The Synthesis of Iso- and Normal Butyl Alcohols in the Presence of Calcium Carbide (B) V.* Comparison of the Results in Dry and Liquid Systems.

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Because the results of autoclave runs III_A Ser. 100, III_A Ser. 113, and IV_A Ser. 124 are quantitative and they (especially III_A Ser. 100) are the first runs in which conclusive evidence of the formation of iso-butyl alcohol has been obtained; and, furthermore, because of the circumstance that these results have proven invaluable for the later investigations on the synthesis of butyl alcohols, they will be given here in some detail. An attempt will be made in this and the following papers, to delve into the mechanism of the reaction as deeply as possible, still keeping within the propriety of the reliability of the data. Since the experimental procedure and methods of analysis have been given(1), they will not be repeated. We shall begin immediately with the discussion of the results which are summarized in Tables 1 to 4 and in Fig. 1 to 5.

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(1) R. Negishi, Papers (B) III and IV, this Bulletin, **17**(1942), 179; **17** (1942), 364.

Table 1. Summarized Results of Runs III_A Ser. 113, III_A Ser. 100, and IV_A Ser. 124. (Catalyst mixed with carbide).

Experimental Number	III_A Ser. 113	III_A Ser. 100	IV_A Ser. 124
Paraffin Oil Introd. (g.)	None	None	300
Residue liq. Recovered (g.)	—	—	288
Carbide (g.)	300 (grains)	300 (grains)	300 (60 mesh)
$CO:H_2$	1:1.85	1:1.89	1:1.3
Reaction Temp. (°C.)	295–305	320	330
Press. Range, kg/cm² at Reaction Temp. °C.	165–135	183–175	200–160
Catalyst No. and Wt. (g.)	15b, 216	15, 212	18ab, 45
Liquid Products	c.c. g.	c.c. g.	c.c. g.
Condenser	46.5 38.8	35.8 30.1	52.2 40.4
Trap	53.3 41.0	50.0 36.2	35.4 24.0
Extract	— 17.1	— 3.9	— —
Condensable Gas (trap)	— 45.7	— 37.6	— 15.7
Total carbide carbon Introd. (g.)	79.05	79.05	83.85
Total Carbide Carbon React. (g.)	79.05	79.05	68.00
Total reacted Carbon (g.)	198.6	181.7	160.9
Total Liq. Carbon (without Extract) on Total React. Carbon (%)	25.6	26.4	27.5
Gaseous and Residue Carbons (g.)+% on Total reacted Carbon	Carbon (%)	Carbon (%)	Carbon (%)
CH_4	5.30 2.7	17.59 9.7	10.71** 6.7
C_2H_6	9.19 4.6	16.16 8.6	
C_2H_4	10.17 5.2	7.82 4.3	8.85 5.5
C_nH_{2n}*	19.82 10.0	11.82 6.5	6.45 4.0
C_2H_2	32.98 16.6	9.79 5.4	4.03 2.5
Carbonate	36.41 18.4	38.91 21.4	33.4 20.8
Hi Polym, and Decomp.	11.86 6.0 (15.0)*** †	32.37 17.8 (41)***	16.07 10.0 (0)*** †
Total Carbon Balance‡	96.6	102.1	91.2‡
Total Weight Balance	98.3	100.0	96.5

* Calculated as C_3H_6.
** Mostly Methane.
*** If all free carbon is from carbide.
† Contains large amount of "yellow powder".
‡ The real accuracy of the results is not as good as what it appears to be. What we are really interested in is the absolute amount of the carbon unaccounted for, and in this series it amounts to 47 g. It is difficult to say how this "unaccounted-for" carbon is distributed among the products given in the Table.

Table 2. Elementary Analysis of Liquid Products.

Exp. No.	Liquid in Condenser			Liquid in Trap		
	C	H	O	C	H	O
III_A Ser. 100	77.90	11.69	10.41	66.80	12.58	20.72
III_A Ser. 113	72.41	11.69	15.85	55.64	15.00	29.36
IV_A Ser. 124	(Cond.+Trap)			68.53	13.10	18.37

Table 3. Distillation Analysis of Condensate.

"Condenser"

Temp. Range (°C.)	Volume (%) III_A Ser. 113	III_A Ser. 100	IV_A Ser. 124*
<100	17.5**	8.4	18.8
100–150	41.6***	24.7	35.4
150–230	27.1	30.1	27.6
230–297.3	11.2	18.3	At 216°C began to crack
Residue	10.7	12.2	10.8
Loss	—	6.3	7.4
Total	108.1†	100	100
Sample Taken (c.c)	42	28.7	—

"Trap"

Temp. Range (°C.)	Volume (%) III_A Ser. 113	III_A Ser. 100
<60	25.35	48.6
60 – 70	22.5	12.4
70 –105	10.5	3.2
105–120	19.8‡	7.0
Residue	7.0	3.4
Total	84.75	74.6
Loss	15.25§	25.4§
Sample (c.c.)	40.0	44.8

* Condenser+Trap.
** Contains some acetone.
*** 44.7% of the cut is isobutyl alcohol (16% of the total "condenser.")
† Due probably to cracking.
‡ 92% of the cut is isobutyl alcohol (18% of the total "Trap.")
§ Dissolved gases.

Table 4. Effect of Temperature and of Carbide on the Formation of Butyl Alcohol.

Exp. No.	System	Reaction Temp. (°C.)	Crude Isobutanol Vol. %* (103–110°C.)	Wt. of Carbide Used (g.)
III_A Ser. 113	Dry	295–305	21.1	300
IV_A Ser. (40+50)	Dry	300–305	8.8	500
III_A Ser. 100	Dry	320	7.1	300
IV_A Ser. 178	Paraffin	300–305	18	300
IV_A Ser. 124	Paraffin	330	16	300
IV_A Ser. 82	Paraffin	360	1.8	300

* Volume (%) based on Total condensates, corrected for the medium forced out.

Discussion. Autoclave run III_A Ser. 100 is the first series of runs in which the main object has been to investigate whether or not butyl alcohols could be definitely prepared from mixtures of carbon monoxide and hydrogen in the presence of a methanol catalyst and calcium carbide. From the previous experiences that, when water vapour is passed over carbide, the optimum temperature for the liquid synthesis is about 340°C[2]; the reaction involving the carbide is exceedingly exothermic; and finally, the lower the temperature, the greater is the carbon monoxide conversion into methyl alcohol, we have at first tried 320°C. The choice of the pressure was perforce determined by circumstances. The effect of pressure, however, is not so important in the static system, especially in the presence of the carbide which possesses large affinities for water and carbon dioxide molecules, by-products of the reaction. The removal of the reaction products shifts the equilibrium sufficiently so that its effect substantially overcomes that of the reduced pressure.

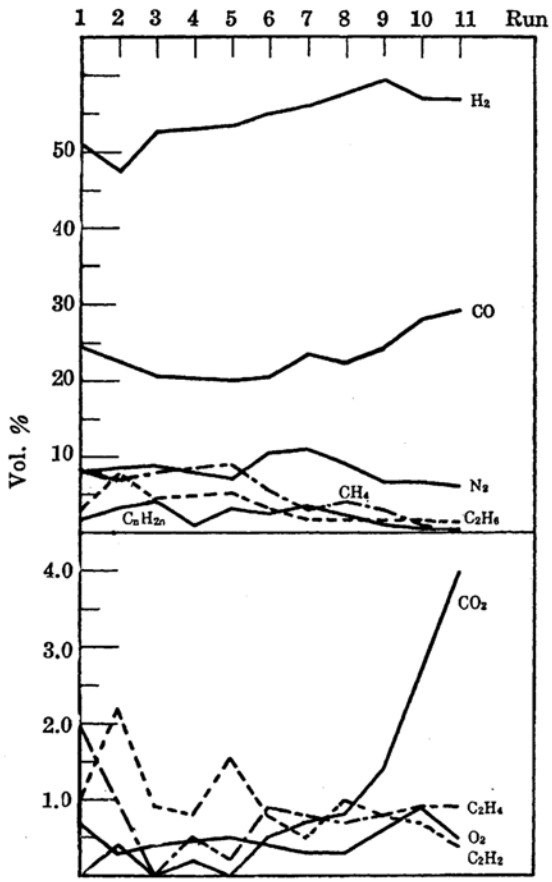

Fig. 1. Gas Composition vs Run (III_A Ser. 100).

As shown in the tables, the formation of iso-butyl alcohol (practically all iso- and no normal) was not large, but they gave indications that in the closed system here employed, the effect of the temperature appeared rather important, and in this case the temperature seemed definitely too high. This is evident from the results of gas analysis given in Table IV in Paper (B) III and in Fig. 1 in this paper and from the high content of decomposed carbon in the residue, as shown in Table I. With this valuable information on hand, we have made autoclave runs III_A Ser. 113 at lower temperatures (and under lower pressure due to circumstances) and IV_A Ser. 124 at higher temperatures but in a liquid medium, which has the same sort of effect as lowering of the reaction temperature, to distribute and dissipate rapidly the excessive heat of reaction. Their

(2) R. Negishi and O. Kamiike, Papers I to VI, *J. Soc. Chem. Ind. Japan*, **44** (1941), 1028; **45** (1942), 137.

results are also given in the tables and figures. The yields of butyl alcohol, on the one hand, have increased appreciably, while those of the saturated gases of lower molecular weights, as well as of the decomposed carbon, on the other hand, have decreased. This is good supporting evidence for the correctness of the assumption that the reaction temperature in III_A Ser. 100 has been too high.

When the results of III_A Ser. 100 and of III_A Ser. 113 are compared with those of non-catalytic, direct synthesis of hydrocarbon liquids from the carbide in dry system, several noticeable differences come to light. First, much larger quantities of hydrocarbon liquids are formed in the present series. In the high pressure non-catalytic reactions[3], at temperatures as low as 310 to 320°C. such a large quantity of liquid products is not possible from the carbide. Neither is it probable even in the ordinary pressure reactions[2] in which fairly large amounts of liquid products have been obtained at 340°C. The products found in the low pressure runs are dark, viscous, and dense, but those in the present series are for the "condenser", light greenish brown and clear with a "crab-like" odour and for "trap", colourless and transparent. Second, the results of the analysis of the gases found in the trap are different in the present and the non-catalytic runs. In the former a large amount of carbon dioxide was found, while it was absent in the latter; no butane[4] in the former, while it was found

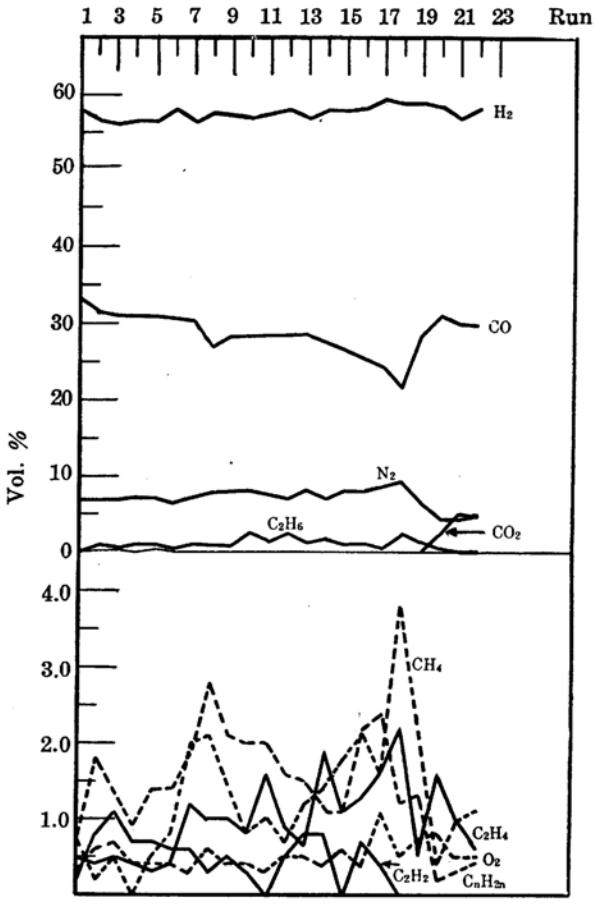

Fig. 2. Gas Composition vs Run (III_A Ser. 113).

(3) R. Negishi, M. Nibayashi, and O. Kamiike, Papers I–III, to be published in Japanese in *J. Soc. Chem. Ind. Japan*, **45** (1942).

(4) Butane is found in the series of runs carried out in liquid medium at higher temperatures, 350–360°C. It seems suggestive that the temperature has a great deal to do with the appearance of butane, but with our present limited data, nothing more can be said.

in some of the latter runs which were carried out at higher temperatures[4].

We can offer no adequate explanation for these differences. As to the increased formation of liquid products, the results of the formation of butanols from methanol[5] in the presence of the carbide are suggestive. we have found that a considerable amount of the methanol introduced has disappeared inexplicably. Probably, part of this methanol has formed hydrocarbon liquids; there are qualitative indications that such is the case. It seems more probable, in our case, that the liquid products are formed rather from the alcohols, methanol and butanol produced, than directly from $CO+H_2$[6] or from acetylene[7]. In connection with the last point, a rough estimate based on the results of III_A Ser. 113 indicates that most of the carbide acetylene has escaped as such or has formed C_nH_{2n} and the "yellow powder", and only about 10% of the carbide has been actually transformed into liquid products. The role

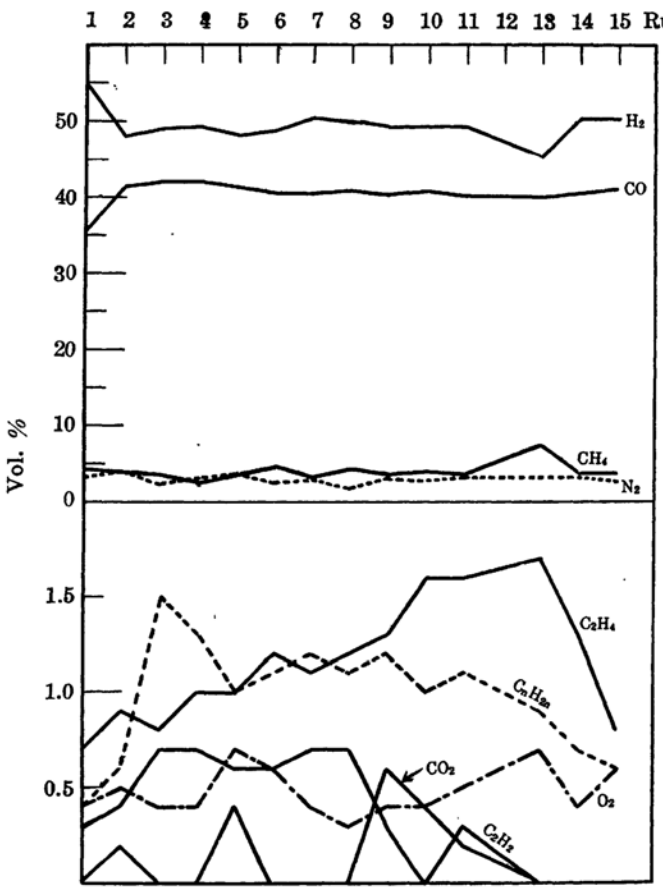

Fig. 3. Gas Composition vs Run (IV_A Ser. 124).

(5) R. Negishi, *Rev. Phys. Chem. Japan*, **15** (1941), 171.

(6) Tsutsumi, *J. Fuel Soc. Japan*, **16** (1937), 481; F. Fischer and H. Kuester, "Gesammelte Abhandlung zur Kenntnis der Kohle," Band 11, 459; H. Pichler and H. Bufflet, *Brennstoff-Chem.*, **21** (1940), 257, 273, 285. According to them, under proper conditions, hydrocarbon liquids of paraffin series and waxes can be synthesized from carbon monoxide and hydrogen under elevated pressures.

(7) H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, **39** (1935), 811; A. Farkas and L. Farkas, *J. Am. Chem. Soc.*, **61** (1939), 3396; G. Egloff and E. Wilson, *Ind. Eng. Chem.*, **27** (1935), 917. According to these investigators, acetylene is readily hydrogenated to ethylene, and the latter has a lower activation energy of polymerization than that of hydrogenation and, furthermore, it is the key molecule for the hydrocarbon synthesis. These facts, therefore, cannot be entirely over-looked in our case.

of the carbide in this series has been to dehydrate the methanol synthesized to produce not only the butanols[5] but also some hydrocarbon liquid products. The fact that most of the carbide acetylene has escaped free may be of great practical importance.

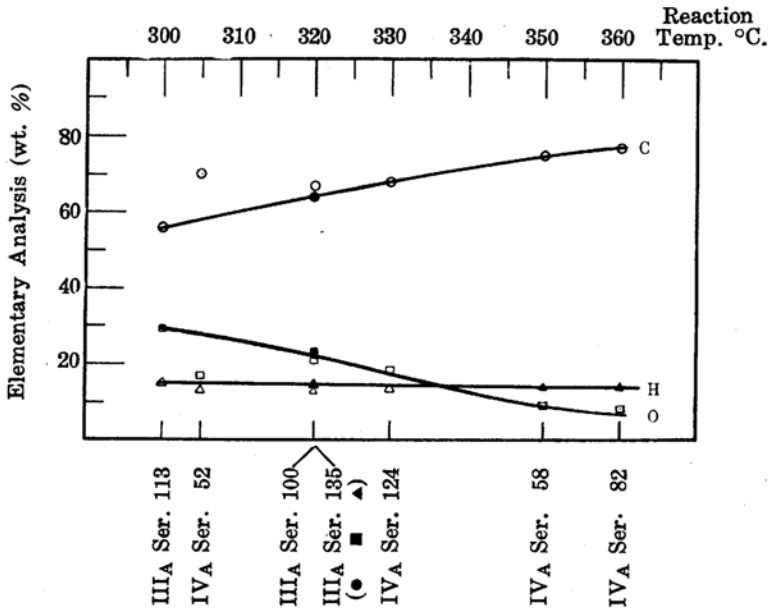

Fig. 4. Effect of Reaction Temperature on Trap Condensates.

As for the second difference mentioned above, i.e., the difference in the composition of the gases found in the trap, we are again without a suitable explanation and can only offer suggestions. The presence of a large amount of CO_2 in the runs, in which a catalyst (oxides of Zn and Cr) has been used, may be correlated with the fact that the following reaction[8] also takes place:

$$CO + H_2O = CO_2[9] + H_2 \qquad (1)$$

and CO_2 more than sufficient to react with CaO may be produced. Our calculation indicates that the source[10] of the water involved in reaction (1) is likely the reduction of carbon monoxide to form methane and ethane.

We shall now compare the results obtained in dry and liquid systems. Although we lack a conclusive support, a considerable body of experimental results we have gathered indicates that the role played by the carbide in the mechanism of the formations of the products in these two

(8) P. K. Frolich and D. S. Cryder, *Ind. Eng. Chem.*, **22** (1930), 1051.

(9) We have found no definite indications that $2CO = CO_2 + C$ takes place under our conditions.

(10) Water may be produced from the decomposition of methanol. We have no indication that CO_2 has been reduced to produce water in our case.

systems are essentially the same. The over-all mechanism of the reaction may be summarized as follows:

(a) Synthesis of methanol from CO and H_2.

(b) Dehydration by the carbide of the methanol to form isobutyl alcohol.[5]

(c) More complete dehydration by the carbide of the alcohols followed by polymerization to produce hydrocarbon liquids.

(d) Polymerization, hydrogenation, and escape of acetylene molecules.

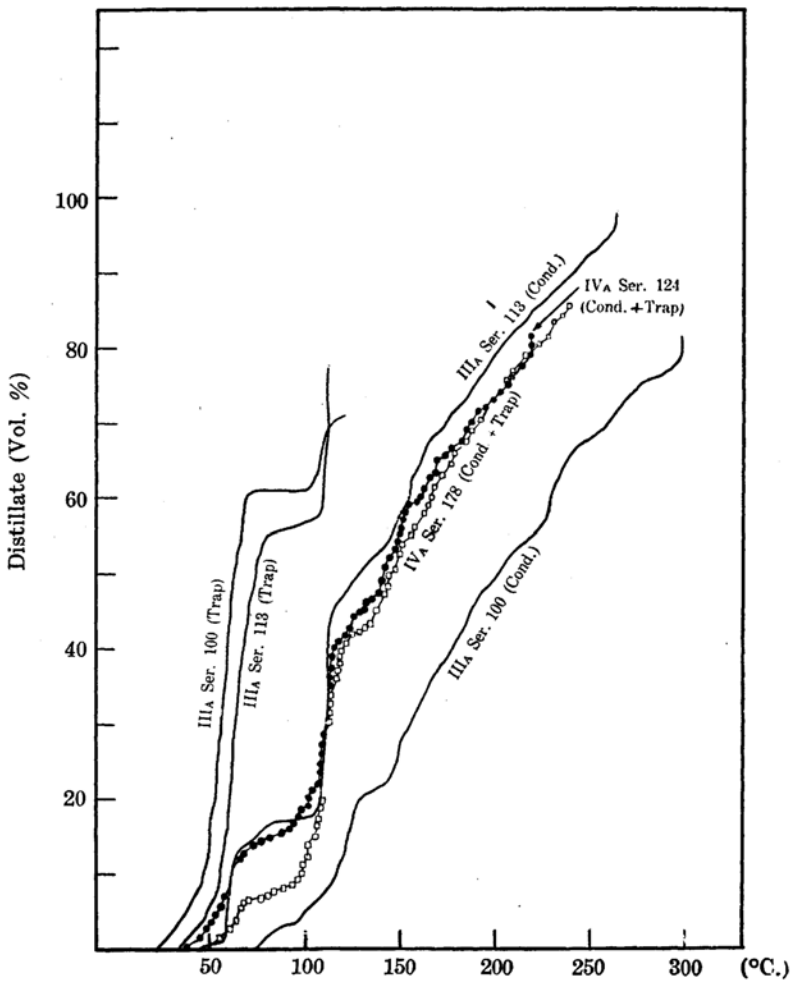

Fig. 5. Distillation Curves.

The differences observed in the systems are rather due to the effects of the heat of reaction involving the carbide; but such differences as no formation of ethane, the lesser amounts of olefins and free acetylene (see Table I) in liquid medium may not be so simply explained.[11]

(11) As in Paper (B) IV, these differences may also be connected with the relative rates of polymerization reactions both in dry and liquid mediums.

Tables 2 and 3 show the results of elementary and distillation analyses of the products formed from the two systems. The results of Table 4 summarize the effect on the butanol yield of temperature, and the distillation curves for some of the runs are shown in Fig. 5. In spite of the fact that IV_A Ser. 124 has been made at 330°C, as compared with 320°C for III_A Ser. 100, the yield of butanol in the former is very much greater. This is an excellent example of the advantage of carying out highly exothermic reactions in a liquid medium where the accumulation of excessive heat of reaction is less likely, and a better distribution of heat is effected. There is another advantage in using a liquid medium which may readily crack.* As is seen in Table I, the residue of IV_A Ser. 124 contains no free carbon; on the other hand, a part of the medium has cracked to give lower boiling substances, as the results of the distillation of the liquid medium separated from the residue of the series show. When it was distilled under the following conditions:

Maximum liquid temperature (in flask) °C	429**
Maximum vapor temperature	398**
Distillation pressure, p mm. Hg	5

approximately 41 c.c. of products boiling below the original paraffin oil (III) was obtained, as compared with 6.7 c.c. in IV_A Ser. 139 in which the medium alone had been treated at 330°C for nearly 2000 minutes. In the former series the decomposition of the carbide had been avoided at the expense of that of the medium. This fact may be of practical significance.

Among the series of the same system, the observed differences are effected by the variation in the temperature, the time of contact, and the amount of the carbide used, just to mention a few. The difference, for example, in the yield of butanol, as in III_A Ser. 52 and III_A 113, which have been carried out at about the same temperature, is probably due to the difference in the amounts of the carbide used. In the former 500 g. while only 300 g. has been used in the latter. Dehydration must have been more complete in the excess of the carbide, as indicated by the results of elementary analysis in Table 2 of Paper (B) III[1] and in Fig. 4. The difference between the yields of butanol, as is also the case with the relative amounts[12] of saturated gases, olefins, free C_2H_2 and free carbon, as shown in Table 1, for III_A Ser. 113 and III_A Ser. 100 is, no doubt, due

* Usually cracking reactions are endothermic.

** Corrected to normal conditions.

(12) A similar sort of relationship was obtained when the first 13 runs of IV_A Ser. 124 were compared with IV_A Ser. 178, which contained just 13 runs. The results (the amount of carbon (g.)) are shown in the Table A. (Condensable gases, i.e., the gases found in the trap, are not included).

Table A.

Exp. No.	C_2H_2	C_2H_2	C_nH_{2n} (as C_3H_6)	Methane
Ser. 178	4.84	11.2	6.22	3.64
Ser. 124	2.16	4.47	5.46	7.70

to the temperature. The effect of the temperature becomes clearer when IV_A Ser. 178 and IV_A Ser. 82 are compared. It is of some note that increasing the temperature has a similar sort of effect as increasing the amount of carbide, as seen from the results of IV_A Ser. 52 and III_A Ser. 100. The decreasing oxygen contents with increasing temperature means, among others, that dehydration reactions become more important with temperature. It is of significance that in our case the reaction temperatures are quite low, and 350°C already seems too high, even in a liquid medium. In most of the direct synthesis of butanols from CO and H_2, the temperature of reaction must be at least above 350°C[13] and usually well over 400°C.

The usual assumption that the average temperature of the reaction vessel is not a true indication of the actual temperature of the reaction is interestingly, though perhaps without much significance, illustrated by Fig. 4 in which the results of the elementary analysis of the trap condensates of the series of runs made both in dry and liquid systems are plotted against the reaction temperatures. When a smooth line is drawn through all the carbon points, it passes through, at 320°C, the point obtained when the catalyst is placed "in cylinder", supported at the center of the autoclave, and finally, through the point obtained at 300°C in dry system. The same sort of behavior is apparent, though to a lesser extent, for the oxygen and hydrogen lines. The carbon and the oxygen points at 320°C in III_A Ser. 100 (in which the catalyst is mixed with the carbide) are above and below the extended lines, respectively. All these relationships show that the actual temperature in III_A Ser. 100 is higher than the average of the system. It is not surprising that the points of III_A Ser. 135 and III_A Ser. 113, though carried out in dry system, would fall on the lines. It has been found that when the catalyst is separated[3] from the carbide, the reaction takes place less rapidly, and the accumulation of heat is not so excessive. At 300°C we have seen that the reaction proceeds rather slowly and, again, we should expect no abnormal effect of the heat of reaction. The points at 305°C do not at all fall on the curves, and this is due to the fact that, in the presence of a large amount of carbide, excessive dehydration takes place; therefore, the conditions of the series are not strictly comparable with the others. The relative positions of the points with respect to the curves are as expected from the above considerations.

In Figs. 1, 2, and 3, the results of gas analysis of each run of the series (III_A Ser. 100, III_A Ser. 113, and IV_A Ser. 124) are given graphically. In Figs. 1 and 2 the CO_2 contents suddenly increase and they become larger than the original value (3.3%). This is good evidence that the water gas reaction also takes place. The content of CO_2 in the gas serves as a fair guide as to the amount of carbide still present in the system. When the carbide exists in sufficient quantities, the content of CO_2 remains practically constant (and very small), while a sudden increase indicates that the carbide has been used up considerably.

This paper will complete the reports on the series of experiments made in our static system. The date and the discussion presented in this

(13) P. K. Frolich and W. K. Lewis, *Ind. Eng. Chem.*, **20**(1928), 285.

series of papers are, at places, fragmentary and incomplete, but we have decided to publish them, because they are sufficiently interesting in themselves, and because the synthesis of butyl alcohols in the presence of calcium carbide is new and has not heretofore been reported in the literature. The next series of investigation will be made with an autoclave into which the reaction gases can be continuously charged. Their results will appear later also in this Bulletin on appropriate occasions.

Summary.

The results of autoclave runs III_A Ser. 100, III_A Ser. 113 in dry and IV_A Ser. 124 carried out in liquid paraffin have been compared and discussed rather quantitatively.

It has been found that the main reactions involving the carbide are the same in the two systems. The differences found are attributable to the accumulation of the heat of reaction, while those among the series of the same system are, in addition, due to such secondary effects as the time of contact and the amount of the carbide present.

From a considerable body of experimental results, it has been indicated that the role of the carbide is to dehydrate the methanol synthesized from carbon monoxide and hydrogen to produce isobutyl alcohol, and with further dehydration of the alcohols, hydrocarbon liquids are produced. Under certain conditions the principal fraction of the carbide acetylene may escape as free or form olefines and yellow powder, with only a slight formation of liquid products.

It has been shown that cracking of the carbide acetylene is avoided at the expense of that of the medium.

It is the authors' pleasure to express their sincere thanks to Professor T. Marusawa for his keen interest and encouragement throughout this series of investigations.

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