Researches on the Chemical Reaction by Use of the Thermal Diffusion Apparatus of Clusius and Dickel. I. Thermal Polymerisation of Methane.*

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(Received June 12, 1941.)

Introduction. Separation of gases by thermal diffusion method is much improved by the application of an apparatus(1), sometimes called thermal diffusion column, by means of which many researches are going on in order to separate isotopes such as those of chlorine, xenon, mercury and carbon(2), while the author has used the apparatus as a rectifying column and discussed its efficiency(3). The author also tried to use the apparatus as a reaction vessel, intending to perform a chemical reaction smoothly and completely as well as to separate the reactants at the same time by the action of thermosyphone found by Clusius and Dickel.

Object of the Research. On the first trial, the thermal polymerisation (or cracking-polymerisation) of methane,

$$CH_4 \rightarrow H_2 + \text{Higher Hydrocarbons},$$

which was found in nineteenth century and was extensively studied by F. Fischer(4) in 1928, was carried out, because the effect would be remarkable in this reaction for the following reason, and on the other hand this reaction is important from the industrial point of view.

The elementary process of the above reaction is considered, at present,(4)(5) though not yet definitely determined in detail, to consist in two stages: the first stage in which methane is cracked in hydrogen and some free radicals* and the second stage in which these free radicals polymerise into higher hydrocarbons, such as benzene and naphtalene. At high temperatures at which the reaction takes place with a measurable speed, both free radicals and hydrocarbons produced are very unstable and decompose easily into hydrogen and elementary carbon.

$$\begin{tikzcd} & CH_4 \rightarrow H_2 + \text{Free Radicals} \arrow[dl] \arrow[dr] & \\ \text{Elementary Carbon} + H_2 & & \text{Higher Hydrocarbons} + H_2 \arrow[ll] \end{tikzcd}$$

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* Main part of this paper was read at the annual meeting of the Chemical Society of Japan (April 5, 1941).

(1) K. Clusius and G. Dickel, *Naturwissenschaften*, **26** (1938), 546.

(2) For instance, a) Cl, K. Clusius and G. Dickel, *ibid.*, **27** (1939), 148, 487; b) Xe, W. Groth, *ibid.*, 260; c) Hg, W. Groth and P. Harteck, *ibid.*, 584; d) C, H. S. Taylor, *Nature*, **144** (1939), 8.

(3) K. Hirota, *J. Soc. Chem. Ind. Japan*, **44** (1941), 391.

(4) F. Fischer, *Brennstoff Chem.*, **9** (1928), 308.

(5) H. M. Stanley and W. Nash, *J. Chem. Soc. Ind.*, **48** (1928), 1.

* The kind of free radicals is considered as CH_3, CH_2 or CH, according to the different theory, but is not the main point of the argument.

So the important condition in getting a yield of hydrocarbons is to prevent the decomposition of free radicals in the hot region and to make those polymerise in the cold region. To meet this, Fischer passed methane very rapidly through a porcelain or quartz tube laid horizontally and heated at 900°C. or above, but his maximum yield of condensed hydrocarbons is 0.126 g. per liter of methane(4)(6), i.e., the conversion of 18% of the original methane. Kobayashi and others(7) modified the method so as to pass the cracked methane through a slightly colder tube in order to acceralate the polymerisation of the free radicals. Dilution of the methane with nitrogen, hydrogen, chlorine, water steam or other gases(8) cannot alter the yield considerably better and rather unfavourably in some cases. Hessel and others(9) used a vertical tube and mixed some gaseous hydrocarbons or chlorine gas into the original methane. All these results obtained with a quartz and a porcelain tube, however, are of the same degree as some of these are shown in Table 1, while it was found that metallic tubes are not suitable on account of its catalytic power of accerelating the decomposition into carbon and hydrogen.

Table 1. Maximum Yield of Condensed Hydrocarbons in the Reaction, $CH_4 \rightarrow H_2$ + Higher Hydrocarbons.*)

Investigators	Vol. % of CH_4 in original gas	Conditions		Condensed Hydrocarbons		
		Temp. (°C.)	Contact Time(sec.)	Light Oil (g./l.)	Tar (g./l.)	Total (g./l.)
Fischer(4)	93	1050	—	0.009	0.0045	0.014
Stanley, Nasch(5)	93	1150	0.6	0.028	0.035	0.063
Fischer, Pichler(6)	—	1300	0.016	0.050 (0.110)	0.076 (0.082)	0.126 (0.192)
Oda(10)	82	1200	0.23	0.026 c.c./l.	0.023	—
Kobayashi, etc.(7)	76	1100	0.45	0.091	0.022	0.113
Hessel, etc.(9)	—	1190	0.29	0.031 (0.117)	0.029 (0.115)	0.050 (0.232)

Now if the reaction is carried on in the thermal diffusion column, we can consider that it will proceed as follows:—

Methane gas, introduced in from the bottom of the column, is cracked into hydrogen gas and free radicals at the electrically heated wire, placed in the central axis of the column. By the action of thermosyphone, the hydrogen molecules, the molecular weight of which is small, rise up along the heated wire and flow out from the top of the column, while the free

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(6) F. Fischer and H. Pickler, *Brennstoff Chem.*, **13** (1932), 381.

(7) K. Kobayashi, K. Yamamoto, H. Ishikawa and S. Hinonishi, *J. Soc. Chem. Ind. Japan*, **37** (1937), 785.

(8) G. Egloff, "The Reaction of Pure Hydrocarbons", 64 (1937).

(9) W. Hessels, D. W. von Krevelen and H. I. Waterman, *J. Soc. Chem. Ind.*, **58** (1939), 321.

* Values in parenthses are obtained by repeated treatment of the gas for four times.

radicals go down along the cold wall, polymerising into higher hydrocarbons. Then we can expect in this process (i) that the decomposition of free radicals and higher hydrocarbons diminishes and (ii) that the reaction takes place completely, because the unreacted methane remains in the column, repeatedly colliding with the wire.

Experiment. The experiments were carried out at one atmospheric pressure. The column was a boron-glass (terex glass) tube of 1.01 meter in length and of 2.0 cm. in diameter with a tungsten wire of 0.75 mm. in diameter and 70 cm. in length and with a cooling glass tube of running water. Methane gas was prepared from sodium acetate and soda lime in an ordinary way. A gas interferometer was used constantly throughout the experiments for the check of gas analysis. Other details of the experimental procedures have been described in anothr journal(11), so only the summarised results are shown in Table 2 and 3.

Table 2. Summarised Experimental Results I.

No. of Exp.	Original Gas		Experimental Conditions				
	Vol. % of CH_4	Vol. % of H.H.C.*	Gas Vol. Used (l.)	Flow Velocity (l./hr.)	Maximum† Temp of the Wire °C.	Temp. of the Cold Wall °C.	Drying Substance
A	90	0.0	2.3	1.3	1200	34	Soda lime
B	89	0.2	7.6	6.8	1300	42	
C**	89	1.2	4.5	6.3	1200	28	
D	93	1.2	1.8	1.3	1300	30	One normal sodium hydro-oxide
E	93	1.2	3.0	1.2	1200	31	
F	93	1.2	1.9	0 4	1300	44	
G	93	1.2	2.2	0.8	1200	30	
H***	93	1.2	5	3.0	1300	35	

† Maximum Temp. of the Wire was obtained pyroptically. This value was probably too low on account of the disturbance caused by a brown product deposited on the cold glass wall.

* H. H. C. means heavy hydrocarbons.

** Part of the reacted gas was let to flow out from the bottom of the column too with the flow velocity of 0.2 liter per hour, and had the composition as follows: CH_4 91%, H_2 2%, etc.

*** Tungsten wire coated with sodium silicate was used.

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(10) R. Oda, *J. Soc. Chem. Ind. Japan,* **37** (1934), B 630.

(11) K. Hirota, *J. Chem. Soc. Japan,* (Printed in Japanese) **62,** (1941), 392.

In the course of these experiments upper part of the wire was observed to be less bright than the lower part, probably owing to the higher concentration of hydrogen as would be expected.

Table 3. Summarised Experimental Results II.

No. of Exp.	Produced Gas				Produced Hydrocarbons			
	Flow Velocity l./hr.	Expansion Ratio	Vol. % of H_2	Vol. % of CH_4	Liqiud (g./l.)	Solid (g./l.)	Total (g./l.)	Ratio
A	0.6	0.5	77	11	0.12	0.04	0.16	3
B	3.7	0.5	79	11	0.03	0.02	0.05	1.5
C	4	0.6	33	59	0.09	>0.005	0.09	<20
D	1.6	1.2	87	6	0.22	0.08	0.30	3
E	1.6	1.3	82	12	0.14	0.01	0.15	14
F	0.4	1.0	80	14	0.10	0.05	0.15	2
G	0.3	0.4	85*	—	0.17	0.07	0.24	3
H	2.0	0.6	60*	—	0.00	0.08	0.08	∞

* These values were estimated from the refractive index of the gas produced.

Discussion. I. The maximum yield of condensed hydrocarbons was 0.30 g. per liter of the original methane used, i.e., the conversion of 42%, and the concentration of hydrogen in the reacted gas amounted to 87% in the same experiment. This results are much superior to those of the researches of other investigators, and, moreover, to those obtained after the treatment of four times(6)(8).

II. Experiment H seems to show that a surface covered with nonmetallic substance favours the undesirable decomposition to carbon and hydrogen, in spite of the reversed result of other investigators, but this might be due to the fact that contact plane of the wire to gas could not be heated fully.

III.(*) From the above experiments the following relations could be deduced easily:—

(i) Comparing A and B to D, E, F and G, small degree of drying seems to act to prevent the decomposition into carbon and hydrogen as indicated in the expansion ratio.

(ii) Comparing D to E, higher temperature seems to act to decrease the ratio of the liquid to the solid product and to increase the total yield.

(iii) The effect of flow velocity exists, if D to F is compared.

But as the number of the experiments is small, it must be examined carefully by later researches if these relations really hold.

IV. The liquid and solid products had the odour of toluene and naphtalene respectively. Both were insoluble in water and liquid paraffine and were hardly soluble in ethyl alcohol but soluble in benzene. These materials could be considered to be higher aromatic hydrocarbons. This conforms with the previous researches in connecton with this point.

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* Content of this paragraph is slightly different from that in ref. (11) on account of the addition of new data.

As it has been shown very effective to use a thermal diffusion apparatus of Clusius and Dickel as a reaction vessel, the author is going not only to study the reaction expensively, but also to apply the method to other reactions.

Summary.

(1) A method of thermal polymerisation of methane proceeding in a thermal diffusion column of Clusius and Dickel has been described and discussed.

(2) By this method a good yield of condensed hydrocarbons and highly concentrated hydrogen gas have been obtained.

(3) Effects of the experimental conditions have been obtained.

In conclusion the author wishes to express his sincere thanks to Dr. R. Yoshimura, Director of the Department, for his interest and encouragement in carrying out this research.

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