The Synthesis of Higher Alcohols in the Presence of Calcium Carbide. (B.) VI.*
Normal Butyl Alcohol from Ethyl Alcohol and Carbide.

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I have shown in several of my papers that normal butanol can be prepared readily from ethyl alcohol in the presence of calcium carbide according to the reaction⁽¹⁾:

$$2C_2H_5OH+CaC_2 \rightarrow C_4H_9OH+CaO+C_2H_2 \text{ (or polymers)}.$$

It has been shown also in those papers that the presence of carbide is theoretically sound and enhances the synthesis quite appreciably.

The purpose of this study is to see whether or not the synthesis has any practical possibilities, and from this point of view, the present investigation has been undertaken, and the results obtained therefrom, will also be discussed mainly from the same standpoint. In order to attain the purpose in a minimum of time, a certain amount of refinement and thoroughness in the research has been sacrificed with the consequence that the data, as a whole, are not free from a certain amount of ambiguity. There are, moreover, a number of difficulties and uncertainties associated with the work, because several drastic limitations have been imposed upon the research as the apparatus used was not especially designed for it.

Experimental Details. Since the experimental details will be fully treated in a forth-coming paper to be published in the Journal of the Fuel Society of Japan, most of them will be omitted in this paper; however, a schematic drawing of the apparatus, a few explanatory notes on the experimental procedure and the scheme of analysis will be given briefly.

A paste consisting of 500 g.* of solid, for example, 100 g. of carbide and 400 g. of calcium carbonate or calcium oxide, and 1000 g. of a paste vehicle** were charged into the autoclave from which the air had been expelled. The temperature was raised to a desired point while the paste was well stirred mechanically. Ethyl alcohol and electrolytic hydrogen were then introduced at a constant rate from their respective inlets. Products were condensed and separated from the gas, which passed through

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* "The Synthesis of Iso- and Normal Butyl Alcohols in the Presence of Calcium Carbide," (B) I–V by the present writer will henceforth be referred to as "The Synthesis of Higher Alcohols in the Presence of Calcium Carbide," (B) I–V.

(1) R. Negishi, *Rev. Phys. Chem. Japan*, **15** (1941), 171; this Bulletin, **17** (1942), 423.

* In later runs 100 to 200 g. of carbide alone and 1000 g. of oil were used. The results of which will be reported elsewhere.

** In this series of experiments lubricating oil, Texaco SAE 50, was used for convenience' sake.

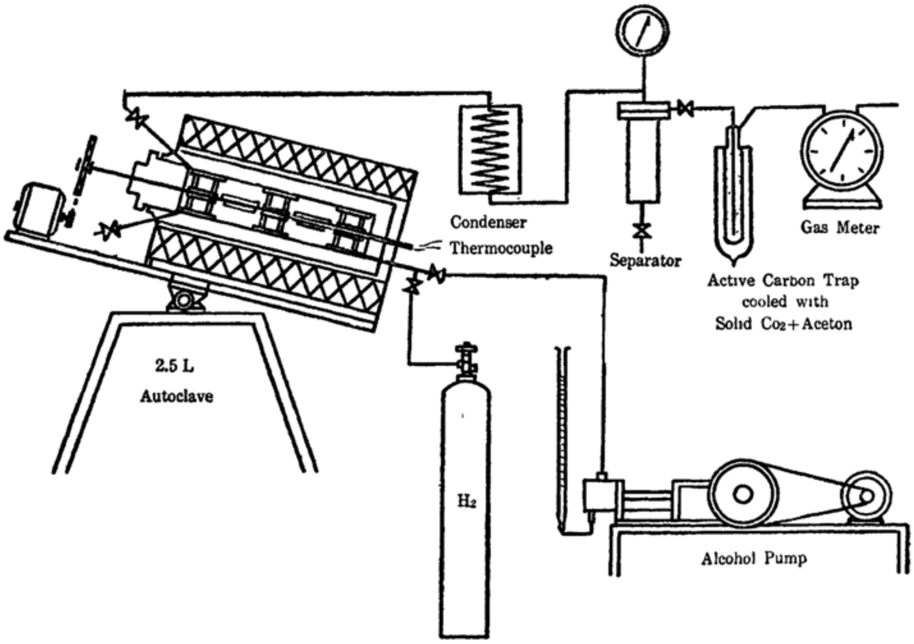

Fig. 1. A Schematic Drawing of the Apparatus.

an active carbon trap which was cooled with acetone and solid carbon dioxide, before escaping into the atmosphere. No carbon and weight balances were taken.

The liquid product, as discharged, was separated by means of crude distillation into the following fractions: below 85°C. (or 90), 85 to 100°C., 100 to 125C., 125 to 170°C., and above 170°C. These fractions were then further analyzed more carefully by means of Podbielniak and azeotropic distillations.

The results of Podbielniak distillation indicated that the fraction boiling below 85°C. was practically all ethyl alcohol, and that the fraction between 85 and 100°C. consisted of about 30% butanol and 70% ethyl alcohol.

100 to 125°C. fraction was the so-called butanol fraction and it was most carefully analyzed. The butanol content in this fraction was determined by azeotropic distillation(2). The total amount of butanol synthesized in any run was determined from the results of above distillation plus the amount of butanol found in other fractions, 85 to 100°C. and 125 to 170°C., by Podbielniak distillation. The synthesized butanol was practically all normal, as it boiled in the neighbourhood of 118°C., and the fraction boiling between 117 and 119°C. showed the following composition:

Found	$C = 64.34$	$H = 13.53$
Calculated as butanol	$C = 64.79$	$H = 13.61$

125 to 170°C. fraction combined with that of 85 to 100°C., as in $\text{IV}_{CA}26$, or this fraction alone, as in $\text{IV}_{CA}41$, was subjected to Podbielniak

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(2) R. Negishi and C. Isobe, this Bulletin, **16** (1941), 278.

distillation and the distillation curves were shown in Figs. 2a and 2b, respectively. In both of these Figs. it is shown that a large portion of this fraction consisted of a higher alcohol, probably normal hexyl alcohol*. Some support for this was indicated by the results of the elementary analysis, shown in Table 1, of the 150 to 160°C. cut (Fig. 3) obtained by Podbielniak distillation of the combined 125 to 170°C. fractions of runs $IV_{CA}12$ to $IV_{CA}17$, from which all substances soluble in 20 times the total volume of the original 125 to 170°C. fractions had been removed. The agreement between the theoretical and observed values was not good, but the deviations in C and O seemed to be in the expected directions.

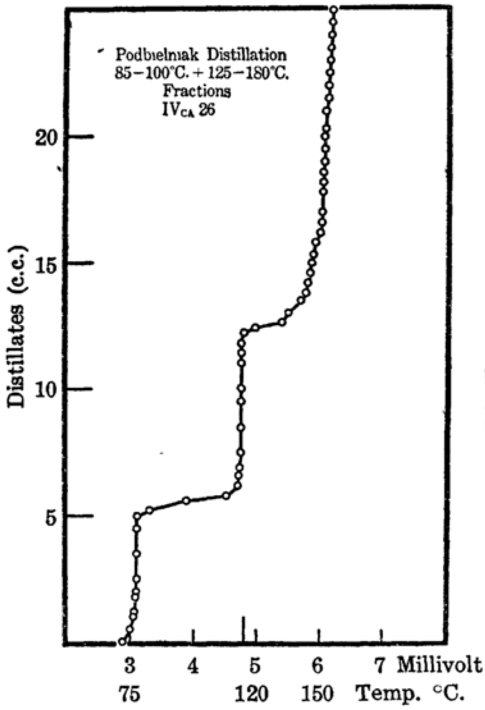

Fig. 2a.

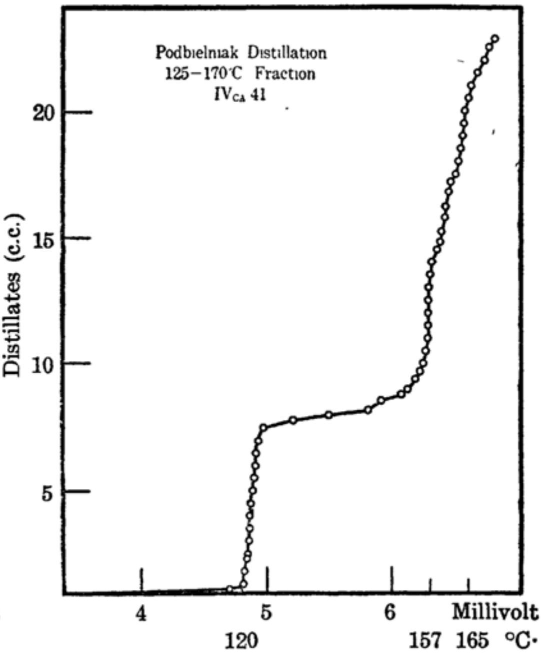

Fig. 2b.

Table 1. The Elementary Analysis of 150 to 160°C. Cut.

Observed	Theoretical ($C_6H_{13}OH$)
B. P. 150 to 160°C.	156°C.
C 73.0	70.6
H 13.6	13.7
O (by diff.) 13.4	15.7

The distillation curve of the combined 125 to 170°C. fractions was shown in Fig. 3, from which it was obvious that not all of the water and butanol had been removed, as indicated by the vertical portions at about 90 and 118°C., respectively.

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* $C_2H_5CH_3CHCH_2CH_2OH$, B.P. 152.1°C. is also possible.

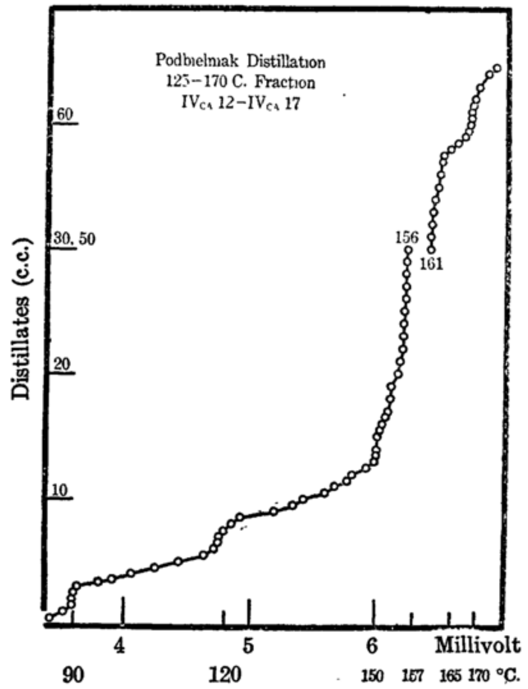

Fig. 3.

By our synthesis not only higher alcohols but also some hydrocarbons had been probably formed(3). The amount of so-called hydrocarbons boiling up to 170°C. was determined by subtracting the alcohol synthesized, estimated from the distillation curve, from the orginal amount of the product before distillation, and by adding the water insoluble substances found in the 100 to 120°C. fraction to the result of subtraction. Naturally, by this method of calculation, some alcohols other than butanol and normal hexanol, as well as all distillation losses would be included as hydrocarbons(4).

Hydrocarbons above 170°C., which might have been formed from carbide was not determined, but the results of $\mathrm{IV}_{CA}41$

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(3) R. Negishi and O. Kamiike, this Bulletin, **17**(1942), 345; *ibid.*, **17**(1942), 355.

(4) In fact, the results of the elementary analysis, given in Table A, of the various distillation cuts, shown in Fig. A, of the combined 125 to 175°C. fractions of runs $\mathrm{IV}_{CA}18$ to $\mathrm{IV}_{CA}29$, indicated that most of the substances were probably alcoholic.

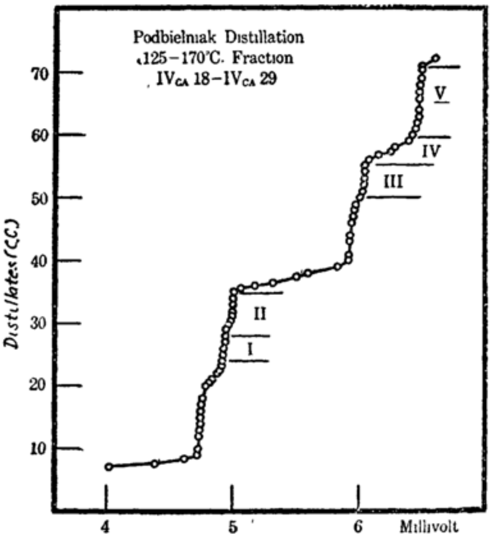

Fig. A.

and IV$_{\mathrm{CA}}$42, which would be referred to later, were suggestive in connection with the point in question. These runs were made under practically the same conditions, excepting only the fact that in the former 200 g. of carbide and 300 g. of calcium oxide was used while in the latter no carbide and 500 g. of calcium oxide. The distillation residues of Samples⁽⁵⁾, II, III, and IV from the runs are shown in Table 2. It may be hazardous to assume that these differences show exactly the amounts of hydrocarbons (and higher alcohols) synthesized from the carbide and alcohol or from the carbide and water, but it is perhaps fairly safe to assume that these differences are good representatives of the order of magnitude and relative amounts of hydrocarbons found in the respective samples.

Table 2. Hydrocarbons in Distillation Residue (Above 170°C.).

Sample No.	IV$_{\mathrm{CA}}$41	IV$_{\mathrm{CA}}$42	Diff. (c.c.)
II	87.5	82	+ 5.5
III	73.0	68	+ 5.0
IV	60.0	62	− 2.0

Results and Discussion. Since the results obtained are, as mentioned already, incomplete and fragmentary, the present discussion would be, at best, descriptive and qualitative. The premature presentation is justified perhaps only by the following fact that this synthesis is new and has not been reported extensively in the literature.

The summarized results are given in Table 3. Only in II$_{\mathrm{CA}}$A38(39) the experimental conditions are quite different from the others. This run has been included, because it seems to make the effect of the excessive carbide much more clear than in other runs in which 100 to 200 g. of carbide is charged. The ratios of ethanol to butanol and carbide to butanol,

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Table A. The Elementary Analysis of Various Cuts in 125 to 175°C. Fraction.

Cut. No.	Elementary analysis			Approx. Mol. Wt.*	Approx. B. P. or Boil. Range.
	C	H	O (by diff.)		
I	67.3	13.5	19.2	82	121
II	69.0	13.9	17.1	78	125
III	72.5	13.6	13.9	103	150–152**
IV	74.6	14.6	10.8	107	152–157**
V	72.0	13.3	14.7	103	157–163**

* By freezing point lowering of benzene.

** Probably 2 or 3°C. too high.

A similar conclusion was gained from the results of the analysis of the water insoluble substances found in the 100–125°C. fractions of the runs from IV$_{\mathrm{CA}}$18 to IV$_{\mathrm{CA}}$29. It would, therefore, be closer to truth to consider that most of the products synthesized by this method are alcoholic with but a slight amount of hydrocarbons mixed with them.

(5) By "Sample" the writer means: In making a run, a discharge of product is made every 30 minutes. A number of discharges (usually 3) are combined together, and this combined discharges has been designated as a "Sample".

Table 3. Non-catalytic Synthesis of n-Butanol from Ethyl Alcohol and Carbide.

General Conditions: (1) Electrolytic hydrogen of 98% purity used.
(2) 1000 g. Lubricating oil used as paste vehicle.
(3) S=Sample(5).

Experimental No.	Carbide (g.) C=Charged R=Reacted	Ethanol reacted (c.c.)	Calcium carbonate (g.) charged	Temp (°C.)	Press. (Kg / cm²)	Effluent gas (l./min.)	Ethanol charged (c.c / hr.)	Products (c.c.)			$\frac{\text{Ethanol}}{\text{Butanol}}$ (c.c./c.c.)	$\frac{\text{Carbide}}{\text{Butanol}}$ (g./c c.)	Time of Reaction (hr.)	
								Butanol	Higher alcohols	Hydro-carbons			For Sample concerned	Total
II_{CA}A38 (39)	C, 500 R, 206	148.4	0	350	50	3	—	12.8	—	48.4(1)	11.2	16.2	15.0	15.0
IV_{CA}11, S III	C, 200 R, 36.7	37.5	300	350	50	3	70	6.2	7.1		6.1	5.9	1.0	5.5
IV_{CA}25, S II, III	C, 100 R, 60	73.4	400	350	10	3	50	14.9	1.3		4.9	4.0	3.0	5.0
IV_{CA}13, S III	C, 200 R, 60	63.0	300	365	10	3	70	13.0	1.5	16.6	4.9	4.6	1.5	5.0
IV_{CA}15	C, 200 R, <200	212.3	300	365	10	3	50	32.3	6.7	43.1	6.6	6.2	6.5	6.5
IV_{CA}15, S IV	R, 42.6	43.3	300	365	10	3	50	8.5	1.5	9.9	5.1	5.4	1.5	6.5
IV_{CA}16, S II, III	C, 100 R, 60	69.4	400	365	10	3	50	18.7	19.0		3.7	3.2	3.0	5.0
IV_{CA}17, S II, III	C, 100 R, 54.5	73.5(2)	400	365	10	3	50	17.3	3.2	17.0	4.3	3.2	3.0	5.5
IV_{CA}23, S II, III	C, 100 R, 60	68.2	400	365	10	4	50	19.6	3.5	9.3	3.5	3.1	3.0	4.5
IV_{CA}24	C, 100 R, <90	120.0	400	365	10	5	50	23.4	10.0	8.2	5.1	3.8	4.5	4.5

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(1) To 200°C.; others usually to 170°C.
(2) From IV_{CA}17 on Ethanol dried with carbide used.

Table 3.—(*Concluded*)

Experimental No.	Carbide (g.) C=Charged R=Reacted	Ethanol reacted (c.c.)	Calcium carbonate (g.) charged	Temp. (°C.)	Press. (Kg./cm^2.)	Effluent gas (l./min.)	Ethanol charged (c.c./hr.)	Products (c.c.)			Ethanol / Butanol (c.c./c.c.)	Carbide / Butanol (g./c.c.)	Time of Reaction (hr.)	
								Butanol	Higher alcohols	Hydro-carbons			For Sample concerned	Total
IV$_{CA}$24, S II, III	R, 60	72.4	400	365	10	5	50	18.4	7.5	5.5	3.9	3.3	3.0	4.5
IV$_{CA}$26, S II, III, IV	C, 100 R, 70	121.0	400	365	20	6	50	25.6	10.0	17.0	4.7	2.7	3.5	5.0
IV$_{CA}$27, S II, III	C, 100 R, 70	71.2	400	365	20	10	50	23.6	5.5	10.5	3.0	3.0	3.0	5.0
IV$_{CA}$28	C, 200 R, 172	202.0	300	365	20	20	50	42.2	5.5	26.1	4.8	4.1	7.5	7.5
IV$_{CA}$28, S II, III, IV	R, 103	112.0	300	365	20	20	50	28.6	3.3	16.4	3.9	3.6	4.5	7.5
IV$_{CA}$29, S II, III	C, 500(3) R, 293	47.6	0	365	10	5	50	12.8			3.7	22.9	3.0	4.5
	R, 67(4)	47.6	0	365	10	5	50	12.8	8.3		3.7	5.2	3.0	4.5
IV$_{CA}$14	C, 200 R, 72.8	77.6 78.7	300 300	365	1	3	70	8.1	—	—	9.8	9.1	2.0	2.5
IV$_{CA}$36(5), S III	C, 100 R, 24.3(4)	26.6 22.6(6)	400	365	10	5	50	8.0	4.2		3.3 2.8(6)	3.0	1.5	4.0
IV$_{CA}$41(5), S V	C, 200 R, 21.1(4)	34.2 25.2(6)	CaO 300	365	10	5	50	10.8	2.7	5.5	3.2 2.3(6)	2.0	1.5	7.0
IV$_{CA}$44, S III, IV	C, 180 R, 66.5	69.5 51.5(6)	CaO 320	365	15	8	50	22.2	5.4	5.6	3.1 2.3(6)	3.0	3.0	6.5
IV$_{CA}$44, S IV	R, 33.2	31.8 22.8(6)	CaO 320	365	15	8	50	11.1	2.6	3.1	2.9 2.0(6)	3.0	1.5	6.5

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(3) 15.9% carbide used.
(4) Calculated on 70% carbide.
(5) 61% carbide used.
(6) Corrected for Ethanol carried away by effluent gas.

respectively, have been determined not on the total product of a complete run, but on the Samples recorded as SI, II, etc. in the first column of Table 3. In many cases, these ratios represent the best results of the individual runs.

There are a number of factors some of which have pronounced effects on the conversion of ethyl alcohol into *n*-butanol and they will be now mentioned and discussed briefly.

(1) *The Effect of Carbide Concentration in the Paste.* There are at least two effects of carbide visible from the results of this series of runs. These effects are inter-related, but for the sake of clearness, they will be treated independently. One of the effects is associated with the fact that, in general, the larger the content of the carbide present in the paste, the larger is the relative amount of hydrocarbons(4) as compared with that of butanol; in other words, the greater the amount of carbide present, the greater is the extent and degree of dehydration, as can be seen from the results of $\mathrm{IV}_{\mathrm{CA}}28$, given in Table 4.

Table 4. The Effect of Carbide on Butanol and Hydrocarbon Synthesis.

Sample No.	Carbide content (g.)	Reacted carbide (g.)*	Reacted Ethanol (c.c.)	Produced (c.c.)			$\frac{\text{Carbide}}{\text{Butanol}}$	$\frac{\text{Ethanol}}{\text{Butanol}}$	$\frac{\text{Butanol}}{\text{Hydrocarbons}}$
				Normal butanol	Higher alc.	Hydrocarbon, 170°C.			
II	165.6–131.2	34.4	41.8	9.4	1.4	6.2	3.7	4.5	1.5
III	131.2– 96.8	34.4	36.9	9.6	1.2	5.7	3.6	3.9	1.7
IV	96.8– 62.4	34.4	34.0	9.5	0.8	4.5**	3.6	3.7	2.1
V***	62.4– 28.0	34.4	33.2	8.8	1.0	4.5	3.9	3.8	2.0

* Assumed reacted linearly with time.

** To 165°C.

*** Least reliable.

The second effect is associated with the fact that the larger the content of the carbide in the reacting system, the larger is the ratio of the reacted ethanol to butanol. This effect is again evident from Table 4. A large part of this alcohol probably forms hydrocarbons, as indicated by $\mathrm{II}_{\mathrm{CA}}\mathrm{A}38$(39).

(2) *The Effect of Temperature.* Due partly to the limitations imposed upon the apparatus, the effect of the temperature has not been investigated extensively. It has been found qualitatively that at temperatures below 350°C., the rate of butanol synthesis seems to be rather slow. Temperatures above 365°C. are not practical with our apparatus, since the amount of the paste medium carried away by the effluent gas becomes too excessive. It may be of some interest to compare the results of $\mathrm{IV}_{\mathrm{CA}}24$, SII, III and $\mathrm{IV}_{\mathrm{CA}}25$, SII, III which have been made under as similar conditions as possible, excepting for the reaction temperatures.

(3) *The Effect of Alcohol Charged per Unit Time.* Our present results indicate that there is not much difference between 50 c.c./hr. and

70/hr.*. It is likely that there must be an optimum rate of introduction, but it has not been determined in the present investigation.

(4) *The Effect of Pressure.* The effect of pressure is probably more significant in connection with the mechanical and engineering points of view than from the chemical point of view. In fact, the overall reaction of the butanol synthesis from ethanol is:

$$2C_2H_5OH = C_4H_9OH + H_2O$$

and the pressure should not exert any effect which seemed to be the case, but its effect is large in connection with performing the experiments. When the pressure is below 10 kg./cm.^{2}, as in $IV_{CA}14$, the paste vehicle carried off by the effluent gas becomes too large, while above 20 kg./cm.$_2$, the amount of gas that has to be introduced to effect nearly the same linear velocity in the paste as that at lower pressures becomes enormous, and here again some inconvenience has been felt. Mostly from the mechanical and experimental considerations, we have experienced that for our present apparatus 10 to 20 kg./cm.^{2}. is about the most suitable range of pressure.

The effects of pressure are so closely related with the rate of effluent gas. This subject will be treated in the next section, for they are without much significance to be treated alone.

(5) *The Effect of Rate of Effluent Gas.* This is one of the most vital effects. The effect has no independent significance, but only when it is considered as an integral part of the whole effects, consisting of those of temperature, pressure, and the amount of the carbide present. However, to make this effect as clear as possible it will be considered separately in this section.

The necessary data are given in Table 5, in which two sets of experiments, one under 10 kg./cm.^{2} and the other under 20 kg./cm.^{2}, have been made. From the Table it seems fairly evident that, at least, the amount of hydrocarbons(4) produced per butanol synthesized decreases with increasing rate of effluent gas(6). This fact has been anticipated more or less, since in order to produce hydrocarbons from ethanol, it is equivalent of saying that one molecule of water is taken away from each molecule of alcohol, while to produce butanol it requires but one molecule of water from two molecules of alcohol.

Because of the limitations imposed upon the apparatus, 20 l./min. was about the upper limits of practicability, since for this rate of gas the amount of the paste medium carried off from the reaction zone by the effluent gas was quite large even under 20 kg./cm.^{2} (and 365°C.).

(6) *The Effect of the Carbide Content.* Up to $IV_{CA}29$ the carbide of 70 to 72% content had been used, and being mixed with an appropriate

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* There was some indication that the time-yield of butanol was larger with 70 c.c./hr. than with 50 c.c./hr., and the latter rate, in turn, was definitely more effective than with 30 c.c./hr.

(6) A comparison of $IV_{CA}13$ and $IV_{CA}41$, in both of which 200 g. of carbide has been used, is suggestive. The ratio of hydrocarbons to butanol is less than 1/2 in $IV_{CA}41$ of that of $IV_{CA}13$, in which the rate of gas is only 3 l./min. as compared with 5 l./min. as compared with 5 l./min. for the former.

amount of calcium carbonate or calcium oxide, a desired carbide content per weight of the paste was prepared. In $IV_{CA}29$, however, 70% carbide was left exposed to the atmosphere until its content had decreased to 15.9%. 500 g. of this carbide, which corresponded to 110 g. of 70% carbide, was mixed with 1000 g. of the oil. The results of this run are shown in Table 3. If the reacted carbide (g.) per c.c. butanol synthesized is calculated on the actual results, it becomes 22.9. If, however, it is calculated not on 15.9 but on 70% content, the ratio becomes 5.2 instead of 22.9. 5.2 is still rather large in comparison with the others ($IV_{CA}24$, SII, III) in which approximately 100 g. of 70% carbide is used. A plausible explanation for this may be found in the reaction:

$$Ca(OH)_2 = CaO + H_2O\,,$$

and this water reacts with the carbide. At 365°C. the vapour pressure of water in the above reaction is about 17.3 mm.(7), but in the presence of carbide, the equilibrium probably will be shifted to the right, and the amount of carbide consumed may be increased appreciably(8).

On the other hand, the amount of ethanol reacted to give one part of butanol is about the same in either case when the carbide (15.9% or 70%) is used, as the comparative results of $IV_{CA}24$, SII, III indicate.

(7) *The Catalytic Effect of Diluents.* In all of these runs calcium carbonate and calcium oxide had been used to "dilute" the carbide concentration in the paste, but they probably exerted no catalytic effects, as the results of blank runs with calcium carbonate and calcium oxide, respectively, had indicated. In $IV_{CA}42$ 500 g. of calcium oxide was used without any carbide, but the other experimental conditions had been made as similar as possible to those of $IV_{CA}41$. The results showed that from 225 c.c. of ethyl alcohol charged, 197 c.c. was accounted for by distillation, and 20 g., or about 25 c.c. from the active carbon trap cooled with solid carbon dioxide and acetone. In other words, out of 225 c.c., 222 c.c. of ethyl alcohol was recovered which was in as good agreement as could be hoped for. A blank run with calcium carbonate was less quantitative, but a similar conclusion could be drawn.

Table 5. The Effect of the Rate of Effluent Gas on Butanol.

Exp. No.	Time of reaction concerned (hr.)	Product/time (c.c./hr.)			Higher alcohol / Butanol	Hydrocarbons / Butanol	Pressure (kg./cm^2.)	Rate of effluent gas (l/min.)
		Butanol	Higher alcohol	Hydrocarbons				
$IV_{CA}17$	3.0	5.8	1.1	5.7	0.2	1.0	10	3
$IV_{CA}23$	3.0	6.5	1.2	3.1	0.2	0.5	10	4
$IV_{CA}24$	3.0	6.1	2.5	1.8	0.4	0.3	10	5
$IV_{CA}26$	3.5	7.3	2.9	4.9	0.4	0.7	20	6
$IV_{CA}27$	3.0	6.7	1.6	3.0	0.2	0.4_5	20	10

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(7) Landolt-Boensteins Tabellen (1936) 2578.

(8) The results obtained from $IV_{CA}38$ and $IV_{CA}41$ are suggestive. In the former CaO, without drying (found to contain apprecible amount of H_2O), was mixed with carbide, while the same amount of CaO dried at 550°C. was used in the latter. The carbide/butanol ratio in the former is 5.8 while it is 3.0 in the latter.

(8) *The Effects of Miscellaneous Factors.* The effects on the time-yield of butanol and hydrocarbons of such factors as the temperature, pressure, and the rate of alcohol charged were not clear from the data presented, but the results of Table 5 seemed to indicate that the larger the rate of effluent gas, the smaller became the formations of butanol and hydrocarbons (or, perhaps, better higher alcohols plus hydrocarbons.).

Theoretically, the introduced gases do not take part in the synthesis; therefore any gas should be equally effective, but several runs made with water gas indicate that, as far as the synthesis of *n*-butanol is concerned, the results obtained are unsatisfactory in every case. At this present stage of investigation, whether water gas really exerts ill effects or not is uncertain. At least, in the direct synthesis of hydrocarbons from carbide(9), it seems to have ill effects. Neither does a pasting vehicle involve in the reaction, and any liquid of sufficiently high boiling point and viscosity may be used. However, other than the lubricating oil nothing else has so far been tried.

The most satisfactory results obtained are shown by $IV_{CA}44$, SIV, in which two parts by volume of ethyl alcohol give one part of normal butanol, 0.2 parts of higher alcohol, probably *n*-hexanol, and 0.3 parts of so-called hydrocarbons boiling up to 165°C. This ratio of ethanol to butanol represents 60% of theoretical. In this calculation the amount of ethyl alcohol carried over by the effluent gas has been taken into account, and in this case, basing on the results of $IV_{CA}41$, it is 9 c.c.

If this synthesis is carried out in a properly designed apparatus in which the temperature of the vapour space above the paste can be controlled independently of that of the paste, not only a more efficient conversion of ethyl alcohol into butanol is possible, but also the experimental conditions may be varied over wide limits, and more definite conclusions as to the effects of gas rate, pressure, and temperature may be obtained.

It may be concluded from the results of this series of investigations that this new process, the non-catalytic synthesis of normal butyl alcohol from ethyl alcohol in the presence of calcium carbide, is not only theoretically appealing but also it has some practical possibilities.

Summary.

The various substances synthesized have been separated into a number of fractions by distillation, and the properties of them have been described briefly.

The following factors which affect the synthesis of butanol have been considered: The effects of (1) the carbide concentration in the paste, (2) the temperature, (3) the rate of alcohol charged, (4) the pressure, (5) the rate of effluent gas, (6) the carbide content, (7) the solid diluents, and (8) miscellaneous factors, such as the species of the introduced gases and the paste vehicles.

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(9) R. Negishi, O. Kamiike and S. Kataoka, *J. Soc. Chem. Ind. Japan*, **45** (1942), 133; *ibid.*, **45** (1942), 529.

Under the optimum conditions, two parts by volume of ethyl alcohol give one part of normal butanol, 0.2 parts of higher alcohol, and 0.3 parts of so-called hydrocarbons, boiling up to 165°C.

It has been concluded that the non-catalytic synthesis of normal butanol from ethyl alcohol in the presence of calcium carbide is not only theoretically interesting, but it may possess also some practical significance.

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