combine. The higher hydrocarbon gases also break up and reunite to form various substances differing from the parent substances. At sufficiently high temperatures, the gas will decompose to carbon and hydrogen. Hydrogen is always one of the products and other gases such as acetylene, ethylene, propylene and butylene vary in amounts with the details of pyrolysis. The principal liquids formed in the pyrolysis are benzene, toluene, and xylene. Fischer (12) found that methane, when properly heated, will yield benzene and naphthalene, whereas earlier investigators thought carbon and hydrogen to be the chief or only products.

Rudder and Biederman (13) investigated the effect of temperature, pressure, and time of reaction on the pyrolysis of methane. In the main, it is shown that the amount of ethylene formed is a maximum at 1200 degrees C. under a pressure of 100 millimeters, and that the amount of acetylene increases very rapidly with temperature. At 1500 degrees C. and a pressure of 40 millimeters, the yield is 58 per cent of the theory. For each temperature there exists an
interval in which the amount of acetylene formed is at a maximum. This interval is shorter as the temperature is increased. The reaction is not changed by addition of such catalysts as hydrogen chloride, thorium, silicon dioxide, and nickel. The acetylene is always accompanied by carbon and hydrogen. Chiko Fujio (14) passed methane at varying velocities between spherical electrodes at voltages from 8000 to 47,000. The products were chiefly hydrogen and acetylene in the proportion of about five to one.

Fischer (15) passed methane and coal gas together through porcelain and quartz tubes at 900° to 1200°C. Tar was precipitated in a cottrell precipitator and the light oils absorbed in activated charcoal. Higher temperatures and low gas velocities favored the formation of carbon and hydrogen.

The results of Wheeler and Wood (16) were quite similar to those of Fischer. Benzene was formed between 875° and 1100°C., the optimum temperature being 1050°C. The yield obtained was two-tenths gallon per 1000 cubic feet.

Jones (17) passed methane through heated quartz tubes of one centimeter bore at a temperature of 700° to 1080°C. Pressures of 10 to 70 centimeters of mercury and various gas velocities were used. The methane decomposed partly into carbon and hydrogen and smaller quantities of olefines. When the methane was subjected to an electric spark, the
same products were formed but with a larger percentage of acetylene.

Stanley and Nasch (18) found that long heating and increased heating surface both tended to increase the amount of carbon in the product. Short heating periods (.4 second) at 1000° to 1200°C. resulted in the formation of acetylene, ethylene, and benzene while the carbon formed was almost negligible. The per cent of methane converted into higher hydrocarbons increased rapidly with increased gas rates reaching a maximum for each temperature. An increase in temperature increases the optimum gas velocity. The accumulation of carbon in the tube was found to decrease the yield of higher hydrocarbons. The presence of steam does not influence the course of the reaction. At 1150°C. gas rates of 13.8 liters per hour using a 12 centimeter tube (5mm. bore) the yield of light oil and tar was 11 per cent and ethylene 8.8 per cent.

A summary of the work done on the pyrolysis of carbon compounds in general is given by Hurd (19). A small section is devoted to the pyrolysis of methane.

Chamberlin and Bloom (20) reported yields of 44 liters of light oils from 1000 cubic meters of gas, using a silica tube. Catalysts such as copper and nickel caused decomposition in carbon and hydrogen. In general, their results were similar to those of Stanley and Nash except
that the temperatures were somewhat lower.

Frey and Hepp (21) found the values of the time of contact for maximum yield of light oils within a temperature range are shown by the empirical formula which is as follows:

\[ T = 691 - 100 \log t \]

Where

\[ T = \text{temperature in degrees C.} \]
\[ t = \text{time in minutes} \]

Wheeler and Word (22) made two types of experiments, the first in which methane was heated in a quartz bulb of 60 cubic centimeters capacity at different temperatures, pressure changes being observed by manometer readings, and the second in which large volumes of methane were passed through heated tubes of various materials. The rapid initial decomposition of methane is chiefly a surface phenomenon but the reaction does not proceed to a state of equilibrium because of the formation of a protective film of hydrogen adsorbed on the silica surface. Prolonged heating of methane produced carbon and hydrogen. Short heating periods favor the formation of molecules of two carbon atoms, while increasing the time of heating diminishes these, and the aromatic compounds are formed.

Berl and Hoffman (23) obtained yields up to 87 per cent of condensation products by heating acetylene around 600 to 700°C. in the presence of beach wood charcoal
catalysts. Highly porous carbon catalyzes the decomposition into carbon and hydrogen and the formation of methane. Contact catalysts such as iron, copper, stannic oxide, and calcium oxide do not promote condensation. The presence of steam favors condensation. Yields of 98.8 per cent have been obtained at 740°C.

Padoviani and Magaldi (24) found that with the elevation of the temperature, the yield of unsaturated hydrocarbons was increased. Increasing the rate of flow increased the production of hydrocarbons up to a certain point and diminished thereafter. Packing the reaction tube with porcelain chips increased production.

DISCUSSION OF LITERATURE

Only literature having a direct bearing on the pyrolysis of methane has been cited. There is much literature to be found on the pyrolysis of the higher members of the paraffin series and of hydrocarbons in general. Considerable work has been done on the production of carbon and hydrogen from methane. Reference to such work, however, has been omitted.

In the literature cited, there is considerable disagreement as to the optimum temperature for the production of liquid products.

Most investigators believe that in the process of
pyrolysis, the methane is first decomposed and then re-
polymerizes into larger molecules. It would seem that both
of these phenomena should be studied carefully in order to
understand the transformation taking place. From exami-
nation of the literature it is very evident that practi-
cally no attention is given to the conditions under which
the polymerization takes place. Some investigators have
expressed the belief that sudden cooling of the gas upon
leaving the reaction tube, would increase the yield of
light oils, but no experimental data is submitted to sub-
stantiate the belief.

APPARATUS

The gas velocity was measured by the use of a small
bore tube across which a differential manometer was placed.
The total volume of gas used during a run was measured with
a commercial gas meter which had been carefully checked for
accuracy. A calcium chloride drying tower was used to free
the gas of water vapor. The reaction chamber consisted of
a silica tube seven-eighths inch in diameter and two feet
long. Chromel wire wrapped directly on the outside of the
tube served as a heating element. The tube was then lagged
with asbestos and eighty-five per cent magnesia, and mounted
in a frame of transite board as shown in figure 1. A rheo-
stat to control the temperature was built into the furnace
frame. A larger tube, one and three-eighths inches in diameter and three feet long was used as a cooling tube. An asbestos collar over the exit end of the reaction tube served as a connection for the cooling tube. Cotton filters consisting of bottles loosely packed with cotton, were used to remove the tar leaving the cooling tube. Several bottles of activated charcoal were used to absorb the light oils. The hydrogen analysis apparatus consisted of two gas burettes connected to an electrically heated copper oxide tube. A base metal thermocouple was used to observe the temperature.

RAW MATERIAL

The gas used in this study was the regular laboratory supply which comes from the McPherson field, the composition of which is as follows:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>.72 per cent</td>
</tr>
<tr>
<td>Oxygen</td>
<td>.50 per cent</td>
</tr>
<tr>
<td>Methane</td>
<td>78.20 per cent</td>
</tr>
<tr>
<td>Ethane</td>
<td>14.20 per cent</td>
</tr>
<tr>
<td>Residue</td>
<td>6.38 per cent</td>
</tr>
</tbody>
</table>

PROCEDURE

Before making a run, all combustible material was burned out of the reaction tube by passing through a slow stream of air while the furnace was heated to a dull red heat. Each of the bottles (h) and (g) and the tube (f)
were carefully weighed and connected in the system as shown in figure 2 except that the connection between the furnace and the tube (f) was not made until the temperature of the furnace was fixed. The temperature was observed by placing a thermocouple in the exit end of the reaction tube. When the furnace had reached the desired temperature, the gas was admitted at the rate to be used during the run. The rheostat was then adjusted to hold the furnace to the desired temperature. The thermocouple was then removed and the tube (f) connected. At the same time the initial reading of the gas meter was taken.

After the runs had continued for the desired length of time, usually five or six hours, the valve (v) was closed, the meter read, and the bottles (h) and (g) and the tube (f) were again weighed. After allowing the furnace to cool, the carbon was removed as completely as possible and weighed. The tar fog which did not condense in the cooling tube was caught in the cotton filter while the light oils were absorbed in the activated charcoal. Hence the increase in weight of the cooling tube and the cotton filter was recorded as tar while the gain in the activated charcoal was recorded as light oils.

NOTES

In run number 1, the cooling tube (f) was not used and the small bore tube leading from the furnace was repeatedly stopped with naphthalene and carbon. In run number 2 and in
following runs the cooling tube \(f\), as shown in figure 2 was used. During the fourth run, an iron catalyst in the form of steel wool was placed in the gas stream at the junction of the reaction tube and the cooling tube \(f\). No naphthalene was observed in the cooling tube and a great deal of carbon collected in the reaction tube near the exit end. This carbon was of a soft, sooty nature differing from the hard metallic-like carbon usually obtained. When a copper catalyst was used (runs number 4 and 5) the yield of light oil and tar was slightly higher than that obtained when no catalyst was used. A large yield of naphthalene was obtained on the walls of the cooling tube. When clay was used as a catalyst in the furnace, (runs number 6 and 7), a decided increase in yield of tar and light oil was noted. In the runs following number 7, no catalyst was used and special attention was given to the yield and variation in the product at different times of contact of the gas with the heated tube.

At times a small deposit of carbon occurred on the walls of the cooling tube \(f\) adjacent to the furnace. In such cases, it was removed and weighed with the carbon obtained from the furnace. In order to insure the complete absorption of the light oils, a sufficient number of bottles of charcoal \(h\) were inserted so that the last bottle collected no light oil.
Fig. 2. Diagram of apparatus used for pyrolysis

(a) Flow meter
(b) Gas meter
(c) Calcium chloride drying tower
(e) Furnace
(f) Cooling tube
(g) Cotton filter
(h) Charcoal absorber
When metals such as chromel and nicrome alloys were placed in the reaction tube, a heavy deposit of carbon collected on the metal. More than the usual amount of carbon also collected in the reaction tube. In runs number 22 and 23, a thermocouple enclosed in asbestos was placed in the reaction tube during the run. As shown by the data, a very large yield of carbon resulted.

DISCUSSION

With the development of new oil fields, there has come a tremendous production of natural gas. In many cases, there is no ready market for this gas and as a result, it is wasted. In 1929 the United States Bureau of Mines found that at some of these fields as much as 250,000,000 cubic feet are being wasted daily.

This great waste has stimulated much investigation to find new ways of utilizing the gas. Three methods of utilization, chlorination, oxidation, and pyrolysis, are receiving considerable attention at the present time. Each of these processes converts the natural gas into one or more useful liquid or solid product.

The transformation of methane into aromatic hydrocarbons necessitates the liberation of hydrogen in the following reaction: \[ 6\text{CH}_4 = \text{C}_6\text{H}_6 + 9\text{H}_2 \]. This increases the number of gas molecules and hence, according to La Chate-
### Table 1. Data Showing Results of Pyrolysis

<table>
<thead>
<tr>
<th>Run</th>
<th>Tar (grams)</th>
<th>Light (oil)</th>
<th>Car (oil)</th>
<th>Per (liter)</th>
<th>Grains</th>
<th>Cubic (Temp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.85</td>
<td>6.69</td>
<td>2.45:12.45:1.125</td>
<td>20:1.0</td>
<td>6.12:2.019:6.00</td>
<td>1:02</td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>1.00</td>
<td>9.00</td>
<td>2.00:1.000</td>
<td>25:2.0</td>
<td>4.00: .500:4.00</td>
</tr>
<tr>
<td>3</td>
<td>11.60</td>
<td>9.20</td>
<td>2.30:19.60: .710</td>
<td>15: .8</td>
<td>10.15:1.350:5.25</td>
<td>1:23</td>
</tr>
<tr>
<td>4</td>
<td>6.90</td>
<td>8.90</td>
<td>2.00:18.80:1.290</td>
<td>20:3.0</td>
<td>7.65:12.600:6.00</td>
<td>1:27</td>
</tr>
<tr>
<td>5</td>
<td>6.50:70.00</td>
<td>1.70:13.50:1.200</td>
<td>22: .6</td>
<td>6.30:2.110:3.15</td>
<td>2:00</td>
<td>1840: copper</td>
</tr>
<tr>
<td>7</td>
<td>10.80:15.70</td>
<td>2.00:26.50:1.500</td>
<td>24: .8</td>
<td>10.20:2.500:5.50</td>
<td>1:26</td>
<td>1840: relay</td>
</tr>
<tr>
<td>8</td>
<td>6.40:11.40</td>
<td>1.50:19.60:1.360</td>
<td>20:1.2</td>
<td>9.00:1.800:3.20</td>
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<td>1700: no</td>
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<td>6.00</td>
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<td>6.40</td>
<td>4.20</td>
<td>2.30:10.60: .660</td>
<td>25:2.3</td>
<td>4.25:2.490:2.50</td>
<td>1.70</td>
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<tr>
<td>11</td>
<td>6.40</td>
<td>8.30</td>
<td>1.50:14.70: .780</td>
<td>19:1.0</td>
<td>7.00:1.700:3.50</td>
<td>2.00</td>
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<td>12</td>
<td>9.50</td>
<td>9.20</td>
<td>2.00:19.70:1.000</td>
<td>24:2.0</td>
<td>9.00:2.000:4.00</td>
<td>2.25</td>
</tr>
<tr>
<td>13</td>
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<td>2.00:25.45: .760</td>
<td>25:2.0</td>
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<td>2.40</td>
<td>1730: no</td>
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<td>1.20:22.30: .780</td>
<td>24:1.5</td>
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<td>4.00:1.400:5.60</td>
<td>1.40</td>
<td>1650: no</td>
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<td>0.00:2.45:1.450</td>
<td>16:1.0</td>
<td>5.00: .310:4.00</td>
<td>1:75</td>
<td>1600: no</td>
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<tr>
<td>18</td>
<td>1.80:2.90</td>
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<td>15:1.5</td>
<td>8.00: .940:3.16</td>
<td>1:40</td>
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<td>1.20:15.50: .680</td>
<td>25:1.2</td>
<td>10.00:1.550:3.00</td>
<td>3.20</td>
<td>1800: no</td>
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<tr>
<td>20</td>
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<td>1.20:15.30:1.440</td>
<td>22:1.0</td>
<td>14.50:1.30:5.50</td>
<td>2.84</td>
<td>1700: no</td>
</tr>
<tr>
<td>21</td>
<td>7.30:8.50</td>
<td>.60:16.80:1.160</td>
<td>23:1.1</td>
<td>7.50:1.100:3.50</td>
<td>1.00</td>
<td>1600: no</td>
</tr>
<tr>
<td>22</td>
<td>5.40:3.00</td>
<td>14.00:8.40: .360</td>
<td>46:2.0</td>
<td>6.00:1.900:1.75</td>
<td>5:43</td>
<td>1700: no</td>
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<tr>
<td>23</td>
<td>13.50:10.30</td>
<td>7.30:24.40: .450</td>
<td>56:2.0</td>
<td>12.00:2.000:5.75</td>
<td>3.20</td>
<td>1700: no</td>
</tr>
<tr>
<td>24</td>
<td>3.90:3.60</td>
<td>2.00:7.50:1.100</td>
<td>20:1.5</td>
<td>7.50:1.000:3.30</td>
<td>2.30</td>
<td>1800: no</td>
</tr>
</tbody>
</table>
lier's principle, the reaction should be promoted by reduced pressure. It was believed, therefore, that if the gas, leaving the reaction tube, were allowed to expand suddenly into a larger tube, reactions of the type given above would be favored.

Most investigators believe that the formation of benzene from methane begins with decomposition followed by polymerization into larger molecules as the gas cools. In order to study this polymerization, the cooling tube (f) was attached to the exit end of the furnace. This unique feature revealed some interesting facts. As the gas leaves the reaction tube consisting of naphthalin, anthracene oils, and tar, it contains a fog varying in color from a white to a dark brown depending upon the temperature of the reaction tube and the velocity with which the gas passes through. At lower temperatures and high gas velocities, the fog had a white color and became dark in color as either the temperature was increased or the velocity decreased. This fog partly condenses on the walls of the glass cooling tube. Most of the condensation takes place on the first few inches of the tube next to the reaction tube. Near the end of this condensation area, there appears a break in the collection on the surface leaving a ring about one-half inch wide around the tube which is, during the first part of the run, practically free from condensation. Often as high as
four of these rings appear. The one nearest the furnace being the much more pronounced. This first ring appears about four to eight inches from the furnace depending on the velocity of the gas. The faster the gas flows, the farther from the furnace the ring appears. In observing the temperature at various points in this tube, a large drop in temperature was noted at this ring. As the condensation of tar continued, the ring became narrow and finally disappeared.

Beyond the point where the tar collected on the tube, large naphthalene crystals were deposited on the tube. In runs lasting four or five hours, these crystals sometimes became large enough to reach across the one and three-eights inch cooling tube.

A direct correlation was found between the color of the fog and the quantity and quality of the yield. When the fog was white, it was found that the total yield was low and that the major part of the product was benzene. When the fog was dark brown, the total yield was high and there was more tar than benzene. The amount of carbon deposited in the furnace increased as the color of the fog became darker.

The formation and deposition of tar and naphthalene on the walls of the cooling tube appeared to be accompanied by absorption of heat, since the gas cooled nearly to room temperature while traveling about 18 inches in the cooling.
tube. To be sure that this drop in temperature was not due to loss by radiation, a stream of air was run through the reaction tube and cooling tube at the same velocity at which the gas had been passed, and a comparison made of the temperatures found at various points in the cooling tube. The results showed that the temperatures in the cooling tube, during the passage of the air were, at all points except near the exit end, about double those observed during the passage of the gas.

The investigation of Schwab and Pretsch (9) has shown that the transformation of methane into other hydrocarbons is a surface phenomenon. Only the molecules striking the heated surface were transformed. If this reaction is a surface phenomenon, as indicated by Schwab and Pretsch, it is very important to know whether the gas flows through the reaction tube in a straight-line or in a turbulent manner. If the gas follows ordinarily straight-line flow, the gas would move faster through the center of the tube and be retarded along the sides. In such a case, it is possible that in reaction tubes of large bore, some of the gas would pass through the center of the tube without coming in contact with the heated wall of the tube. In a reaction tube of a smaller bore, this might not happen. Evidence of the type of flow through the reaction chamber was sought during this investigation and it is believed from the indications noted, that the gas passes through the re-
action tube in a straight-line flow. The fog produced in the furnace in all cases was observed to enter the cooling tube and travel the entire length of the tube in straight-line flow giving no visual evidence of turbulence.

The light oil recorded in the data, was approximately 95 per cent benzene and 5 per cent toluene and the tar was approximately 52 per cent naphthalene and 48 per cent anthracene oils. In runs numbers 8 to 18, no catalyst was used and special attention was given to the quality and quantity of the products at various temperatures and gas velocities. The results are shown graphically in figures 3, 4, and 5. The color of the fog was observed to vary consistently with the total yield. When the yield was about eight-tenths gram per cubic foot, the fog was white and gradually became darker as the yield increased. The yield gradually increased with decreasing gas velocity reaching a maximum beyond which the fog suddenly became black and practically nothing but carbon and hydrogen were produced.

The maximum possible yield of benzene from one cubic foot of methane is about 16.4 grams while one cubic foot of ethane should produce twice this amount. With a gaseous mixture of 78.2 per cent methane and 14.2 per cent ethane, as used in this research, the maximum possible yield would be about 17.5 grams of benzene. The best total yield of light oils and tar obtained in this work was about 15 per cent of this amount.
Gas velocity in cubic feet per hour.

Fig. 3. Showing yield of oil and tar per cubic foot of gas.

A = yield 1650°F.
B = yield at 1700°F.
Fig. 4. Showing ratio of light oils to tar.
A = Ratios at 1650°F.
B = Ratios at 1700°F.
Fig. 5. Showing yield of light oils

\[ x = \text{yield at } 1650^\circ F. \]
\[ o = \text{yield at } 1700^\circ F. \]
CONCLUSIONS

1. Aromatic hydrocarbons such as benzene, toluene, and naphthalene are formed by heating natural gas.

2. The minimum temperature at which the transformation took place, at an appreciable rate, was 1600 degrees F. while at temperatures above 1850 degrees F. the gas velocity for optimum yield was so high as to be impracticable.

3. At a given temperature there is an optimum velocity above or below which the yield is decreased.

4. At a given gas velocity there is an optimum temperature above or below which the yield decreases.

5. Iron and alloys of chromium and nickel caused the reaction to proceed largely to carbon and hydrogen.

6. The use of a large cooling tube produced visual evidence that the gas flowed in a straight-line flow.

7. The optimum temperature for the production of light oils was 1700 degrees F.

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