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Polymerization of Olefin Gases with Sulfuric Acid Catalyst.

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I. Polymerization of Propene.

(1) Apparatus and Procedure.

Sample propene was obtained by dehydration of isopropanol with bentonite as catalyst. The reaction apparatus as shown in Fig. 1-1, was a U-shaped tube, and the larger arm of which contained many glass beads to increase contact surface. 110-115 g of sulfuric acid was used for each experiment.

Propene gas was conducted into the reaction tube from its smaller arm at a rate of 5 l/hr. Unreacted gas, after bubbling through sulfuric acid layer, was collected from the top of the larger arm of the reactor, and the polymer products separated out on the acid surface. When the waste acid was poured into cold water, dark colored oil separated on water surface, which was called "acid wash oil".

The concentrations of sulfuric acid used were 86%, 91%, 96% and 99%, and the reaction temperatures, were 0°C, 25°C, 50°C and 75°C.

(2) Experimental Results.

(i) The absorption rate of propene by sulfuric acid increased with acid concentration up to 96% acid, then slightly decreased. At 50°C, about 98% of conducted propene was absorbed by 96% acid, while the yields of polymer oil and acid wash oil were 31.2% and

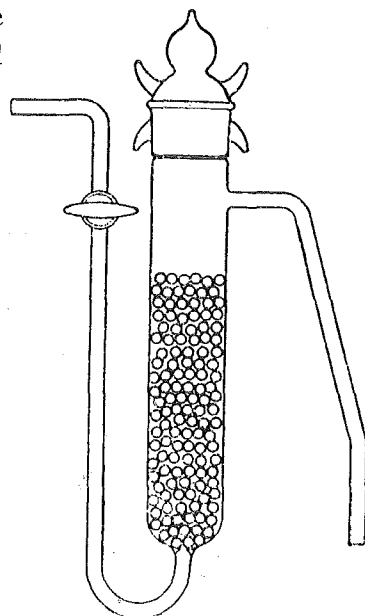


Fig. 1-1 Reaction Apparatus.

of reacted propene respectively. The maximum amount of polymer oil was obtained 21.7% by 96% acid, but yield of acid wash oil was highest with 99% acid. The effect of acid concentration, observed at 50°C, is shown in Fig. 1-2.

(ii) The optimum temperature for the production of liquid polymer was 25°C for 99% acid (49.2% of reacted propene), and 50°C for 96% acid (31.2%). In both cases, the amount of acid wash oil increased with reaction temperature.

The effect of reaction temperature, with 96% and 99% acid, is shown in Fig. 1-3 and 1-4.

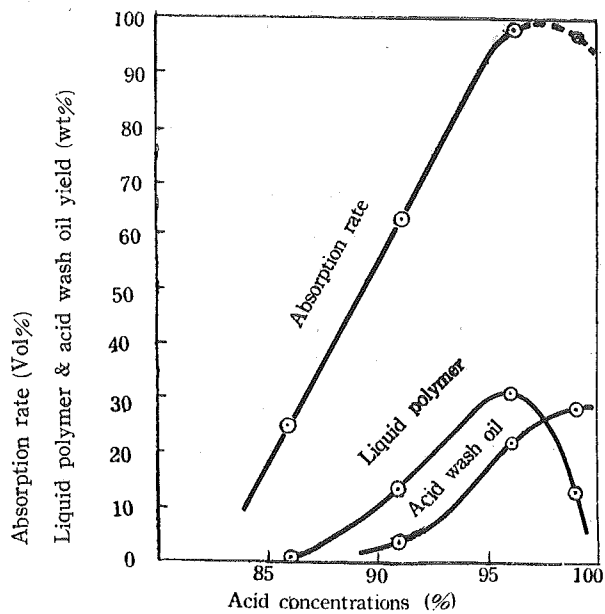


Fig. 1-2 Effect of Acid Concentration observed at 50°C

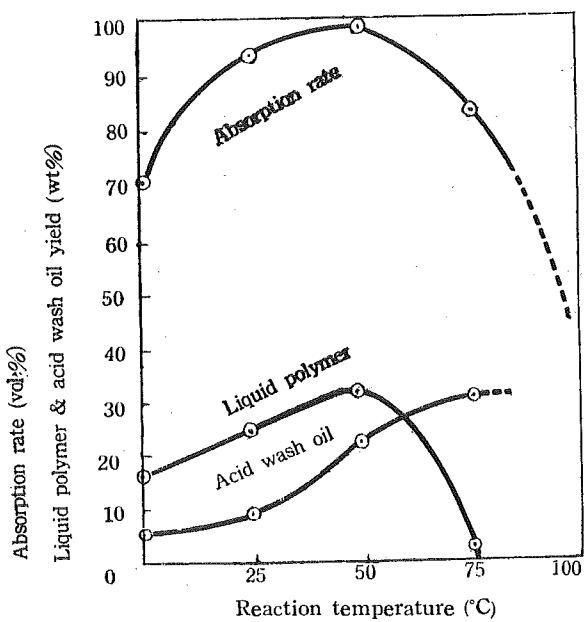


Fig. 1-3 Effect of Reaction Temperature with 96% Acid.

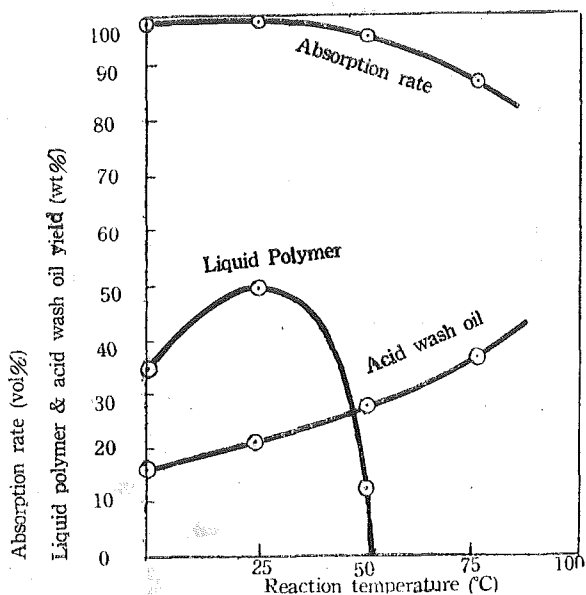


Fig. I-4 Effect of Reaction Temperature with 99% Acid.

(iii) Although propene was easily absorbed by conc. sulfuric acid, high yield of liquid polymer could not be obtained. It was probably due to the fact that isopropyl sulfate was comparatively stable under the reaction conditions, as the liquid polymer was considered to be produced by the decomposition of this ester. Hence, the sulfuric acid process was not recommendable for the production of liquid propene polymer.

(iv) The process of propene polymerization in the presence of conc. sulfuric acid seemed to be a very complicated one. It was not "true polymerization" but "conjunct polymerization". For one example, the liquid polymer obtained by 96% acid at 50°C boiled between 67.5 ~ 283°C, and was mainly consisted of paraffinic hydrocarbons instead of olefinic hydrocarbons in the case of true polymerization as shown in the following table. And an appreciable amount of sulfur trioxide evolved during the reaction. The acid wash oil was consisted of highly unsaturated hydrocarbons among which probably contained some of ring structure.

Table I-I Some Characteristics of Propene Polymer by 96% Acid at 50°C.

Fraction	Sp. gr. (D ₁₅ ¹⁵)	Mean mol. wt.	Vol. %	Components (wt.%)			
				Olefin	Arom.	Naph.	Para.
67.5~200°C	0.7427	138	49.9	4	0	0	96
200~250°C	0.7757	165.5	37.7	12	0	0	88
250~283°C	0.8157	219.0	8.3	—	—	—	—
Gas & loss			4.1				
			100.0				

II. Polymerization of Normal Butene.

(1) Apparatus and Procedure.

Reaction apparatus and polymerization procedure were just the same as used for propene polymerization. Normal butene was prepared by dehydration of normal butanol.

(2) Experimental Results.

(i) When the concentration of acid was kept constant, absorption rate of butene increased with temperature up to a certain maximum point, then slightly decreased. The optimum temperatures were 75°C for 85% acid, 50°C for 90% acid, 25°C for 95% acid and 0°C for 100% acid. The yield of liquid polymer also increased with temperature at first, but rapidly fell at higher temperatures. The temperature for yield maximum was always lower than that for absorption maximum. The yield of acid wash oil increased with temperature. Over 80% of reacted butene was converted into liquid polymer at optimum conditions.

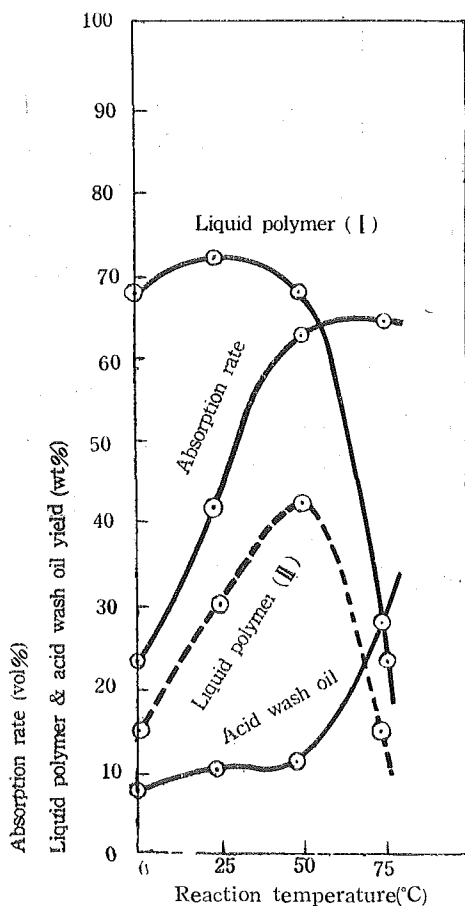


Fig. 2-1 Polymerization of n-butene with 85% acid.

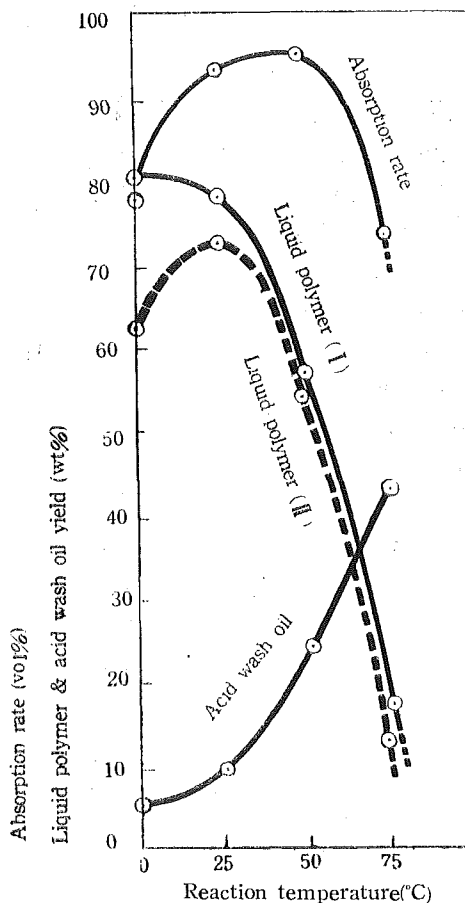


Fig. 2-2 Polymerization of n-butene with 93% acid.

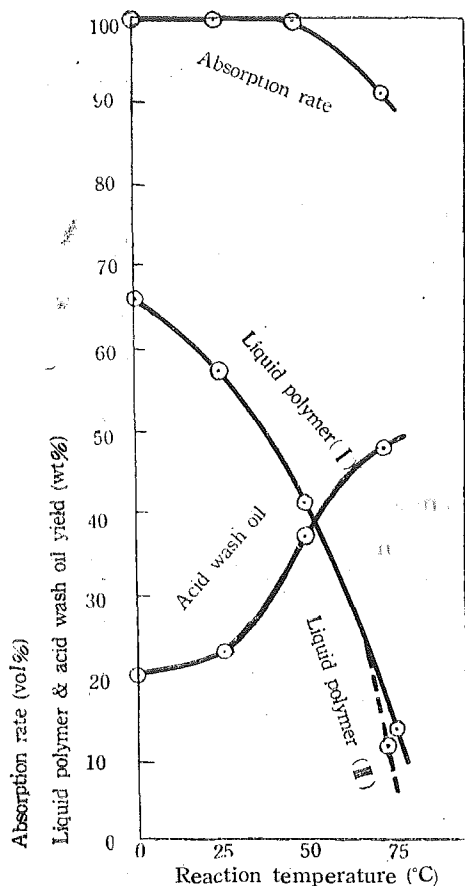


Fig. 2-3 Polymerization of n-butene with 95% acid.

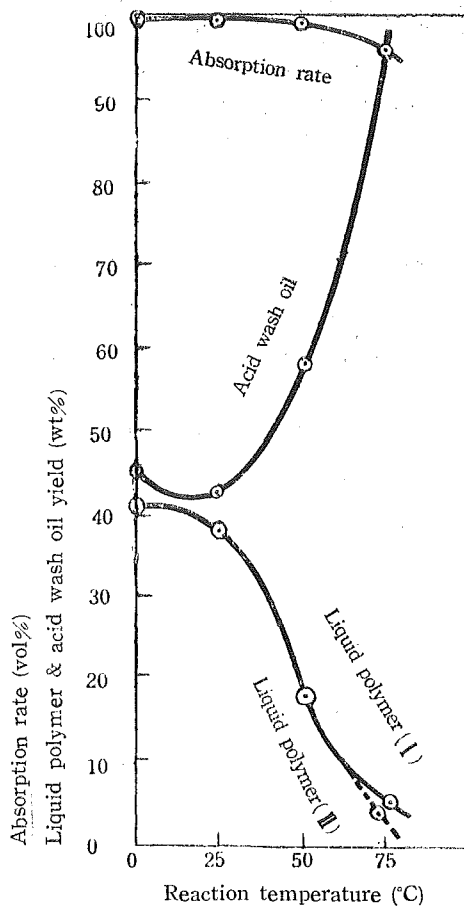


Fig. 2-4 Polymerization of n-butene with 100% acid.

Molecular weight and specific gravity of liquid polymer decreased with reaction temperature, i. e., light polymer oil was obtained at high temperatures.

(ii) At all reaction temperatures adopted, normal butene was almost totally absorbed by 95% and higher concentration acids. The absorption rate was considerably effected by a slight change in acid concentration, as it increased very rapidly with the increase of acid concentration up to 95%. The maximum yield of liquid polymer was obtained by 90% acid below room temperature.

(iii) Under the reaction conditions adopted, there prevailed conjunct polymerization of butene. But, at lower temperatures, true polymerization was mainly observed only by 85% acid. The conjunct polymerization products had a wide boiling range and lower boiling fractions of which were highly paraffinic. The existence of octanes and dodecanes was clearly observed by distillation test in the liquid polymer obtained by 90% acid.

(iv) Polymerization data were shown in Fig. 2-1 ~ Fig. 2-4. In these figures,

curve of liquid polymer (I) showed weight % to reacted butene and curve of liquid polymer (II) showed that to conducted butene.

(v) Some characteristics of liquid polymers were summarized in Table 2-1 and their distillation data in Table 2-2.

Table 2-1 Some Characteristics of
Liquid Polymers.

Expt. No.	Acid conc. (%)	React. temp. (°C)	Sp. gr. (D ₁₅ ¹⁵)	Mean mol. wt.	Bromine no.
209	85	0	0.7972	235.5	48.5
210	85	25	0.7913	231.5	36.5
211	85	50	0.7879	221.0	38.1
212	85	75	0.7600	218.0	34.5
213	90	0	0.7959	255.0	18.2
214	90	25	0.7830	226.5	26.4
215	90	50	0.7670	217.5	27.2
216	90	75	0.7560	208.5	22.5
202	95	0	0.7818	229.5	14.2
201	95	25	0.7624	187.5	17.0
203	95	50	0.7640	194.2	9.6
204	95	75	0.8120	187.3	14.1
205	100	0	0.7817	239.0	7.6
206	100	25	0.7705	233.0	2.6
207	100	50	0.7251	227.0	15.0
208	100	75	—	218.0	—

Table 2-2 Distillation Data of Liquid Polymers

Expt. No.	Acid conc. (%)	React. temp. (°C)	I. b. pt. (°C)	Dry pt. (°C)	I. b. p. ~ 150°C (vol%)	150 ~ 210°C (vol%)	210 ~ 250°C (vol%)	250 ~ dry pt. (vol%)	Residue (vol%)	Loss (by diff.)
209	85	0	125	259	—	20	46	21	11	2
210	85	25	175	277	—	8	52	26	8	6
211	85	50	110	254	5	34	30	13	12	6
212	85	75	130	266	10	25	28	16	19	2
213	90	0	124	299	1	11	19	58	8	3
214	90	25	117	287	14	10	18	42	11	5
215	90	50	112	270	17	22	25	23	11	2
216	90	75	137	268	8	27	23	17	10	15
202	95	0	106	292	12	24	17	34	12	1
201	95	25	110	280	19	33	15	15	14	4
203	95	50	110	243	20	34	31	—	13	2
204	95	75	140	276	—	33	22	20	21	4
205	100	0	93	266	21	26	21	13	12	7
206	100	25	111	227	15	42	34	—	8	1
207	100	50	116	282	3	27	21	20	17	12
208	100	75	129	303	—	28	16	30	23	3

III. Polymerization of Isobutene.

(1) Apparatus and Procedure.

Apparatus and procedure were just the same as used for propene and normal

butene polymerization already described in I. and II. Isobutene was prepared by dehydration of isobutanol.

(2) Experimental Results.

(i) Isobutene being more reactive than normal butene, maximum yield of liquid polymer was obtained near 0°C by 85 ~ 90 % acid. When concentrated acid was used, reaction temperatures higher than 25°C were quite unsuitable for the production of liquid polymer.

(ii) Reaction tendency of isobutene in the presence of sulfuric acid was very similar to that of normal butene. But, isobutene polymer contained larger amount of low boiling components and showed higher degree of unsaturation as compared with normal butene polymer. About 85% of reacted butene was converted into liquid polymer by 90% acid at 0°C, and by 85% acid at 25°C. In both cases, the yield of acid wash oil was only 1 ~ 2 %.

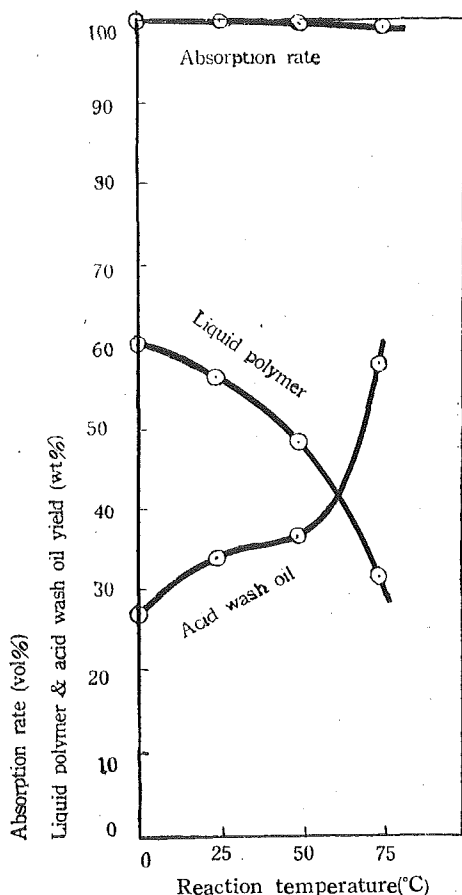


Fig. 3-1 Polymerization of i-butene with 85% acid.

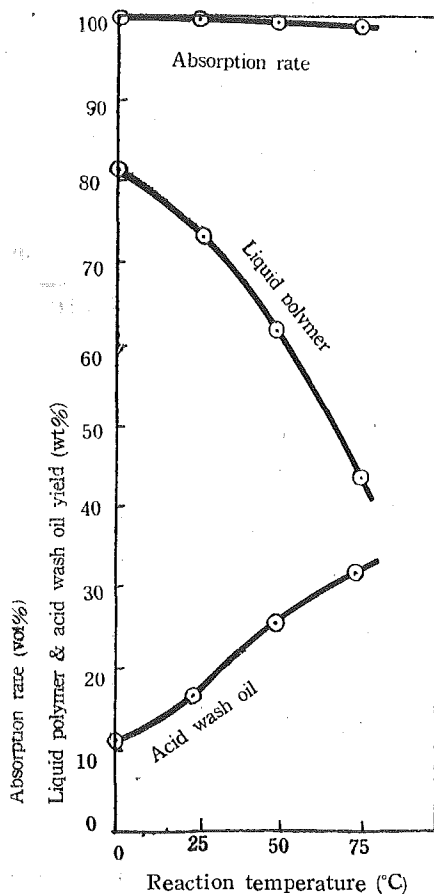


Fig. 3-2 Polymerization of i-butene with 90% acid.

(iii) Isobutene was considered to be the most suitable olefin for the production of liquid polymer by sulfuric acid polymerization.

(iv) Polymerization data were shown in Fig. 3-1 ~ Fig. 3-4.

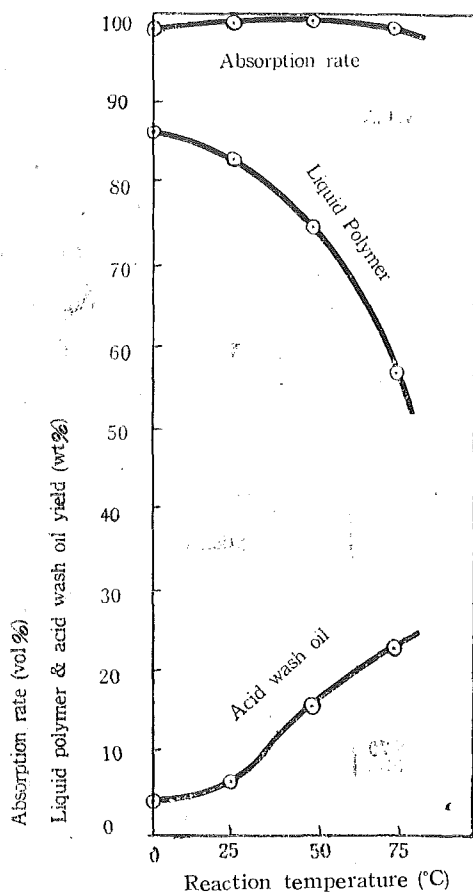


Fig. 3-3 Polymerization of i-butene with 95% acid.

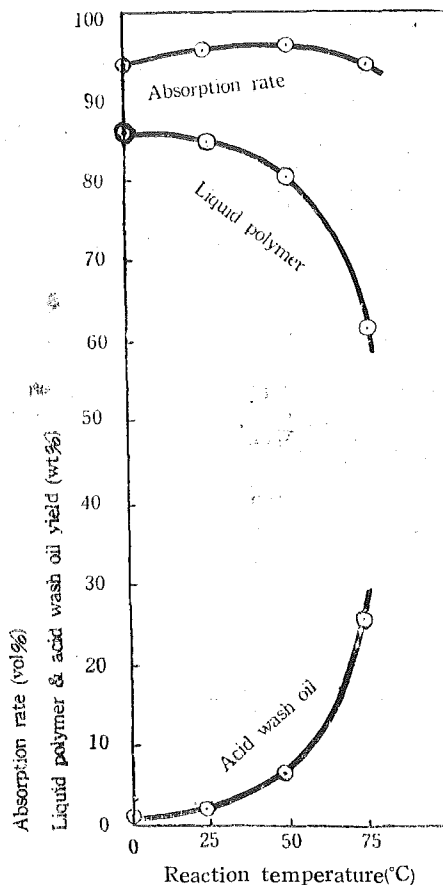


Fig. 3-4 Polymerization of i-butene with 100% acid.

(v) Some characteristics of liquid polymers were summarized in Table 3-1 and their distillation data in Table 3-2.

Table 3-1 Some Characteristics of Liquid Polymers.

Expt. No.	Acid conc. (%)	React. temp. (°C)	Sp. gr. (D_{15}^{15})	Mean mol. wt.	Bromine no.
217	85	0	0.7869	233.6	60.0
218	85	25	0.7796	208.5	57.4
219	85	50	0.7763	200.1	56.9
221	85	75	0.7713	182.4	67.6
221	90	0	0.7807	215.7	45.3
222	90	25	0.7791	193.2	52.7
223	90	50	0.7723	187.3	46.3
224	90	75	0.7747	169.9	58.0

225	95	0	0.7819	232.6	18.0
226	95	25	0.7818	220.5	18.6
227	95	50	0.7849	211.6	17.7
228	95	75	0.7843	190.7	31.8
229	100	0	0.7820	232.7	17.7
230	100	25	0.7832	211.3	18.3
231	100	50	0.7814	200.9	18.4
232	100	75	0.7882	187.6	22.2

Table 3-2 Distillation
Data of Liquid Polymers.

Expt. No.	Acid conc. (%)	React. temp. (°C)	Lb. pt. (°C)	Dry pt. (°C)	Lb. p. ~ 150°C (vol%)
217	85	0	144	266	—
218	85	25	133	281	—
219	85	50	136	284	12
220	85	75	116	217	9
221	90	0	108	276	12
222	90	25	90	247	14
223	90	50	116	246	12
224	90	75	140	273	4
225	95	0	112	304	7
226	95	25	115	216	22
227	95	50	110	273	5
228	95	75	113	233	—
229	100	0	106	285	8
230	100	25	108	288	13
231	100	50	114	282	8
232	100	75	169	276	—

Expt. No.	150~210°C (vol%)	210~250°C (vol%)	250~ dry pt. (vol%)	Residue (vol%)	Loss (by diff.)
217	49	19	27	2	3
218	44	30	16	5	5
219	49	23	—	14	2
220	70	12	—	9	0
221	30	18	30	6	4
222	49	30	—	5	2
223	50	23	—	14	1
224	60	19	6	10	1
225	22	21	31	10	9
226	58	8	—	8	4
227	21	24	30	17	3
228	43	41	—	12	4
229	17	22	35	18	0
230	15	17	39	9	7
231	20	20	27	22	3
232	17	23	32	22	6

IV. Polymerization of Isobutene with Concentrated Sulfuric Acid by Means of Packed-tower Type Reactor.

(1) Apparatus and Procedure.

The reaction apparatus, as shown in Fig. 4-1, was a packed tower, which

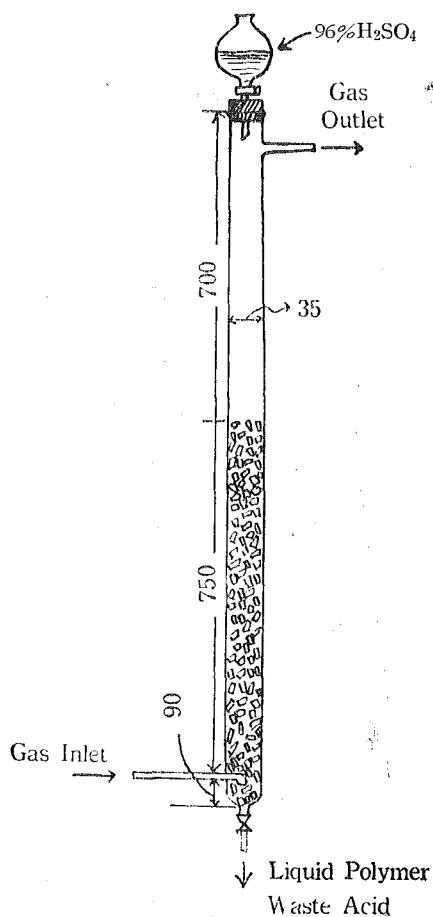


Fig. 4-1 Reaction Apparatus.

contained a large number of 0.5 cm dia. and 2 cm long glass chips. 96% sulfuric acid was added from the top of the reactor and was contained in the packing zone of the tower. Sample isobutene entered the reactor from an inlet tube at its bottom and, while bubbling up through acid layer, a large portion of which was absorbed and polymerized. The unreacted gas left the reactor through an outlet tube at its top. The liquid polymer, which condensed on the acid surface, was withdrawn from the bottom together with the waste acid. The acid wash oil was recovered from the waste acid as described in I.

(2) Experimental Results.

(i) Experimental data for isobutene polymerization were summarized in Table 4-1.

Table 4-1 Polymerization Data.

Exp. No.	140	141	142	143	144	145
sulfuric acid wt. (g)	1290	736	552	368	184	33
used vol. (cc)	700	40	300	200	100	(2)
sample olefin vol. (l/ N. T. P.)	110	113	107.5	126.8	115.2	69.2
acid-olefin ratio (wt.)	4.7:1	2.6:1	2.05:1	1.16:1	0.64:1	0.19:1
React temp. (°C)	25	23	23	20	21	18
Rate of gas flow (l/hr)	110	113	129	143	115	104
Reacted olefin vol. (l/ N. T. P.)	110	113	107.5	126.8	115.2	57.6
Absorption rate (%)	100	100	100	100	100	83.3
Liquid polymer						
{ vol. (cc)	225	250	230	260	303	150
{ yield (%)	63.5	69.5	67.7	65.3	84.2	81.7
Sp. gr. of polymer (D ₁₅ ¹⁵)	0.7763	0.7831	0.7911	0.7950	0.7987	0.7838
Acid wash oil						
{ vol. (cc)	74	73	69	51	30	0
{ wt. (g)	64.4	63	62	48	27	0
{ yield (%)	23.4	24.1	23.0	15.1	9.4	0

(ii) Distillation data of liquid polymers were shown in Table 4-2.

Table 4-2 Distillation Data of Liquid polymers.

Expt. No.	140	141	142	143	144	145
acid-olefin ratio	4.7:1	2.6:1	2.05:1	1.16:1	0.64:1	0.19:1
Init. b. pt. (°C)	26	36	67	35	36	25
Dry pt. (°C)	265	274	284	268	258	230
I. b. p. ~100°C (%)	8.2	6.4	3.4	5.2	2.1	18.4

(1) At first, 400cc of acid was contained in the reactor, and 300cc of acid was added continuously during the experiment. Waste acid was also withdrawn continuously to keep the level of acid layer constant.

(2) Acid was used as thin film on glass packing surface.

100~150°C	(%)	10.3	17.0	12.1	9.6	6.4	26.6
150~200°C	(%)	21.9	18.6	13.8	10.2	17.0	45.5
~200°C total	(%)	40.4	42.0	29.3	25.0	25.5	90.5
200~250°C	(%)	16.6	22.6	16.6	16.0	42.6	—
250~Dry pt.	(%)	22.9	24.1	42.7	46.2	19.2	—
Residue	(%)	19.2	10.6	11.2	12.8	11.9	7.8
Loss	(%)	0.9	0.7	0.2	0	0.8	1.7

(iii) Some characteristics of liquid polymers were shown in the following Table 4 - 3.

Table 4-3 Some Characteristics of Liquid Polymers.

Expt. No.		140	141	142	143	144	145
200°C frac. I. b. p. ~200°C frac.	Sp. gr. (D_{15}^{15})	0.732	0.751	0.749	0.752	0.771	0.763
	Br. no.	2.4	4.7	5.1	16	65	84
	96% H_2SO_4 soluble (wt%)	21.3	31.0	28.4	47.8	71.7	87.8
	Sp. gr. of 96% H_2SO_4 insoluble (D_{15}^{15})	0.731	0.732	0.732	0.701	0.735	0.746
	Aniline pt. of " (°C)	80	81	81	81	80	82.8
200~250°C frac.	Sp. gr. (D_{15}^{15})	0.788	0.813	0.789	0.782	0.810	—
	96% H_2SO_4 soluble (wt%)	27.8	68.9	58.7	46.6	78.3	—
	Sp. gr. of 96% H_2SO_4 insoluble (D_{15}^{15})	0.763	0.781	0.771	0.777	0.764	—
	Aniline pt. of " (°C)	87	90	87	88	86	—
250°C over frac.	Sp. gr. (D_{15}^{15})	0.825	0.825	0.815	0.814	0.816	—
	96% H_2SO_4 soluble (wt%)	60.1	92.7	78.8	84.6	92.8	—
	Sp. gr. of 96% H_2SO_4 insoluble (D_{15}^{15})	0.799	0.788	0.797	0.785	0.802	—
	Aniline pt. of " (°C)	92	92	92	89	86.5	—

(iv) The values of acid-olefin ratio were comparable to the contact time between olefin and acid. As shown in experimental results, only a small amount of acid was necessary to convert total isobutene into polymer. The existence of excess acid did not increase polymer yield, but it gave great influences on the properties of liquid polymer. Low conversion rate in Expt. 145 might be explained by the fact that thin acid film was gradually washed away during experiment.

(v) In Expt. 145, with the smallest amount of acid, there prevailed true polymerization. The main components of liquid polymers were dimer and trimer of isobutene. In Expt. 144, with the acid-olefin ratio 0.64: 1, true polymerization was still predominant. But, the liquid polymer became rich in high boiling compo-

nents. With higher acid-olefin ratios, conjunct polymerization occurred appreciably. Low boiling fraction of the liquid polymers became paraffinic and high boiling fraction contained unsaturated hydrocarbons of complex structure.

(vi) Precise investigation showed that the acid wash oil contained unsaturated ring hydrocarbons.

V. Polymerization of Isobutene with Concentrated Sulfuric Acid at Low Temperatures.

(1) Apparatus and Procedure.

The reaction apparatus was a three-necked flask equipped with a stirrer. Sample isobutene gas was liquefied in the flask cooled at -20°C . 96% sulfuric acid was added dropwise under stirring. The acid addition had to be regulated not to rise the liquid temperature above -20°C . After total acid was added, stirring was continued for a certain duration of time. The reaction time included time required for acid addition. When the reaction was over, the acid layer was syphoned out and the hydrocarbon layer was warmed to room temperature to expel unreacted isobutene. The liquid polymer thus obtained was then washed, dried and distilled.

(2) Experimental Results.

(i) The data of polymerization experiments were shown in Table 5-1.

Table 5-1 Polymerization of Isobutene at Low Temperatures.

Expt. No.	167	169	170	171	172
React. temp. ($^{\circ}\text{C}$)	-20	-20	-20	-20	-20
React. time (hr)	1/4	1	1/4	1	2
Acid-olefin ratio	0.12:1	0.056:1	0.24:1	0.12:1	0.056:1
Sample olefin vol. (N. T. P. gas)	92.1	47.8	48.2	48.6	47.7
Reacted olefin vol. (N. T. P. gas)	92.1	28.8	48.2	48.6	32.8
Absorption rate (%)	100	60.0	100	100	69
Liquid polymer (cc)	245	59	123	143	66
Sp. gr. of polymer (D_{25}^{25})	0.7838	0.7488	0.7826	0.7665	0.7408
Liquid polymer yield (%)	84	62	80	91	69
Dist. test of liquid polymer					
Init. b. pt. ($^{\circ}\text{C}$)	30	20	33	20	20
Dry pt. ($^{\circ}\text{C}$)	218.5	164	238.7	233	176.5
Dimer fraction ($\sim 150^{\circ}\text{C}$) (%)	48.8	47.6	27.5	33.0	44.7
Trimer fraction ($150\sim 210^{\circ}\text{C}$) (%)	26.1	40.0	37.7	43.2	38.2
Dimer/Trimer ratio	1:0.53	1:0.84	1:1.37	1:1.31	1:0.85

(ii) It was possible to obtain comparatively low boiling polymers by true polymerization in the presence of concentrated sulfuric acid at low temperatures below 0°C. But, for the production of butene dimer, phosphoric acid polymerization gave better results. The liquid polymers by phosphoric acid polymerization usually had the dimer/trimer ratio of 1:0.2, while the best dimer/trimer ratio in the current experiments with sulfuric acid was 1:0.53 in Expt. 167.

VI. Polymerization of Butenes with Pumice Catalyst Impregnated with Concentrated Sulfuric Acid.

(1) Apparatus and Procedure.

The reaction apparatus was just the same as used for the experiments described in Chapter IV. But, instead of glass packings, small pieces of pumice impregnated with concentrated sulfuric acid were contained in the reactor. Almost all liquid polymer was withdrawn from the bottom of the reactor. 96% and 90% acids were used. Experiments were conducted at room temperature and afterwards at low temperatures.

(2) Experimental Results.

(i) Preliminary experiments, shown in Table 6-1~6-5, gave the following conclusions.

(a) Isobutene was the best charging stock for "solid sulfuric acid" polymerization. It gave liquid polymer in good yield. While, normal butene was quite unsuitable for this purpose, its sulfuric acid ester being stable at room temperature.

(b) 90% acid gave better results than 96% acid in polymer yield and catalyst life.

(c) Isobutene had some activity to decompose normal butene ester and change it into polymer.

Table 6-1. Polymerization of Isobutene with
90% H₂SO₄-Pumice Catalyst.

H ₂ SO ₄ : 84 g	Pumice : 100 g		Olefin flow rate : 5 l/hr		
Expt. No. (5 runs)	3-1	3-2	3-3	3-4	3-5
Sample olefin vol. (l/ N. T. P)	9.82	10.50	9.35	8.91	9.27
Absorbed olefin vol. (l/ N. T. P.)	9.81	10.04	9.35	8.89	9.22
Absorption rate (%)	99.9	99.9	100	99.7	99.5
Liq. polymer / ^{10 l} sample olefin (cc)	23.9	24.8	21.9	20.8	25.4
Liq. polymer / ^{10 l} absorbed olefin (cc)	23.9	24.8	21.9	20.9	25.6
Sp. gr. of liq. polymer (D ₄ ²⁰)	0.7839	0.7582	0.7569	0.7515	0.7742
Acid sludge / ^{10 l} sample olefin (cc)	7.6	3.5	2.9	3.1	3.9

Table -2 Polymerization of Isobutene with
96% H₂SO₄-Pumice Catalyst.

H ₂ SO ₄ : 72 g		Pumice 100 g		Olefin flow rate : 5 l/hr	
Expt. No. (5 runs)	1 - 1	1 - 2	1 - 3	1 - 4	1 - 5
Sample olefin vol. (l/ N. T. P.)	10.05	9.9	10.3	10.1	10.4
Absorption rate (%)	99.9	99.9	99.9	99.9	99.9
Liq. polymer / ^{10 l} Sample olefin (cc)	18.1	17.5	21.7	20.2	19.6
Sp. gr. of liq. polymer (D ₁₅ ⁴)	0.7758	0.7608	0.7560	0.7556	0.7543
Acid sludge / ^{10 l} Sample olefin (cc)	6.9	3.5	3.6	2.4	1.5

Table 6-3 Polymerization of n-Butene with
96% H₂SO₄-Pumice Catalyst.

H ₂ SO ₄ : 76 g		Pumice : 126 g		Olefin flow rate : 5 l/hr	
Expt. No. (5 runs)	5 - 1	5 - 2	5 - 3	5 - 4 *	5 - 5
Sample olefin vol. (l/ N. T. P.)	10.05	9.25	8.90	9.05	9.57
Absorbed olefin vol. (l/ N. T. P.)	9.99	6.95	3.19	5.08	3.11
Absorption rate (%)	99.4	75.0	35.8	56.2	32.5
Liq. polymer / ^{10 l} sample olefin (cc)	1.1	0.8	0.7	0.6	0.3
Liq. polymer / ^{10 l} absorbed olefin (cc)	1.1	1.2	2.2	1.2	0.96
Sp. gr. of liq. polymer (D ₁₅ ⁴)	—	—	—	—	—
Acid sludge / ^{10 l} sample olefin (cc)	8.8	2.3	3.8	3.8	3.9

Table 6-4 Polymerization of n-Butene with
90% H₂SO₄-Pumice Catalyst.

H ₂ SO ₄ : 58 g		Pumice : 126 g		Olefin flow rate : 5 l/hr	
Exp. No. (5 runs)	6 - 1	6 - 2	6 - 3	6 - 4 *	6 - 5 *
Sample olefin vol. (l/ N. T. P.)	9.59	8.78	9.40	9.74	7.68
Absorbed olefin vol. (l/ N. T. P.)	9.50	7.29	4.54	2.67	4.24
Absorption rate (%)	99.1	83.0	48.3	27.4	55.2
Liq. polymer / ^{10 l} sample olefin (cc)	1.9	2.1	0.5	0.3	0.3
Liq. polymer / ^{10 l} absorbed olefin (cc)	1.9	2.5	1.1	1.1	0.7
Acid sludge / ^{10 l} sample olefin (cc)	12.2	5.7	6.6	7.0	6.9

* These runs were conducted after draining the acid sludge over night.

Table 6-5 Polymerization of Isobutene with
the Waste Catalyst used for Expt. 6.

Catalys : 121 g		Olefin flow rate : 5 l/hr.			
Expt. No. (4 runs)	7 - 1	7 - 2	7 - 3	7 - 4	
Sample olefin vol. (l/ N. T. P.)	9.60	9.38	9.30	10.25	
Absorbed olefin vol. (l/ N. T. P.)	9.13	7.79	7.65	7.98	
Absorption rate (%)	95.1	83.0	81.1	77.8	
Liq. polymer / ^{10 l} sample olefin (cc)	21.4	22.2	24.0	21.8	
Liq. polymer / ^{10 l} absorbed olefin (cc)	22.4	26.7	29.2	26.7	
Sp. gr. of liq. polymer (D ₁₅ ⁴)	0.7705	0.7608	0.7739	0.7543	
Acid sludge / ^{10 l} sample olefin (cc)	2.5	1.6	1.7	0.4	

(ii) Comparative polymerization experiments were conducted with a large amount of isobutene in the presence of 90% acid-pumice and 96% acid-pumice catalysts, and those verified the conclusions obtained by the preliminary experiments (See (i) (a) and (b)). The experimental results were summarized in Table 6 - 6.

 Table 6-6 Comparative Polymerization Experiments with
90% H₂ SO₄ -Pumice and 96% H₂ SO₄ -Pumice Catalysts.*

Expt. No.	2	4
No. of runs	21	17
Conc. of H ₂ SO ₄ (%)	96	90
H ₂ SO ₄ (g)	98	151
Pumice (g)	210	210
Olefin vol. used for each run (l/ N. T. P.)	ca. 10	ca. 21
Olefin flow rate (l/hr)	5	5
Sample olefin vol. (l/ N. T. P.)	198.4	302.2
Absorbed olefin vol. (l/ N. T. P.)	188.5	291.3
Absorption rate (%)	95.0	96.2
Liq. polymer/10 l sample olefin (cc)	21.0	24.2
Liq. polymer/10 l absorbed olefin (cc)	22.0	25.6

(iii) As shown in Table 6 - 7 and 6 - 8, the composition of liquid polymer changed with the reaction time. The liquid polymer became richer and richer in low boiling components according as the reaction time passed.

* Experiments were discontinued, when absorption rate dropped to 85%.

Table 6-7. Distillation Data of Isobutene Polymer
with 90% Acid Catalyst.

Expt. No.	I. b. pt. (°C)	Dry pt. (°C)	I. b. pt. ~150°C frac. (%)	150~210°C frac. (%)	210~dry pt. frac. (%)	Residue (%)
2-1, 2-2	38	235	28.0	55.2	13.7	3.1
2-3, 2-4	27	224	37.8	51.9	6.5	3.8
2-5, 2-6	31	215	45.6	44.8	6.8	2.8
2-7, 2-8	54	214	51.8	41.0	4.7	2.5
2-9, 2-10	60	205	53.9	44.0	—	2.1
2-11, 2-12	30	169	56.9	40.4	—	2.7
2-13, 2-14	66	184.5	58.3	40.9	—	0.8
2-15, 2-16	36	181	61.0	38.3	—	0.7
2-17, 2-18	—	—	—	—	—	—
2-19, 2-20	36	201	—	—	—	—

Table 6-8. Distillation Data of Isobutene Polymer
with 90% Acid Catalyst.

Expt. No.	I. b. pt. (°C)	Dry pt. (°C)	I. b. pt. ~150°C frac. (%)	150~210°C frac. (%)	210~dry pt. frac. (%)	Residue (%)
4 — 1	51.5	242	20.3	61.8	16.9	2.0
4 — 2	75	225	26.8	58.1	12.6	2.5
4 — 3	103	183	36.2	55.4	—	10.4
4 — 4	43	207	41.6	55.4	—	2.0
4 — 5	36	203	46.3	55.4	—	0.3
4 — 6	38	214	47.6	46.7	4.6	1.1
4 — 7	36	210	36.0	62.2	—	1.8
4 — 8	37	205	49.5	48.4	—	2.1
4 — 9	35	204	45.5	54.5	—	0
4 — 10	34	206	61.9	38.1	—	0
4 — 11	84	207	48.8	50.9	—	0.3
4 — 12	49	214	59.0	34.4	4.4	2.2
4 — 13	58	203	58.3	41.4	—	0
4 — 14	54	210	53.6	46.4	—	0
4 — 15	36	198	64.3	35.7	—	0
4 — 16	41	175	64.9	35.1	—	0
4 — 17	44	198	58.4	41.6	—	0

(iv) Polymerization experiments with mixed gas of isobutene and normal butene were also conducted. The summarized results were shown in Table 6-9.

Table 6-9 Polymerization of Mixed Gas of Isobutene and Normal Butene with Sulfuric Acid-Pumice Catalyst.

	96% Acid : 70~85 g		Pumice : 100g		Olefin flow rate : 5 l/hr		
Expt. No.	13	12	10	9	14	16	17
No. of runs*	5	5	5	5	5	5	5
i-Butene/n-butene ratio	1:9	2:8	4:6	5:5	6:4	8:2	9:1
Total olefin vol. (l/N.T.P.)	46.4	48.3	46.2	48.1	46.7	47.3	46.6
Absorbed olefin vol. (l/N.T.P.)	36.5	41.4	42.7	46.3	45.2	47.2	46.5
Mean absorption rate (%)	78.8	83.7	92.5	96.2	96.8	99.8	99.9
Total Liquid polymer (cc)	11.7	39.5	56.0	73.6	84.5	107	101
Liq. polymer/absorbed olefin (cc)	3.2	9.8	13.1	15.9	18.7	22.6	21.9

As shown in Fig. 6-1, the larger was the amount of isobutene in the mixed gas, the longer was the life of the catalyst.

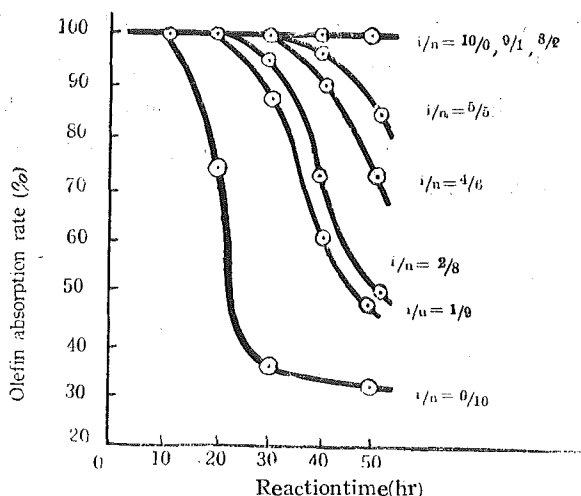


Fig. 6-1 Relation between Isobutene-Normal Butene Ratio and Catalyst Life.

Pure isobutene produced 21.9 cc of liquid polymer and pure normal butene 1.1 cc of liquid polymer per 10 l of absorbed gas respectively. Hence, the 50/50 mixture of isobutene and normal butene was to produce 11.5 cc of liquid polymer, assuming both olefins reacted independently. While, as shown in Table 6-9, the mixture produced 15.9 cc of liquid polymer. In this case, normal butene was changed into liquid polymer in better yield in the presence of isobutene than in the case of pure normal butene alone. This fact was probably due to the inter-

*Ca. 10 l gas was used for each run.

polymerization of both olefins.

(v) In the experiments above described, polymerization was conducted at room temperature (20–25°C). In a series of experiments, the reactor was cooled at 13°C by means of water jacket. In this case, for example, 84.7 l of isobutene was introduced in the reactor at a flow rate of 5 l/hr, and 99.9% of isobutene was absorbed to yield 26.8 cc of liquid polymer per 10 l of reacted isobutene. Hence, it may be concluded that low reaction temperature favors liquid polymer production.

(vi) In the packed-tower type reactor, polymerization reaction was observed to occur at first in the lowest small portion of the catalyst. And, when all the sulfuric acid in that portion seemed to become inactive, the reaction zone moved into the next higher portion of the catalyst. The liquid polymer flowed down through the waste catalyst and was collected at the bottom of the reactor. The higher was the flow velocity of olefin, self-evidently the wider was the reaction zone in the catalyst. Specific gravity of liquid polymer increased with the increase of flow velocity. This fact may be explained as following: As mentioned above, when the flow velocity of olefin was high, polymerization reaction took place in a comparatively wide range of the catalyst tower. So, on the average, the liquid polymer flowed down through a thick layer of catalyst. This caused further polymerization of liquid polymer to increase its specific gravity. In the case of low flow velocity, the reaction zone being narrow, there occurred no appreciable secondary polymerization of liquid polymer due to the residual activity of the waste catalyst.

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