

**THE DECOMPOSITION OF
HYDROCARBONS AND THE
INFLUENCE OF HYDROGEN IN
CARBURETED WATER GAS
MANUFACTURE. DISSERTATION**

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The Decomposition of Hydrocarbons and the Influence of Hydrogen in Carbureted Water Gas Manufacture. Dissertation by Eugene Hendricks Leslie

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MANUFACTURE. DISSERTATION**

**The Decomposition of Hydrocarbons
and
The Influence of Hydrogen in
Carbureted Water Gas Manufacture**

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE FACULTY OF PURE SCIENCE
COLUMBIA UNIVERSITY IN THE
CITY OF NEW YORK

BY

Eugene Hendricks Leslie, B.S.

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**THE DECOMPOSITION OF HYDROCARBONS AND THE
INFLUENCE OF HYDROGEN IN CARBURETED
WATER GAS MANUFACTURE**

I—HISTORICAL REVIEW

The task of reviewing and assembling the large amount of material which has been written on the reactions of the hydrocarbons under the influence of heat is in no sense an easy one. On account of the variety of the materials which have been worked upon, the extreme complexity of the changes which take place in any case, the differences in the types of apparatus used, and the apparent inclination of many writers to allow the reader to do the greater part of the interpretation of the results, which in many cases is well nigh impossible, the presentation of this material in condensed form is accompanied by readily appreciated difficulties. Such a summary must necessarily confine itself to the work of those who seem to have added most to the knowledge in this field.

In the discussion which follows the topics taken up will be:

I—The work relative to the primary decomposition of high molecular weight paraffin and naphthene hydrocarbons.

II—The various ideas in regard to the mode of reaction of the products of the primary decomposition.

III—The pyrogenic reactions of the simpler compounds such as methane, ethane, ethylene, and similar hydrocarbons.

IV—Aromatic hydrocarbons.

V—The influence of hydrogen on these reactions.

VI—The transfer of heat in gas machines.

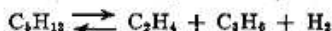
VII—Our own experiments.

I—PRIMARY DECOMPOSITION

It is evident that when a high molecular weight paraffin splits up into two simpler molecules both of these cannot be saturated hydrocarbons. An olefin and a paraffin result.

It might be thought that two olefins and hydrogen

could be formed. If this were the case the decomposition of pentane would be represented:



If this were the manner of the decomposition the gases arising should contain at least 33 per cent of hydrogen whereas we know that low temperature gases contain very little hydrogen.

The other possibility that two paraffins might result with simultaneous separation of carbon is also not the case as can be seen from the analysis of low temperature oil gases shown graphically elsewhere in this paper, and also from the fact that low temperature oil cracking produces only very small amounts of carbon. That such a change is possible at low temperatures, however, in a hydrocarbon system of this sort can be seen from the fact that McAfee¹ in the aluminum chloride catalytic process obtained low boiling saturated hydrocarbons with none of the unsaturated hydrocarbons. The carbon separated out in the form of a granular coky mass. Even when the starting material was unsaturated the final products were saturated hydrocarbons and carbon. That the course of the reaction in the presence of aluminum chloride is different from that of the thermal decomposition at low temperatures is obvious.

That the primary decomposition is actually a breaking down to paraffin and olefin has been well established by the work of investigators which will be cited below, and is borne out by our own experiments which will be discussed later.

The next question which naturally arises is where does the long paraffin chain split, in the middle or near the end? And if the rupture is near the end which is the product of low molecular weight, the olefin or the paraffin? In the discussion of these questions the work of several investigators will be cited.

Vohl² believed that the higher paraffins decomposed primarily into a paraffin of high molecular weight and an olefin with few carbon atoms. His views, however, have not been accepted and are not in accordance with the greater portion of the experimental evidence recorded in the literature.

Thorpe and Young³ heated solid paraffins in sealed tubes, and found that under the combined influence

¹ *J. Ind. Eng. Chem.*, **7** (1915), 737-741; *Met. Chem. Eng.*, **13** (1915), 592-597.

² *Dingler's polytech. J.*, **177**, 69.

³ *Proc. Roy. Soc.*, **31**, 184-201.

of heat and pressure a mixture of olefins and paraffins of lower boiling point was obtained. They believed this mode of decomposition to be general, but were unable to bring forward experimental evidence as to whether the change gave rise to an olefin of low molecular weight with a larger paraffin residue, or *vice versa*.

Prunier¹ found that butylene, propylene, ethylene, and some crotonylene were formed when light petroleum vapors were passed through a glowing tube.

H. E. Armstrong² reported the finding of considerable quantities of amylene and hexylene along with aromatic hydrocarbons in the compression liquids from Pintsch gas manufacture. Paraffins were not present. A gaseous compound was dissolved in these liquids which gave a bromide of the formula $C_6H_8Br_2$, and which, according to Armstrong, was probably methylallene, $CH_2-CH=C=CH_2$.

Brochet³ identified normal butylene, normal amylene, normal hexylene, and piperylene in the compression liquids from Pintsch gas manufacture.

Lewes⁴ found hexylene and heptylene in the tar obtained by the cracking of Russian oil.

Brooks⁵ examined a compression liquid from the Pintsch gas process and found it to contain 48.0 per cent of unsaturated products removable by cold concentrated sulfuric acid. The rest was chiefly benzene. Experiments carried out by him showed that solar oil when treated at temperatures between 430° C. and 600° C. yielded 3 to 20 per cent of gasoline boiling below 150° C. This product was highly unsaturated. Treatment with cold concentrated sulfuric acid caused a 20 per cent loss. When nickel was used along with the oil more gas was produced and the product contained more unsaturated hydrocarbons.

Armstrong and Miller⁶ examined the liquid products which resulted when oil gas was compressed, and found that it contained considerable quantities of amylene and its next two higher homologs, but not the corresponding paraffins. This apparently is evidence in favor of the view that the initial decomposition of the oil is such as to give rise to a high molecular weight olefin and a low molecular with paraffin;

¹ Ber., 6 (1873), 72.

² J. Soc. Chem. Ind., 3 (1884), 462-468.

³ Compt. rend., 114 (1892), 60.

⁴ J. Soc. Chem. Ind., 11 (1892), 584, *et seq.*

⁵ J. Frank. Inst., 180 (1915), 653-673.

⁶ J. Chem. Soc., 49 (1886), 74-93.

for if paraffin and olefin of nearly the same molecular weight had been formed we should expect that a preponderance of paraffins would have been found in the liquid resulting from the compression. It is well known that the paraffins with carbon chains of three atoms or over are more stable with respect to the influence of heat than the corresponding olefins.

Norton and Andrews¹ passed vapors of hexane and pentane through glass or porcelain tubes 15 mm. in diameter and 70 cm. long heated to a bright red heat. In their experiments on hexane a liquid collected in the receiver which was approximately 10 per cent by weight of the hexane used, and which contained unchanged hexane, hexylene, amylene, and a little benzene. The hexylene and amylene were not present in large amount, but this would not be expected when the temperature of their experiments is taken into consideration. They found large amounts of propylene and ethylene which they collected by passing the gases through bromine, and these hydrocarbons no doubt arose from the secondary decomposition of amylene.

J. F. Tocher² destructively distilled octane and decane. He says in the discussion of his results that they "bear out that at low temperatures octane and decane are decomposed into ethylene and higher olefins, methane, and hydrogen, while at higher temperatures no higher olefins are formed, the gaseous products being simply ethylene, methane, and hydrogen." Thus again emphasis is laid on the presence of higher olefins without the corresponding paraffins.

Haber³ studied the decomposition of normal hexane believing that its mode of decomposition was similar to that of the still higher paraffins. He vaporized the hydrocarbons and passed the vapors through a tube $\frac{1}{8}$ in. in diameter and 25 in. long heated to temperatures at intervals between 448° and 800° C. The low temperature was used to avoid the secondary decomposition which plays so important a part at higher temperatures. The hexane was not appreciably decomposed at 518° C. At 600° to 700° C. the gaseous products contained slightly over 50 per cent olefins, 34 to 37 per cent saturated hydrocarbons (of which approximately 70 per cent was methane) and 10 to

¹ *Am. Chem. J.*, **8** (1886), 1-9.

² *J. Soc. Chem. Ind.*, **12**, 231-237.

³ *J. Gasbel*, **29** (1896), 377-382, 395-399, 435-439, 452-455, 799-805, 813-818, 830-834; *Ber.*, **29** (1896), 2691-2700.