# ON THE THERMAL DECOMPOSITION OF CRESOLS.

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It is a well known fact that the constituents of coal tar vary with the conditions under which coal is treated ; the tar obtained from coals by low temperature carbonisation contains much cresol and no phenol nor benzene or merely traces, while the tar produced by high temperature distillation has less cresol but much phenol, benzene and toluene.⑴ These facts suggest that at a high temperature, cresol should decompose into benzene, toluene and phenol as illustrated in the following scheme :

$$\begin{array}{llll} & \nearrow C_6H_5OH + CH_3 & \text{demethylation} & (1) \\ C_6H_4CH_3OH & \rightarrow C_6H_5CH_3 + H_2O & \text{dehydration} & (2) \\ & \searrow C_6H_6 + H_2O + CH_3 & \text{dehydration \& demethylation} & (3) \end{array}$$

On referring to the literature on the present subject, we noticed that J. Kraemer⑵ has confirmed phenol by passing it through a glass or iron tube heated to a red heat, and it was decomposed into benzene and higher aromatic hydrocarbons. The removal of oxygen from phenol was also noted by W. Smith,⑶ when phenol or cresol was introduced into a glowing glass tube, filled with charcoal or iron filings, a small amount of benzene or toluene was produced together with a large amount of gaseous substances. On bringing phenol vapour into contact with a heated platinum wire, H.

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(1) A. Warnes, "Coal tar distillation" (1923), 65 ; C. Lander and R. MacKay, "Low temperature carbonisation" (1924), 71, 79 ; H. Strache und R. Lant, "Kohlenchemie" (1924), 381 ; F. Wirth, "Brennstoff Chemie" (1926), 396.

(2) J. Kraemer, *Ann.*, **189** (1877), 129.

(3) W. Smith, *J. Soc. Chem. Ind.* **9** (1890), 447.

Meyer(1) has identified benzene in the reaction product. Demethylation of cresol was reported by F. Fischer(2); according to his report, cresol vapour passed with hydrogen or carbon monoxide through a tube heated to 700°–800°C., yields phenol as well as benzene. E. Müller(3) has reported that cresol, when passed through an iron tube heated to 700°–800°C., was found to decompose chiefly into methane, carbon monoxide, hydrogen and carbon, and a small amount of benzene and tarry matter were also produced; and that the proportion of the chief reaction products is as follows:

$$C_6H_4CH_3OH \longrightarrow CO+CH_4+2H_2+5C.$$

**1. The Thermal Decomposition of *m*-Cresol.** The writer's supposition for the thermal decomposition of the cresol, which was mentioned above, was partly confirmed by the experiments of many investigators in subjecting phenol to a high temperature with or without catalysts. However, the mechanism and conditions for the formation of benzene, toluene and phenol from cresol remained in a state of uncertainty. The present research was undertaken with the intention of obtaining confirmation of the true nature of the pyrogenic decomposition of cresols and also to settle the conditions under which the hydrocarbons and phenol are formed.

The best method of utilizing the tar acids composing the major part of the tar formed by the low temperature carbonization of coals, a matter which concerns the important problem of the economical uses of coals as fuel, will naturally be acquired from the study of the pyrogenic reaction of cresols.

In the experiment, *o*-, *m*-, and *p*-cresols were passed, at the rate of 3.5–4.5 gr. per hour into a glass tube heated to 600°, 650°, and 700° respectively, in a combustion furnace. The temperature of the reaction tube was measured by means of a thermocouple inserted into the tube, and the reaction products—gas and tar, were separately collected in receivers connected by means of a delivery tube to one end of the tube, as may be seen in Fig. 1 mentioned in the experimental part.

The gaseous product was analysed with the Bone-Wheeler gas analysis apparatus, of methane, hydrogen, carbon monoxide, and carbon dioxide. The tar separated from water, was analysed for hydrocarbon, phenols and polymers; the phenol and the cresol which were separated from the hydrocarbons by means of an 8% caustic soda solution, had their content

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(1) H. Meyer und A. Hofmann, *Monatsh.*, **38** (1917), 343.

(2) F. Fischer, *Abh. d. Kohle*, **4** (1919), 373; **5** (1920), 413.

(3) E. Müller, *J. prakt. Chem.*, [2] **58** (1898), 1.

estimated by the aid of density with reference to that of a mixture of a known quantity of two phenols.

When 20 gr. of *m*-cresol were passed in 5 hours through a glass tube heated to 600°, a gaseous product was noticed to be produced in the first few minutes, and then followed the tar-formation with diminution of the gas-production in process of time, and only 15.5% of the cresol decomposed, and the product was composed mostly of a polymer of high boiling point with 160 c.c. of gas composed of methane, carbon monoxide, carbon dioxide, and hydrogen. The formation of phenol and hydrocarbons was noticed to increase with the rise of the reaction temperature as will be shown in the Table.

The yield of gaseous substances from *m*-cresol at 650° was very meagre, but increased pari passu with the rate of decomposition of the cresol with the rise of the reaction temperature. The composition of the gas formed at 600° being rich in $CO_2$ and poor in $H_2$, is quite different from that generated at 650°, in which hydrogen is predominant, and the content of CO and $CH_4$ shows but slight variation through the whole range of the reaction temperatures. Phenol and benzene began to appear in a measurable quantity at 650°, and at high reaction temperature the yield of both phenol and benzene increased, viz., the formation of phenol is favourable at a low temperature; while the production of benzene and carbon monoxide was increased with the rise of the reaction temperature.

From this fact, it will be understood that the formation of phenol and benzene is due to the thermal decomposition of the polymer which is produced as a primary reaction product. As to this polymer, we have many evidences for considering it a mixture of some diphenyl ether derivatives. P. Sabatier(1) has reported that phenols when heated to 400°–500° in the presence of alumina yield chiefly aromatic ethers, and diphenyl ether according to the writer's experiment was decomposed by passing it through a glass tube heated to 700° into water, benzene, phenol, some polymers and carbon, and the gaseous products were composed mainly of carbon monoxide and hydrogen, and an inferior content of methane and carbon dioxide. Similar statements about the decomposition of phenyl ethers under different conditions were previously made by C. Graebe(2) and W. Ipatiew(3).

Taking these facts into account, the thermal decomposition of phenols would be represented in the following schemes:

$$(1)\quad ROH \longrightarrow ROR + H_2O$$

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(1) P. Sabatier, "Die Catalyse in der Organischen Chemie" (1927), 281.

(2) C. Graebe, *Ber.* **29** (1896), 1877.

(3) W. Ipatiew, *Ber.* **60** (1927), 1963.

$$(2)\quad ROR \longrightarrow \begin{cases} R'+H_2O \\ ROH+RH \\ \text{polymer} \\ CO,\ H_2,\ CH_4,\ H_2O \text{ and carbon} \end{cases}$$

phenol, for example, is condensed first by splitting off one mol of water from two mols of phenol into phenyl ether which then decomposes into benzene and phenol on the one side, and on the other polymerises into complex compounds and eventually into carbon, liberating such simple substances as water, carbon monoxide, carbon dioxide, hydrogen and methane.

In the thermal decomposition of cresol, besides toluene, benzene and phenol would be produced, as the result of demethylation happening simultaneously with the formation and decomposition of cresylether. The rate of detachment of the methyl group from the cresol molecule is assumed to depend mostly on the relative position of the methyl group visa vis the hydroxyl group.

As a matter of fact, the formation of hydrocarbon and phenol from cresol predominates at low temperatures, while the decomposition of the phenol into hydrocarbon is favorable at high temperatures with the formation of carbon monoxide and water, and the writer has noticed diphenyl occurring in the reaction product.

**2. The Comparison of the Thermal Decomposition of *m*-, *o*-, and *p*-Cresols.** When *o*- and *p*-cresols were treated at 700° in a glass tube, under conditions similar to those of *m*-cresol, the decomposition of the substances proceeded in a similar manner to the isomeric substance but differing in the proportionate quantities of the reaction products as may be seen in the following Table.

| Cresol | | *m* | *o* | *p* |
|---|---|---|---|---|
| Decomposed cresol | % | 51.0 | 88.0 | 93.5 |
| Benzene hydrocarbon | % | 8.0 | 11.5 | 13.0 |
| Phenol | % | 9.5 | 22.5 | 20.0 |
| Polymer | % | 17.5 | 24.5 | 21.5 |
| Water | % | 1.5 | 3.5 | 3.0 |
| Gas | c.c./gr. | 108 | 165 | 150 |
| (Vol. %) | CO | 40.5 | 29.3 | 36.7 |
| | $CH_4$ | 35.8 | 47.6 | 45.6 |
| | $H_2$ | 23.2 | 22.2 | 17.1 |

The rate of decomposition of the cresols is in the order *p*, *o* and *m*, but the formation of the gaseous products is greatest with the ortho compound and least with the meta, and the para-compound stands between those two.

The proportions of CO, $CH_4$ and $H_2$ in the gaseous product from the meta-compound is different from that produced from the ortho and the para-isomers, and this fact will afford some notion of the composition of the liquid products from *m*-cresol, in which hydrocarbons of a low boiling point such as benzene and toluene compose the major part, but phenol is the chief reaction constituent from other cresols. Such a difference in the reaction products from the three isomers of cresol is partly due to the easiness by which the elimination of the methyl group from the cresol molecule will take place according to the position combined the group to the carbon atom of the benzene nucleus.

As a matter of fact, the methyl group situated in ortho or para position to the hydroxyl group in the cresol molecule is easily removed in course of the pyrogenesis of the substances, and consequently the phenol-yield is great in *o*- and *p*-cresols, and it is established that *m*-cresol is the most stable and *p*-cresol the most unstable toward thermal treatment.

3. **Effect of the Material of the Reaction Tube.** In order to investigate the catalytic effect of the wall-materials of the reaction tube on the thermal decomposition of cresols, porcelain, copper and iron tubes were employed, through which *m*-cresol was passed under similar experimental conditions as described in the experimental part, and the amount of cresol affected by the reaction was greatest with the copper tube; and the effect of the material is in the order: copper, iron, porcelain, and glass; while for the formation of gaseous products, the order is iron, copper, porcelain, and glass.

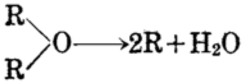
The gas from *m*-cresol which is passed into an iron tube, is chiefly composed of hydrogen and CO, with a small amount of methane, a result quite different from what happens when glass, porcelain or copper tubes are employed. In the latter three cases the constituents of the gaseous products are similar, the chief constituents being CO and methane, and glass and porcelain seem to affect the cresol catalyticaly as may be assumed from the gaseous constituents, in a similar manner, to the decomposition of cresol. This assumption of the catalytic effect of the tube materials is evidently approved on examination of the liquid reaction products which are composed of benzene hydrocarbon (H.C.) and phenol in the following ratio with the several tubes:

| Material of tube | | Glass | Porcelain | Copper | Iron |
|---|---|---|---|---|---|
| Decomposed cresol | % | 41 | 75.5 | 92.5 | 77.5 |
| $\frac{\text{H.C.}}{\text{Phenol}}$ | | $\frac{8.0}{9.5}$ | $\frac{13.5}{8.0}$ | $\frac{20.5}{5.5}$ | $\frac{8.5}{4.5}$ |
| Cresol changed into gas & carbon | % | 14.5 | 33.5 | 46.5 | 53.0 |
| Decomposed *m*-cresol | % | 51.0 | 75.5 | 92.5 | 77.5 |
| Benzene hydrocarbon | % | 8.0 | 13.5 | 20.5 | 8.5 |
| Phenol | % | 9.5 | 8.0 | 5.5 | 4.5 |
| Polymer | % | 17.5 | 18.0 | 16.5 | 6.5 |
| Water | % | 1.5 | 2.5 | 3.5 | 5.0 |
| Gas | c.c./gr. | 108 | 183 | 314 | 342 |
| (Vol. %) | CO | 40.5 | 41.0 | 43.1 | 22.1 |
| | $CH_4$ | 35.8 | 34.5 | 33.5 | 7.0 |
| | $H_2$ | 23.2 | 22.9 | 18.3 | 67.7 |

The relative amount of the hydrocarbon and phenol in the reaction product is the same whether porcelain or iron tubes be employed, though the copper tube shows a different result. The formation of phenol and the hydrocarbon being attributed to the decomposition of the polymer is supposed to proceed equally in glass or porcelain tubes, according to the following scheme:

$$R\text{-}O\text{-}R \longrightarrow R + ROH$$

but the formation of the hydrocarbon is facilitated with the iron and copper tubes, as may be manifest in the scheme:



$$\begin{matrix} R \\ R \end{matrix}\!\!>O \longrightarrow 2R + H_2O$$

When the iron tube was employed the gaseous substances were predominant in the reaction product, which formed at the expense of the polymer, and the latter was partly transformed into the hydrocarbon and phenol.

From these facts it may be concluded that the materials used for the reaction tube will promote catalytically any one of the reactions occurring in the thermal treatment of cresols, and the formation of phenol and polymers from cresols is favoured by the use of a glass or porcelain tube, and the production of benzene is promoted with the use of a copper tube; but with the employment of an iron tube a complete decomposition into gas, water and carbon is accelerated.

**4. Effect of Catalysts.** The occurrence of benzene, toluene and phenol in the coal tar by the high temperature distillation of coals was attributed in the foregoing paragraph to the fact that the tar acids formed as one of the primary reaction products in the tar generated by the carbonization are cracked to form these substances in passing the heated zone of coke or coal in a retort, which consists of the mineral matter together with some organic substances of complex nature. The thermal decomposition of cresols in the presence of some catalysts which are similar in composition to coal ash is very important in order to learn the mechanism of the reaction of the formation of the light fractions of the tar from coal materials.

There is some resemblance between the composition of some Japanese coal ash and of Japanese acid earth, both containing alumina and silica as a chief constituent as shown in the following Table :⁽¹⁾

| | Shimbara coal ash | Japanese acid earth |
|---|---|---|
| $SiO_2$ | 59.2 | 65.19 |
| $Al_2O_3$ | 26.2 | 16.36 |
| $Fe_2O_3$ | 5.6 | |
| $MnO_2$ | trace | — |
| CaO | 4.8 | 0.73 |
| MgO | 1.2 | 2.72 |
| $Na_2O+K_2O$ | 1.7 | 0.11 |

It is, therefore, not inconceivable that the catalytic action of the Japanese acid earth and alumina are analogous to that of coal ash. *o*-Cresol was passed into glass tube which contains Japanese acid earth or alumina, to see the catalytic effect on the decomposition of the substance.

In each case, the formation of a polymer and phenol is evidently favoured at a low temperature, and the yield of benzene hydrocarbon and carbon monoxide is increased with the rise of the reaction temperature due to the cracking of the polymer.

To discover a special feature of the catalysts for the decomposition of the cresol, the reaction products at 700° were studied.

The rate of decomposition of cresol is increased in the presence of the catalysts, and the alumina tends to promote the gasification of the substance. The hydrogen content in the produced gas increased with alumina, due to the expense of methane by the action of water in the presence of the

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(1) *Research Report of the Naval Fuel Depot, Japan,* **1** (1926), 40.

catalyst. The decomposition of polymers into hydrocarbons is obviously accelerated in presence of these catalysts, in which some difference was noticed when the liquid product was examined precisely according to the difference in the chemical constituents of the catalysts.

| | | Blank | Acid earth | $Al_2O_3$ |
|---|---|---|---|---|
| Changed cresol | % | 88.0 | 91.5 | 94.0 |
| Benzene hydrocarbon | % | 11.5 | 13.5 | 13.0 |
| Phenol | % | 22.5 | 16.5 | 12.5 |
| Polymer | % | 24.5 | 18.5 | 12.5 |
| Water | % | 3.3 | 5.0 | 4.0 |
| Gas | c.c./gr. | 165 | 198 | 327 |
| (Vol. %) | CO | 29.3 | 28.5 | 22.3 |
| | $CH_4$ | 47.6 | 46.8 | 33.7 |
| | $H_2$ | 22.2 | 24.0 | 36.9 |

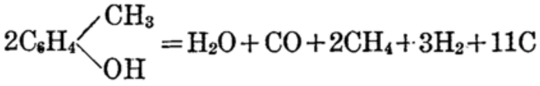
**5. Effect of Deposited Carbon.** In the course of the pyrogenetic reaction of cresols, the writer has noticed that in the first several minutes of the reaction, gaseous substances only are produced, followed by the formation of tar, the nature of the latter substance would not be the same as passing of time of reaction.

These observations led the writer to the notion that in the beginning of the process of pyrogenesis, the complete decomposition of cresols into gaseous compounds and carbon will prevail, and the latter substance accumulated in the reaction tube will retard the gasification, but promote the oxidation or removal of hydrogen from cresols to a polymer which will in turn change into phenol and benzene.

In passing *p*-cresol into the glass tube with alumina at 700°, the main reaction products in the first hour consisted of hydrogen, methane, carbon monoxide and water, with some quantities of carbon and some polymers. The composition of the gaseous products was determined to be

$$CO\ (CO_2),\ 1;\quad CH_4,\ 1.5;\quad H_2,\ 3.8.$$

The formation of these substances is supposed to occur by the reaction represented by the equation which differs slightly from that reported by E. Müller⁽¹⁾



$$2C_6H_4\begin{cases}CH_3\\OH\end{cases}=H_2O+CO+2CH_4+3H_2+11C$$

In the latter phase of the reaction, polymers and phenol are the chief reaction product, and their formation will be connected with the deposition of carbon in the reaction tube. The physical and chemical properties of carbon produced by the thermal decomposition of organic compounds, vary with not only the nature of the substance from which the carbon is produced, but the external conditions such as the temperature and the pressure⁽²⁾ under which the carbonization takes place, also the physical nature of the surface⁽³⁾ of the tube on which the carbon is precipitated. In fact, some differences have been noticed in the appearance of the carbon deposited on the surface of glass, porcelain, copper and iron tubes, and the difference in composition of the reaction products from cresols is partly due to the physical and chemical nature of the carbon deposited on the tube-walls.

## Experimental Part.

Cresols from Kahlbaum, distilled for purification after being treated with anhydrous sodium sulphate, show the following physical constants:

| Cresol | B. p. | $d^{25°}_{4°}$ | $n^{25°}_{D}$ |
|---|---|---|---|
| *o*– | 187.5°—183.3° | 1.0426 | 1.5398 |
| *m*– | 198.5°—199.5° | 1.0304 | 1.5350 |
| *p*– | 197.5°—198.5° | 1.0310 | 1.5335 |

A reaction tube of 2 cm. in diameter and 1 m. in length, made of glass, porcelain, copper, or iron, was heated in a combustion furnace, and the

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(1) E. Müller, loc. cit.

(2) W. J. Mellor, "Comprehensive treaties on inorganic and theoretical chemistry," V, (1924).

(3) K. A. Hofmann und U. Hofmann, *Ber.*, **59** (1926), 2433.

temperature of the inside of the tube was measured by means of a thermocouple; the cresols were gradually dropped into a reaction tube by means of a capillary tube attached to the tube, and the reaction product was collected in a receiver which was cooled with a freezing mixture of ice and salt, and the generated gas which escaped from the receiver was collected on a 10% sulphuric acid solution in a bottle. (Fig. 1).

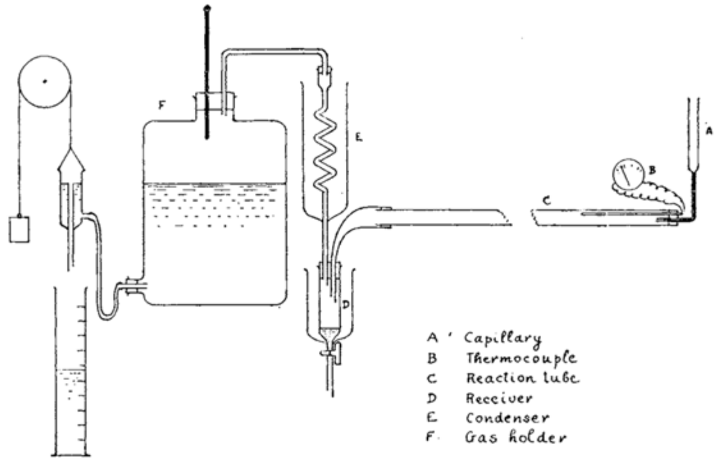

Fig. 1

The gas produced was analysed with a Bone-Wheeler⁽¹⁾ gas analysis apparatus, and the content of $CO_2$, $CO$, $CH_4$ and $H_2$ specially estimated in each experiment. The tarry matter condensed in the receiver was subjected to fractional distillation after water was separated, into three parts; the first part boiled from 78° to 120°, the second part b.p. 120°–200°, the residue b.p. up 200°, and each fraction was treated with 8% caustic soda solution to separate the phenolic substances from the neutral ones and redistilled. The main fractions were estimated to be composed of the following constituents.

1. The neutral fraction b.p. (79°–120°) benzene and toluene
2. ,, acidic ,, b.p. (178°–200°) phenol and cresols
3. ,, residue ,, b.p. (200° — ) polymer

The phenol-content in the acidic fraction (178°–200°) was calculated by weight from its density by consulting the following Table and Fig. 2.

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(1) C. Grice and W. Paymann, *Fuel in Science and Practice* (1924), 236.

| *o*-Cresol | | *m*-Cresol | | *p*-Cresol | |
|---|---|---|---|---|---|
| Phenol % | $d_{4°}^{25°}$ | Phenol % | $d_{4°}^{25°}$ | Phenol % | $d_{4°}^{25°}$ |
| 0 | 1.0426 | 0 | 1.0304 | 0 | 1.0310 |
| 8.4 | 1.0448 | 18.6 | 1.0377 | 17.7 | 1.0380 |
| 14.9 | 1.0470 | 25.9 | 1.0406 | 25.4 | 1.0408 |
| 26.4 | 1.0501 | 44.7 | 1.0480 | 35.9 | 1.0454 |
| 47.8 | 1.0565 | 50.2 | 1.0502 | 51.7 | 1.0514 |
| 67.7 | 1.0623 | 65.4 | 1.0565 | 72.7 | 1.0601 |
| 76.7 | 1 0651 | 76.7 | 1.0610 | | |

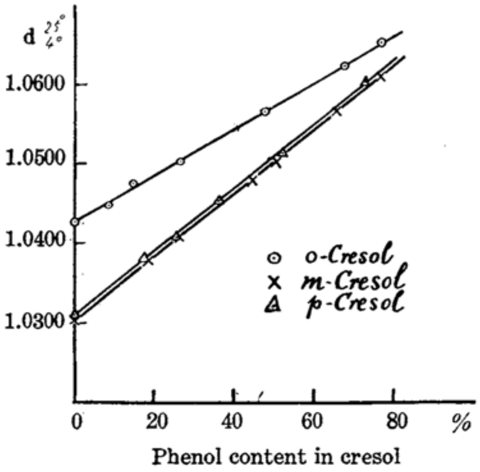

Fig. 2.

The data shown in the Table was obtained by the writer by mixing the known weight of two substances.

Benzene and toluene which occur in the neutral fraction were identified by transforming them into their amino derivatives by the usual method, and also phenol was confirmed by converting into the diazo-derivative.

**1. Experiment with a Glass tube.** *m*-, *o*- and *p*-cresols were passed at the rate of 3.6–4.2 gr. per hour, into a glass tube heated to 600°, 650° and 700° respectively. At the beginning of the reaction, some gaseous product only was formed, followed by the formation of a liquid substance. The products were analysed and the results are shown in Tables 1, 2 and 3. It was noticed that the inner surface of the tube was covered by a film of carbon, and the higher the reaction temperature the greater the thickness of the carbon film. The appearance of the carbon film is black at 600°, bluish black at 650°, with a grey and dull metallic lustre at 700°.

Table 1.

*m*-Cresol

| Reaction temp. | Sample used gr. | Passing rate of sample gr./hour | Decomposition products | | |
|---|---|---|---|---|---|
| | | | Liquid gr. | Gas c.c. at 0°, 760 mm. | Carbon |
| 600°C. | 20.0 | 4.0 | 18.7 | 160 | + |
| 650° | 20.0 | 4.0 | 18.1 | 620 | + |
| 700° | 20.0 | 4.0 | 17.5 | 2150 | + |

Liquid

| Reaction temp. | Neutral (79°–120°) | | | Acidic (178°–200°) | | | Residue (200°–) | Water |
|---|---|---|---|---|---|---|---|---|
| | gr. | $d_{4°}^{25°}$ | $d_{D}^{25°}$ | gr. | $d_{4°}^{25°}$ | $n_{D}^{25°}$ | gr. | gr. |
| 600° | trace | — | — | 16.9 | 1.0307 | 1.5322 | 0.9 | trace |
| 650° | 0.3 | — | 1.4911 | 14.9 | 1.0328 | 1.5334 | 1.9 | 0.2 |
| 700° | 1.6 | 0.8672 | 1.4903 | 11.7 | 1.0368 | 1.5356 | 3.5 | 0.3 |

(Yield in % for sample)

| Reaction temp. | *m*-Cresol | Hydrocarbon | Phenol | Polymer | Water | Hydrocarbon (mol %) / Phenol (mol %) |
|---|---|---|---|---|---|---|
| 600° | 84.5 | trace | trace | 4.5 | trace | — |
| 650° | 70.0 | 1.5 | 4.5 | 9.5 | 1.0 | 2.1/5.0=0.42 |
| 700° | 49.0 | 8.0 | 9.5 | 17.5 | 1.5 | 11.1/10.6=1.05 |

Gas

| Reaction temp. | Yield c.c./gr. | Composition (in vol. %) | | | |
|---|---|---|---|---|---|
| | | $CO_2$ | CO | $CH_4$ | $H_2$ |
| 600° | 8 | 35.6 | 22.5 | 36.6 | 5.2 |
| 650° | 31 | 0.9 | 34.9 | 42.1 | 22.1 |
| 700° | 108 | 0.5 | 40.5 | 35.8 | 23.2 |

Table 2.

*o*–Cresol

| Reaction temp. | Sample used gr. | Passing rate of sample gr./hour | Decomposition products | | |
|---|---|---|---|---|---|
| | | | Liquid gr. | Gas c.c. at 0°,760mm. | Carbon |
| 600°C. | 20.0 | 4.0 | 18.9 | 340 | + |
| 650° | 20.0 | 3.8 | 17.5 | 1560 | + |
| 700° | 20.0 | 3.6 | 15.1 | 3300 | + |

Liquid

| Reaction temp. | Neutral (79°–120°) | | | Acidic (178°–200°) | | | Residue (200° –) gr. | Water gr. |
|---|---|---|---|---|---|---|---|---|
| | gr. | $d_{4°}^{25°}$ | $n_D^{25°}$ | gr. | $d_{4°}^{25°}$ | $n_D^{25°}$ | | |
| 600° | 0.1 | – | 1.4892 | 16.3 | 1.0444 | 1.5412 | 2.0 | 0.1 |
| 650° | 1.1 | 0.8709 | 1.4964 | 11.2 | 1.0495 | 1.5404 | 4.0 | 0.4 |
| 700° | 2.3 | 0.8756 | 1.4946 | 6.9 | 1.0615 | 1.5432 | 4.9 | 0.7 |

(Yield in % for sample)

| Reaction temp. | *o*-Cresol | Hydrocarbon | Phenol | Polymer | Water | $\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$ |
|---|---|---|---|---|---|---|
| 600° | 76.0 | 0.5 | 5.5 | 10.0 | 0.5 | 0.7/ 6.1=0.11 |
| 650° | 42.5 | 5.5 | 13.5 | 20.0 | 2.0 | 7.6/15.8=0.48 |
| 700° | 12.0 | 11.5 | 22.5 | 24.5 | 3.5 | 15.5/25.7=0.62 |

Gas

| Reaction temp. | Yield c.c./gr. | Composition (in vol. %) | | | |
|---|---|---|---|---|---|
| | | $CO_2$ | $CO$ | $CH_4$ | $H_2$ |
| 600° | 17 | 2.9 | 18.6 | 64.1 | 14.4 |
| 650° | 78 | 2.1 | 22.5 | 63.8 | 11.6 |
| 700° | 165 | 0.8 | 29.3 | 47.6 | 22.2 |

Table 3.

*p*–Cresol

| Reaction temp. | Sample used gr. | Passing rate of sample gr./hour | Decomposition products | | |
|---|---|---|---|---|---|
| | | | Liquid gr. | Gas c.c. at 0°,760mm. | Carbon |
| 600°C. | 20.0 | 3.8 | 18.3 | 410 | + |
| 650° | 20.0 | 3.8 | 15.7 | 2840 | + |
| 700° | 20.0 | 4.2 | 13.1 | 3000 | + |

Liquid

| Reaction temp. | Neutral (79°–120°) | | | Acidic (178°–200°) | | | Residue (200°—) gr. | Water gr. |
|---|---|---|---|---|---|---|---|---|
| | gr. | $d^{25°}_{4°}$ | $n^{25°}_{D}$ | gr. | $d^{25°}_{4°}$ | $n^{25°}_{D}$ | | |
| 600° | 0.2 | — | 1.4889 | 15.5 | 1.0373 | 1.5327 | 1.8 | 0.1 |
| 650° | 1.4 | 0.8691 | 1.4959 | 9.4 | 1.0490 | 1.5374 | 3.7 | 0.5 |
| 700° | 2.6 | 0.8711 | 1.4911 | 5.4 | 1.0610 | 1.5400 | 4.3 | 0.6 |

(Yield in % for sample)

| Reaction temp. | *p*-Cresol | Hydrocarbon | Phenol | Polymer | Water | Hydrocarbon (mol %) / Phenol (mol %) |
|---|---|---|---|---|---|---|
| 600° | 72.5 | 1.0 | 5.0 | 9.0 | 0.5 | 1.3/5.9=0.23 |
| 650° | 26.0 | 7.0 | 21.0 | 18.5 | 2.5 | 9.7/25.8=0.37 |
| 700° | 6.5 | 13.0 | 20.5 | 21.5 | 3.0 | 18.0/23.7=0.76 |

Gas

| Reaction temp. | Yield c.c./gr. | Composition (in vol. %) | | | |
|---|---|---|---|---|---|
| | | $CO_2$ | CO | $CH_4$ | $H_2$ |
| 600° | 20 | 1.7 | 20.3 | 62.0 | 16.0 |
| 650° | 142 | 0.9 | 28.4 | 57.5 | 13.5 |
| 700° | 150 | 0.7 | 36.7 | 45.6 | 17.1 |

**2. Experiment with Porcelain, Copper and Iron Tubes.** Three tubes made of porcelain, copper and iron was used instead of the glass tube, in the experiment with *m*-cresol which was carried out under the conditions shown in the Table, and the results are as follows :

## Table 4.

### (A) Porcelain tube

| Reaction temp. | Sample used gr. | Passing rate of sample gr./hour | Decomposition products | | |
|---|---|---|---|---|---|
| | | | Liquid gr. | Gas c.c. at 0°,760 mm. | Carbon |
| 600°C. | 20.0 | 4.0 | 17.2 | 140 | + |
| 650° | 20.0 | 3.6 | 17.0 | 680 | + |
| 700° | 20.0 | 3.6 | 14.0 | 3670 | + |

### Liquid

| Reaction temp. | Neutral (79°–120°) | | | Acidic (178°–200°) | | | Residue (200°—) gr. | Water gr. |
|---|---|---|---|---|---|---|---|---|
| | gr. | $d^{25°}_{4°}$ | $n^{25°}_{D}$ | gr. | $d^{25°}_{4°}$ | $n^{25}_{D}$ | | |
| 600° | trace | — | — | 14.7 | 1.0310 | 1.5330 | 1.2 | 0.1 |
| 650° | 0.5 | 0.8630 | 1.4936 | 13.4 | 1.0328 | 1.5353 | 2 0 | 0.2 |
| 700° | 2.7 | 0.8684 | 1.4920 | 6.5 | 1.0400 | 1.5366 | 3.6 | 0.5 |

### (Yield in % for sample)

| Reaction temp. | *m*-Cresol | Hydrocarbon | Phenol | Polymer | Water | Hydrocarbon (mol %) / Phenol (mol %) |
|---|---|---|---|---|---|---|
| 600° | 72.0 | trace | 1.5 | 6.0 | 0.5 | trace/1.7 |
| 650° | 62.5 | 2.5 | 4.5 | 10.0 | 1.0 | 3.5/5.0=0.70 |
| 700° | 24.5 | 13.5 | 8.0 | 18.0 | 2.5 | 18.6/9.4=1.97 |

### Gas

| Reaction temp. | Yield c.c./gr. | Composition (in vol. %) | | | |
|---|---|---|---|---|---|
| | | $CO_2$ | $CO$ | $CH_4$ | $H_2$ |
| 600° | 7 | 29.8 | 24.8 | 40.5 | 4.9 |
| 650° | 34 | 4.2 | 35.7 | 37.9 | 22.2 |
| 700° | 183 | 1.7 | 41.0 | 34.5 | 22.9 |

## Table 5.

### (B) Copper tube

| Reaction temp. | Sample used gr. | Passing rate of sample gr./hour | Decomposition products | | |
|---|---|---|---|---|---|
| | | | Liquid gr. | Gas c c. at 0°, 760 mm. | Carbon |
| 600°C. | 20.0 | 4.7 | 18.2 | 950 | a few |
| 650° | 20.0 | 4.0 | 15.2 | 3260 | a few |
| 700° | 20.0 | 3.8 | 11.6 | 6280 | a few |

### Liquid

| Reaction temp. | Neutral (79°–120°) | | | Acidic (178°–200°) | | | Residue (200°—) gr. | Water gr. |
|---|---|---|---|---|---|---|---|---|
| | gr. | $d_{4°}^{25°}$ | $n_D^{25°}$ | gr. | $d_{4°}^{25°}$ | $n_D^{25°}$ | | |
| 600° | 0.1 | — | — | 15.8 | 1.0313 | 1.5320 | 1.0 | 0.1 |
| 650° | 1.9 | 0.8694 | 1.4930 | 9.4 | 1.0367 | 1.5348 | 2.9 | 0.6 |
| 700° | 4.1 | 0.8704 | 1.4900 | 2.6 | 1.0472 | 1.5375 | 3.3 | 0.7 |

### (Yield in % for sample)

| Reaction temp. | *m*-Cresol | Hydrocarbon | Phenol | Polymer | Water | Hydrocarbon (mol %) / Phenol (mol %) |
|---|---|---|---|---|---|---|
| 600° | 76.5 | 0.5 | 2.5 | 5.0 | 0.5 | 0.7/2.6=0.27 |
| 650° | 39.5 | 9.5 | 7.5 | 14.5 | 3.0 | 12.1/8.2=1.48 |
| 700° | 7.5 | 20.5 | 5.5 | 16.5 | 3.5 | 28.5/6.2=4.60 |

### Gas

| Reaction temp. | Yield c.c./gr. | Composition (in vol. %) | | | |
|---|---|---|---|---|---|
| | | $CO_2$ | $CO$ | $CH_4$ | $H_2$ |
| 600° | 43 | 21.4 | 37.2 | 39.8 | 1.5 |
| 650° | 163 | 4.6 | 40.0 | 29.8 | 25.6 |
| 700° | 314 | 5.2 | 43.1 | 33.5 | 18.3 |

Table 6.

(C) Iron tube

| Reaction temp. | Sample used gr. | Passing rate of sample gr./hour | Decomposition products | | |
|---|---|---|---|---|---|
| | | | Liquid gr. | Gas c.c. at 0°,760 mm. | Carbon gr. |
| 600°C | 20.0 | 3.5 | 12.9 | 4080 | + |
| 650° | 20.0 | 4.0 | 12.8 | 5430 | 2.5 |
| 700° | 20.0 | 3.8 | 10.0 | 6850 | 5.0 |

Liquid

| Reaction temp. | Neutral (79°–120°) | | | Acidic (178°–200°) | | | Residue (200°) gr. | Water gr. |
|---|---|---|---|---|---|---|---|---|
| | gr. | $d_{4°}^{25°}$ | $n_D^{25°}$ | gr. | $d_{4°}^{25°}$ | $n_D^{25}$ | | |
| 600° | 0.4 | 0.8663 | 1.4870 | 10.4 | 1.0313 | 1.5328 | 1.0 | 0.3 |
| 650° | 0.4 | 0.8704 | 1.4914 | 9.6 | 1.0328 | 1.5334 | 1.3 | 0.7 |
| 700° | 1.7 | 0.8726 | 1.4930 | 5.4 | 1.0367 | 1.5350 | 1.3 | 1.0 |

(Yield in % for sample)

| Reaction temp. | *m*-Cresol | Hydrocarbon | Phenol | Polymer | Water | Hydrocarbon (mol %) / Phenol (mol %) |
|---|---|---|---|---|---|---|
| 600° | 50.5 | 2.0 | 1.5 | 5.0 | 1.5 | 2.8/1.8=1.56 |
| 650° | 44.5 | 2.0 | 3.5 | 6.5 | 3.5 | 2.8/3.8=0.74 |
| 700° | 22.5 | 8.5 | 4.5 | 6.5 | 5.0 | 11.8/5.3=2.26 |

Gas

| Reaction temp. | Yield c.c./gr. | Composition (in vol. %) | | | |
|---|---|---|---|---|---|
| | | $CO_2$ | CO | $CH_4$ | $H_2$ |
| 600° | 204 | 6.2 | 25.4 | 11.3 | 57.1 |
| 650° | 271 | 4.9 | 25.0 | 4.3 | 65.9 |
| 700° | 342 | 3.2 | 22.1 | 7.0 | 67.7 |

**3. Experiment with Catalysts.** Japanese acid earth or alumina was used in the thermal decomposition of *o*-cresol as a catalyst to investigate their effect on the reaction. Commercial Japanese acid earth was washed repeatedly with water, dried at 100° and then heated to 500°, and alumina from the market was used.

In the experiment, 10 grams of the catalysts, thus prepared, were spread to a length of 70 cm. in the glass tube and heated to the desired reaction temperature for one hour in a current of air, and then *o*-cresol was passed at the rate of 3.3–4.2 gr. per hour through the tube. After the reaction, the surface of the catalyst was noticed to be covered with carbon. The experimental result are shown in Tables 7 and 8.

Table 7.

Japanese acid earth

| Reaction temp. | Sample used gr. | Passing rate of sample gr./hour | Decomposition products | | |
|---|---|---|---|---|---|
| | | | Liquid gr. | Gas c.c. at 0°,760 mm. | Carbon |
| 600°C. | 20.0 | 3.4 | 16.9 | 970 | + |
| 650° | 20.0 | 4.2 | 16.4 | 380 | + |
| 700° | 20.0 | 4.0 | 12.9 | 3970 | + |

Liquid

| Reaction | Neutral (79°-120°) | | | Acidic (178°-200°) | | | Residue (200°—) gr. | Water gr. |
|---|---|---|---|---|---|---|---|---|
| | gr. | $d_{4^\circ}^{25^\circ}$ | $n_D^{25^\circ}$ | gr. | $d_{4^\circ}^{25^\circ}$ | $n_D^{25^\circ}$ | | |
| 600° | 0.7 | 0.8787 | 1.4952 | 13.3 | 1.0456 | 1.5400 | 2.0 | 0.6 |
| 650° | 1.3 | 0.8732 | 1.4949 | 11.6 | 1.0504 | 1.5412 | 2.7 | 0.6 |
| 700° | 2.7 | 0.8748 | 1.4944 | 5.0 | 1.0618 | 1.5428 | 3.7 | 1.0 |

(Yield in % for sample)

| Reaction temp. | *o*-Cresol | Hydrocarbon | Phenol | Polymer | Water | Hydrocarbon (mol %) / Phenol (mol %) |
|---|---|---|---|---|---|---|
| 600° | 59.5 | 3.5 | 7.0 | 10.0 | 3.0 | 4.9/ 7.9=0.62 |
| 650° | 42.0 | 6.5 | 16.0 | 13.0 | 3.0 | 9.0/18.5=0.49 |
| 700° | 8.5 | 13.5 | 16.5 | 18.5 | 5.0 | 18.7/18.9=0.99 |

Gas

| Reaction temp. | Yield c.c./gr. | Composition (in vol. %) | | | |
|---|---|---|---|---|---|
| | | $CO_2$ | CO | $CH_4$ | $H_2$ |
| 600° | 48 | 0.7 | 11.6 | 43.3 | 44.3 |
| 650° | 19 | 0.5 | 15.3 | 47.4 | 36.9 |
| 700° | 198 | 0.7 | 28.5 | 46.8 | 24.0 |

Table 8.

Alumina

| Reaction temp. | Sample used gr. | Passing rate of sample gr./hour | Decomposition products | | |
|---|---|---|---|---|---|
| | | | Liquid gr. | Gas c.c. at 0°, 760 mm. | Carbon |
| 600°C. | 20.0 | 3.3 | 13.8 | 2690 | + |
| 650° | 20.0 | 4.0 | 12.3 | 2990 | + |
| 700° | 20.0 | 4.2 | 10.2 | 6530 | + |

Liquid

| Reaction temp. | Neutral (79°–120°) | | | Acidic (178°–200°) | | | Residue (200°—) gr. | Water gr. |
|---|---|---|---|---|---|---|---|---|
| | gr. | $d_{4^\circ}^{25^\circ}$ | $n_D^{25^\circ}$ | gr. | $d_{4^\circ}^{25^\circ}$ | $n_D^{25^\circ}$ | | |
| 600° | 0.7 | 0.8760 | 1.4900 | 10.2 | 1.0483 | 1.5404 | 1.7 | 0.8 |
| 650° | 1.5 | 0.8743 | 1.4947 | 7.2 | 1.0537 | 1.5423 | 2.6 | 0.8 |
| 700° | 2.6 | 0.8750 | 1.4935 | 3.7 | 1.0623 | 1.5430 | 2.5 | 0.8 |

(Yield in % for sample)

| Reaction temp. | *o*-Cresol | Hydrocarbon | Phenol | Polymer | Water | $\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$ |
|---|---|---|---|---|---|---|
| 600° | 41.0 | 3.5 | 10.0 | 8.5 | 4.0 | 4.5/11.2=0.40 |
| 650° | 22.0 | 7.5 | 14.0 | 13.0 | 4.0 | 10.4/16.3=0.64 |
| 700° | 6.0 | 13.0 | 12.5 | 12.5 | 4.0 | 18.0/14.1=1.28 |

Gas

| Reaction temp. | Yield c.c./gr. | Composition (in vol. %) | | | |
|---|---|---|---|---|---|
| | | $CO_2$ | CO | $CH_4$ | $H_2$ |
| 600° | 135 | 3.0 | 8.6 | 35.9 | 52.6 |
| 650° | 150 | 7.3 | 14.9 | 44.4 | 33.2 |
| 700° | 327 | 7.1 | 22.3 | 33.7 | 36.9 |

Table 9.

| No. of interval | Time hour | Sample passed gr. | Decomposition products | |
|---|---|---|---|---|
| | | | Liquid gr. | Gas c.c. at 0°,760 mm. |
| I | 1 | 10.7 | 2.8 | 4690 |
| II | $3\frac{2}{3}$ | 39.2 | 32.9 | 5232 |
| III | $4\frac{1}{2}$ | 49.1 | 40.7 | 4185 |

Liquid

| No. of interval | Fraction | gr. | $d^{25^\circ}_{4^\circ}$ | $n^{25^\circ}_{D}$ |
|---|---|---|---|---|
| I | Neutral ( 79°–120°) | 0.3 | — | 1.4881 |
| | Acidic (178°–200°) | 0.7 | 1.0500 | 1.5377 |
| | Residue (200° ——) | 1.2 | | |
| | Water | 0.6 | | |
| II | Neutral ( 79°–120°) | 1.8 | 0.8677 | 1.4924 |
| | Acidic (178°–185°) | 3.2 | 1.0608 | 1.5439 |
| | ,, (185°–190°) | 2.3 | 1.0483 | 1.5375 |
| | ,, (190°–195°) | 9.8 | 1.0347 | 1.5345 |
| | ,, (195°–200°) | 4.5 | 1.0330 | 1.5341 |
| | Residue (200° ——) | 4.7 | | |
| | Water | 0.5 | | |
| III | Neutral ( 79°–120°) | 1.9 | 0.8684 | 1.4903 |
| | Acidic (178°–185°) | 3.0 | 1.0546 | 1.5391 |
| | ,, (185°–190°) | 4.0 | 1.0462 | 1.5366 |
| | ,, (190°–195°) | 13.0 | 1.0347 | 1.5356 |
| | ,, (195°–200°) | 7.8 | 1.0326 | 1.5349 |
| | Residue (200° ——) | 5.5 | | |
| | Water | 0.3 | | |

Liquid (% for sample)

| No. of interval | *p*-Cresol | Hydrocarbon | Phenol | Polymer | Water |
|---|---|---|---|---|---|
| I | 3.8 | 3.8 | 2.8 | 11.2 | 5.6 |
| II | 39.0 | 4.6 | 11.5 | 12.0 | 1.3 |
| III | 46.8 | 3.8 | 9.8 | 11.2 | 0.6 |

Table 9.—(*continued*).

Gas (composition in vol. %)

| No. of interval | $CO_2$ | CO | $CH_4$ | $H_2$ | $C_nH_{2m}$ |
|---|---|---|---|---|---|
| I | 3.4 | 10.8 | 23.6 | 59.6 | 2.8 |
| II | 3.4 | 21.2 | 33.0 | 39.6 | 2.6 |
| 1II | 3.1 | 24.3 | 39.5 | 30.1 | 2.5 |

**4. Experiment on the Effect of the Deposited Carbon.** 99 grams of *p*-cresol were passed in 9 hours into a glass tube with three porcelain boats which were situated separately at certain intervals in the tube, each containing about 10 gr. of alumina. The reaction products, gas and tar were collected successively in three intervals ; the first one hour, then 3.5 hours for the second fraction, and finally 4.5 hours for the third, and each collection was analysed, and the results are shown in Table 9.

In order to learn the chemical nature of the carbon deposited on the catalyst in the boats, the whole content of these boats was subjected to combustion, and carbon and hydrogen were estimated as in the elemental analysis of an organic compound.

| Position in reaction tube | Capillary side | Centre | Receiver side |
|---|---|---|---|
| C % | 97.3 | 95.3 | 92.5 |
| H % | 2.0 | 3.1 | 3.1 |
| O % | 0.7 | 1.6 | 4.4 |
| C/H | 4.05/1 | 2.56/1 | 2.48/1 |

As will be seen from the above Table, the so-called carbon deposited on alumina is mostly composed of carbon, and its composition varies with the position in which the boat is situated in the tube. When cresol comes into contact with the heated surface of alumina, it would undergo repeated polymerisations and decompositions, splitting off oxygen and hydrogen, and producing such a carbon-rich substance as the so-called carbon(1).

**5. Diphenyl Ether.** Diphenyl ether prepared from chlorobenzene and sodium phenolate, showed b.p.$=(97.5°–98.5°)_{3mm.}$, $d_{4°}^{25°}=1.0716$, $n_D^{25°}=1.5782$, was passed into a glass tube heated to 700°, at the rate of 15.4 gr. per hour, and thus, 30.8 gr. of diphenyl ether yielded 27.0 gr. of the tarry substance, 0.3 gr. of water, 1900 c.c. of gas and some carbon. Analytical results of the tar are shown in the following Table.

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(1) M. Berthelot, "Essai de mecanique chimique", II, (1879), 137.

The neutral fraction.

| Fraction | gr. | % | | |
|---|---|---|---|---|
| 1. 78°—100° | 3.5 | 11.4 | $d^{25°}_{4°}=0.8753$, $n^{25°}_{D}=1.4974$ | benzene (24.7 mol %) |
| 2. 220°—260° | 5.8 | 18.8 | $d^{25°}_{4°}=1.0734$, $n^{25°}_{D}=1.5958$ | mainly diphenyl ether |
| 3. 260°—330° | 1.9 | 6.2 | | ,, diphenylene oxide |
| 4. residue | 3.6 | 11.8 | | |

The acidic fraction.

| Fraction | gr. | % | | |
|---|---|---|---|---|
| 1. 178°—185° | 4.1 | 13.3 | m.p. [39.5°—40.5°] | phenol (34.1 mol %) |
| 2. 280°—290° | 0.4 | 1.3 | | |
| 3. residue | 0.2 | 0.6 | | |

Benzene in the neutral fraction was confirmed by the usual chemical method. The fraction b.p. 220°–260° of the neutral part was assumed to be a mixture of diphenyl ether and diphenyl from the physical constants. From the fraction b.p. 260°–330° of the neutral part, a substance of m.p. 80°–81° by recrystallisation from alcohol was isolated, which was identified as diphenylene oxide by converting it into picrate with a m.p. of 96°–97°.

The composition of the gas was determined and shown by volume.

| CO | $H_2$ | $CH_4$ | $C_nH_{2m}$ | $C_2H_4$ | $CO_2$ |
|---|---|---|---|---|---|
| 51.9 | 38.9 | 7.6 | 0.7 | 0.4 | 0.5 |

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