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Polymerization of Normal Butene with Mixed Acid Catalysts (2).

Reactions of Butenes with Sulfuric Acid.

By

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Introduction.

In the previous paper,* the polymerization of *n*-butene with mixed acid catalysts composed of sulfuric acid and phosphoric acid was reported.

The mixed acid catalysts gave better polymer yield and had longer life than sulfuric acid alone. But even in the case of the mixed acid, catalyst life was comparatively low.

To clarify the reason for the catalyst deterioration, detailed investigation on the reactions between butene and acid catalysts was necessary.

In this report, descriptions are presented of the behaviours of butenes during the course of polymerization with sulfuric acid catalyst.

Experimental.

1. Apparatus and procedure.

The reaction vessel was a four-necked round bottom flask as described in the previous paper.* Butene gas was bubbled under agitation into 87% sulfuric acid contained in the flask.

The conducted butene was partly polymerized to liquid polymer which separated out over the acid layer and partly was absorbed by the acid. Hence, the amount of polymerized and absorbed butene was taken as the amount of the reacted butene. The amount of the sulfuric acid used for each run was 50 g.

The liquid polymer was separated from the acid after standing

* The same authors, Memoirs of the Faculty of Engineering, Hokkaido University, Vol. 9, No. 1. (1952).

over night.

Weight increase of the waste acid was measured after the polymer separation.

About one gram of sample was drawn off from the waste acid, and it was titrated with N/2 NaOH solution using methyl orange as an indicator. The amount of N/2 NaOH solution required for neutralizing 1 g. of the waste acid was calculated from the titration data.

2. Experimental Results.

The results of polymerization experiments with *n*-butene and *i*-butene in the presence of 87% sulfuric acid are summarized in Tables 1 to 3 and illustrated in Figs. 1 to 3.

Discussion of the Results.

During the course of polymerization, a part of the butene was absorbed by the acid. The absorbed butene, which was shown as the weight increase of the catalyst, was supposed to form acid ester by combining with sulfuric acid.

TABLE 1. Polymerization of *n*-Butene with 87% H₂SO₄.

(React. Temp. 50°C, Catalyst Acid 50 g, Gas flow rate 12 l/hr)

Conducted <i>n</i> -butene S. T. P.	ℓ	10	15	20	25	30	35	40	45	50	55	60
Reacted <i>n</i> -butene S. T. P.	ℓ	9.0	13.5	17.0	19.6	21.5	22.8	23.6	24.0	24.3	24.6	24.8
Conversion rate Over all	%	94.0	90.0	85.0	78.5	71.7	65.2	59.0	53.4	48.6	44.8	41.8
Each stage	%	94.0	82.0	70.0	52.0	38.0	26.0	16.0	8.0	6.0	6.0	4.0
Polymer yield	g	19.3	23.2	26.3	28.8	31.2	32.8	34.0	34.5	35.0	35.2	35.2
	%	82.2	68.7	62.8	58.8	58.1	57.6	57.6	57.5	57.5	57.3	56.8
Wt. increase of Catalyst (Ester)	g	3.5	10.0	15.5	19.6	22.0	23.8	24.5	25.2	25.8	26.1	26.2
	%	14.9	29.6	36.5	40.0	40.9	41.8	41.9	42.0	42.4	42.4	42.6
Total product (Ester + Polymer)	g	22.8	33.2	41.8	48.4	53.2	56.6	58.5	59.7	60.8	61.3	61.4
	%	97.1	98.3	99.3	98.8	99.0	99.4	99.5	99.5	99.9	99.7	99.4
Consumption of ^N / ₂ NaOH cc/g waste acid		30.08	24.93	20.79	17.46	15.14	14.94	14.84	14.74	14.68	14.44	13.98

TABLE 2. Polymerization of *n*-Butene with 87% H₂SO₄.
(React. Temp. 30°C, Catalyst Acid 50 g, Gas flow rate 12 l/hr)

Conducted <i>n</i> -butene S. T. P.	ℓ	10	15	20	25	30	35	40	45	50	55	60
Reacted <i>n</i> -butene S. T. P.	ℓ	9.8	14.2	18.1	21.2	23.6	25.0	26.0	26.0	26.0	26.0	26.0
Conversion rate Over all	%	98.0	95.0	90.6	85.0	78.5	71.5	65.0	57.8	52.0	47.3	43.3
Each stage	%	98.0	88.0	78.0	62.0	48.0	28.0	20.0	20.0	20.0	20.0	20.0
Polymer yield	g	10.5	14.7	18.3	20.9	23.0	24.0	24.7	25.4	25.5	25.5	25.5
	%	42.9	41.2	40.5	39.4	39.0	38.4	38.0	37.8	37.8	37.8	37.8
Wt. increase of Catalyst (Ester)	g	13.0	19.5	25.4	30.6	34.5	37.0	39.0	39.5	39.5	39.5	39.5
	%	53.2	55.0	56.2	57.7	58.5	59.2	60.0	58.5	58.5	58.5	58.5
Total product (Ester+Polymer)	g	23.5	34.2	43.7	51.5	57.5	61.0	63.0	64.9	65.0	65.0	65.0
	%	96.1	96.2	96.7	97.1	97.5	97.6	98.0	96.3	96.3	96.3	96.3
Consumption of ^N / ₂ NaOH cc/g waste acid		25.5	20.0	15.0	12.5	11.5	11.2	11.2	11.2	11.2	11.2	11.2

TABLE 3. Polymerization of *i*-Butene with 87% H₂SO₄.
(React. Temp. 50°C, Catalyst Acid 50 g, Gas flow rate 12 l/hr)

Conducted <i>i</i> -butene S. T. P.	ℓ	10	15	20	25	30	35	40	45	50	55	60
Reacted <i>i</i> -butene S. T. P.	ℓ	10	15	20	25	30	35	40	45	50	55	60
Conversion rate Over all	%	100	100	100	100	100	100	100	100	100	100	100
Each stage	%	100	100	100	100	100	100	100	100	100	100	100
Polymer yield	g	23.5	35.2	47.0	58.8	70.5	82.2	94.0	105.7	117.6	129.0	141.0
	%	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0
Wt. increase of Catalyst (Ester)	g	1.0	2.0	2.8	3.6	4.4	5.2	5.9	6.6	7.2	8.0	9.0
	%	4.0	5.34	5.6	5.76	5.87	5.94	5.9	5.87	5.76	5.82	6.0
Total product (Ester+Polymer)	g	24.5	37.2	49.8	62.4	74.9	87.4	99.9	112.3	124.8	137.0	150.0
	%	98.0	99.34	99.6	99.76	99.87	99.94	99.9	99.87	99.76	99.82	100.0
Consumption of ^N / ₂ NaOH cc/g waste acid		32.90	31.29	29.67	28.67	27.55	26.65	25.84	25.23	24.83	23.92	22.51

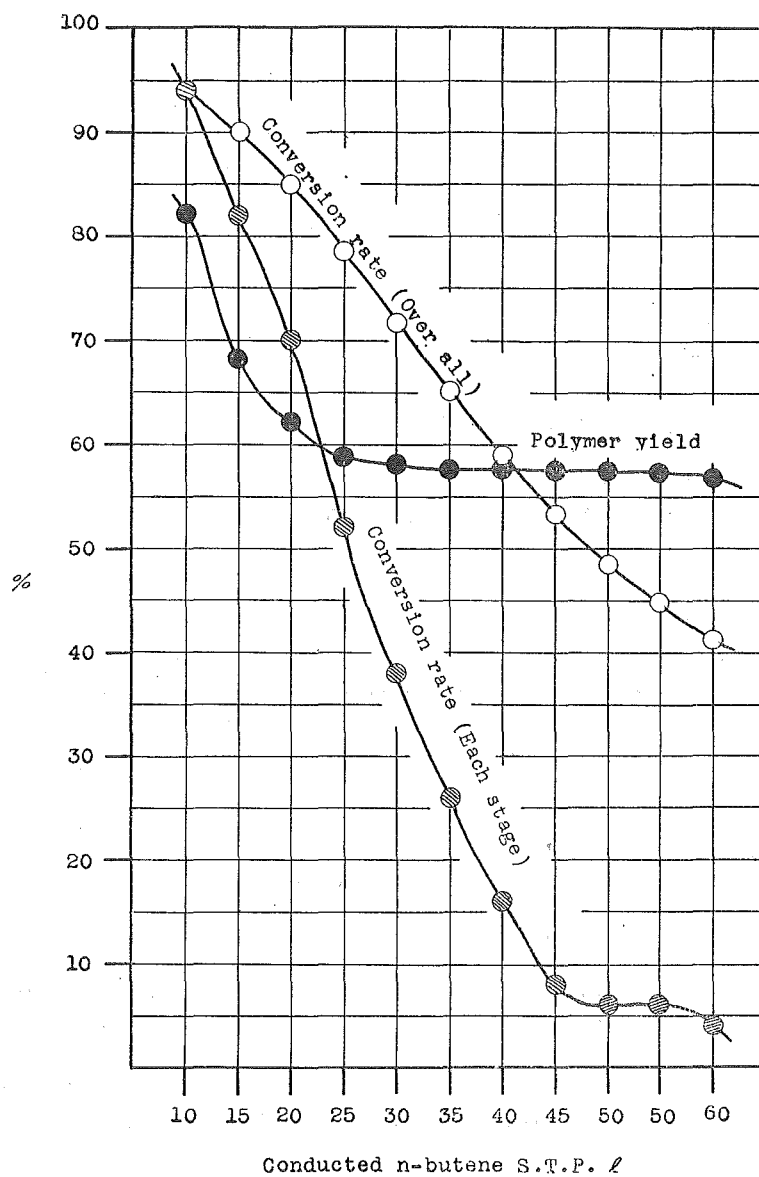


Fig. 1. Polymerization of *n*-Butene with 87% H_2SO_4 .
(React. Temp. 50°C)

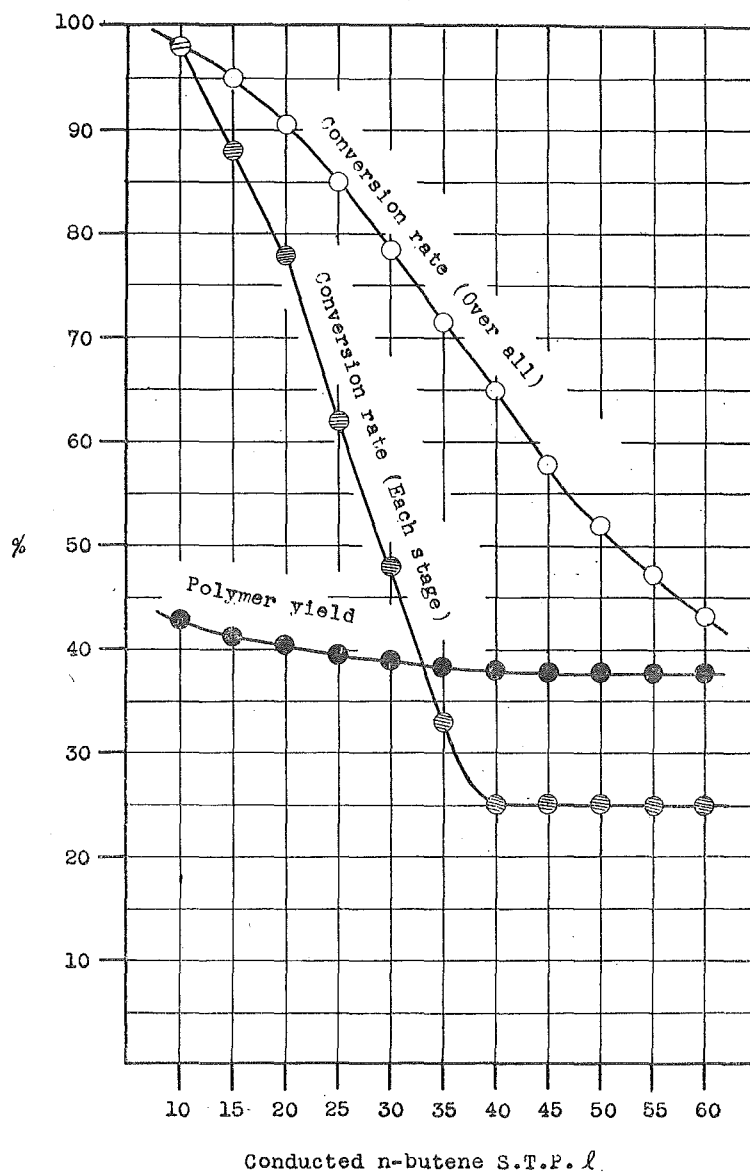


Fig. 2. Polymerization of *n*-Butene with 87% H₂SO₄.
(React. Temp. 30°C)

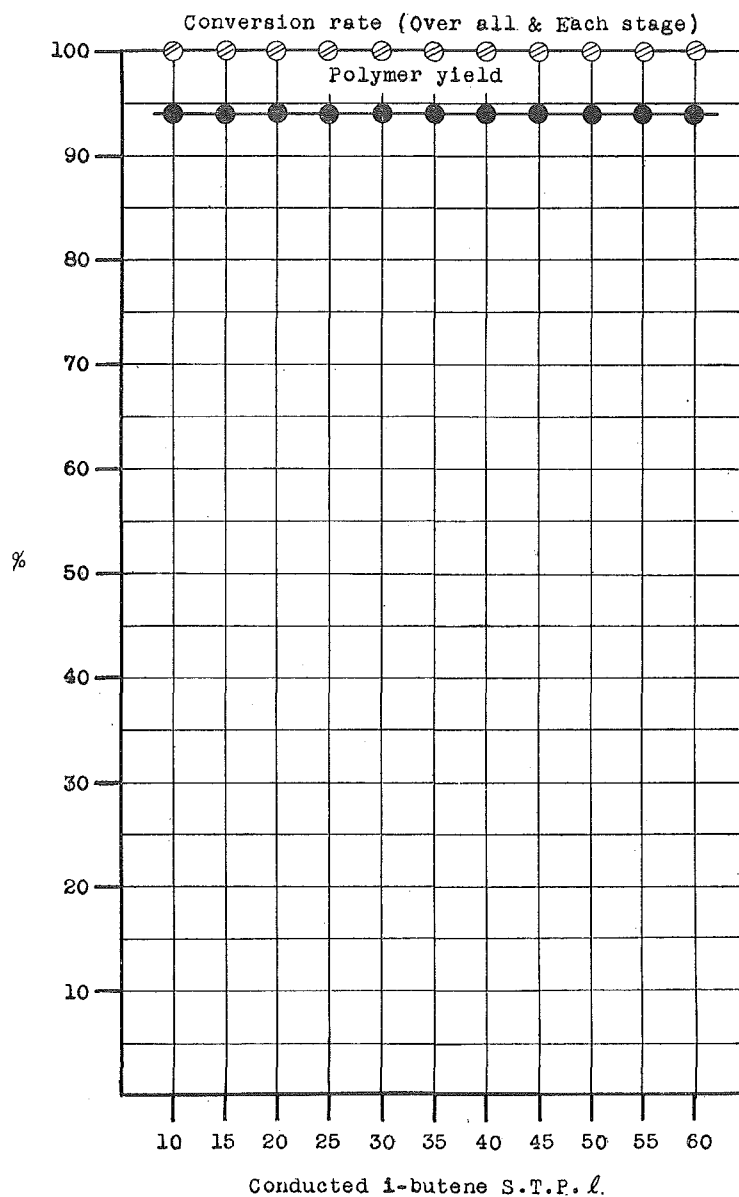


Fig. 3. Polymerization of *i*-Butene with 87% H₂SO₄.
(React. Temp. 50°C)



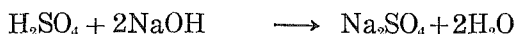
If x g. of 100% sulfuric acid in 1 g. of a % sulfuric acid was consumed to form acid ester, $(1+0.57x)$ g. of ester-containing acid was produced. Thus, in 1 g. of the ester-containing acid, the amounts of acid ester and free acid (100% H_2SO_4) may be calculated as shown below;

$$\text{Weight of acid ester} = \frac{1.57x}{1+0.57x} g$$

$$\text{Weight of free acid} = \frac{\frac{a}{100} - x}{1+0.57x} g$$

Hence, if y cc of N/2 NaOH solution is required for neutralizing 1 g. of ester-containing acid (waste acid), this amount of soda solution

is consumed to neutralize $\frac{1.57x}{1+0.57x} g$ of acid ester, and $\frac{\frac{a}{100} - x}{1+0.57x} g$ of free acid by the following equations.



$$\therefore y = \frac{20.4x}{1+0.57x} + \frac{0.408a - 40.8x}{1+0.57x} = \frac{0.408a - 20.4x}{1+0.57x}$$

$$\therefore x = \frac{0.408a - y}{0.57y + 20.4}$$

$$\begin{aligned} \text{Weight of acid ester} &= \frac{1.57x}{1+0.57x} = \frac{1.57(0.408a - y)}{20.4 + 0.57 \times 0.408a} \quad \dots (1) \\ \text{in 1 g of waste acid} \end{aligned}$$

$$\begin{aligned} \text{Weight of free acid} &= \frac{\frac{a}{100} - x}{1+0.57x} = \frac{(1 + 0.0057a)y - 0.204a}{20.4 + 0.57 \times 0.408a} \quad (2) \\ \text{in 1 g of waste acid} \end{aligned}$$

By the above two equations (1) & (2), the amounts of acid ester and free acid in 1 g. of waste acid may be calculated from the volume of N/2 NaOH solution required for neutralizing 1 g. of waste acid (y).

The calculated values of acid ester and free acid are shown in Tables 4 to 6 and illustrated in Figs. 4 to 6 corresponding to Tables 1 to 3 respectively.

TABLE 4.
Catalyst Acid Composition.
(Based on 1 g Catalyst Acid)

Conducted <i>n</i> -butene S. T. P. ℓ	Free Acid g	Ester g
10	0.668	0.206
15	0.479	0.405
20	0.327	0.566
25	0.205	0.694
30	0.120	0.784
35	0.112	0.792
40	0.109	0.796
45	0.105	0.800
50	0.103	0.802
55	0.094	0.811
60	0.077	0.829

TABLE 5.
Catalyst Acid Composition.
(Based on 1 g Catalyst Acid)

Conducted <i>n</i> -butene S. T. P. ℓ	Free Acid g	Ester g
10	0.4998	0.3833
15	0.2980	0.5965
20	0.1145	0.7894
25	0.0227	0.8861
30	—	0.9247
35	—	0.9363
40	—	—
45	—	—
50	—	—
55	—	—
60	—	—

TABLE 6.
Catalyst Acid Composition.
(Based on 1 g Catalyst Acid)

Conducted <i>i</i> -butene S. T. P. ℓ	Free Acid g	Ester g
10	0.771	0.097
15	0.713	0.159
20	0.653	0.222
25	0.616	0.261
30	0.575	0.304
35	0.542	0.339
40	0.512	0.370
45	0.490	0.394
50	0.475	0.409
55	0.442	0.447
60	0.390	0.499

As shown clearly in the above figures, catalyst sulfuric acid gradually changes to acid ester by combining with butenes in the course of polymerization. In the case of *n*-butene, ester formation velocity seems to be much higher than in the case of *i*-butene. Low reaction temperatures seem to favor ester formation.

For example, after treating ca. 25 liters of *n*-butene, 50 g. of 87% sulfuric acid is almost completely converted into acid ester under the reaction temperature of 30°C.

The catalytic activity of the acid ester for the polymerization of *n*-butene seems to be negligible over the reaction temperature range employed. Hence, when almost the whole of the catalyst acid has changed to acid ester, the polymerization reaction of *n*-butene is substantially discontinued.

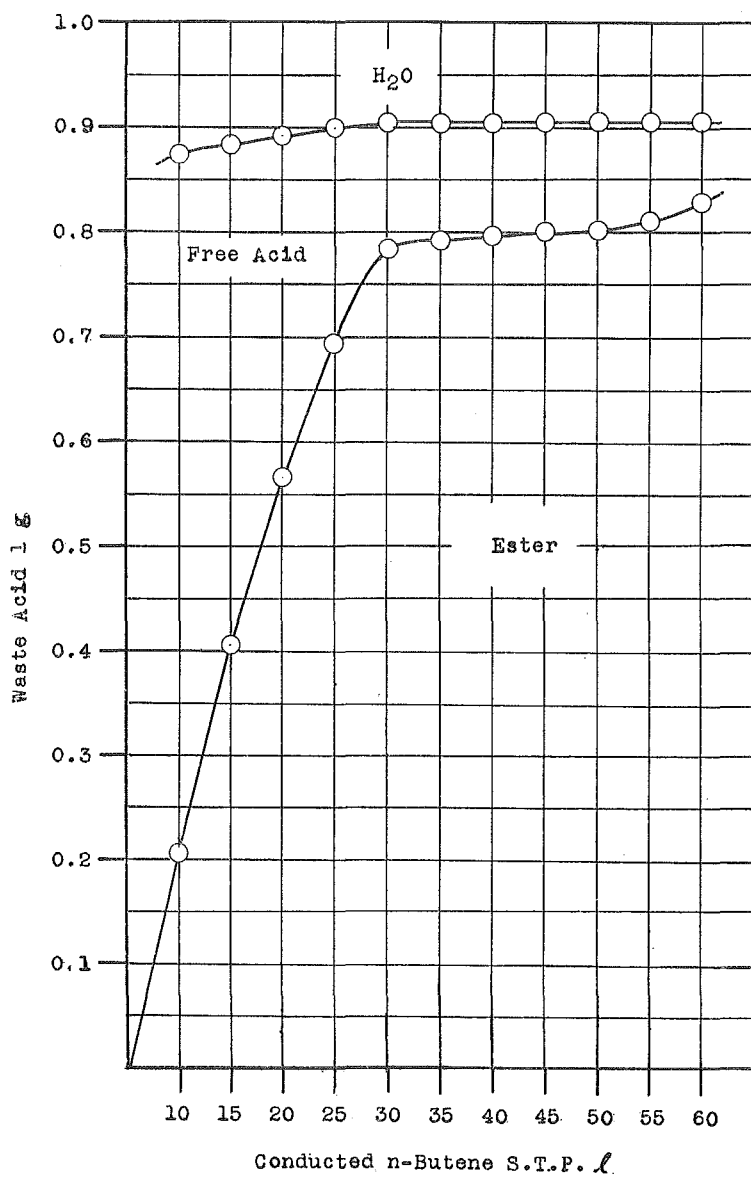


Fig. 4. Waste Acid Composition.
(*n*-Butene, 50°C)

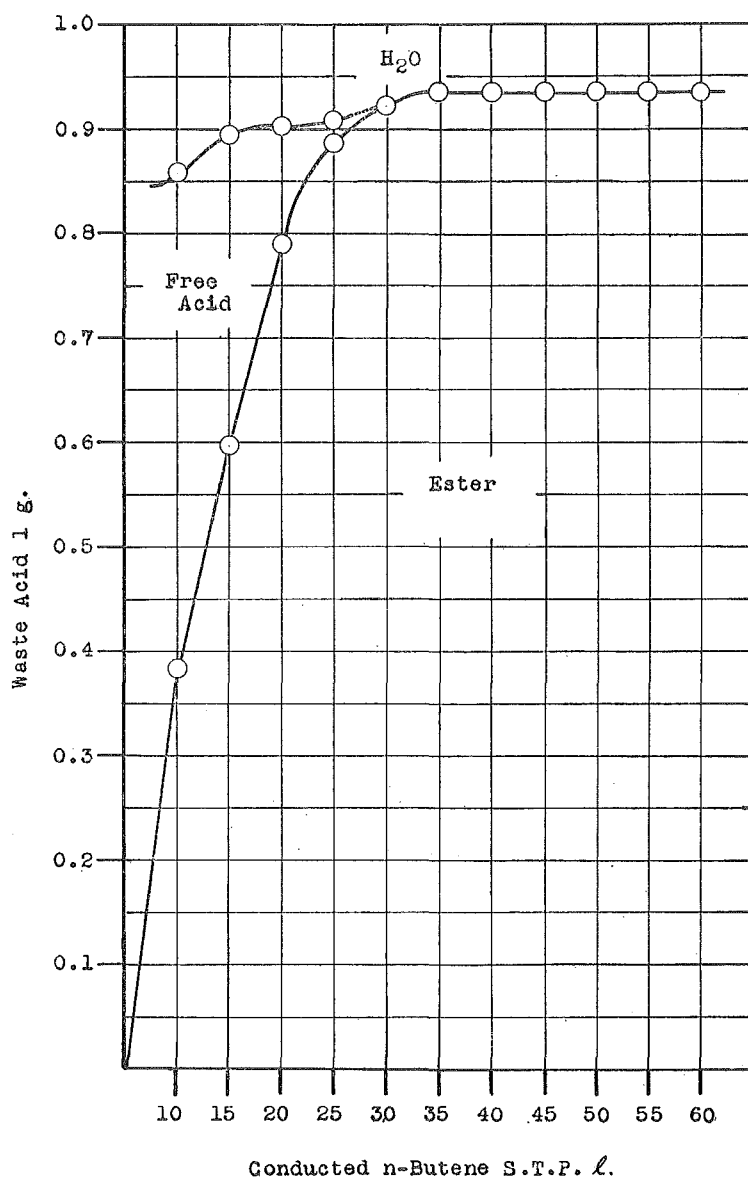


Fig. 5. Waste Acid Composition.
(*n*-Butene, 30°C)

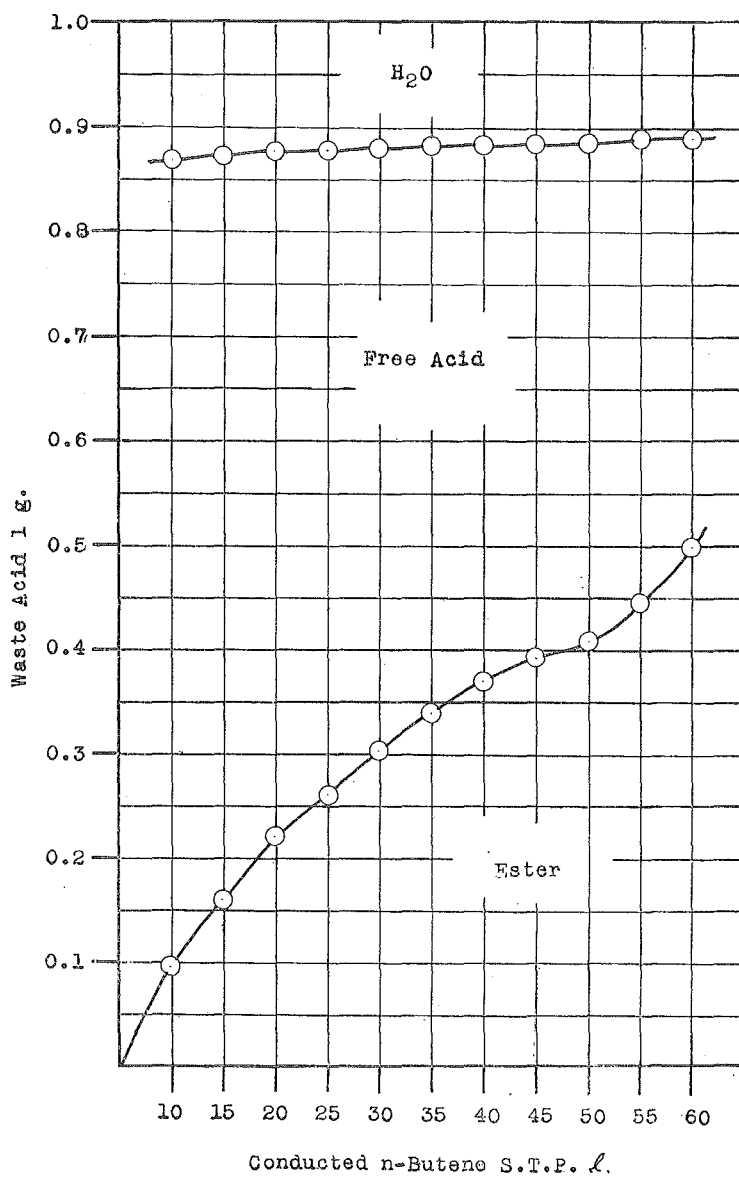


Fig. 6. Waste Acid Composition.
(*i*-Butene, 50°C)

But this acid ester still possesses appreciable catalytic activity for the polymerization of *i*-butene. About 20 liters of *i*-butene were conducted into 50 g. of acid ester obtained in the experiment shown in Table 2 at 30°C and following results were obtained;

Conducted <i>i</i> -butene (S. T. P.)	20 ℓ
Reacted <i>i</i> -butene (S. T. P.)	12.7 ℓ
Conversion rate	68.5 %
Polymer yield	34.0 g (99% of theoretical amount)
Weight increase of catalyst	0 g
N/2 soda equivalents were just the same (11.2 cc for 1 g. catalyst) before and after the reaction.	

The obtaining of almost the exact theoretical polymer yield was worth notice.

These esters are stable up to 80°C. When heated to over 100°C, decomposition occurs. But, heating or long standing of these esters never causes formation of liquid polymer.

Considering from the above shown experimental results, polymerization and ester formation of butenens are competitive reactions in the presence of acid catalysts. As far as the present experimental results are concerned, acid ester is never the intermediate product of polymerization reaction. Ester formation is only a side reaction and polymerization reaction seems to proceed according to the proton exchange mechanism as proposed by Prof. Horiuchi.

Thus, catalyst acid deterioration caused by ester formation is inevitable in so far as the catalyst acid is used in liquid phase and under comparatively low reaction temperatures.

The addition of phosphoric acid (especially pyrophosphoric acid) to sulfuric acid catalyst is fairly effective for the elongation of the life of the catalyst, as the butyl phosphoric acid ester is much more unstable than the sulfuric acid ester.

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