Hydrogenation and Polymerisation Reactions of Acetylene.* II.** Polymerisation Reaction by Use of the Thermal Diffusion Column.

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I. Introduction. The first attempt to obtain liquid hydrocarbons from acetylene by polymerisation reaction, utilizing its high reactivity, was tried by Berthelot(1) about eighty years ago. Since then, many researches were carried out and patents also were claimed. In Japan this reaction was also studied by many investigators(2), especially in the Tokyo Imperial Industrial Research Institute, and the operation in an industrial scale is reported to be accomplished (2g).

One of the present authors (O.K.) has investigated the hydrogenation and polymerisation reaction of acetylene, applying high tension discharge, and has obtained satisfactory results(3). On the other hand, the other author (K.H.) has investigated the polymerisation reaction of methane(4) and the desulfurisation reaction(5) by use of the thermal separation apparatus of Clusius and Dickel(6), expecting from theoretical standpoint that these reactions may take place in favourable manner. The obtained results have been shown to be satisfactory.

From the above experimental results and from theoretical considerations, expecting the possibility to obtain a good yield, the authors have carried out the polymerisation reaction of acetylene in the thermal separation column. The result is good just as expected. The followings are the theoretical and experimental details.

II. Results of Prevalent Methods. As the historical development concerning this reaction is precisely summarised by Egloff(7) and others(8), here will be described some important points.

(*) Translated by the authors from *J. Soc. Chem. Ind. Japan*, in press.

(**) First report, this Bulletin, **18** (1943), 1.

(1) Berthelot, *Ann. Chim. Phys.*, (4), **9** (1866), 402.

(2) (a) G. Kita, T. Mazume, S. Wada, and R. Abe, *J. Soc. Chem. Ind. Japan*, **29** (1926), 738, 843; (b) S. Iki and R. Ogura, *ibid.*, **30** (1927), 461; (c) S. Hujio, *ibid.*, **31** (1928), 77; (d) K. Hukagawa, *J. Chem. Soc. Japan*, **50** (1929), 689; (e) Y. Kato and H. Aikawa, *J. Electrochem. Assoc. Japan*, **3** (1935), 261; (f) I. Orito, *ibid.*, **7** (1939), 51; (g) T. Hujisaki, *J. Fuel Soc. Japan*, **20** (1941), 782.

(3) O. Kimura, *J. Soc. Chem. Ind. Japan*, **44** (1941), 750. This Bulletin, **18** (1943), 1.

(4) K. Hirota, *J. Chem. Soc. Japan*, **62** (1941), 392; *Bull. Chem. Soc. Japan*, **16** (1941), 274.

(5) K. Hirota, *J. Soc. Chem. Ind. Japan*, **44** (1941), 1045, 459B.

(6) K. Clusius and G. Dickel, *Naturwiss.*, **26** (1938), 546.

(7) Egloff, "Reaction of pure Hydrocarbons," 1937.

(8) Orito, *loc. cit.*; Hujisaki, *loc. cit.*

As was described in the first report, the main reactions and the relating free energies of the system, acetylene and hydrogen, are as follows:

	(kcal./mol.)	298°K.	500°K.	1000°K.
(1) Hydrogenation reaction:				
$C_2H_2+H_2 \rightarrow C_2H_4$	ΔF_0	$-$ 35.0	$-$ 29.6	$-$ 13.8
$C_2H_2+2H_2 \rightarrow C_2H_6$		$-$ 59.1	46.1	+ 15.5
(2) Polymerisation reaction:				
$3C_2H_2 \rightarrow C_6H_6$	ΔF_0	$-$121.9	$-$105.6	$-$ 64.3
(3) Decomposition reaction:				
$C_2H_2 \rightarrow 2C+H_2$	ΔF_0	$-$ 50.8	$-$ 48.1	$-$ 41.3

As seen in the above table, these reactions take place with large diminution of free energy in the temperature range from 25°C. to 700°C. Besides these reactions, there also occur such reactions as the formation of methane and ethane etc., but these reactions are considered to be secondary ones. In the system of acetyelne only, which is dealt with in this paper, the primary reactions are the polymerisation and the decomposition of acetylene. By the secondary reaction, however, the hydrogenation of acetylene and the formation of methane may also occur, as there exist hydrogen and free carbon through the decomposition of acetylene. In order to get liquid product by the polymerisation of acetylene in good yield, therefore, it is necessary to avoid not only the decomposition of acetylene, but also that of polymerised oil.

Such being the matters, the principle of the prevalent methods to obtain liquid product from acetylene consists in flowing the original gas through a pipe heated to a certain temperature. In greater parts of the experiments, the temperature of reaction lies between 450°C. and 1000°C.; 600°C. being considered to be the most suitable temperature to obtain light oil. At lower temperatures, the decomposition of acetylene and therefore the deposition of free carbon hardly occurs, and the product is rich in light oil, though the rate of reaction is slow; at higher temperatures vice versa. From these reasons, the intermediate temperature such as 600°C. is profitable. The effect of flow velocity is also remarkable, and the yield of oil increases as the velocity becomes slow, but the diminution of the space time yields and the increase of deposition of free carbon occurs at the same time. To avoid the formation of the free carbon, such improvements as to dilute acetylene with hydrogen, nitrogen, methane etc., were also tried by several investigators, but the effect was not so remarkable, except the experiment which was carried out by E. Berl and K. Hoffmann(9) obtaining a yield of 98.8% by dilution with steam.

Among these factors, the most important ones are the material of the reaction vessel and the substanced inserted in it. For instance, most metals accelerate the decomposition of acetylene into hydrogen and free carbon as well as the production of methane and ethylene catalytically, while glass and porcelain hardly accelerate the decomposition. The

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(9) E. Berl and K. W. Hoffmann, *Z. angew. Chem.*, **44** (1931), 259.

existence of carbon is reported to be rather favourable to some extent, which suggests that a slight decomposition reaction is not so harmful, but the decomposition not only diminishes the yield, but also inclines to give rise to explosion. As the polymerisation and decomposition reactions of acetylene are very exothermic, heat energy is liable to be accumulated locally in the reaction vessel, and consequently the decomposition of the reaction products occurs. In order to avoid the local accumulation of the reaction heat, insertion of a certain metal, which is a good conductor of heat but has no catalytic activity, in the reaction vessel is reported to give good result, while cooling of the inside of the reaction vessel is also reported to be effective. These results may be considered to be caused by the prevention of local accumulation of the reaction heat. There is also an experiment(10) that acetylene is passed through several reaction vessels consecutively, the temperatures of which are gradually lowered one by one. Superposition of such physical factors as electrical discharge has been also studied by several authors. The first report of this work can be counted as one of these investigations. As stated above, this reaction is accompanied with many difficulties, although the principle is rather simple; a further investigation is yet necessary.

III. The Principle of the Present Method. One of the present authors (K.H.) studied the chemical reactions in a thermal separation column of heated filament type(6), and obtained good effect in each case. This fact suggests us that the polymerisation of acetylene may also proceed with good yield by use of the apparatus. Theoretically this effect can be explained as follows: In the thermal separation column which is shown schematically in Fig. 1, F, F′ is the metallic filament, W is the wall of the reaction vessel, W′ is that of cooling jacket, A is the inlet of the original gas, and B is the outlet of the resulting gas. When a mixture of two gases is enclosed in the apparatus, the enrichment of the heavier component may occur in the colder region by the combined action of the thermal diffusion and the counter flow in the apparatus. Now, suppose that the acetylene is introduced in such an apparatus, the filament of which is heated sufficiently to cause polymerisation, then the reaction will be carried on under such favourable circumstances as follows: (1) the movement of the polymerised products from reaction zone to cold region, (2) the prevention of the decomposition of the produced substances, and (3) the removal of the reaction heat. Owing to these circumstances, a good yield of liquid product might be expected in this apparatus, but one more important condition is necessary, i.e., the selection of the heating wire, which serves as the hot wall. For instance, tungsten wire gave a good result, as seen in the following data, while nichrome wire gave bad

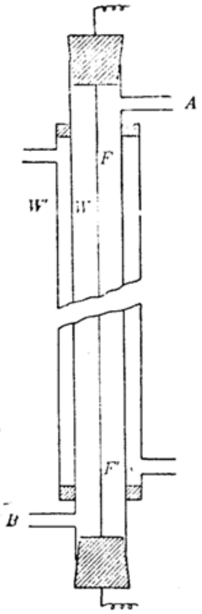

Fig. 1. Reaction Apparatus.

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(10) R. Meyer and A. Tanzen, *Ber.*, **46**(1913), 3183.

result on the contrary, owing to its catalytic power of decomposing acetylene.

It is worth while to mention that Kovaché and Trichot⁽¹¹⁾ adopted an apparatus in which the above effect might occur, although it was not noticed by the authors. The reaction vessel is a perpendicular porcelain tube and heated from outside. At the center of the vessel is situated a copper tube cooled by water which prevents the accumulation of the reaction heat. By this apparatus, it is reported that a considerably good result was obtained, but the production of free carbon could not completely be avoided. It is noticed by the authors that the reason why above mentioned apparatus is adopted by them is to avoid the accumulation of reaction heat, but we suppose that the good yield is rather resulted from the co-operation of the effect of thermal diffusion and the counter flow. It was also described by them that the mixture of benzene vapour and nitrogen was flowed through the reaction vessel just in the same condition as the polymerisation reaction of acetylene, but the decomposition of benzene was not observed within experimental error. This remarkable fact may only be explained by the above thermal diffusion effect.

IV. Apparatus and Experimental Procedures. The experiment was carried out nearly in the same way as described in the first report except the substitution of the thermal separation column for the reaction vessel (Fig. 1). The reaction column was made of Terex glass, 100 cm. in length and 1.5 cm. in diameter. As the filament FF′, a tungsten wire was used, the length of which was 85 cm. and the diameter 0.2 mm. Acetylene, prepared from calcium carbide and water and purified in the usual way, was flowed into the reaction vessel through the upper inlet A at a constant rate and the resulting gas was flowed out from the outlet B continuously. The purity of acetylene was 99%. The heavier part of the polymerised oil was condensed in the lower part of the vessel, while the volatile part, included in the resulted gas, was caught by a trap immersed in solid carbon dioxide-alcohol mixture. The amount of these oils was measured after every run, and the refractive index and the density were measured in every part of the fractionated oil. The analysis of the resulting gas was carried out according the Schuftan's Method⁽¹²⁾. The temperature of the filament was measured by means of an optical pyrometer. The accuracy of the measurement is relatively good at high temperatures, but at low temperatures, e.g., at 700°C., the error is considered to be about ±50°C. Then the lower temperature was also estimated on the assumption that the consumption of electrical energy was proportional to the temperature, the highest temperature being taken to be a standard. Naturally this estimation was not correct, because the higher the temperature, the greater is the consumption of heat energy by convection and radiation. Consequently the value thus obtained must be lower than the true one, and this tendency was ascertained actually in the comparison with the value obtained by the optical pyrometer.

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(11) Kovache and Trichot, *Chimie et Industrie*, **13**(1925), 361, 537.

(12) "Gasanalyse in der Technik," Leipzig, (1931). O. Kamiike, *et al.*, *J. Soc. Chem. Ind. Japan*, **44**(1941), 1030.

V. Experimental Results and Discussions. Experimental results are summarised in Tables 1, 2 and 3. Table 2 is the data of the gas analysis and Table 3 is the physical properties of the fractionated oil.

Table 1. Experimental Results.

No. of Exper.	Temp. of Filament. (°C.)	Watt (Temp.)	Flow velocity. (l./hr.)	Gas flowed. l. (N.T.P.)	Gas flowed out. l. (N.T.P.)	Gas consumed. l. (N.T.P.)	Contraction. (%)	Oil produced. (c.c.)	Yield of oil per 1 *l.* original gas. c.c./l.	Yield of oil per 1 *l.* consumed gas. cc./l.
1	700	139 (440)	1	4.7	4.17	0.5	11	0	0	0
2	”	136 (430)	2	4.7	4.50	0.2	4	0	0	0
3	800	233 (730)	1	7.5	3.44	4.1	54	5.3	0.71	1.2_9
4	”	242 (760)	2	8.5	4.26	4.2	50	5.5	0.65	1.3_1
5	”	220 (690)	3	11.5	6.00	5.5	48	6.8	0.60	1.2_3
6	”	210 (660)	4	11.6	8.92	2.7	23	3.0	0.27	1.1_1
7	”	210 (660)	6	10.3	8.17	2.1	20	2.0	0.19	0.9_5
8	”	196 (610)	8	9.8	7.94	1.9	19	1.6	0.16	0.8_5
9	1000	320 (1000)	1	6.6	1.08	5.5	84	7.2	1.09	1.3_1
10	”	320 (1000)	2	10.3	3.50	6.9	67	8.1	0.79	1.1_7
11	”	320 (1000)	3	10.4	3.40	7.1	68	8.6	0.83	1.2_1
12	”	312 (980)	4	11.6	4.17	7.4	64	9.1	0.79	1.2_3
13	”	312 (980)	6	9.8	4.23	5.6	57	6.8	0.69	1.2_1

Table 2. Gas Analysis.

No. of Exper.	CO_2	C_2H_2	C_2H_4	C_nH_m	O_2	CO	H_2	CH_4	N_2
1	3.2	88.4	0.0	0.0	0.0	1.6	0.0	0.0	6.8
2	4.4	87.6	0.0	0.2	0.0	1.8	0.0	0.0	0.0
3	1.4	81.8	0.2	1.0	0.0	2.8	0.4	0.0	10.2
4	3.1	85.1	0.4	0.6	0.0	2.8	2.2	0.0	17.6
5	3.0	81.0	0.2	0.4	0.0	2.8	2.2	0.0	10.4
6	1.8	93.4	0.0	0.0	0.3	0.4	0.0	0.0	4.1
7	3.0	84.6	0.2	0.0	0.6	1.0	0.0	0.0	9.6
8	3.5	90.5	0.4	0.0	0.0	1.4	0.0	0.0	4.2
9	1.3	63.1	0.6	0.4	0.0	2.2	4.0	23.7	4.2
10	4.4	79.6	0.4	0.6	0.4	2.6	4.8	0.0	7.6
11	5.2	83.6	0.6	0.2	0.2	1.8	4.2	0.0	7.0
12	3.5	79.8	0.4	0.2	0.0	3.0	6.2	0.0	7.0
13	5.4	77.0	0.6	2.8	0.0	2.2	6.0	0.0	6.0

Table 3. Physical Properties.

Temp. (°C.)	Temp. of Fractions (°C.)	Proportion (%)	Refractive index at 17°C., D line	Density at 25°C.
800	Volatile part	28.6	1.5017*	0.8443*
	<100	10.0	1.5125	0.8811
	100–120	8.5	1.5139	0.8881
	120–140	7.6	1.5257	0.8938
	140–160	7.6	1.5497	0.9193
	160–190	12.6	1.5670	0.9532
	>190	25.0	—	—
1000	Volatile part	15.4	1.5017*	0.8443*
	<100	16.3	1.5178	0.8831
	100–120	22.8	1.5232	0.8925
	120–150	10.6	1.5439	0.9198
	150–200	16.2	1.5745	0.9666
	>200	18.7	—	—

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* The density and the refrective index of the volatile part are that of the mixture of the products of reaction temperature 800°C. and 1000°C.

To show the effect of temperature and flow velocity, the volume contraction in percentage and yields of oils are plotted against the flow velocity for each temperature in Fig. 2 and 3. From these data, the following tendencies concerning the yields of the oils and the compositions of the resulting gases can be seen:

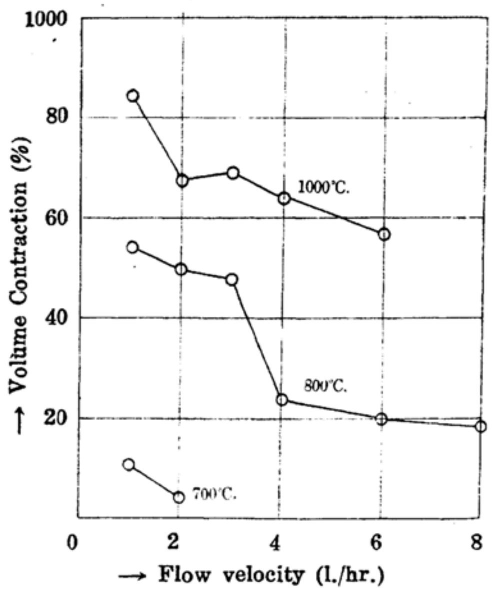

Fig. 2. Gas Contractions.

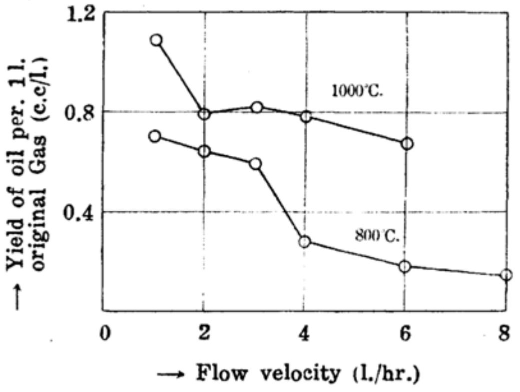

Fig. 3. Yield of oil.

(1) The effect of the reaction temperature is very essential, while that of the flow velocity of the gas is not so much.

(2) The oil produced per unit volume of acetylene flowed into the vessel is larger in quantity at higher temperatures than at lower temperatures, while that per unit volume of the comsumed acetylene is nearly the same in each run and close to the theoretical yield.

(3) The sub-reaction hardly occurs, as ascertained by the result of gas analysis that the quantities of such gases as H_2, C_2H_4, and C_nH_m are small, except at 1000°C. and at much small flow velocity.

(4) The volatile component is larger in quantity as the heating temperature becomes lower.

The tendencies (2) and (3) are remarkable, because they indicate that the polymerisation is the main reaction. These are the essential differences from the prevalent investigations, in which the sub-reactions and consequently the production of hydrogen, methane, and ethylene are inevitable as seen in Table 4. The data in Table 4 are taken from the experiment of E. N. Hague and R. V. Wheeler(13) as a typical example of this reaction.

Table 4. Experimental Results of Hague and Wheeler.

Temp.	Yields in percent by weight of acetylene treated			Gas analysis, percent by volume				
(°C.)	Total liq.	C_6H_6 fraction	Carbon	C_nH_m	C_2H_2	C_2H_4	H_2	CH_4
600	30.8	—	—	0.8	53.2	4.2	27.9	8.3
650	61.1	26.4	9.7	1.2	29.5	6.9	34.0	23.0
700	61.1	24.8	16.7	1.2	2.4	10.4	43.8	37.1
750	46.7	18.3	22.1	0.2	0.7	8.8	50.1	37.5

The above conclusion that the polymerisation is the main reaction will be also shown from the fact that the carbon deposition is hardly seen in the reaction vessel and moreover from the following material balance. As the gas contraction can be assumed to be caused merely by the polymerisation of acetylene, as shown in (2), the theoretical yield of oil from acetylene is 1.29 c.c./l., or 1.22 c.c./l., if we assume the density of oil to be 0.95 or 0.90, respectively. The greater part of the yields obtained agrees with the theoretical one within experimental errors, as seen in Table 1. The volatile part of the oil can be estimated to be benzene from the density and the refractive index as well as from the boiling point. About 70% of the condensed oil distils out below 200°C. In addition, some substance which boils at room temperature was also caught in the volatile part, but it could not be analysed as the amount was too small. Judging from its odour as well as from the fact that the resulted gas scarcely contains olefins, the authors suppose that it might be diacetylene (C_4H_4). If this is the case, it supports the mechanism proposed by Pease and Taylor(14).

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(13) E. N. Hague and R. V. Wheeler, *J. Chem. Soc.*, **1929**, 391.

(14) Pease and Taylor, *J. Am. Chem. Soc.*, **51** (1929), 3470; *J. Phys. Chem.*, **39** (1935), 811.

It will be mentioned that the reaction temperature of this research seems to be higher than that of the prevalent ones by about 100°C., but it cannot be concluded that there exists some disagreement, because the recorded temperatures in our experiments are that of the heating filament and not of the reaction zone.

At such a high temperature as 1000°C., after long time of the reaction, a slight deposition of carbon was observed on the tungsten wire, the appearance of which was very characteristic. The microscopic photograph of it is shown in Fig. 4. As seen in the figure, the deposited carbon grows horn-like with metallic luster, and bends upward presumably by the effect of convection flow.

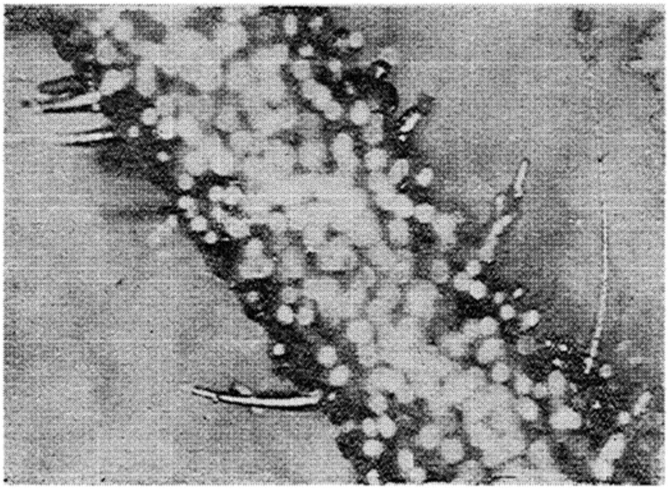

Fig. 4. Microscopic Photograph.

The reaction was also studied with nichrome wire instead of tungsten. In this case, the deposition of free carbon occurred as soon as the filament was heated, and the production of oil was scarcely found.

VI. Conclusion. It was shown that, by use of the thermal separation column of heated wire type as the reaction vessel, acetylene polymerises to liquid hydrocarbons almost perfectly under the most favourable conditions. The authors believe that the reason why the above good yield is obtained will be due to the combined effect of thermal diffusion and the counter flow.

Summary.

(1) The possibility of polymerisation reaction of acetylene with a good yield by use of the thermal diffusion column as reaction vessel has been discussed theoretically.

(2) The polymerisation of acetylene has been carried out with tungsten wire as heating filament at 700°C.–1000°C.

(3) The experimental results have shown that acetylene is converted into liquid hydrocarbons almost perfectly, and that the amount of hydrogen, methane, and ethylene are small in the resulting gas, and moreover the deposition of carbon is scarcely observed.

In conclusion, the authors express their sincere thanks to Dr. M. Sato, the Director of the Laboratory and Dr. R. Yoshimura, the Chief of the Department of Inorganic Chemistry, for their encouragement throughout this research and to the former also for the permission of the publication of this paper.

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