Hydrocarbons from Carbide (A) IV. Non-Catalytic Polymerization under Ordinary Pressure. Acetylene-Carbide System and General Remarks.

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(Received February 10, 1942.)

This paper will conclude our investigations on the non-catalytic direct synthesis of hydrocarbon liquid products from calcium carbide under ordinary pressure. The paper consists of two parts: the first part deals with the studies on acetylene-carbide system and the second gives a supplementary discussion and, at the same time, a resumé of the results of the entire series of investigations, consisting of the following systems:

Hydrogen—carbide,
Carbon dioxide—carbide,
Carbon monoxide (and water gas)—carbide,
Hydrogen chloride—carbide, and
Acetylene—carbide.

With the accumulation of the results with various gases, we feel more confident that we are now in a better position to picture the true affairs of the polymerization of nascent acetylene molecules, even in a system where the carrier gas itself may undergo polymerization. In fact, we have hoped that the total liquid yield may be increased by the polymerization of the very gas introduced, and for this reason, we have attempted to study the effects of acetylene and its mixtures with hydrogen or carbon dioxide. We have further hoped that by the introduction of acetylene, the formation of free acetylene from the carbide may be prevented, or suppressed, and thereby the nascent acetylene may be made more available for liquid synthesis.

In this paper we have made most of the runs at 340°C., which seems to be the most satisfactory temperature, and one run at 420°C. to make more clear the real effect of the carrier gas on the total yield of liquid products. Preparation of acetylene and experimental method have been already given in Paper (A) II⁽¹⁾.

Results and Discussion. Results are given in Table 11.* The first question that may be raised is whether the introduction of acetylene suppresses the formation of free acetylene from the carbide or not. Our data given in Table 12, seem to indicate it positively. In the table the results of only those experiments have been considered** in which except for

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(1) R. Negishi and O. Kamiike, this Bulletin, **17** (1942), 118; also R. Negishi and O. Kamiike. *J. Soc. Chem. Ind.*, Japan. **45** (1942), 135.

* Numbering of the Tables and Figures is consecutive from (A) II to the final paper.

** Percentage of free C_2H_2 varied from 20.3 to 36.1 for all the other runs at 340°C. involving mixtures of gases.

Table 11. Acetylene Systems.

Experimental No.	I_L 70	I_L 75	I_L 68	I_L 71	II_L 22
Reaction Temp. (°C.)	340	340	340	340	420
Gas	C_2H_2	$C_2H_2+H_2$	$C_2H_2+CO_2$	$C_2H_2+CO_2$	C_2H_2
Saturation Temp. (°C.)	79.7	79.8	78.8	79.8	65.5
Ratio Gas to Water	$C_2H_2:H_2O$	$C_2H_2:H_2:H_2O$	$C_2H_2:CO_2:H_2O$	$C_2H_2:CO_2:H_2O$	$C_2H_2:H_2O$
(Partial Press.)	1:0.86	1 : 1 : 2.67	1 : 3 : 4	1 : 3 : 4	2.7 : 1
Time of Contact (sec.)	25.9	28.9	18.3	22.9	23.7
Liquid Products (g.)	22.4	17.5	22.9	18.8	8.3
Water (g.)	1.5	0.7	7.2	3.8	1.0
Oil % on Reacted Carbide Carbon	40.6	34.5	36.9	30.0	130
Oil (total Wt.) % on Reacted Carbide C_2H_2	47.2	38.0	40.7	33.6	137
Carbon Balance	102.3	96.0	95.8	104.5	99.0
Weight Balance	102.2	98.8	100.4	99.5	99.3

Table 12.

Exp. No.	I_L 34	I_L 35	I_L 44	I_L 57	I_L 65	I_L 70	I_L 68	I_L 71	I_L 75
Gas	H_2	N_2	CO	CO_2	CO_2+HCl	C_2H_2	$C_2H_2+CO_2$	$C_2H_2+CO_2$	$C_2H_2+H_2$
Free C_2H_2 (%)	+36.1	+26.7	+34.3	+27.8	+28.3	−8.4	+16.6	−42.2	−15.7

acetylene and HCl systems pure gases are used. The plus sign means that free acetylene has been formed while the minus means that the introduced acetylene has reacted; in other word, it is equivalent of saying that there is no formation of free acetylene. Minus 42.2% is definitely too high, and plus 16.6 is difficult to explain.*

Another question that may arise is whether or not the total liquid yield, based on the reacted carbide acetylene (and carbon), increases in these systems. The answer is again positive but with certain reservations. The results of Table 11 indicate that the effect of acetylene on the total yield is striking only when its concentration is relatively high, as for example, I_L–70 and II_L–22. When acetylene is diluted with an inert gas, such as H_2 or CO_2, and its concentration becomes relatively low, its effect on the total liquid yield disappears, as shown by I_L–75, I_L–68, and I_L–71. However, the presence of acetylene, even in a small concentration, has a striking effect on the suppression of the formation of free aceytlene, as has been mentioned in the preceding paragraph. These effects, coupled with the fact that some of the introduced acetylene is actually used up, suggest that the role of the introduced acetylene is to form principally gaseous products, which in the absence of the acetylene are formed at the expense

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* It may be added here that the results of I_L–68 are less reliable.

of the carbide, or that of the nascent acetylene molecules. It is interesting that the liquid yield at 420°C. is much larger than at 340°C., quite contrary to the results of the other systems, although the effect of the acetylene concentration cannot be entirely dismissed. Nevertheless, this point is in accord with the fact that the liquid formation by non-catalytic acetylene polymerization becomes appreciable only above 400°C. and optimum in the range, 500 to 700°C.(2)

The effect on the liquid yield of a diluent gas is small, and the final yield is mainly determined by the concentration of the water vapor. It may be added, however, that there exists an optimum concentration of the water vapor. A ratio not differing too far from 0.8 to 1.0 seems most favorable under our experimental conditions.

The results of elementary analysis are given in Table 13. The results of gas analysis are given in Table 14, and here, again, they should be considered, as in a previous paper(3), qualitatively rather than quantitatively. In spite of the fact that some of the hydrogen used in effecting desorption is mixed in the effluent reacted gas, the hydrogen contents in runs I_L–70 and I_L–71, which are at 340°C., are lower than that of II_L–22, which is at 420°C. and in which no desorption has been effected. A similar situation exists for the methane contents of these runs, and these facts are consonant with the effect ascribable to the difference in the reaction temperatures.

Table 13. Elementary Analysis.

Exp. No.		I_L 68		I_L 70		I_L 71		I_L 75		II_L 22	
		Trap.	Cond.	Trap.	Cond.	Trap.	Cond.	Trap.	Cond.	Trap.	Cond.
Element	C....	74.98	84.69	67.98	86.27	79.76	82.66	79.69	86.72	74.10	81.96
”	H....	9.37	8.62	10.21	8.73	9.97	8.61	9.01	9.26	10.30	8.19
”	O....	15.65	6.69	21.81	5.00	10.27	8.73	11.20	4.01	15.60	9.85

Table 14. Gas Analysis (Average values).

Exp. No.	I_L 68	I_L 70		I_L 71			I_L 75		II_L 22	
Gas		Reacted	Desorp.	Reacted	Desorp.	Orig.	Reacted	Orig.	Reacted	Orig.
CO_2	38.2	2.4	0.6	36.5	4.0	74.3	1.0	0.8	1.6	6.9
C_2H_2	34.4	79.2	22.1	47.7	14.1	24.7	30.8	45.5	75.4	92.9
C_2H_4	0.1	0.2	0.6	0.2	0.4	—	0.6	0.0	0.5	—
C_nH_{2n}	0.2	0.6	1.1	0.4	0.7	—	0.8	0.0	0.9	—
O_2	0.7	0.6	0.6	0.6	0.5	—	0.8	1.0	0.5	—
CO	0.3	0.3	0.4	0.3	0.3	—	0.3	0.0	0.3	—
H_2	21.3	9.6	62.3	8.8	70.3	—	57.4	47.9	12.4	—
CH_4	1.7	4.0	8.7	1.7	7.0	—	4.1	0.4	6.1	—
N_2	2.0	3.3	3.1	3.8	3.0	1.0	3.7	4.2	1.0	0.2

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(2) G. Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., N.Y., (1937); C. Ellis, "The Chemistry of Petroleum Derivatives," Reinhold Publishing Corp., N.Y., Vols. I and II, (1934 and 1937).

(3) R. Negishi and O. Kamiike, this Bulletin **17** (1942), 244.

When the contents of methane in the effluent gas of desorption in I_L–70 and I_L–71 are considered, it is evident that they are higher than those in the respective effluent gases during the normal course of reaction. The difference must be real. When the temperature is increased to effect desorption, quite an appreciable amount of water is always condensed out along with the liquid products, even when a dry gas is used. The source of this water is not clear, but that is of no consequence in our present discussion. What appears significant is that this water reacting with the carbide, produces acetylene which probably is then transformed into methane more effectively at higher temperature. As has been mentioned before(3), the effect of desorption is apparent only in I_L–71 in which carbon dioxide is present.

This system will conclude the experimental work on the non-catalytic direct synthesis of hydrocarbons from calcium carbide under ordinary pressure, and in the next section of this paper, we shall treat the subject from a broader perspective to give more coherence to the isolated facts obtained in the individual systems so far investigated.

Concluding Remarks. As we have already seen, hydrogen and nitrogen are without effect(1); carbon dioxide has a pronounced beneficial effect(3) while carbon monoxide has rather harmful ones(3); acetylene increases the total yield owing to the circumstance that it itself polymerizes under certain conditions; and, finally, hydrogen chloride has shown to give somewhat harmful effects only when its concentration is high(3). We have also seen that desorption shows effects only when CO_2 (and its mixtures) is used as a carrier gas. Although these gases have varied in their effects on the total liquid products, they are without appreciable influence on the character of the products. This point has been briefly mentioned elsewhere(3), but it becomes quite plausible in the light of the more complete set of data, which are shown in Table 15.

As can be readily seen from Table 15, the oxygen contents of the condensates in the condenser and in the trap differ widely, as is also the case with their H/C ratios. When the average ratios of H/C, 0.1309 and 0.1028, for the liquid in the trap and the condenser, respectively, are compared, there will be a difference of 27% between them, provided no correction for the oxygen content is taken into account; when corrected, the corresponding values are 0.0959 and 0.0890, and the difference is about 8% which is a notable reduction from that of the uncorrected. Moreover, the individual ratios for the corrected values differ from the average less markedly. This is interesting, because it gives some support to the validity of our assumptions that the oxygen is principally alocoholic and that the gases used are without influence on the character of the products.

The results of elementary analysis of the condenser condensates* also give good supporting evidence for the independence of nascent acetylene

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* The results of the trap are not so uniform as those of the condenser, but this is due to the fact that the amount of the condensates in the former is very much smaller (at times, less than 10% of the condenser, or about 1 c.c.), and the results of analysis are less accurate. There is another probable source of error, which is more pronounced in the trap than in the condenser. It is the amount of water which may have dissolved in the respective condensates. A larger H/C ratio of trap as compared with that of condenser is suggestive.

Table 15.

Exp. No.	Gas Used		Elementary Analysis		H/C Ratio				On Reacted Carbide Carbon (%)	
					Found		Correct. for MeOH Oxygen		Methane C in Reacted Gas	Decomp.+ Poly. Carbon in Residue
			Trap	Cond.	Trap	Cond.	Trap	Cond.		
$\mathrm{I_L}$35*	N_2	C	74.79	86.57	0.1295	0.099	0.100	0.0894	3.5	20.7
		H	9.96	8.61						
		O	13.25	4.82						
$\mathrm{I_L}$34	H_2	C	75.36	85.99	0.1355	0.0975	0.1024	0.0862	6.1	18.8
		H	10.22	8.39						
		O	14.40	5.62						
$\mathrm{I_L}$57	CO_2	C	74.98	83.19	0.1250	0.1053	0.0853	0.0864	3.9	23.1
		H	9.37	8.76						
		O	15.65	8.05						
$\mathrm{I_L}$41	CO_2+H_2	C	83.02	84.02	0.1214	0.1000	0.1070	0.0841	2.3	24.5
		H	10.10	8.47						
		O	6.88	7.52						
$\mathrm{I_L}$44	CO	C	82.02	84.60	0.1182	0.1027	0.1008	0.0881	7.3	48.9
		H	9.71	8.69						
		O	8.27	6.71						
$\mathrm{I_L}$50	$CO+H_2$	C	Combined	85.20	Combined	0.1025	Combined	0.0898	3.4	43.1
		H		8.76						
		O		6.04						
$\mathrm{I_L}$64	HCl, 3.5+CO_2	C	74.29	79.79	0.1360	0.1100	0.0989	0.0833	3.5	23.4
		H	10.10	8.78						
		O	15.61	11.43						
$\mathrm{I_L}$65	HCl, Dil.+CO_2	C	67.70	84.96	0.1550	0.1042	0.1020	0.0957	2.3	28.3
		H	10.48	8.85						
		O	21.82	6.19						
$\mathrm{I_L}$70	C_2H_2	C	67.98	86.27	0.1500	0.1015	0.0923	0.0906	12.5	44.63
		H	10.21	8.73						
		O	21.81	5.00						
$\mathrm{I_L}$75	C_2H_2 $+H_2$	C	79.69	86.72	0.1130	0.1070	0.0871	0.0937	6.4	41.50
		H	9.01	9.26						
		O	11.20	4.01						
$\mathrm{I_L}$68	C_2H_2 $+CO_2$	C	74.98	84.69	0.1250	0.1015	0.0862	0.0873	3.8	28.4
		H	9.37	8.62						
		O	15.65	6.69						
			Average		0.1309	0.1029	0.0959	0.0890		

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* Least reliable.

polymerization, which we shall henceforth refer to as the specificity of nascent acetylene polymerization. As evident from Table 15, the results are quite similar in every case except for those of $\mathrm{I_L}$–64. The fact that a ratio of H/C is near that of C_2H_2 but always larger is probably real and significant. The meaning of this is, among others, first, the mechanism of the main reaction of the nascent acetylene molecules may be written as

$$n(C_2H_2) = (C_2H_2)_n,$$

second, there is a slight amount of hydrogenation of the products, even in the absence of any catalyst. This is what we have anticipated in one of our papers(4) At the instance the carbide reacts with water, there may exist some rather reactive hydrogen molecules or atoms, some of which may take part in hydrogenation(5). The ratio of the average value of H/C to that of acetylene gives a measure of the degree of hydrogenation; it is 1.07, or about 7% is hydrogenated.

We cannot draw a conclusion as to the mechanism of the main reaction merely from the circumstance alone that the ratio of H/C is near that of acetylene, since it is quite possible that the average value of elementary analysis of the numerous components* contained in the products may be that of acetylene as far as its H/C ratio is concerned. However, it may be carried to the conclusion by a combination of the following evidences. Properly controlled low-temperature polymerization of acetylene(7) will convert it into monovinylacetylene; a dimer, divinylacetylene; a trimmer(8); and a tetramer(9)(5). Spark, Rosen, and Frolich in their interesting paper(10), "Dimerization of Petroleum Hydrocarbons," have assumed that complicated hydrocarbons can be built up by a series of dimerizations involving the well-known 1, 3 rearrangement of hydrogen and have applied this principle to acetylene. According to them a dimer, vinylacetylene, is formed which may undergo either to vinyldivinylacetylene, $CH_2\text{-}CH\text{-}C{\equiv}C\text{-}CH{=}CH\text{-}CH{=}CH_2$, or to styrene by ring closure. Styrene has been identified(6)(11). Recently, butadiene has been

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(4) R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, **15** (1941), 31.

(5) H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, **39** (1935), 811. They have concluded from their homogeneous thermal polymerization of acetylene and its hydrogenation in the temperature range 495 to 535°C. that the principal processes (polymerization and hydrogenation) are interpreted as bimolecular with energies of activation of 40,500 and 42,000 calories, respectively. The efficiency of the association is high, but in the presence of excess of hydrogen, the hydrogenation process becomes predominant.

* Indicated by the absence of sharp breaks in the distillation curve and by the large number of the products, as shown in Table 16, identified by Schlapher and Stadler(6) in their analysis of the cuprene-tar, the liquid products obtained during the formation of cuprene.

(6) Schlapher and Stadler, *Helv. Chim. Acta*, **9** (1926), 185.

(7) C. Ellis, Ref. 2, Vol. II, p. 701 ff. (1937).

(8) Acetylenebivinyl, $CH_2{=}CHCH{=}CHC{\equiv}CH$, another trimer of acetylene has been obtained by A. K. Klebanskii, U. A. Dranitzina, and I. M. Dobromilskaya, Compt. rend. acad. sci., (URSS), **2** (1935), 229.

(9) Pease, *J. Am. Chem. Soc.*, **51** (1929), 3470. He concludes that the rate determining process is the primary reaction involving two molecules of acetylene, and the major reaction involves four molecules of acetylene giving a tetramer. Taylor and Van Hook (*loc. cit.*) assume that the main reactions of acetylene in the presence of hydrogen are

$$4C_2H_2 = (C_2H_2)_4 \quad \text{and}$$

$$C_2H_2 + H_2 = C_2H_4.$$

(10) W. J. Spark, R. Rosen, and P. K. Frolich, *Trans. Faraday Soc.*, **35** (1939), 1040.

(11) M. E. Cupery and W. H. Carothers, *J. Am. Chem. Soc.*, **56** (1934), 1625.

prepared directly from acetylene⁽¹²⁾. In the light of the foregoing evidences, it is not unreasonable to assume that the main mechanism of the nascent acetylene polymerization is as written above; moreover, it becomes probable that some sort of chain-compounds are formed first which are then transformed into aromatic and condensed hydrocarbons⁽¹³⁾. In connection with this transformation, a recent paper by Thomas, Egloff, and Morrell⁽¹⁴⁾ is highly suggestive.

We shall say a word concerning the beneficial effect of carbon dioxide in passing. It is difficult to point out definitely what the effect is but we believe that it is associated, to no small extent, with the destruction of $Ca(OH)_2$ (and CaO). According to Berl and Hofmann⁽¹⁵⁾, CaO is unfavorable to acetylene polymerization and turns the reaction toward the formation of methane, hydrogen, and carbon. When our results in

Table 16. Physical Constants of Cuprene-Tar.

Compound	Formula	d^{20}	Boiling Pt. °C at 760 mm.	Mol. Wt.	H/C
Hexenes	C_6H_{12}	0.681–0.6938	64.1–68.1	84	0.167
Octene	C_8H_{16}	0.7155	123	112	0.167
Benzene	C_6H_6	0.8707	80.08	78	0.0833
Toluene	C_7H_8	0.8658	110.5	92	0.0952
Xylenes	C_8H_{10}	0.8612–0.8745	138.4–144.4	106	0.1041
Ethylbenzene	C_8H_{10}	0.8669	136.1	106	0.1041
Styrene	C_8H_8	0.9074	146	104	0.0833
Methylstyrene	C_9H_{10}	—	—	118	0.0927
Trimethylbenzenes	C_9H_{12}	0.8634–0.895	164.64–176.1	120	0.1112
Ethylmethylzenzenes	C_9H_{12}	0.862–0.873	162–162.5	120	0.1112
Propylbenzenes	C_9H_{12}	0.862–0.864	152–159.45	120	0.1112
Naphthalene	$C_{10}H_8$	1.145	217.9	128	0.0666
Methylnaphthalenes	$C_{11}H_{10}$	1.052–1.029	242–245	142	0.0758
Ethylnaphthalene	$C_{12}H_{12}$	1.059	258 (decomp)	156	0.0833
Dimethylnaphthalenes	$C_{12}H_{12}$	1.001–1.008	261–266	156	0.0833
Anthracene	$C_{14}H_{10}$	1.025	354–5	178	0.0596
Hexahydronaphthalene	$C_{10}H_{14}$	0.934	168.7–180	134	0.1166
Butylbenzenes		0.862–0.8673			
Cymenes		0.8510–0.876	175–177		
Propyltoluenes		0.864	176–184		
Diethylbenzenes		0.860–0.865	182–184.5		
Dimethylethylbenzenes		0.861–0.877	185–189		
Tetramethylbenzenes		0.880–0.901	195–204		

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(12) A. A. Balandin, Ya. T. Eidus, and E. M. Terent'eva, *Compt. rend. acad. sci.*, (URSS), **27** (1940), 343.

(13) E. Bergman, *Trans. Faraday Soc.*, **35** (1939), 1025; G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7** (1939), 725.

(14) C. L. Thomas, G. Egloff, and J. C. Morrel, *Chem. Rev.*, **28** (1941), 1. This interesting paper summarizes the reactions of hydrocarbons in electrical discharges, but the mechanism of acetylene polymedization in general is also included.

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

Table 15 are examined, whenever CO_2 is used, a ratio of methane carbon, as well as that of free carbon, to carbide carbon is smaller.*

Hydrogen chloride seems without appreciable effect, and this is probably due to the fact that it may not react with CaO but slightly. In I_L–62 (Table 6(3)), where the average concentration of the acid is 26% by weight, the carbonate carbon in the residue is 10.4% while that in the hydrogen system(1) is from 3.7 to 12.9%; in I_L–75 (Table 11) in which a mixture of acetylene and hydrogen is used, it is 8%. Since HCl seems without effect on the carbonate, it may neither have any effect on CaO**.

The facts that the presence of the carbide increases the magnitude of $-\Delta F$(4) and that the nascent acetylene molecules possess high reactivity might lead to a conclusion that there would be an improvement in the yield of hydrocarbon liquids. The answer to this point is hinted at when the results of I_L–57 (Table 3(3)) are compared with those obtained by Shiomi and Iwamoto(16) and Amemiya(17), as shown in Table 17. As can be seen from Table 17, under the respective optimum conditions the polymerization of nascent acetylene gives, even in the absence of catalyst, the highest yield both in volume and weight. The fact that the lower the reaction temperature, the lighter are the products is probably due to the predominance of catalytic effect over that of $-\Delta F$, or the chemical tendency, which favors the formation of heavier products in the carbide reactions(4).

Table 17. Comparison between Polymerizations of Ordinary and Nascent Acetylene.

Experimenter	Catalyst	Temp. (°C.)	Max. Yield		Approx. Density
			c.c./cbm.	gr./cbm.	
Shiomi and Iwamoto ..	Co:Ni:Cr_2O_3 Acid clay	208	405	320	0.778*
Amemiya	Fe:Ni Kieselguhr	290	455.6**	389	0.855
Negishi and Kamiike..	None	340	486	460	0.9–1.0

* For the fraction boiling between 170 and 200°C.

** The more recent result by him is (ref. 17b), under the following conditions: Catalyst Fe:Ni:Co:Kieselguhr (90:5:5:1000) +2% K_2CO_3, 3 g. as metal; reaction gas $C_2H_2:H_2=1:4$; flow rate 200 c.c./min.; reaction Temp.°C. (270?), 478.5 c.c./cbm.

In Shiomi and Iwamoto's experiment, given in Tables 18 and 19,, it is obvious that the fraction boiling up to 300°C. is about twice as large and the densities of various fractions are much less than ours. In their investigations they have obtained only 26.9% aromatic; similarly, Amemiya has obtained about 23%* aromatic for the fractions boiling up to 350°C. In ours, on the other hand, we are quite reasonable in assuming,

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* High polymers and free carbon are determined together, and there is some uncertainty in the values of the individual components.

** Since the results of I_L–62 are least reliable, this argument must be taken with certain reservations.

(16) Shiomi and Iwamoto, *J. Soc. Chem. Ind., Japan,* **41** (1938), 831.

(17) T. Amemiya, *ibid.,* **42** (1939), 692; (b) *J. Fuel Soc., Japan,* **21** (1941), a45.

*** Calculated from his data given in Ref. 17b, pp. a56 and a57.

Table 18. Results of Distillation.

Negishi and Kamiike			Shiomi and Iwamoto	
Distillation Range Temp. (°C.)	Vol. (%)	Density at 25°C.	Range of Distillation	Fraction Vol. (%)
<100	1.8	—	—	—
100–150	5.7	0.837*	<150	28.7
150–200	7.8	0.9084	150–200	15.5
200–250	22.3	0.957	200–270	23.6
250–300	10.1	0.971	270–300	11.5
300–326	25.4	—	Above 300	19.6
Residue..........	22.1 (Wt. %)			

* For fraction below 150°C.

Table 19. Density of Products.

Temp. Range (°C.)	< 110	110–140	140–170	Above 170	Experimenter
Density_4^{20}	0.685	0.739	0 749	0.778	Shiomi and Iwamoto
Temp. Range	Below 150		150–200		Negishi and Kamiike
Desnty at 25°C.	0.837		0.9084		

judging from the boiling ranges and densities, that the major fraction of the products is aromatic. This assumption becomes more plausible in the light of the identification made by Schlapher and Stadler⁽⁶⁾ of the cuprenetar (Table 16). The physical constants of the substances identified, as well as some of the unidentified substance having the empirical formula, $C_{10}H_{14}$, in the Table have been taken from the Science of Petroleum⁽¹⁸⁾.

Finally, we may say that many of our observations in this series of investigations are without adequate interpretation; to mention a few, the real effects on the liquid yield of carbon monoxide, hydrogen chloride, and desorption and the real nature of the individual components in the product. The role of a catalyst must be made clear in near future, but at this stage of progress, we may say with some confidence that in these reactions involving the carbide, it is not the question of the activation of the reactants, but of the selectivity, or the specificity, of the catalyst that is most pertinent.

Summary.

It has been shown that when acetylene is used as a carrier gas, the percentage of the total liquid products, based on the reacted carbide acetylene (or carbon), increases owing to the polymerization of the carrier gas itself, provided its concentration is sufficiently high. If the concentration is low, the effect of the introduced acetylene appears limited merely to the suppression of the formation of free acetylene.

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(18) The Science of Petroleum, Vol. 11 (1928), Oxford Press.

An explanation for a higher content than in the reacted gas of methane in the effluent gas used for desorption has been given for the acetylene system.

The supplementary data in support and evidence for the reasonableness of the over-all mechanism of nascent acetylene polymerization, which may be written

$$n(C_2H_2) = (C_2H_2)_n,$$

have been given.

It has been indicated that the efficacy of the synthesis of hydrocarbon liquids directly from calcium carbide is higher than even the catalytic polymerization, so far reported in literature, of ordinary acetylene.

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