



A STUDY OF DECOMPOSITION PROCESSES APPLICABLE TO CERTAIN PRODUCTS OF COAL CARBONIZATION

BY

MANSION JAMES BRADLEY

A. B. McMaster University, 1915A. M. McMaster University, 1915

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE



1921

Reprinted from Chemical and Metallurgical Engineering Vol. 27, No. 15. Oct. 11, 1922 UNIV. OF California

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ACKNOWLEDGMENT

The writer wishes to express his sincere thanks to Proi. S. W. Parr. whose suggestion, assistance, guidance and encouragement made this thesis possible. Deep appreciation is felt for the valuable training in the fundamentals of research. It is expected that this stimulated appreciation of chemical investigation will increase with time because research is appreciation.

He also wishes to thank Dr. T. E. Layng, not only for help and instruction in assembling the apparatus, but more especially for the many valuable suggestions and advice during the investigation.

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Decomposition Processes Applicable to Certain Products Of Coal Carbonization

An Experimental Study in Which Mixed Xylenes Were Decomposed Under Varied Conditions of Temperature. Pressure and Atmosphere—Effects of Different Contact Surfaces— Identification of Many of the Important Decomposition Products

BY M. J. BRADLEY* WITH S. W. PARR

HE extensive experimental work carried on in these laboratories on the coking of Illinois, Eastern bituminous, Utah. Canadian and many other . coals has demonstrated the possibility of increasing the yield of tar oils approximately one hundred-fold, depending upon the variety of coal used in the low-temperature carbonizing process. The distillate obtained in this manner contains a large quantity of low-boiling, aromatic oils, some of which under normal commercial conditions have a limited application in the industries. For instance, xylene could be obtained in large quantities even under present conditions, if its industrial demand were such as to warrant the expense of recovery and purifying. This hydrocarbon, having a boiling range from 137 to 141 deg. C., has too low a vapor pressure to be an efficient motor fuel, but if by pyrogenic decomposition it can be converted into benzene, which boils at 80 deg. C., its value as a motor fuel is greatly increased. Xylene can also be decomposed in such a manner as to form higher boiling compounds. many being solids at ordinary temperatures. Anthra-

^{*}An abstract of work carried out by M. J. Bradley in partial fulfillment for the degree of Poctor of Philosophy at the University of Illinois.

'cene and methyl-anthracenes can be obtained in this manner, but, by known methods, in small yields.

In this research an endeavor was made to find out the mode of decomposition and formation of the various products obtained from xylene in order to be able to increase the yields of the desired compounds, and if possible to use this knowledge in working over crude tar oils in order to obtain similar products. In the following experimental work some striking results were obtained which seemed to be directly opposed to those recorded by other investigators.¹ Pure xylene was passed through an electrically heated furnace, at various temperatures, under different pressures and in the presence of such contact surfaces as iron oxides, reduced iron, copper, tin, molybdenum, chromium, the alloy Illium, aluminum, nickel, cobalt, manganese, charcoal, pumice and refractory. The condensible compounds were collected, weighed and analyzed and the non-condensible measured and analyzed. The vapor condition inside of the furnace was varied by introducing, at the same time with the xylene, air, superheated steam, carbon dioxide, carbon monoxide, hydrogen, nitrogen or ethylene.

APPARATUS USED IN EXPERIMENTAL WORK

The essential parts of the apparatus are shown in the photographs accompanying this paper. The complete outfit, being of a conventional type, requires little explanation, with the possible exception of the furnace. It was made by taking 6 ft. of 4-in. wrought-iron pipe, threading on flanges and thermocouple pockets and then having these joints acetylene-welded to insure having no leaks under conditions of high temperature and pressure. The caps were cast particularly for this furnace and extended 1½ in. into the end of the pipe and were fitted with three $\frac{3}{2}$ -in. threaded openings leading into the furnace.

The pipe was thinly coated with alundum cement, wound in five sections, each having 36.5 ft. of nickelchromium resistance wire, and again coated with cement. It was surrounded by a wooden box, 20 in. square and as long as the furnace, which contained the pulverized-asbestos and Sil-O-Cel insulation. Each

¹In order to conserve space, no discussion of other investigations is included in this paper, but a list of articles on the pyrogenic reactions of aromatic hydrocarbons which appeared to be most important in connection with the present problem is given at the end.

heating element, when connected directly across the 110-volt line, permitted a maximum current of 20 amperes to pass through, but this could be reduced to 5 amperes by means of an external resistance connected in series at the switchboard. At no time was more than 10 amperes permitted to go through the heating elements. By this means the heat of the furnace could be kept constant at any desired temperature between 250 and 900 deg. C.

The top end was fitted with feed pipes for xylene, superneated steam and other gases, also with a pressure and reduced pressure gage. On the exit at the bottom end was a safety relief valve, or constant pressure valve, which could be adjusted to let the gases escape into the line leading to the gas meter at any desired pressure.



FIG. 1-UPPER END OF FURNACE

This outfit has been operated at pressures as high as 180 lb. per square inch. The temperature was measured by means of a thermocouple. The cold junction was kept at zero by means of a Thermos bottle well and ice water, and the e.m.f. was read on a millivoltmeter which had been standardized at known temperatures. By this method the temperature could be read accurately within 4 or 5 deg. The thermocouple pockets K (see Figs. 1 and 2) extended into the middle of the furnace and thus gave the temperature of the area where the largest volume of vapors passed.



FIG. 2-LOWER END OF THE FURNACE

METHOD OF OPERATION

The mechanical arrangement of the apparatus is apparent from the explanation of the progressive steps of a typical run. The xylene was placed in the reservoir A (Figs. 1 and 2), fed by means of a regulating valve through the sight-glass or bypass B into the upper end of the furnace C. Here also could be introduced gas, such as hydrogen, nitrogen, carbon dioxide or ethylene, from the cylinder I or steam from the high-pressure steam line J could be introduced through the gas-fired superheater H. Another attachment, not shown in the illustration, permitted the use of compressed air.

In passing down through C the vapors came in contact with the various contact surfaces used. The highest boiling condensate was collected in receiver I, the medium oils in No. 2, while the gases, after passing through the water-cooled condensers D, were scrubbed with heavy oil in receiver 3. The gas leaving receiver 3 passed through pipe E to be measured by the meter Fand was then burned, or analyzed by means of the modified Orsat apparatus G.

When running under increased pressure, extra lengths of piping, fitted with a gate valve, were attached to the ends of the condensers. By keeping the lower valve closed and the upper one open, the condensate collected between them and could be easily removed, by closing the upper valve and opening the lower one, without causing any change in the pressure within the furnace.

METHOD OF ANALYZING PRODUCTS

The condensible products were weighed, fractionated through a 6-in. wash column of glass beads until all the liquids boiling below 145 deg. C. were removed. The liquid boiling above 145 deg. C., designated in the following results as high-boiling product, was then transferred to an ordinary distilling flask and the fractionation continued until all but coke was driven over. These operations were carried out in electrically heated pot furnaces built to accommodate the particular flask used and maintained at a constant temperature by means of external resistances. Thus each furnace could be regulated so that no distillate would be driven over above a certain temperature. One furnace was used for each cut, up to 105 deg. C.; from 105 deg. C. to 130 deg. C.; from 130 deg. C. to 145 deg. C.; and finally one for the higher boiling compounds. This method saved much time, as it was possible to have several fractionating flasks going at the same time as the furnace and gas analyses.

The solids obtained from the high-boiling oils were purified and analyzed by a combination of various methods as described by Charlton (17), Clark (21), Cook (22) and others (see bibliography at end of article). Partial separation was obtained by making the distillation cuts at various temperatures and then lowering the temperature sufficiently to freeze out the solids. In some cases steam distillation, fractional solution, class reactions and other methods were used to advantage, but these operations are too long to be described in this paper.

The products not removed in the scrubbing process were measured by a standard wet meter and then burned. The sample taken for analysis was collected

before passing through the meter. The gases were analyzed by means of a modified Orsat apparatus constructed by the author. It is shown in Fig. 3 with the oxygen and nitrogen reservoir permanently attached to the manifold ready for use and the furnace removed. showing the copper oxide tube. Another modification of this apparatus is shown in a text² describing a number of processes and apparatus developed in this laboratory. The carbon dioxide was removed with 35 per cent KOH solution; oxygen by potassium pyrogallate; acetylene by ammoniacal silver chloride: ethylene by bromine water; aromatics by 20 per cent fuming sulphuric acid; hydrogen and carbon monoxide by combustion with copper and ceric oxides; ethane and methane by slow combustion by means of a platinum coil in pure oxygen; and the nitrogen was estimated by difference.

The gas sample was taken in at the top of the burette and measured at atmospheric pressure by means of twin burettes joined at bottom. The copper oxide

²S. W. Parr, "The Analysis of Fuel, Gas, Water and Lubricants," 3rd edition, 1922, McGraw-Hill Book Co., Inc., New York City.



FIG. 3—MODIFIED ORSAT GAS ANALYZING APPARATUS, SHOWING THE WATER-COOLED FURNACE REMOVED

tube was made of Pyrex glass and contained about 30 grams of granular copper oxide which passed through a 10-mesh and remained on a 20-mesh screen. To this was added about 0.9 gram of finely powdered ceric oxide, which seemed to activate the copper oxide and greatly to hasten the combustion of hydrogen. In fact, where the carbon monoxide content was low or previously removed by acid cuprous chloride, 70 to 80 c.c. of hydrogen could easily be completely burned in 5 minutes. In the presence of considerable quantities of carbon monoxide the combustion was slower. The combustion tube was frequently oxidized with pure oxygen.

The absorption pipettes contained thin-walled glass tubing to give surface and speed up the absorption. The slow combustion pipette for ethane and methane was made from a 300-c.c. thick-walled Kjeldahl Pyrex flask, which proved very satisfactory. The temperature of the platinum coil was regulated by means of a chromel resistance in series shown on the front of the stand. It is realized that an exact separation of acetylene and ethylene cannot be obtained in the above manner, but by leaving the gases in contact with the ammoniacal silver chloride solution during a constant time interval in each analysis, a relative idea of the two constituents can be obtained. The complete analysis could be made in this apparatus in less than 30 minutes.

SPECIFICATION OF THE HYDROCARBONS

The mixed xylene, which was the commercial product such as is usually marketed in 10-gal. cans, was used in the major portion of this work. After redistilling, it was water-white, contained no suspended material, was free from moisture, had no foreign odor, practically all distilled over between 137 and 142 deg. C. and had a specific gravity of 0.8664 at 15.5 deg. C.

The benzene, toluene and naphthalene used were the commercial product in stock in the chemistry storeroom. They were not analyzed or purified in any manner, as only a few runs were made with them to compare with the results obtained on xylene under similar conditions.

The results on the decomposition of xylene are summarized in Table I and the outstanding features are discussed briefly in the comments on each series.

RESULTS OF TESTS

Each run selected for use in the table is a typical result obtained in a series of eight to twelve similar

runs made while the furnace was heated up and with similar conditions inside the furnace-that is, as to contact surfaces and lining. The results are given as obtained for various temperature ranges, different pressures and under the influence of other gases which were introduced into the furnace at the same time as the xylene. The amount of xylene used was 1,000, 500 or 200 grams and was fed through the furnace in 2-hour or 1-hour periods. The sample of gas for analysis was taken when the run was about three-quarters completed. The loss in per cent is given on the basis of the weight of the original xylene; the different fractions of the condensate and coke obtained are given on the same basis. The results tabulated for fractions boiling above 145 deg. C. are not given on a particular run, but on heavy boiling product obtained in several runs in the same series.

A number of preliminary runs between 200 and 600 deg. C. at 50 deg. C. intervals were made on 1,000-gram samples of xylene to see if the iron surface of the furnace would promote any reactions. The loss was less than 1 per cent and the volume of gas was so small that it was not analyzed; the condensate was practically unchanged xylene.

CHARCOAL AS A CATALYST

For series 1, No. 26 being a sample, 2 kg. of wood charcoal, cut in small cubes about $\frac{3}{4}$ in. square, were placed inside of the furnace. The first run was made at 250 deg. C., but no appreciable reactions were noted. As the temperature rose, more gas was given off and contained increasing amounts of CO. Xylene seemed very stable under these conditions up to temperatures above 650 deg. C., when about one-fourth of it was lost. At lower temperatures considerable ethane was found in the escaping gas, while the proportion of methane was small. At 600 deg. C. the ethane content was at its maximum, about 7.5 per cent, and with 20.0 per cent of methane present, but as the temperature rose, the ethane decreased rapidly, while the percentage of methane increased. On the conclusion of the series, considerable carbon, from the decomposition of xylene, was found adhering to the furnace walls.

Before commencing series 2, the furnace was cleaned by means of a wire brush and 2 kg. of new charcoal cubes inserted. To insure against leaks, the furnace was subjected to 125 lb. pressure of live steam before TARTE I_SUMMARY OF EXPERIMENTAL RESULTS IN THE DECOMPOSITION OF XVIENE

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	C%2244A

[11]

heating up. This steaming of the charcoal seemed to activate it so the reactions commenced at lower temperatures, for instance at 550 deg. C. over 20 per cent ethane was found in the outgoing gas and about 25 per cent of the condensate was toluene. At 600 deg. C. the ethane had disappeared and the toluene fraction decreased, while the hydrogen and methane were greatly increased. During the run at 700 deg. C. the temperature of the furnace fell rapidly and a great increase in the volume of gases took place. The furnace became activated in such a manner that the xylene was completely decomposed into gaseous products and amorphous carbon. Run 33 summarizes the results. Several other runs at lower temperatures gave similar products; even introducing hydrogen from a cylinder at various pressures up to 150 lb. did not stabilize the reactions in such a way as to obtain any condensate. The xylene was completely decomposed into hydrogen, methane and carbon.

EFFECTS OF OXYGEN AND HYDROGEN

Before beginning series 3 about 8 cu.ft. of air was passed through the heated furnace; approximately 14 per cent of CO, was found in the issuing gases. The air poisoned or deadened the activity of the furnace, with the result that 44 per cent of the xylene was unchanged at 500 deg. C. The air was discontinued during run 50. In this series it was found that charcoal, when heated to 700 deg. C. under reducing conditions and then cooled out of contact with air, would, at ordinary temperatures, take up air readily. On again heating, the oxygen came off as carbon oxides. the dioxide at lower and the monoxide at higher temperatures. It was extremely difficult to remove the oxygen even at 700 deg. C. in the presence of hydrogen, diminishing amounts being given off after several days' treatment.

Before series 4 the furnace had been thoroughly cleaned of carbon and new charcoal added. While heating up it was kept under reducing conditions with hydrogen from a cylinder. During this series considerable toluene was formed, especially at 650, 700 and 750 deg. C. At the latter temperature, under excess hydrogen from the cylinder, a yield of 56 per cent was obtained, while without the hydrogen only 43 to 45 per cent was obtainable. In this case hydrogen seemed to stabilize rather than promote the decomposition of toluene. Superheated steam deadened the activity of the furnace in such a way as to stabilize the xylene passing through, although after steaming and then reducing for a short time the furnace became activated in such a manner as to decompose the xylene completely. This was also found to be true without any charcoal in the furnace. That is, the iron surfaces could be freshly oxidized or activated by means of steam when heated between 600 and 790 deg. C. and after reducing slightly became activated so that the xylene was completely decomposed into carbon, hydrogen and methane. Run 61 shows the results of the first run after passing superheated steam through the furnace; after reducing with hydrogen for a short time, the xylene was completely decomposed, but could be partly stabilized by passing CO or CO, into the furnace at the same time as the hydrocarbon. Hydrogen even at 140 lb. pressure did not stabilize any of the liquid products, once the furnace was in this activated condition. The carbon deposited was intensely black and fluffy, contained some small percentage of liquid hydrocarbon and about 11 per cent of iron, which was found to be a mixture of the magnetic oxide and other oxides, along with very small particles of finely divided metallic iron. It was impossible to tell from these results whether it was the iron or the charcoal surfaces which was causing the complete decomposition of the liquid hydrocarbons.

EFFECT OF METAL FURNACE WALL

In series 5 a lining tube of No. 18 sheet copper was placed snugly in the furnace so that no iron surfaces were left exposed. Copper seemed to have a tendency to decompose xylene into lower rather than higher boiling compounds, as shown in run 78. Oxidizing the copper made it somewhat more active, but on reducing it again complete decomposition of the xylene did not take place. What decomposition did take place seemed to form liquid and gaseous products rather than amorphous carbon, which was formed only in extremely small amounts.

In series 6 the furnace was copper lined and contained $2\frac{1}{2}$ kg. of charcoal cubes. Typical results obtained in this series is shown in run 88. The reactions below 600 deg. C. were unimportant, but as the temperature rose the loss became greater. The loss was cut down somewhat by introducing hydrogen into the furnace, which appeared to stabilize and increase the toluene fraction. However, it was found impossible to activate the furnace and charcoal as described for series 2 and 3.

In series 7 the furnace was copper lined and the contact surface consisted of $3\frac{1}{2}$ kg. of oxidized Illium turnings, mechanically mixed among small pieces of pumice. These runs demonstrated that around 700 deg. C. the decomposition of xylene was greatest and giving the maximum quantity of the lower boiling fractions.

Series 8 was made over small pieces of pumice which had been dipped in nickel nitrate and then reduced at 500 deg. C. with hydrogen. This was to get the metal in a finely divided condition and over as much surface as possible. Several runs were made between 500 and 800 deg. C., run 104 being a sample. Nickel under these conditions did not promote the formation of liquid products, but rather favored complete decomposition of the hydrocarbons into hydrogen, methane and carbon. In fact, the deposited carbon soon filled the furnace so that the series had to be discontinued. At this time the copper lining was found to have become broken in several places, leaving iron surfaces exposed, which no doubt had influenced the reactions.

Before commencing series 9 the furnace was relined with tinned copper, the tin surface being on the inside. Run 113 gives a typical example of results obtained. The series seemed to indicate that in the neighborhood of 700 deg. C. tin promoted the formation of low-boiling liquids. No other contact materials were in the furnace during these runs.

EFFECT OF NICKEL, MOLYBDENUM AND COBALT

Series 10 was run through the tinned-copper lining and using $2\frac{1}{2}$ kg. of charcoal cubes which had been dipped in a thin paste of nickel oxide and dried at 110 deg. C. In this case the nickel oxide and furnace were not reduced before commencing the runs. The results obtained were similar to those of the iron-charcoal series-that is, the xylene tended to be completely broken down into carbon, hydrogen and methane. Even at as low a temperature as 450 deg. C., 83.5 per cent total loss was obtained. During run 125 hydrogen was introduced at 15 lb. pressure, but did not stabilize any of the liquid hydrocarbons. Small amounts of water were collected in the condensate in every run. The furnace was soon choked up by the deposited carbon. During this series practically all the tin surface scaled off the copper lining.

The next series, No. 11, was run in the copper-lined furnace after over $\frac{1}{2}$ lb. of metallic molybdenum powder had been scattered among the small pieces of pumice stone. As in the preceding series, considerable moisture was collected in the condensate. No appreciable decomposition of the xylene took place below 600 deg. C., but above this temperature the reactions greatly favored the formation of benzene and of methane rather than hydrogen and carbon. Run 133 gives a fair idea of results obtained.

Series 13 was run with the copper-lined furnace containing 5 kg. of 1-cm. cobalt cubes. To reduce all the oxide surfaces the furnace was heated to 500 deg. C. and maintained under 60 lb. pressure of hydrogen for several hours. Even after this treatment moisture was collected in the condensate. Cobalt promotes the decomposition of xylene at low temperatures; even at 450 deg. C. about 35 per cent was lost, and at 550 to 575 deg. C. considerable toluene was formed, as shown in run 142.

MANGANESE AND ALUMINUM

In series 14 manganese in a fine powder was scattered among the small pieces of pumice stone. This metal promoted the decomposition of xylene at lower temperatures than any tried previously and the products formed were liquid rather than gaseous. Run 151 indicates the decomposition products obtained.

In series 15, 440 grams of aluminum powder was scattered among the small pieces of pumice stone and several runs were made at various temperatures. Below 600 deg. C. very little decomposition of xylene took place, but what was changed went to hydrogen and deposited carbon. Run 163, at 680 deg. C., indicates that aluminum does not favor the formation of higher boiling compounds from xylene. It should be mentioned that the copper lining during this series had given way in several places so that some iron was exposed.

Before series 16 the copper lining was removed from the furnace, the latter cleaned by means of a wire brush, reduced while hot with hydrogen and when cold was coated with a lining made by mixing 80 per cent Hytempite with 20 per cent alundum cement. After drying and baking, several runs were made without other contact surfaces. Under these conditions the xylene did not decompose much below 600 deg. C., while above this temperature liquids rather than gaseous compounds were formed. Run 167 gives results at 550 deg. C. and shows the amount of ethylene formed.

CRACKING IN ATMOSPHERE OF ETHYLENE

For series 20 a cylinder of commercial ethylene was connected to the upper end of the furnace. The refractory lining was in good repair and no other materials were introduced for contact surfaces. The preliminary runs introducing ethylene at 45 lb. pressure into the furnace gave some interesting data regarding the stability of ethane, methane and ethylene under these conditions. At 415 deg. C. the waste gases contained 89.4 per cent of ethylene, no ethane and 8.5 per cent of methane; at 475 deg. C. it contained 73.9 per cent of ethylene, 4.6 per cent of ethane and 10.0 per cent of methane. The maximum amount of ethane was obtained at 500 deg. C.; the methane increased with temperature, and at 675 deg. C. the outgoing gases contained 84.1 per cent of methane. Below 475 deg. C. very little decomposition of xylene took place, the loss being less than 5 per cent. In the runs below 475 deg. C. there was always a gain in weight in the liquid condensate, although little xylene was decomposed. This was found to be due to the xylene dissolving considerable volumes of the ethylene, which was readily given off when redistilling. Around 600 deg. C. the furnace decomposed xylene and ethylene very rapidly, the latter going principally to methane. In order to keep the furnace atmosphere mostly ethylene, the pressure outlet gage was set at 2 lb. and the ethylene introduced into the furnace very rapidly. Under these conditions the maximum yield of high-boiling compounds was obtained. The results are given in run 286. Many other runs under various conditions of pressure, rates of feed and gaseous atmospheres were made, but the percentage of higher boiling compounds were lower than in the run tabulated.

In series 21 the refractory-lined furnace was found to decompose xylene as described for series 16. It was now desirable to see if the lower boiling liquids could be stabilized by deliberate control of the gaseous atmosphere inside the furnace. In run 287 the furnace was maintained under 125 lb. pressure with hydrogen from a cylinder while the xylene was being introduced. The results indicate that the major portion of the xylene was decomposed into lower boiling liquids.

In series 25 the low-boiling liquids were slightly increased by increasing the hydrogen concentration in the furnace. The maximum yield is shown in run 288. This result is calculated from the weight of xylene used, while by referring to the equation C_8H_{10} + $2H_2 \rightleftharpoons 2CH_4 + C_6H_6$, it is evident that this would equal about 93.7 per cent of the possible theoretical yield. The carbon deposited in these runs was very different in appearance from that described previously. It was a metallic gray color and was granular or sandy, while the other deposits had been intensely black and slightly oily.

RUNS USING BENZENE, TOLUENE AND NAPHTHALENE

The runs with benzene were made through the iron furnace containing $2\frac{1}{2}$ kg. of charcoal, the purpose being to try to check the results of Cobb and Hollings (23). They found that benzene passing through coke heated to 800 deg. C. could be entirely stabilized by means of excess hydrogen. In these experiments it was found that when the charcoal and furnace were activated it was impossible to stabilize the benzene even at 500 deg. C. Pressures as high as 125 lb. of hydrogen per square inch were used. On the other hand, if the charcoal and furnace had been treated with superheated steam, air or carbon dioxide, benzene could be entirely stabilized at temperatures as high as 800 deg. C. with very small pressures of hydrogen.

Cobb and Hollings (23) had found that when toluene was passed through red hot coke it was more stable alone than in the presence of excess hydrogen—that is, hydrogen promoted the decomposition of toluene into benzene and methane. In series 4 hydrogen was found to increase the toluene fraction slightly. Pure toluene was used under similar conditions and found to be somewhat more stable in the presence of hydrogen, except when the furnace was in the activated condition, when it was entirely decomposed with or without hydrogen.

In making the runs with naphthalene, it was preheated in an electrically heated retort connected to the upper end of the furnace. The naphthalene vapors were carried into the furnace by means of the gases which were bubbled through. It was noticed that practically as soon as the run commenced the temperature of the furnace dropped. Even when the current passing through the heating elements was materially increased, the temperature fell slowly. This would indicate that the reactions taking place inside the furnace were absorbing considerable heat. Another feature, particularly noticeable in the nitrogen run, was that the gas recovered did not equal the amount passed into the furnace from the cylinder, even with the addition of the gas from decomposition of the naphthalene. The charcoal may be partly responsible for this result.

In the runs using carbon dioxide as the carrying gas the product contained a heavy, black, high-boiling oil, some free carbon and a very light, fluffy, red material with very little odor of naphthalene. With hydrogen the product was dark gray, containing also traces of the light reddish material. The product from the nitrogen runs was a compact greenish color and from carbon monoxide the reddish fluffy material formed the bulk of the recovery.

The bulk of the recovered product was naphthalene, with small amounts of benzerythrene and α -methyl-naphthalene. A considerable amount of β - β -dinaphthyl, m.p. 187-8 deg. C., was obtained and identified by the picrate, m.p. 183 deg. C. The α - α and α - β forms were present in very small amounts.

GASEOUS PRODUCTS SYNTHESIZED

The process of decomposition of hydrocarbons can never be regarded as a simple effect of heat, independent of contact surfaces and the gaseous atmosphere in which it is conducted. The way in which we were able to modify the results of decomposition in various directions was by the deliberate control of these two factors. The gaseous products obtained in these experiments were extremely important and played as important a part in the final products as the gas introduced. Their effects can be considered from two standpoints-mechanical and chemical. An inert gas, like nitrogen, would not enter directly into chemical reaction under these conditions, but would play a very important part by washing the products of decomposition from the surface of the contact material, assist their volatilization by lowering their concentration in the vapor phase, and hurry them away from the region of decomposition. In the case of hydrogen, being much lighter, it has a greater diffusing power, the molecules travel at a higher speed and thus penetrate small areas where the larger gas molecules never reach. The all-important action of hydrogen, however, is chemical. It tends to reduce the single ring benzene hydrocarbons to benzene itself. A similar action may be inferred, as is very probable, on the attached groups of more complicated ring structures resulting in the formation of naphthalene and anthracene. It seems that this was the part played by hydrogen in the majority of the experiments carried out. However, other factors must be able to modify this tendency of hydrogen, because in the experiments giving the largest yields of the toluene fraction it was found possible to increase this fraction by introducing hydrogen from a cylinder. It was possible to change the production of hydrogen in these experiments by changing the temperature or the activity of the furnace.

Methane could also be produced in varying quantities, depending upon the furnace conditions. Bone and Coward (24) concluded that methane decomposes chiefly directly into hydrogen and carbon, the process being reversible and a surface phenomenon at least up to 1,200 deg. C. At the temperature these experiments were run methane is practically stable and its chemical reaction would be negligible, but its mechanical action would be very important, as in the case of nitrogen.

The carbon dioxide formed was in small quantities and was always in equilibrium with carbon monoxide. They seemed to deaden or poison the activity of the furnace, although it is possible CO_2 caused partial combustion.

Acetylene was formed in small quantities and although many investigators claim that the building up process is through the ability of acetylene to polymerize, it was concluded from these experiments that acetylene played a very small part. At higher temperatures it was more likely to be decomposed to carbon and hydrogen than to be built up.

ETHYLENE FORMATION

The production of ethylene in these reactions was very desirable, because it was noticed that wherever the percentage of ethylene in the outgoing gas approximated 3 or 4 per cent, the yields of the higher boiling compounds were appreciably increased. In general, it was found that ethylene decomposed into a mixture of ethane and methane in the neighborhood of 500 deg. C. Above 500 deg. C. the ethane content gradually decreased and around 650 deg. C. disappeared entirely with a resultant increase in methane. Ethylene seems to be able to decompose in several ways, which no doubt explains its usefulness in the building up process.

Bone and Coward (24) concluded that the primary action of heat on ethylene is to eliminate hydrogen. The residue \equiv CH thus formed may decompose or be hydrogenated to methane, or it may unite with another such residue to form acetylene. Hollings and Cobb (23) found that at lower temperatures, around 800 deg. C., it decomposed into methane and acetylene, while at higher temperatures it went into methane and hydrogen.

In some of these experiments as high as 15 per cent of the waste gas was found to be ethane. It was also found that very little ethane was formed below 475 deg. C. and that it was all practically decomposed at 700 to 725 deg. C., except in the presence of steam, which seemed to stabilize it at slightly higher temperatures. These temperatures are far lower than found by Hollings and Cobb (23), who found that the decomposition of ethane was rapid but not complete in 46 seconds at 800 deg. C. At 1.100 deg. C. only 88 per cent was decomposed, the chief products being ethylene and methane. No doubt the molecular decomposition of ethane played an important part in these experiments. According to J. J. Thomson (25), such residues as \equiv CH, = CH, and - CH, may exist momentarily in the free state. The four possibilities open to the residue - CH, are: (1) To form ethylene by uniting with another similar residue; (2) to break down into carbon and hydrogen: (3) to be hydrogenated to methane; (4) to attach to some heavier molecular formation-a partial decomposition of the benzene nucleus or homologs.

The above is only a partial list of the gaseous constituents in the furnace atmosphere during decomposition; undoubtedly many more complex groups or radicles from the higher boiling compounds exerted an important influence on the decomposition processes.

LIQUID HYDROCARBONS IDENTIFIED

Some of the liquid hydrocarbons which were purified and definitely identified by physical contents or known derivatives are listed below. Other compounds were obtained but have not been identified.

n-Hexane, b.p. 68 deg. C., was obtained in the ethylene series of runs in considerable quantities along with an unsaturated hydrocarbon, which had very similar physical

properties, probably hexylene. They were partly separated by the usual methods and the last traces of the unsaturated compound were removed by selenium oxych'oride. This reagent reacts too violently to use, however, where any considerable quantity of the unsaturated compound is present.

siderable quantity of the unsaturated compound is present. Cyclo Hexane, b.p. 80 deg. C., was obtained in small quantities, and after a partial separation from benzene, was purified by the above reagent. However, a solution of benzene in selenium oxychloride will readily dissolve cyclohexane. In cases where only traces of benzene were present the separation was rapid and complete.

Benzene, b.p. 80.5 deg. C., was obtained in several runs. The maximum yield obtained was 93.0 per cent of the possible theoretical.

Toluene, b.p. 110 deg. C., was obtained in many of the runs over charcoal. The maximum yield of the crude product was about 66.0 per cent of the possible theoretical.

a- and β -Methyl-Naphthalenes, b.p. 240-3 deg. C., were identified by the picrate, m.p. 112 deg. C.

Di-Tolyls (mixed), b.p. 275-8 deg. C., were identified by the acid derivatives. They were oxidized by prolonged boiling in chromic and glacial acetic acids.

1.2.Dimethyl-Naphthalene, b.p. 262-4 deg. C., was identified by the picrate.

Diphenyl-Ethane, b.p. 286 deg. C., was obtained in small quantities.

Some of the Solids Obtained

The solids synthesized were numerous and complex. In a single series of runs the high-boiling constituents were very similar, but in different series the variation was marked. In the series using cobalt and manganese the high-boiling oils contained a larger percentage of solids containing anthracene. The partial list follows:

Diphenyl, m.p. 70 deg. C., was obtained in considerable quantities in the fraction boiling from 340 to 255 deg. C. On standing, it settled out as a white solid. This compound could come from two benzene molecules with the liberation of hydrogen. Dufton and Cobb (18) have proved this to be a reversible reaction by passing diphenyl and hydrogen through a hot silica tube and producing benzene.

Naphthalene, m.p. 80 deg. C., was obtained in considerable quantities, as closely as could be determined, in approximately 4 per cent yields on the original xylene used. In view of the conflicting reports in the literature concerning the formation of naphthalene at low temperatures and from similar liquids, toluene especially, particular care was taken in the purification and identification of this compound. The presence of stilbene may give a clue to its formation.

presence of stilbene may give a clue to its formation. *Phenanthrene*, m.p 98-100 deg. C., was obtained in small yields. It was difficult to oxidize, but the picrate was easily obtained.

Stilbene, m.p. 124 deg. C., was found in small quantities; apparently it had been mostly condensed to naphthalene.

Pyrene, m.p. 145-7 deg. C., was identified by the picrate, m.p. 220 deg. C.

Methyl-Anthracene, m.p. 200-5 deg. C., was obtained in good yields. Both alpha and beta forms were present and

were separated by means of the methyl-anthracene-carbonic acids, which have considerable difference in the melting point temperature.

p-Diphenyl-Benzene, m.p. 207 deg. C., was also formed Anthracene, m.p. 212-14 deg. C., was formed in consider-able yields. It was rather difficult to purify it. 2.3.Dimethyl-Anthracene, m.p. 244-6 deg. C., was puri-fied and identified by the quinone, m.p. 180-2 deg. C. Chrysene, m.p. 248-50 deg. C., was obtained in small amounts in the runs with ethylene and xylene under high

pressures.

Another compound which has been separated is similar to asphaltenes in its appearance, behavior toward solvents, especially ether and hexane, and contains sulphur. The sulphur must have come from the contact surfaces inside the furnace.

SUMMARY AND CONCLUSIONS

Some of the more important results as indicated by the foregoing investigation are given in the following summary:

1. Mixed xylenes were decomposed by heat and contact surfaces, under the stabilizing influence of hydrogen and methane, almost theoretically into benzene and methane. Sixty-nine per cent of the original xylene was converted into crude benzene, which boiled below 100 deg. C. This is approximately 94.0 per cent of the possible theoretical.

2. At slightly lower temperatures, under the same condition of contact surfaces but in a gaseous atmosphere in which ethylene greatly predominated, 77 per cent of the mixed xylenes were built up into higher boiling compounds, the majority of which were solids at ordinary temperatures.

3. Mixed xylenes, under other conditions of temperature and contact surfaces, were converted into crude toluene in quantities approximating 64.0 per cent of the theoretical.

4. Mixed xylenes, under the influence of heat and iron surfaces, were decomposed quantitatively into amorphous carbon and gaseous products. Metallic oxide surfaces, especially after being slightly reduced at temperatures where they decompose xylene freely, accelerate this reaction. Small particles of iron oxides and reduced iron were found in the deposited carbon.

5. The reduced metallic surfaces, or freshly oxidized surfaces at the same temperature are much less reactive and tend to promote partial decomposition.

6. Non-metallic substances such as charcoal, pumice or refractory material at like temperatures tend to

decompose xylenes into unsaturated and higher boiling compounds. The decomposition to carbon is materially lessened.

7. Activation of heated iron and carbon surfaces could be induced by treating with superheated steam during a short period and afterward slightly reducing with hydrogen.

8. A deadening effect, opposite in characteristics to the above, was caused when carbon dioxide, carbon monoxide, air or superheated steam was passed through the activated furnace. This condition seemed to be the same, as is ordinarily described, as poisoning of the catalyzer. Under these conditions the liquid hydrocarbons were most stable.

9. Contact surfaces are very important to hydrogenation and dehydrogenation of aromatic hydrocarbons.

10. The gaseous atmosphere in which pyrogenic decomposition takes place exerts an extremely important influence on the yields and products of decomposition. Gases like methane and nitrogen between temperatures of 600 to 700 deg. C. have mostly a mechanical action. Ethylene, acetylene, hydrogen and ethane between the same temperatures have also a mechanical bearing on the end products, but their all-important action is chemical. Ethylene, acetylene and ethane were found to be entirely decomposed at temperatures above 725 deg. C.

11. The decomposition of ethylene was controlled so that practically pure methane or mixtures of methane and ethane were obtained as end products.

12. Pressure under some conditions favors molecular condensation, particularly if the pressure is made up of unsaturated gases. In other cases, where the pressure was made up by hydrogen, it caused the decomposition of the heavier molecules into the single ring compounds. Pressure in all cases lessened the percentage of unsaturated hydrocarbons in the final products.

13. Decomposition of hydrocarbons increases with rise in temperature, the larger molecules being less stable than the smaller ones at temperatures above 700 deg. C. The lower the temperature at which decomposition takes place the more economical the reaction. Lower temperatures can be used in the presence of activated surfaces.

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Contribution from the Chemical Laboratories,

University of Illinois. Urbana, Ill.

VITA

The writer of this thesis received his early education in the grade school at Leskard, and high school at Bowmanville, Ontario. He entered McMaster University in the fall of '09 and graduated with the degrees of Bachelor of Arts in the honor science course, and Master of Arts in Chemistry in 1915.

After graduation he entered war munition work. From September, 1915, to March, 1916, analyzing high explosives at the plant of The Canadian Explosives, Ltd., Montreal. From March, 1916, to November of the same year analyzing 9.2 inch shell steel, at the plant of the Canada Cement Co., Montreal. During November he was at the plant of the Armstrong-Whithworth Co., Longuiel, Quebec, analyzing tool steel. From December, 1916, to October, 1917, he was with the British Munitions Board, stationed at the acetone plant of the Canadian Products Co., Shawinigan Falls, Quebec.

Since October, 1917, he has been at the University of Illinois doing graduate work. While here he has held the following positions in the Department of Chemistry: October, 1917, to February, 1918, graduate assistant; and from February, 1918, to the present time, half-time assistant.





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