STUDIES ON ETHINYLATION REACTIONS, I

Synthesis of Butynediol in a Continuous Process

By Keizo Suzuki

Introduction

Studies on the kinetics of the reaction of acetylene with aqueous formaldehyde solution in the static method were already reported in *This Journal*[1,2]. From those results the following points are summarized as the good conditions of butynediol synthesis: the reaction temperature is optimum at 120°C, a concentrated aqueous solution of formaldehyde should be used, the methanol content should be diminished, the pH value must not be held below 3, and so on.

In the previous report, however, the reaction rate is slow owing to the smallness in the ratio of the quantity of the catalyst to that of the liquid sample, and the relatively earlier stage of the reaction is treated, and also the static method is adopted. Accordingly, it is difficult to extend these experimental results directly to the practical butynediol synthesis. For the practical purpose, the results of butynediol synthesis obtained in the continuous process are reported in this paper, referring to those results in the previous works.

In the continuous process of butynediol synthesis, the so-called "trickling tower process," where the liquid sample is trickled over the catalyst layer and both acetylene gas and the liquid are passed down through the catalyst layer from the top, has been employed hitherto[3]. In this experiment, however, the following method (counter-current flow method) is used: the catalyst layer is always immersed in the liquid, and the liquid sample is passed down from the top, and acetylene gas reversely from the bottom to the top. The reasons why this method is adopted are as follows. In this experiment the elevated conditions that the reaction temperature, the formaldehyde concentration and the pressure of acetylene gas are 120°C, 30 % and $10 \sim 20 \, \mathrm{kg/cm^2}$, are taken in comparison with the case (about 100°C, 10 % and 5 atm respectively) of trickling tower process in the past, in which it is considered that the cuprene formation and the fatigue of the catalyst become remarkable. Then, the liquid phase and counter-current flow method is superior in avoiding the disaster as much as possible, and also in obtaining the uniform temperature distribution in the reaction vessel.

Experimental Apparatus and Procedures

1) R. Kiyama, J. Osugi and K. Suzuki, *This Journal*, **22**, 22 (1952)
2) R. Kiyama, J. Osugi and K. Suzuki, *ibid.*, **22**, 59 (1952)
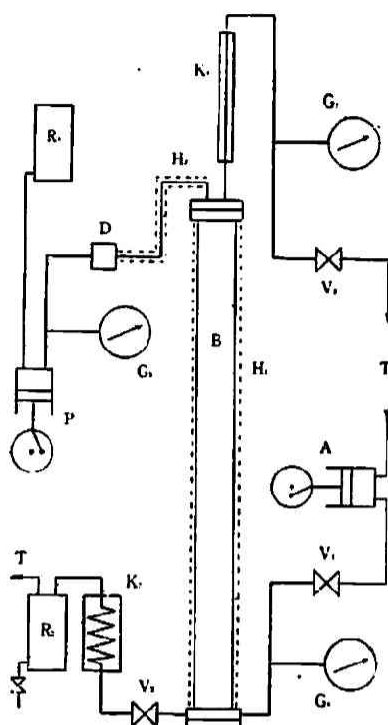3) J. W. Copenhaver and M. H. Bigelow, *Acetylene and Carbon Monoxide Chemistry*, p. 98 (1949)

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Fig. 1 ·Schematic layout of
apparatus

A : gas compressor,   K₁: cooler,
G₁,···, G₃: pressure gauges,
V₁, V₂: high pressure valves,
T : gas tank

The schematic layout of the apparatus is shown in Fig. 1, where the gas stream system is shown on the right hand of the reaction vessel B in the centre of the figure, and the liquid stream system on the left hand.

The reaction vessel B (150 cm in length, 5 cm in inner diameter, 7 cm in outer diameter) is closed with flanges. At the upper flange are set the inlet of the liquid sample, the outlet of the exhausted acetylene gas and the protective pipe inside which the thermocouple is inserted, while at the lower flange the inlet of acetylene gas and the outlet of the reaction products are fitted.

The protective pipe(made of stainless steel)of the thermocouple is inserted to the bottom of the reaction vessel, and catalyst described below is packed directly on the bed covering the inlet of acetylene gas and the outlet of the reaction products. The height of the catalyst layer is 115 cm, and at the dead space of the upper part (35 cm in height) glass tubes are packed to prevent from the detonation.

The reaction vessel is externally heated with the electric heater H₁, and the temperature at each position inside the reaction vessel is measured by the copper-constantan thermocouple inserted in the protective pipe.

The liquid stream system is arranged in the following order: the reservoir of liquid sample R₁, liquid pump P, non-return valve D, the preheater for liquid sample H₂, reaction vessel B, valve V₃, cooling bath K₂ and the reservoir of reaction products R₂. The liquid pump P (6mm in its piston diameter) is used in the range $40 \sim 100$ r. p. m. and its flow quantity is $1 \sim 3$ l/hr. As the preheater H₂, the electric heater set on the pipe connecting the liquid pump with the reaction vessel is used, and the preheating temperature is measured by means of the thermocouple set on the pipe near the inlet of reaction vessel.

The reaction products are stored in the reservoir R₂ through valve V₃. As the liquid quantity, in this case, increases owing to the reaction products, the sum of the sucked quantity of liquid pump and the increased quantity is drawn out by controlling valve V₃ in order to keep the level of the liquid immersing the catalyst layer constant. The reaction products stored in the reservoir R₂ are drawn out after measuring the volume at a definite time, and part of them is analysed.

By changing the number of times that the reaction liquid is passed through the

catalyst layer under a definite temperature distribution, the amount of reaction in the case where the contact time is different is obtained, and then the reaction curves are drawn.   The data in the continuous process can be perfectly obtained by the above procedures.

Catalyst

The catalyst of copper-bismuth adsorbed on a silica gel carrier is employed, and its preparation is the same as in the previous report[1].   The catalyst used, which is 0.82 in the apparent specific gravity and 0.36 cm in the diameter assumed as a sphere, contains 8 % Cu and 2 % Bi.

As it is reported that the catalyst activated in the mild condition is durable and active[3], the temperature, the pressure of acetylene gas and the formaldehyde concentration in the aqueous solution (pH 4 ~ 5) for the condition of activation are taken in the gradual increase from 70°C to 100°C, from 5 kg/cm² to 20 kg/cm² and from 5 % to 30 % respectively in the operation of about 50 hours.   Then, the completion of activation procedures is confirmed by the fact that the catalyst is brought to the reproducible condition from the analysis of the reaction products.

Analysis

The analyses of the experimental materials and propargyl alcohol formed are the same as in the previous report[1]. As to the analysis of butynediol, however, the following method is established and used.

The distillation method is not used for the small quantity of sample, and there lies the disadvantage that it takes a long time in the drying method in vacuum, though these methods were used in the previous work.   The spectroscopic analysis, moreover, is not adequate, because the reaction liquid colours owing to the corrosion and its colour is difficult to remove. Then, the method of the addition reaction of bromine to butynediol as shown in the following equation is examined.

$$HOH_2CC \equiv CCH_2OH + 2Br \rightarrow HOH_2CBrC = CBrCH_2OH.$$
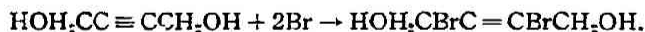
The quantity of bromine consumed in the same way by propargyl alcohol, whose concentration is analysed by the silver nitrate method previously reported, must be subtracted from the total consumed quantity of bromine.   In order to examine the effect of formaldehyde contained in the reaction liquid, moreover, the blank test for the samples, in which formaldehyde is contained in various concentrations, is performed according to the following analytical method.   As the analytical error is about 0.10 ~ 0.15 % from the results, the correction for formaldehyde is unnecessary even in any concentration of formaldehyde.

Take 1 ml of the sample in the flask cooled by ice water, and then add 1 ml of a bromine solution (bromine is dissolved in the solution of 2 part of methanol and 1 part

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of water*), whose concentration is a mole/ml. The flask is immediately stoppered and shaken, and then kept at ice temperature in a dark place for about 90 minutes. Afterwards, the concentration of the excessive bromine b mole/ml is determined by the iodometry. The quantity of bromine used, al mole, in this case, is taken so as to be about twice the sum of x and p mole/ml which are the concentrations of butynediol and propargyl alcohol in the sample respectively. As the consumed quantity of bromine which is equivalent to the sum of p and x mole/ml is $(a-b)l$ mole, the concentration of butynediol is

$$x = (a-b)l - p \quad (\text{mole}/ml)^{**}.$$

The satisfactory results are obtained without the effects of the materials contained by the above analytical procedures.
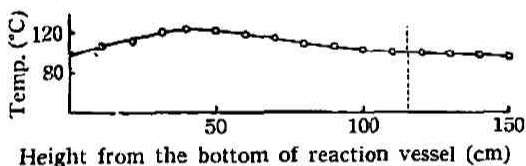
Experimental Results

Fig. 2 Temperature distribution
in the reaction vessel

The temperature distribution in the reaction vessel is shown in Fig. 2, where the dotted line shows the upper position of the catalyst layer. The temperature distribution is kept as similarly as possible in each experiment and the temperature at the maximum of the curve is designated as the reaction temperature.

The experimental results obtained on the effects of the initial concentration of formaldehyde, the pressure of acetylene gas and the methanol content on the reaction are graphically shown in Figs. 3～5 under the reaction conditions of 120°C as the reaction temperature, 0.9～1.3 and 0.8～0.9 l/l hr in S. V. (space velocity) of gas and liquid respectively, and pH 5 in the liquid sample, where the concentration of formaldehyde decreased (F), and those of propargyl alcohol (P) and butynediol (B) formed are respectively plotted against 1/S. V. of liquid. Moreover, the relations between S. T. Y. (space time yield) of butynediol and S. V., and the plots of P/B (the concentration in moles of the propargyl alcohol formed per 1 mole of the butynediol formed) and the conversion percentage of formaldehyde (the percentage of ratio of the formalde-

Experimental conditions
(Fig. 3 ～ Fig. 8) at 120°C

Exp. No.	Liquid sample HCHO (g/100 cc)	CH₃OH	Pressure (kg/cm²)
○ 20	16.2	41.6	10
△ 21	32.7	41.2	〃
● 22	〃	〃	20
□ 23	31.9	18.5	10

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* In the case of using an aqueous solution of bromine, the plus error of about 0.4 % is found, though the addition reaction finishes in 10～15 minutes. While in a methanol solution of bromine the accurate analytical value is obtained, but it takes more than 5 hours to complete the reaction owing to the slowness of the reaction.

** From the results obtained in the investigation on the effect of water in the sample, 1 ml of water gives the plus error of 0.08 % in the analytical value. As this value, however, is within the analytical error, the effect of water may be neglected.
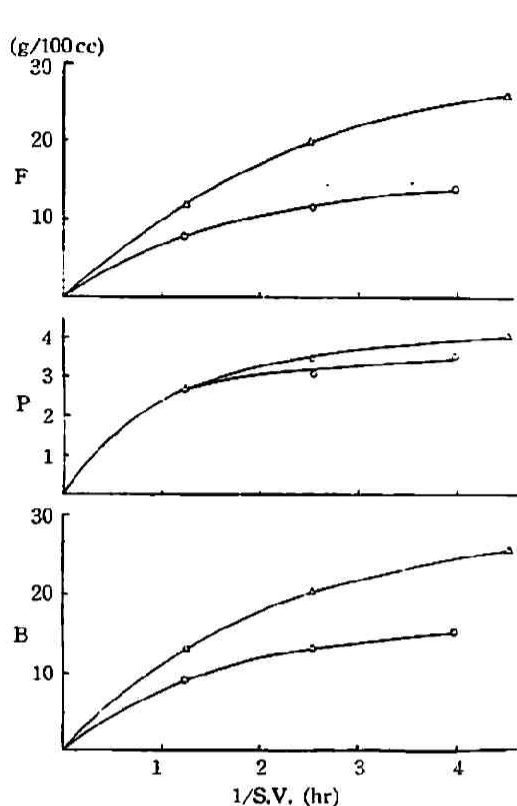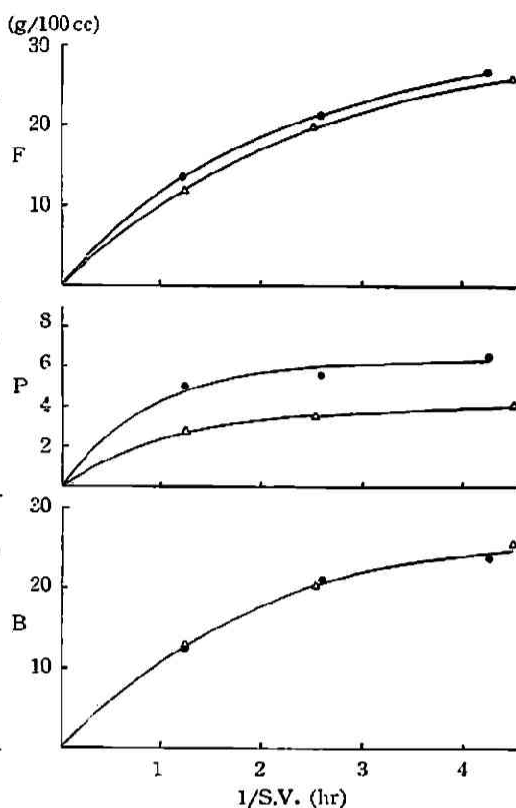
Fig. 3 Initial formaldehyde conc. effect

Fig. 4 Pressure effect

hyde concentration consumed to its original concentration against 1/S. V. are shown in Figs. 6~8 respectively. The experimental conditions are remarked in the previous table.

These results are summarized as follows. The synthetic condition of butynediol is better in the case of the higher initial concentration of formaldehyde (Exp. Nos. 20 and 21 in Fig. 6, cf. Fig. 3) and in that of the minor content of methanol (Exp. Nos. 21 and 23 in Fig. 6, cf. Fig. 5), and the pressure effect of acetylene gas is not recognized (Exp. Nos. 21 and 22 in Fig. 6, cf. Fig. 4). And from Fig. 7 it is also found that the cases of the higher initial concentration of formaldehyde and the minor content of methanol are suitable to the butynediol synthesis, but the pressure rise is not adequate because the concentration of the propargyl alcohol formed becomes high. It is found in Fig. 8 that the conversion percentage of formaldehyde becomes high when the methanol content and the initial concentration of formaldehyde are low, and the pressure of acetylene gas is high*.

It is considered to be reasonable to select S. V. 0.5 ~ 0.6 l/l hr from the curves of

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* The conditions of propargyl alcohol formation are better in the cases where the initial concentration of formaldehyde, the pressure of acetylene gas and the methanol content are higher (Figs. 3~5). It is noticeable, however, that P/B is larger in the lower initial concentration of formaldehyde (Fig. 7).
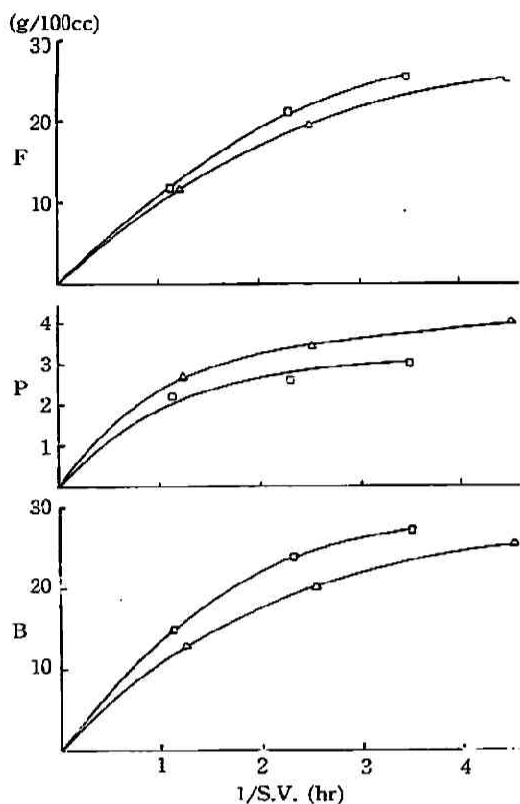
(g/100cc)

Fig. 5   Methanol content effect

Fig. 6   Relations between S. T. Y. of butynediol
and S. V.

Fig. 7   Relations between P/B and 1/S. V.

Fig. 6*.   The components of the reaction
products in the results of Exp. No. 23, which
is obtained under the best condition in this
experiment, where S.V. is 0.6, are as follows:
15.2 % formaldehyde (52 % in the conver-
sion percentage), 2.5 % propargyl alcohol
and 20.2 % butynediol.

Moreover, the experimental results of
the effects of temperature and of stirring
on the reaction are obtained, which is des-
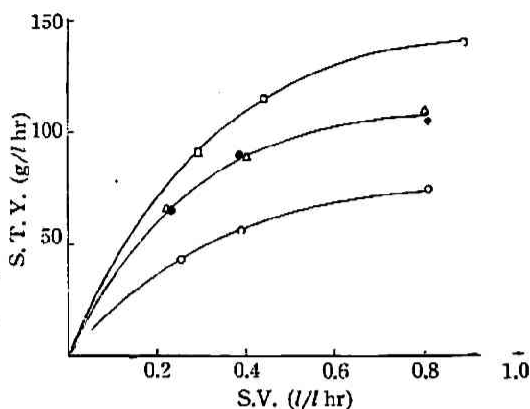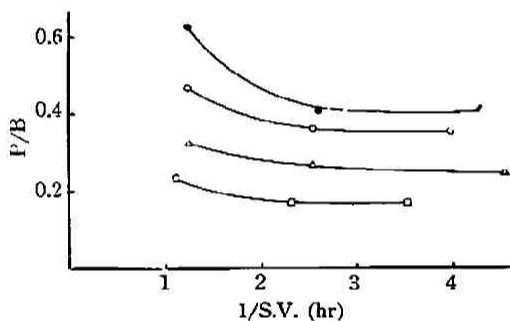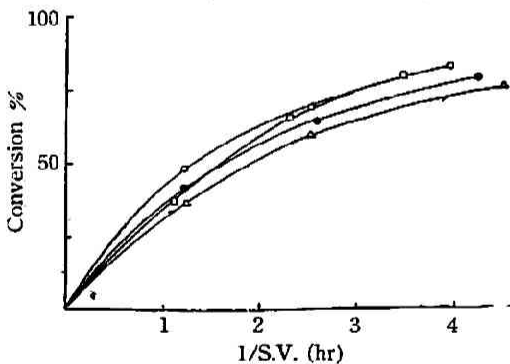cribed in the following section.

Fig. 8   Relations between conversion
per cent and 1/S. V.

Kinetical Considerations

If the rate of formaldehyde decrease is assumed to be the first order as to the
formaldehyde concentration in the solution, the following relation is derived,

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*   Up to the neighbourhood of 0.5～0.6 in S. V., the slope of the curves in Fig. 6 is rela-
tively steep.

$$\frac{1}{\text{S.V.}} = \frac{1}{k} \ln \frac{a}{a-x},$$

where a is the initial concentration of formaldehyde, x the concentration of the formaldehyde decreased at $1/\text{S. V.}$ and k the rate constant. In order to examine whether the above relation is valid or not, the relations between $1/\text{S.V.}$ and $\log(a-x)$ are graphically shown from the experimental results. As shown in Fig. 9, it is confirmed that the linear relations being obtained, the

Fig. 9   Relations between $\log(a-x)$ and $1/\text{S.V.}$
○ Exp. No. 20, △ Exp. No. 21, □ Exp. No. 23

rate equation of formaldehyde decrease is the first order.

The values of the rate constant in the results of Figs. 3～5 are given in Table 1 from the above relation. Table 2 shows the values of the apparent activation energy

Table 1   Values of rate constant (at 120°C)

Space velocity (l/l hr)
{ gas   0.9～1.3
{ liquid 0.8～0.9

Exp. No.	Liquid sample HCHO (g/100 cc)	CH₃OH (g/100 cc)	Pressure (kg/cm²)	Rate constat k (hr⁻¹)
20	16.2	41.6	10	0.48
21	32.7	41.2	〃	0.37
22	〃	〃	20	0.44
23	31.9	18.5	10	0.51

Table 2   Activation energy (at 10kg/cm² pressure)

Exp. No.	Temperature (°C)	Space velocity gas (l/l hr)	liquid (l/l hr)	Liquid sample HCHO	propargyl alc. (g/100 cc)	CH₃OH	Rate constant k (hr⁻¹)	Activation energy (kcal)
{ 11	115	2.2	0.8	16.7	1.8	13.6	0.66	4.8
{ 12	120	〃	0.7	〃	〃	〃	0.72	
{ 16	120	2.3	1.1	32.4	0	40.6	0.54	5.1
{ 17	115	〃	0.7	〃	〃	〃	0.50	

Table 3   Stirring effect on the values of rate constant (at 10 kg/cm² pressure)

Exp. No.	Temperature (°C)	Space velocity gas (l/l hr)	liquid (l/l hr)	Liquid sample HCHO	propargyl alc. (g/100 cc)	CH₃OH	Rate constant k (hr⁻¹)
{ 9	110	1.6	0.5	16.7	1.8	13.6	0.57
{ 14	〃	2.2	1.8	〃	〃	〃	0.70
{ 21	120	1.1	0.8	32.7	0	41.2	0.37
{ 19	〃	1.4	1.2	〃	〃	〃	0.50
{ 16	〃	2.3	1.1	32.4	〃	40.6	0.54

related to the rate constant k, from which it is known that the values are rather small. The effect of stirring on the value of the rate constant k is shown in Table 3, from which it is found that there is the tendency that the rate constant becomes larger when the values of S. V. of gas and liquid increase, that is, the stirring effect is large.

Now, these results in the present experiment should be considered referring to the rate determining step of the reaction mechanism in the previous report. The ratio of the quantity of catalyst to that of the liquid in the reaction vessel being about ten times as much as the previous case, the reaction rate should be about ten times as high if the rate determining step and the reaction conditions are the same. In the previous report the rate of formaldehyde decrease is the zero order at the earlier stage of the reaction, but the rate gradually diminishes with the lapse of $6 \sim 10$ hours in the reaction time[2]. Therefore, even if the zero order mechanism may be held in the present experiment, it is only at the earlier stage. It is difficult, however, to observe the reaction process at such an earlier stage by the continuous method, and so the experimental results obtained by the static method, in which the liquid stream system shown in Fig. 1 is cut off, are shown in Fig. 10. From this figure the rate of formaldehyde decrease is constant until the lapse of $70 \sim 80$ minutes, and then in the successive process the rate becomes the first order as to the formaldehyde concentration. From these results it seems probable to consider that the zero order
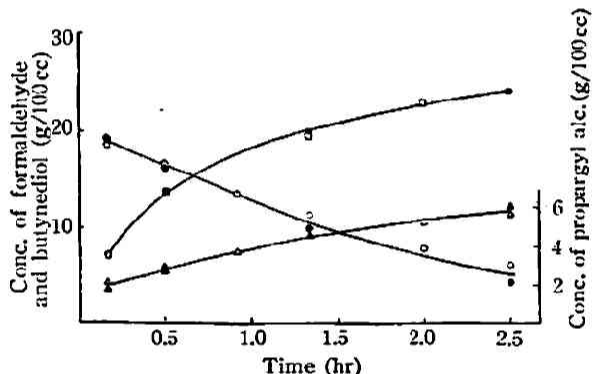

Fig. 10 Reaction curves (in static method)
at 110°C, 30 kg/cm² pressure
● ○ : formaldehyde, ▲ △ : propargyl alc.,
■ □ : butynediol
● ▲ ■ : samples drawn out from the upper part of the reaction vessel
○ △ □ : samples drawn out from the lower part of the reaction vessel

reaction also occurs at the very earlier stage even in the continuous process, but the reaction turns to the first order owing to the changes of medium which are brought about by the reaction products.

From the above described results that the rate of formaldehyde decrease is the first order as to the formaldehyde concentration, the small values in the activation energy related to the rate constant of the first order is much the same as that of diffusion, and the value of the rate constant depends on stirring, and also from the results considered referring to the reaction mechanism in the previous work, it seems that the diffusion process of formaldehyde to the catalyst surface is the rate determining step in such a case of this experiment that the concentration of the butynediol formed becomes high.

As shown in the experimental results the rate of formaldehyde decrease depends

on the pressure, while in the previous work it does not depend. This discrepancy may be understood if considered that acetylene gas is adsorbed on the catalyst unsaturately owing to the rapidity of the reaction in the present.

Conclusions

The investigations on the butynediol synthesis are performed in the continuous process. The best result in this experiment is obtained in the case (Exp. No. 23) where the reaction temperature is 120°C, the initial concentration of formaldehyde 32 % (18 % methanol content, pH ca. 5) and the pressure $10 kg/cm^2$*, and the optimum S. V. is about 0.6 l/l hr. In this case, S. T. Y. of butynediol is 130 g/l hr, the conversion percentage of formaldehyde 52 % and the yield of butynediol against the formaldehyde consumption 85 %. This value of S. T. Y. is $2 \sim 3$ times as much as that in the literature already published[3]. If an aqueous formaldehyde solution in which the methanol content is far smaller is employed, and the high stirring is made, it is expected that further good results may be obtained.

The life of catalyst is concerned about under such a severe condition of reaction as in the present experiment (as to the temperature and the formaldehyde concentration). But it seems that the continuous operation employed in this experiment, where the catalyst layer is always immersed in liquid, and gas and liquid are counter-current, is superior in the protection of catalyst to the trickling method, and the fatigue of catalyst is not found even after its use for about 200 hours.

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* The effect of pressure on the butynediol synthesis is not found above $10 kg/cm^2$, and so it is unnecessary to increase the pressure above $10 kg/cm^2$.