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

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(Received Oct. 1, 1951)

Introduction.

In the previous paper,[1] a study was reported of polymerization of butenes with sulfuric acid catalyst to obtain mainly octenes. Low reaction temperature and short time of contact favored the production of low molecular polymers and sulfuric acid of over 87% concentration caused appreciable polymerization of butenes. In the presence of sulfuric acid, reaction temperatures higher than 100°C were quite inadequate to obtain liquid polymer from butenes. Isobutene gave liquid polymer in good yield with sulfuric acid catalyst. While, normal butene showed poor polymer yield, probably its sulfuric acid ester being stable, and, in this case, the activity of sulfuric acid decreased very rapidly.

In the present paper, polymerization of normal butene in the presence of mixed acid catalyst is reported. The mixed acid catalyst consisted of 87% sulfuric acid and phosphoric acid (ortho- or pyro-phosphoric acid). With this catalyst, normal butene was converted into liquid polymer in good yield. Dimers, trimers and tetramers of butene were the main components of the liquid polymer.

In this series of experiments, the polymerization conditions were so controled as to produce chiefly trimers and tetramers of butene. These long chain olefins have recently been used for various purposes in organic synthesis.

Experimental.

1. Apparatus and Procedure.

The polymerization apparatus was a three-necked round bottom flask of 300cc capacity equipped with an agitator. Normal butene gas was bubbled into the catalyst acid contained in the flask under agitation. The temperature of the contents

(1) H. Ohtsuka et al., Memoirs of the Faculty of Engineering, Hokkaido University, ⑧, No 3 Part I.

was regulated by immersing the flask in a water bath or in an oil bath.

The conducted butene gas was partly polymerized to liquid in the presence of the acid catalyst and the unreacted gas left the flask through a reflux condenser. The liquid polymer thus produced was separated from the acid after cooling and then washed, dried and fractionated into the following four fractions:

1) Up to 150°C Butene dimers (Octenes)
2) 150 – 210°C Butene trimers (Dodecenes)
3) 210 – 274°C Butene tetramers (Cetenes)
4) Over 274°C Heavy polymers.

About 20 litres of normal butene was used for each experiment and gas flow rate was ca. 12 litres per hour. The normal butene was prepared by the dehydration of fermentation butyl alcohol with bentonite as a dehydration catalyst. Normal butene thus prepared contained only trace of isobutene according to the analysis. The amount of the mixed acid used for each run was 50 g.

In a series of experiments the tetramer fraction of butene was added to the catalyst acid for the purpose of retarding heavy polymer production. The amount of addition was 15 g for each experiment.

2. Experimental Results.

(1) Polymerization of Normal Butene with the Mixed Acid of 87% Sulfuric Acid and 90% Orthophosphoric Acid. (Without the Addition of Butene Tetramer.)

The results of this series of experiments are summarized in Tables 1 to 4, and illustrated in Figs. 1 to 4.

Table 1. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 50% / 90% Phosphoric Acid 50% }

React. temp. (°C)		60	65	70	75
Conducted butene	(*l*,N.T.P.)	19.0	19.0	19.0	19.1
Reacted butene	(*l*,N.T.P.)	3.1	4.2	5.7	6.2
Conversion rate	(%)	16.3	22.1	30.2	32.4
Polymer yield	(g)	1.0	1.6	2.4	2.7
	(%)	12.9	15.2	16.8	17.4
Polymer component					
Dimer frac.	(%)		7.8		
Trimer frac.	(%)		62.4		
Tetramer frac.	(%)		29.8		
Heavy polymer	(%)		—		
Gas & loss	(%)		—		

Table 2. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 60% / 90% Phosphoric Acid 40% }

React. temp. (°C)		60	65	70	75	80	85
Conducted butene	(*l*, N.T.P.)	19.0	19.0	19.1	18.9	18.0	18.0
Reacted butene	(*l*, N.T.P.)	6.5	7.7	10.4	14.5	14.7	14.2
Conversion rate	(%)	34.2	40.5	54.6	76.7	82.0	79.0
Polymer yield	(g)	3.4	5.5	10.5	18.5	24.1	22.5
	(%)	20.9	28.6	40.4	51.0	65.5	63.5
Polymer component							
Dimer frac.	(%)	—	—	7.6	6.5	3.3	2.2
Trimer frac.	(%)	—	—	56.0	52.5	46.5	45.8
Tetramer frac.	(%)	—	—	28.6	31.9	45.6	47.1
Heavy polymer	(%)	—	—	3.8	5.4	4.6	4.9
Gas & loss	(%)	—	—	4.0	3.7	—	—

Table 3. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 70% / 90% Phosphoric Acid 30% }

React. temp. (°C)		60	65	70	75
Conducted butene	(*l*, N.T.P.)	19.0	19.1	19.0	18.9
Reacted butene	(*l*, N.T.P.)	14.5	16.0	16.4	15.6
Conversion rate	(%)	76.5	84.0	86.5	82.5
Polymer yield	(g)	15.0	21.3	26.2	25.4
	(%)	41.4	53.3	64.0	65.0
Polymer component					
Dimer frac.	(%)	5.3	4.8	5.4	4.3
Trimer frac.	(%)	44.6	42.2	40.1	37.4
Tetramer frac.	(%)	40.0	44.6	47.8	48.1
Heavy polymer	(%)	5.3	5.6	4.6	7.1
Gas & loss	(%)	4.8	2.8	2.1	3.1

Table 4. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 80% / 90% Phosphoric Acid 20% }

React. temp. (°C)		55	60	65	70	75
Conducted butene	(*l*, N.T.P.)	18.5	19.0	18.9	19.0	18.9
Reacted butene	(*l*, N.T.P.)	16.8	18.3	17.8	16.8	15.3
Conversion rate	(%)	91.0	96.5	94.5	88.5	80.8
Polymer yield	(g)	28.6	32.6	28.6	25.6	22.4
	(%)	68.0	71.2	64.2	61.0	58.6
Polymer component						
Dimer frac.	(%)	5.3	3.1	2.5	2.3	1.8
Trimer frac.	(%)	29.7	33.2	31.4	30.5	28.1
Tetramer frac.	(%)	59.5	58.0	59.2	58.0	58.5
Heavy polymer	(%)	3.5	4.3	4.9	6.3	8.1
Gas & loss	(%)	2.0	1.4	2.0	2.9	3.5

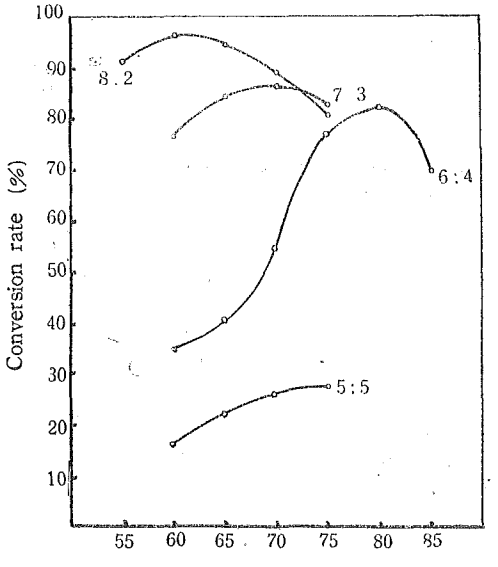


Fig. 1 Conversion Rate

Note: {8:2} means the mixed acid of
{87% Sulfuric acid 80%
{90% Orthophosphoric acid 20%

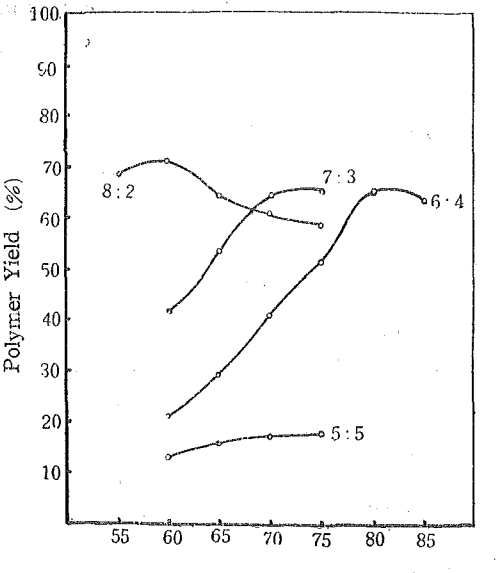


Fig. 2 Polymer Yield

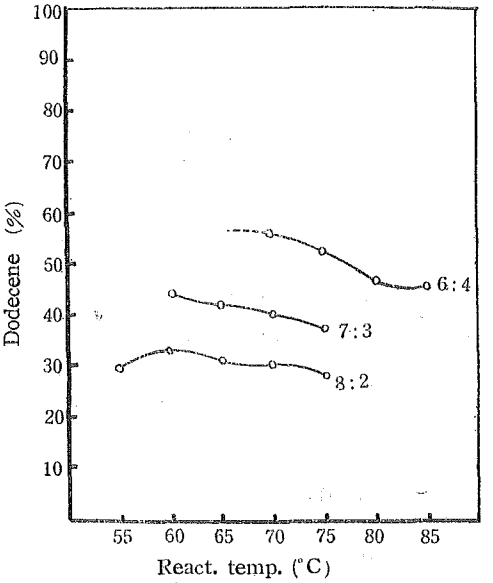


Fig. 3 Dodecene % in Polymer

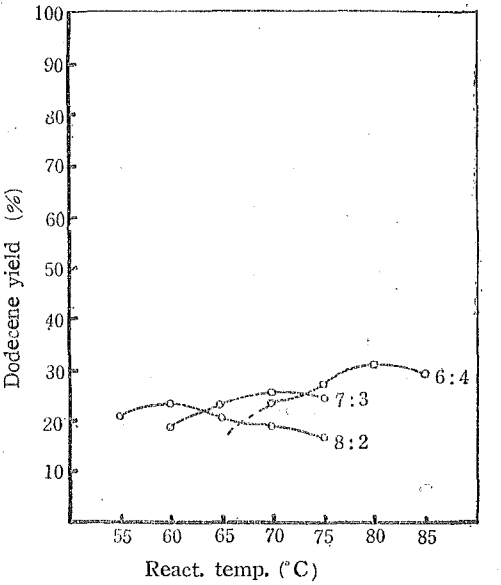


Fig. 4 Dodecene Yield

(2) Polymerization of Normal Butene with the Mixed Acid of 87% Sulfuric Acid and 90% Orthophosphoric acid.
(With the Addition of Butene Tetramer.)

The results of this series of experiments are summarized in Tables 5 to 8, and illustrated in Figs. 5 to 8.

Table 5. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 50% / 90% Phosphoric Acid 50% }

React. temp. (°C)		60	65	70	75	80
Conducted butene	(*l*, N.T.P.)	19.0	18.9	18.9	18.9	18.0
Reacted butene	(*l*, N.T.P.)	5.7	7.1	8.7	10.0	9.1
Conversion rate	(%)	30.0	37.5	46.0	52.8	50.0
Polymer yield	(g)	1.6	3.6	7.4	11.0	9.6
	(%)	11.3	20.3	34.0	44.0	42.3
Polymer component						
Dimer frac.	(%)	—	—	16.3	18.4	11.5
Trimer frac.	(%)	—	—	83.7	74.5	67.7
Tetramer frac.	(%)	—	—	—	—	14.6
Heavy polymer	(%)	—	—	—	—	3.0
Gas & loss	(%)	—	—	—	7.1	3.2

Table 6. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 60% / 90% Phosphoric Acid 40% }

React. temp. (°C)		60	65	70	75	80	85
Conducted butene	(*l*, N.T.P.)	19.0	19.0	19.0	19.0	18.2	18.0
Reacted butene	(*l*, N.T.P.)	10.6	11.3	12.4	13.6	15.6	13.9
Conversion rate	(%)	55.7	59.5	65.2	71.7	80.5	77.3
Polymer yield	(g)	4.9	6.8	12.5	17.0	24.2	20.0
	(%)	18.5	24.1	40.4	50.0	62.0	57.5
Polymer component							
Dimer frac.	(%)	—	19.0	16.0	15.3	6.2	8.5
Trimer frac.	(%)	—	81.0	76.0	70.0	55.4	53.0
Tetramer frac.	(%)	—	—	6.4	13.5	28.1	27.0
Heavy polymer	(%)	—	—	—	—	10.3	11.5
Gas & loss	(%)	—	—	1.6	1.2	—	—

Table 7. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 70% / 90% Phosphoric Acid 30% }

React. temp. (°C)		60	65	70	75
Conducted butene	(*l*, N.T.P.)	18.9	19.0	19.1	19.0
Reacted butene	(*l*. N.T.P.)	14.1	16.0	17.2	16.2

Conversion rate	(%)	74.5	84.2	90.0	85.5
Polymer yield	(g)	14.3	21.1	24.1	22.3
	(%)	40.6	52.8	56.2	55.0
Polymer component					
Dimer frac.	(%)	8.4	7.6	5.8	5.4
Trimer frac.	(%)	67.0	65.4	62.8	59.7
Tetramer frac.	(%)	19.6	24.0	26.6	29.6
Heavy polymer	(%)	2.1	1.9	2.5	3.6
Gas & loss	(%)	2.9	1.1	2.3	1.7

Table 8. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 80% / 90% Phosphoric Acid 20% }

React. temp. (°C)		55	60	65	70	75
Conducted butene	(*l*,N.T.P.)	18.5	19.0	19.0	18.9	19.0
Reacted butene	(*l*,N.T.P.)	16.8	18.2	17.8	17.6	17.1
Conversion rate	(%)	91.0	96.0	94.0	93.0	90.2
Polymer yield	(g)	24.8	29.6	28.3	25.6	22.9
	(%)	59.0	65.0	63.5	58.3	53.5
Polymer component						
Dimer frac.	(%)	9.3	4.4	3.9	3.1	2.6
Trimer frac.	(%)	44.4	45.0	41.8	39.1	38.0
Tetramer frac.	(%)	43.6	44.3	48.2	51.2	50.7
Heavy polymer	(%)	2.7	2.7	3.5	3.9	5.3
Gas & loss	(%)	—	3.6	2.6	2.7	3.4

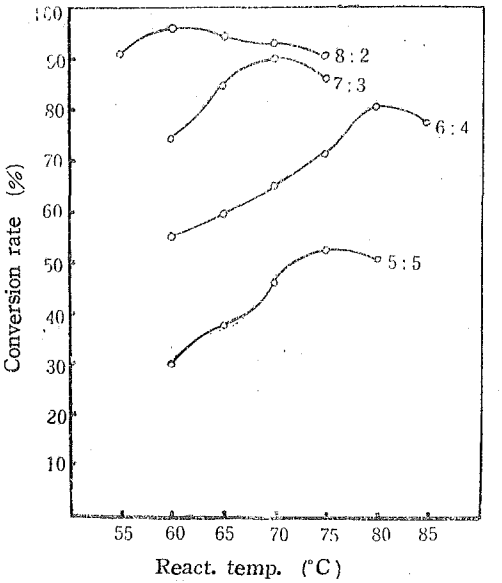


Fig. 5 Conversion Rate

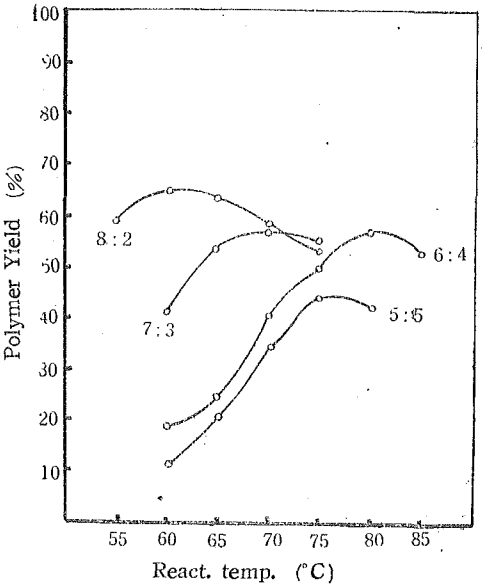


Fig. 6 Polymer Yield

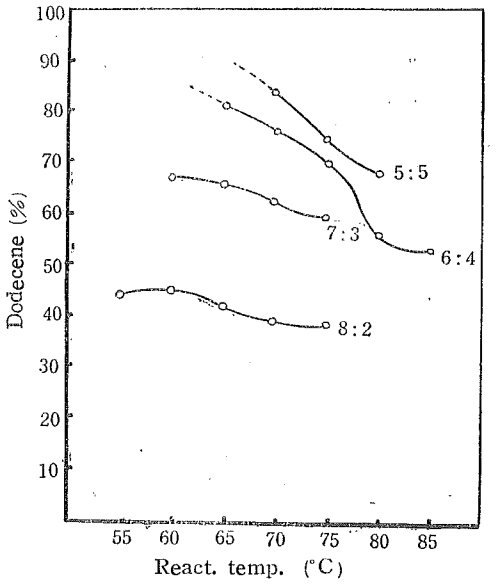


Fig. 7 Dodecene % in Polymer

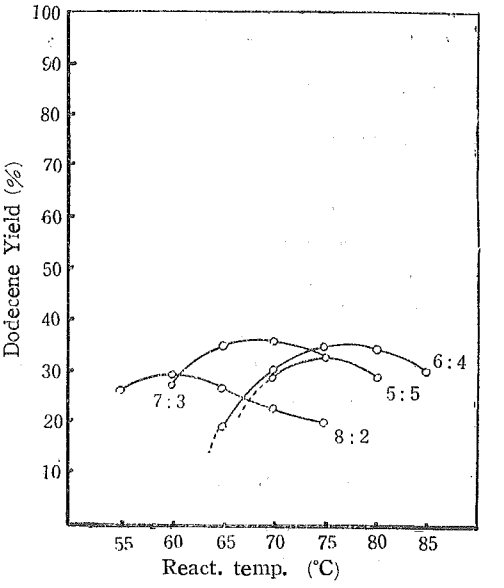


Fig. 8 Dodecene Yield

(3) Polymerization of Normal Butene with the Mixed Acid of 87% Sulfuric Acid and Pyrophosphoric Acid. (Without the Addition of Butene Tetramer.)

In this series of experiments pyrophosphoric acid was used as a component of the mixed acid in place of orthophosphoric acid. Pyrophosphoric acid was prepared by heating orthophosphoric acid at ca. 215°C. The heat treatment of orthophosphoric acid was continued until one drop of the acid gave no more yellow precipitate by addition of ammonium molybdate solution.

The pyrophosphoric acid thus prepared contained only a trace of metaphosphoric acid.

The results of this series of experiments are summarized in Tables 9 to 12, and illustrated in Figs. 9 to 12.

Table 9. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 50% / Pyrophosporic Acid 50% }

React. temp. (°C)		60	65	70	75	80	85
Conducted butene	(l, N.T.P.)	19.0	19.0	18.8	19.0	18.9	19.0
Reacted butene	(l, N.T.P.)	18.4	18.3	18.0	18.0	16.8	15.8
Conversion rate	(%)	97.0	96.5	95.7	95.0	89.0	83.3
Polymer yield	(g)	32.0	33.5	33.2	33.1	29.8	26.0
	(%)	69.5	73.3	73.7	73.5	71.0	65.8
Polymer component							
Dimer frac.	(%)	2.5	2.7	2.7	2.4	3.2	3.8
Trimer frac.	(%)	22.5	29.5	34.1	36.6	37.0	37.3
Tetramer frac.	(%)	71.3	64.0	58.5	56.1	50.4	48.9
Heavy polymer	(%)	1.9	1.8	2.4	2.4	7.1	8.0
Gas & loss	(%)	1.8	2.0	2.3	2.5	2.3	2.0

Table 10. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 60% / Pyrophosphoric Acid 40% }

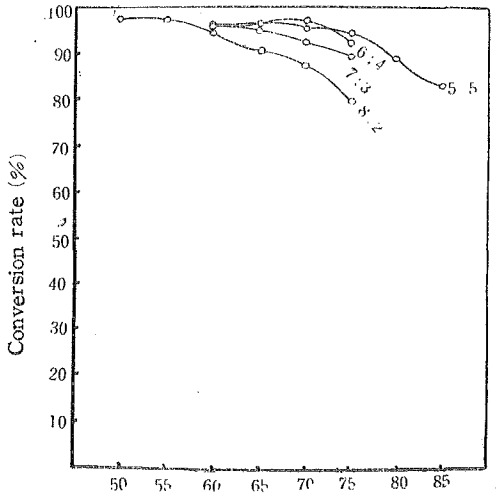
React. temp. (°C)		60	65	70	75
Conducted butene	(*l*, N.T.P.)	19.0	19.0	19.0	19.0
Reacted butene	(*l*, N.T.P.)	18.2	18.4	18.5	17.5
Conversion rate	(%)	96.0	97.0	97.5	92.3
Polymer yield	(g)	33.0	34.0	33.8	31.2
	(%)	72.5	73.6	73.2	71.4
Polymer component					
Dimer frac.	(%)	2.1	2.3	3.6	3.8
Trimer frac.	(%)	23.9	28.2	32.0	33.4
Tetramer frac.	(%)	70.7	66.0	60.4	58.4
Heavy polymer	(%)	1.5	1.5	2.3	2.6
Gas & loss	(%)	1.8	2.0	1.7	1.8

Table 11. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 70% / Pyrophosphoric Acid 30% }

React. temp. (°C)		60	65	70	75
Conducted butene	(*l*, N.T.P.)	18.9	19.0	18.9	18.9
Reacted butene	(*l*, N.T.P.)	18.0	18.0	17.4	16.9
Conversion rate	(%)	95.3	95.0	92.0	89.3
Polymer yield	(g)	31.7	32.6	29.6	26.4
	(%)	70.5	72.5	68.0	62.5
Polymer component					
Dimer frac.	(%)	2.5	3.4	4.0	2.3
Trimer frac.	(%)	23.7	24.5	29.4	26.1
Tetramer frac.	(%)	68.3	66.0	60.2	63.7
Heavy polymer	(%)	3.2	3.7	4.1	5.3
Gas & loss	(%)	2.3	2.4	2.3	2.6

Table 12. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 80% / Pyrophosphoric Acid 20% }

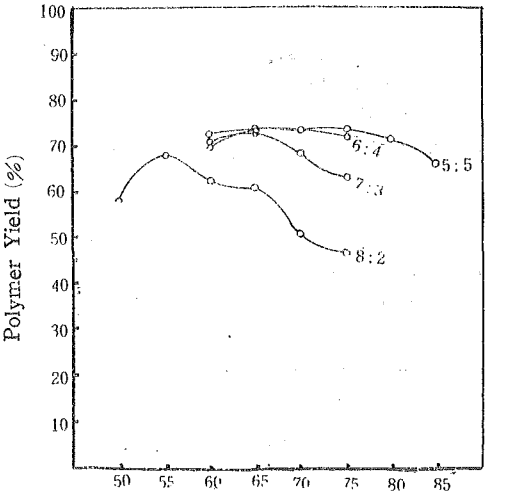
React. temp. (°C)		50	55	60	65	70	75
Conducted butene	(*l*, N.T.P.)	18.5	18.0	19.0	18.9	18.9	19.0
Reacted butene	(*l*, N.T.P.)	18.1	17.6	18.0	17.1	16.5	15.1
Conversion rate	(%)	97.6	97.6	94.6	90.5	87.5	79.7
Polymer yield	(g)	26.0	30.0	28.0	26.2	21.0	17.7
	(%)	57.7	68.4	62.3	61.2	50.8	47.0
Polymer component							
Dimer frac.	(%)	—	1.4	2.9	3.1	3.3	3.4
Trimer frac.	(%)	13.1	23.3	19.6	20.2	22.4	18.1
Tetramer frac.	(%)	67.3	60.0	71.1	68.4	63.8	65.0
Heavy polymer	(%)	14.4	11.3	4.3	5.3	6.7	9.0
Gas & loss	(%)	5.2	4.0	2.1	3.0	3.8	4.5



React. temp.(°C)

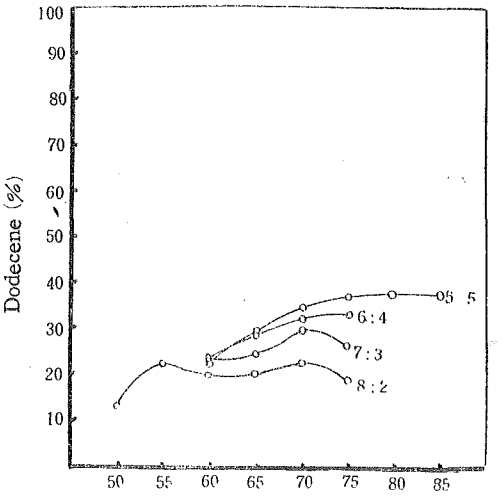
Fig. 9 Conversion Rate

Note : [8 : 2] means the mixed acid of
{87% Sulfuric acid 80%
}Pyrophosphoric acid 20%



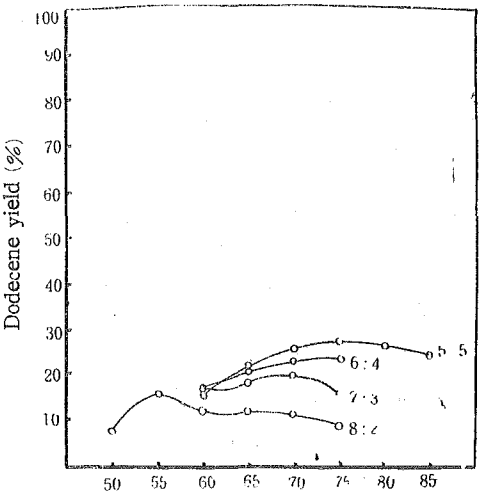
React. temp. (°C)

Fig. 10 Polymer Yield



React. temp. (°C)

Fig. 11 Dodecene % in Polymer



React. temp. (°C)

Fig. 12 Dodecene Yield

(4) Polymerization of Normal Butene with Mixed Acid of 87% Sulfuric Acid and Pyrophosphoric Acid.
(With the Addition of Butene Tetramer.)

The results of this series of experiments are summarized in Tables 13 to 16, and illustrated in Figs. 13 to 16.

Table 13. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 50% / Pyrophosphoric Acid 50% }

React. temp. (°C)		55	60	65	70	75
Conducted butene	(*l*, N.T.P.)	18.5	18.9	18.9	19.0	19.0
Reacted butene	(*l*, N.T.P.)	18.1	18.8	18.8	18.8	18.8
Conversion rate	(%)	98.0	99.6	99.7	99.0	99.0
Polymer yield	(g)	32.6	36.9	37.0	35.0	34.2
	(%)	72.0	78.5	76.7	74.5	72.7
Polymer component						
Dimer frac.	(%)	—	3.0	3.2	3.4	4.1
Trimer frac.	(%)	27.9	37.4	39.5	40.9	40.0
Tetramer frac.	(%)	66.5	57.5	55.1	53.2	52.6
Heavy polymer	(%)	2.3	—	—	0.9	1.2
Gas & loss	(%)	3.3	2.1	2.2	1.6	2.1

Table 14. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 60% / Pyrophosphoric Acid 40% }

React. temp. (°C)		55	60	65	70	75
Conducted butene	(*l*, N.T.P.)	18.5	19.0	19.0	19.0	19.0
Reacted butene	(*l*, N.T.P.)	17.9	18.8	18.8	18.8	18.7
Conversion rate	(%)	97.0	99.0	99.0	99.0	98.7
Polymer yield	(g)	32.7	35.4	34.0	33.2	30.9
	(%)	73.0	75.5	72.5	70.6	66.0
Polymer component						
Dimer frac.	(%)	1.2	5.7	5.3	5.4	4.2
Trimer frac.	(%)	24.8	33.4	42.7	37.4	34.7
Tetramer frac.	(%)	68.5	58.5	48.6	54.0	57.4
Heavy polymer	(%)	3.1	—	1.2	1.2	1.6
Gas & loss	(%)	2.4	2.4	2.2	2.0	2.1

Table 15. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 70% / Pyrophosphoric Acid 30% }

React. temp. (°C)		55	60	65	70	75
Conducted butene	(*l*, N.T.P.)	18.6	18.9	19.1	18.4	18.4
Reacted butene	(*l*, N.T.P.)	18.2	18.8	19.0	17.5	17.0

Conversion rate	(%)	98.0	99.5	99.5	95.0	92.3
Polymer yield	(g)	30.6	32.0	30.9	26.2	22.6
	(%)	67.0	68.0	65.0	60.0	53.3
Polymer component						
Dimer frac.	(%)	1.9	3.7	7.1	6.9	3.6
Trimer frac.	(%)	21.2	36.9	48.6	43.2	32.3
Tetramer frac.	(%)	68.7	55.7	40.5	44.7	57.1
Heavy Polymer	(%)	6.1	1.9	2.6	3.8	4.4
Gas & loss	(%)	2.1	1.8	1.2	1.4	2.6

Table 16. Polymerization of Normal Butene with the Mixed Acid of { 87% Sulfuric Acid 80% / Pyrophosphoric Acid 20% }

React. temp. (°C)		55	60	65	70	75
Conducted butene	(l, N.T.P.)	18.5	19.0	19.0	19.0	18.9
Reacted butene	(l, N.T.P.)	18.3	18.8	17.9	17.4	15.7
Conversion rate	(%)	99.0	99.3	94.5	91.7	83.0
Polymer yield	(g)	25.7	28.0	24.2	20.9	16.7
	(%)	56.2	59.7	54.0	48.0	42.5
Polymer component						
Dimer frac.	(%)	3.1	2.5	5.0	4.3	4.8
Trimer frac.	(%)	14.4	16.4	33.4	30.6	24.5
Tetramer frac.	(%)	74.7	75.4	55.0	58.0	59.3
Heavy polymer	(%)	5.5	2.9	3.3	3.8	6.6
Gas & loss	(%)	2.3	2.8	3.3	3.3	4.8

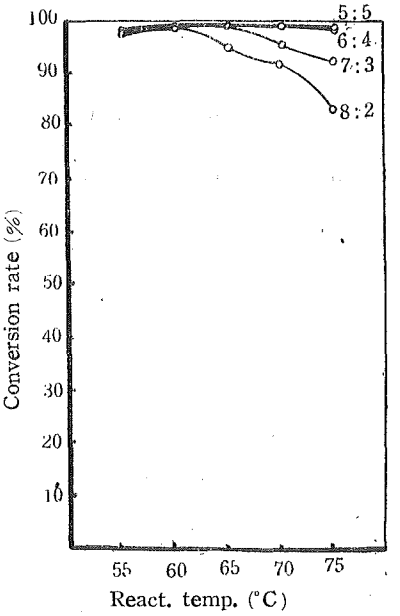


Fig. 13 Conversion Rate

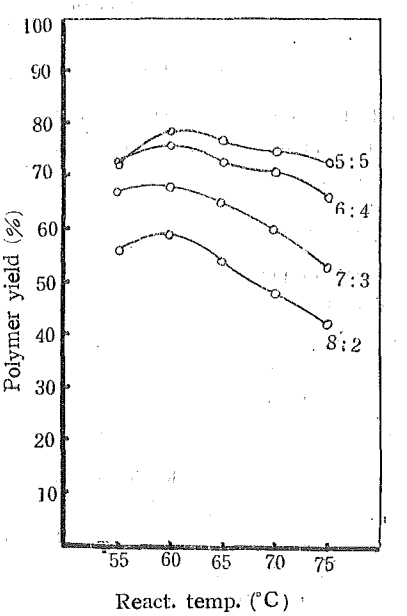


Fig. 14 Polymer Yield

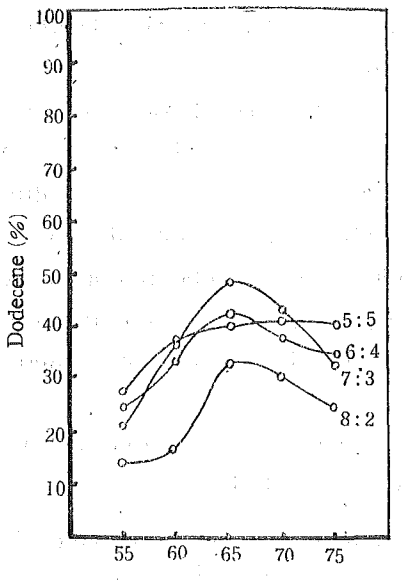


Fig. 15 Dodecene % in Polymer

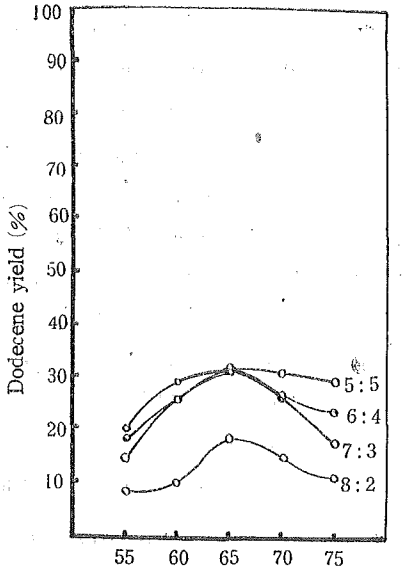


Fig. 16 Dodecene Yield

Discussion of the Results.

(1) In the presence of the mixed acid consisting of 87% sulfuric acid and 90% orthophosphoric acid, n-butene polymerized readily into liquid polymer, which was chiefly composed of trimers and tetramers of butene. In general, the trimer content of the liquid polymer decreased with the increase of the reaction temperature and with the increase of the amount of sulfuric acid in the mixed acid catalyst.

The polymer yield was 65 — 70% at maximum based on the n-butene absorbed. The maximum yield of trimer was obtained with the mixed acid of 87% sulfuric caid 60% – 90% orthophosphoric acid 40% and at the reaction temperature of 80°C. The yield was 30.5% with a tetramer production of 29.9%. The maximum yield of tetramer was 41.3% with a trimer production of 23.6%, which was obtained with the mixed acid of 87% sulfuric acid 80% – 90% orthophosphoric acid 20% and at the reaction temperature of 60°C.

It was clearly observed that the addition of butene tetramer promoted the trimer production by retarding the production of the tetramer and other higher polymers. With the addition of butene tetramer, the maximum yield of trimer was elevated to 35% with a tetramer production of only 6.8% in the presence of the mixed acid of 87% sulfuric acid 60% — 90% orthophosphoric acid 40% and at the reaction temperature of 75°C. (See Tables 1 to 8 and Figs. 1 to 8)

(2) When pyrophosphoric acid was used as a component of the mixed acid in place of 90% orthophosphoric acid, the activity of the mixed acid became much higher. Even the mixed acid of 87% sulfuric acid 50%-pyrophosphoric acid 50%

absorbed almost 100% of conducted n-butene at 60 — 85°C and the absorbed butene was converted into liquid polymer in the yield of over 70%.

The use of pyrophosphoric acid in place of orthophosphoric acid favored the tetramer production especially at low reaction temperatures. The maximum yield of trimer, which was 26.8%, was obtained with the mixed acid of 87% sulfuric acid 50%-pyrophosphoric acid 50% and at the reaction temperature of 75°C. At the same time, tetramer was produced in the yield of 41.2%. The maximum yield of tetramer was 51.2% with the trimer production of 17.3%, which was obtained with the mixed acid of 87% sulfuric acid 60%-pyrophosphoric acid 40% and at the reaction temperature of 60°C.

With the addition of tetramer, the trimer yield was increased to over 30% under optimum conditions. (See Tables 9 to 16, Figs. 9 to 16.)

(3) The mixed acid converted absorbed n-butene into liquid polymer in much larger yield than did sulfuric acid. Accordingly, the catalyst life of the mixed acid for n-butene polymerization was longer than that of sulfuric acid. But, even in the case of the mixed acid, after treating 40 liters of n-butene, the catalytic activity of the acid dropped to about one half of the value that was observed during the treatment of the first 20 litres of n-butene. Hence, elongation of the catalyst life was a matter of moment in the research. This problem will be discussed in the following paper.