

ENCLOSURE (B)2

SUMMARY

To prepare an aviation gasoline from iso-butene, it was found that the ~~best catalyst for polymerization was a mixture of phosphoric acid and barium sulphate.~~ Iso-octane prepared from n-butene by use of this catalyst was hydrogenated to iso-octane consisting of 2, 3, 4-trimethyl pentane, 2, 2, 3-trimethyl pentane and 2, 2, 4-trimethyl pentane.

I - INTRODUCTION

The polymerizing action of sulphuric acid and phosphoric acid has been known for some time, and when the lower polymerides of iso-butene are required, polymerization is most conveniently effected by acid catalyst, e.g. sulphuric or phosphoric acid. Phosphoric acid is one of the most successful polymerization catalysts, in supported form, so-called "solid phosphoric acid" catalyst, in commercial use on a large scale in the production of high octane number polymer gasolines from cracked gasolines.

The author (H. FUJIMOTO) supposed that the polymerization activity of solid phosphoric acid catalyst depends on the catalyst support and studied, from 1937 to 1939 at TOKUYAMA, various materials such as $BaSO_4$, $CaSO_4$, $PbSO_4$, MgO , HgO , SiO_2 , $Mn_3(PO_4)_2$, $Ni_3(PO_4)_2$, H_3PO_4 , and $Hg_4P_2O_7$ as supports and found that sulphates of Ba, Ca and Sr were the most successful materials for polymerization of iso-butylene. A catalyst composed of 95% of $BaSO_4$ and 5% of H_3PO_4 was used in a commercial unit at TOKUYAMA, (employing C_3 and C_4 hydrocarbon gas mixture as feed stock) and it was indicated that the catalyst gave better results with regard to activity and especially in its selectivity, compared with U. O. P. catalyst.

Next Y. MCMOTARI and Y. KAKIUCHI tried to prepare high octane gasoline by polymerizing n-butene in the presence of the above mentioned catalyst and to analyze it by means of Raman effect.

II - DETAILED DESCRIPTION

A diagram of the test apparatus used in the following experiments is given in Figure 1(B)2.

A. POLYMERIZATION OF ISO-BUTENE

Experimental results on polymerization of iso-butene at atmospheric pressure in the presence of the various catalysts are shown in Table I(B)2. The iso-butenes were prepared from iso-butanol by decomposition over alumina at 450°C. Catalyst size was about 5 mesh.

TABLE I(B)2

	H_3PO_4 (wt %)	Temp. (°C)	Gas S.V. (V/v/hr.)	Yield of Polymer (wt %)
$BaSO_4$	5-10	125-150	270	90
$CaSO_4$	10-20	125-150	500	90
$PbSO_4$	5-15	125	500	80
MgO	71	125	275	80
HgO	25 and 40	120	100	80
SiO_2	30	170	40	72
$Mn_3(PO_4)_2$	55-60	125	500	68
$Ni_3(PO_4)_2$	40	150	36	65
$Hg_3P_2O_7$	0	200	280	16
$Hg_4P_2O_7$	0	180	200	80

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On the basis of the above data BaSO_4 and H_3PO_4 appeared to be the most effective catalyst. The following data were obtained to determine the optimum composition and operating conditions for this catalyst.

TABLE II(B)2

	Reaction Temp. (°C)	Gas rate (cc/hr/cc)	Polymer (%)	d_{40}^{20} of Polymer
$\text{BaSO}_4:\text{H}_3\text{PO}_4 =$ 95:5	75	300	52.2	0.7136
	100	300	81.3	0.7220
	125	300	88.6	0.7236
	150	300	92.6	0.7246
	175	300	86.8	0.7205
	200	300	78.8	0.7124
$\text{BaSO}_4:\text{H}_3\text{PO}_4 =$ 90:10	75	300	69.8	0.7245
	100	300	77.8	0.7172
	125	300	88.2	0.7234
	150	300	86.4	0.7242
	175	300	86.1	0.7207
	200	300	73.2	0.7182
$\text{BaSO}_4:\text{H}_3\text{PO}_4 =$ 85:15	125	300	58.0	0.7186
	150	300	63.0	0.7175
	175	300	80.3	0.7206
	200	300	81.1	0.7171
	225	300	72.1	0.7163
$\text{BaSO}_4:\text{H}_3\text{PO}_4 =$ 80:20	100	300	26.3	0.7221
	125	300	60.1	0.8171
	150	300	75.2	0.7144
	175	300	84.1	0.7148
	200	300	78.0	0.7147
	225	300	67.2	0.7136
$\text{BaSO}_4:\text{H}_3\text{PO}_4 =$ 75:25	125	300	24.3	0.7238
	150	300	57.5	0.7215
	175	300	68.6	0.7182
	200	300	70.8	0.7136
	225	300	75.8	0.7140

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B. POLYMERIZATION OF n-BUTENES

Experiments showed that n-butenes react with $H_3PO_4-BaSO_4$ (10:90) catalyst at relatively low temperatures and under atmospheric pressure to form high octane number polymer. These results were as follows:

1. Relative rates of polymerization of 1-butene and 2-butene

1-Butene was obtained from normal butanol by dehydration in the presence of alumina at 400°C with purity of 94.7%, as determined by the low temperature fractional distillation method of Podbielniak; 2-butene was prepared from 2-butanol with purity 98.8%.

TABLE III(B)2

	1-butene	2-butene
Temp. (°C)	150	150
Pressure	atmospheric	atmospheric
Gas rate cc/hr/cc cat	150	150
Yield of polymer -wt%	41.0	33.2
Dimer fraction -wt%	68.7	71.0
Octane No. of hydrogenated polymer	89.5	88.0

2. Effects of operating conditions

Varying temperature with $H_3PO_4-BaSO_4$ (10:90) catalyst at constant gas rate and atmospheric pressure, influenced the octane rating of the iso-octane fraction: (see Table IV(B)2).

TABLE IV(B)2

MIXTURE OF 1-BUTENE AND 2-BUTENE (94.7% 1-BUTENE)

Temp. (°C)	Gas Rate cc/hr/cc cat.	wt % Polym.	% Dimer Fraction	Hydro. Dimer Octane No.
150	300	9.9	78.9	90.8
170	300	16.7	81.2	88.6
200	300	25.1	80.2	86.3

Variation of the gas-rate at constant temp. of 150°C, and 200°C and atmospheric pressure did not appreciably influence the octane No. of the iso-octane fractions.

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TABLE V(B)2

Gas Rate	Temp. (°C)	(%) Polym.	(%) Dimer	Hydro. Dimer Octane No.
150	150	20.7	78.7	90.5
300	150	9.9	78.9	90.8
150	200	49.1	78.3	86.0
300	200	25.1	80.2	86.3

Variation of the pressure at constant temperature 150°C, influenced the yield of iso-octanes.

TABLE VI(B)2

Press(kg/cm ²)	Gas Rate cc/hr/cc	(%) Polym.	(%) Dimer	Hydro. Dimer Octane No.
0	150	20.7	78.7	90.5
5	150	28.1	56.4	90.2

Change of temperature under 5 kg/cm² pressure influenced the octane No. and the yield (Table VII(B)2).

TABLE VII(B)2

Temp. (°C)	Press(kg/cm ²)	Gas Rate	(%) Polym.	(%) Dimer	Hydro. Dimer Octane No.
150	5	150	28.1	56.4	90.2
175	5	150	44.8	62.2	88.9
200	5	150	75.8	50.8	83.8

3. Catalyst

Effect of content of phosphoric acid (Table VIII(B)2) at atm. pressure:

TABLE VIII(B)2

% of H ₃ PO ₄	Temp. (°C)	Gas Rate	(%) Polym.
10	150	150	6.0
13	150	150	13.7
15	150	150	24.9
17	150	150	20.1
20	150	150	8.1

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Effect of state of Phosphoric acid:

TABLE IX(B)2

	Temp.(°C)	Gas Rate	(%) Polym.
Ortho-phosphoric acid	150	150	40.7
Pyro phosphoric acid	150	150	24.7

It is seen that ortho phosphoric acid-barium sulphate is much more active for the polymerization of butene-1.

Effect of 5% by weight of phosphate promoter added to (90:10 catalyst):

TABLE X(B)2

Promoter	(%) Polym.	Promoter	(%) Polym.
None	35.5	B PO ₄	0
Na ₃ PO ₄	0	Al PO ₄	0
K ₃ PO ₄	0	Pb ₃ (PO ₄) ₂	2.3
Cu ₃ (PO ₄) ₂	32.5	Cr PO ₄	4.8
Ag ₃ PO ₄	40.0	Fe ₃ (PO ₄) ₂	0
CO ₃ (PO ₄) ₂	0	Fe ₃ PO ₄	6.4
Zn ₃ (PO ₄) ₂	1.8	CO ₃ (PO ₄) ₂	0
Cd ₃ (PO ₄) ₂	29.8	Ni ₃ (PO ₄) ₂	12.4
Hg ₃ (PO ₄) ₂	34.6		

Note: Temp(°C) 150, Gas rate 150.

From these results, it was deduced that Ag and Hg-phosphates were the most active promoters, but yield improvement was insufficient to justify use of promoter.

C. ANALYSIS OF THE SAMPLE BY MEANS OF RAMAN EFFECT

The sample taken was the so-called iso-octane fraction produced by the polymerization of 1-butene under conditions of atm. pressure, temperature of 150°C, space velocity of 300 and % of polymerization 9.9. The octane rating of the sample was 90.8.

The Raman spectrum of the sample was photographed and the spectrum density was measured with the eye. The result was compared with the known data of pure samples and a rough estimate of the percent of principal components of the sample was made as follows:

2, 3, 4	- Trimethylpentane	35-40 %
2, 2, 3	- Trimethylpentane	35-40 %
2, 2, 4	- Trimethylpentane	20-25 %

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The physical constants of the sample are given in table XI(B)2.

TABLE XI(B)2

	Obs.	Calc.
Density (d_4^{20})	0.7116	0.712
Refractive Index (n_D^{20})	1.4013	1.401
Mean M. W.	115	114.1

III. CONCLUSIONS

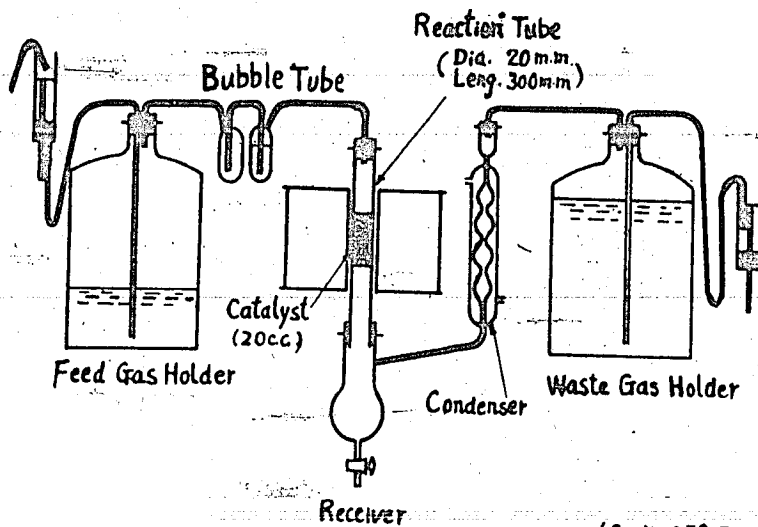
On the basis of the data obtained, the following conclusions can be drawn:

1. $BaSO_4-H_3PO_4$ catalyst is an active catalyst for the polymerization of isobutenes.
2. The preferred composition of catalyst is $BaSO_4/H_3PO_4=95/5-90/10$.
3. The best temperature for the polymerization of iso-Butenes is between 125° and $150^\circ C$, and the yield of polymer is 90%.
4. The best conditions for the polymerization of n-butene to obtain the 91 octane polymer are as follows:

Temperature $150^\circ C$
 Pressure Atmospheric
 S. V. 150

5. A hydrogenated 91 octane polymer consists mainly of 2, 3, 4-trimethylpentane, 2, 2, 3-trimethylpentane and 2, 2, 4-trimethylpentane.

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Figure 1(B)2
APPARATUS FOR POLYMERIZATION OF BUTENE

ENCLOSURE (B)₂

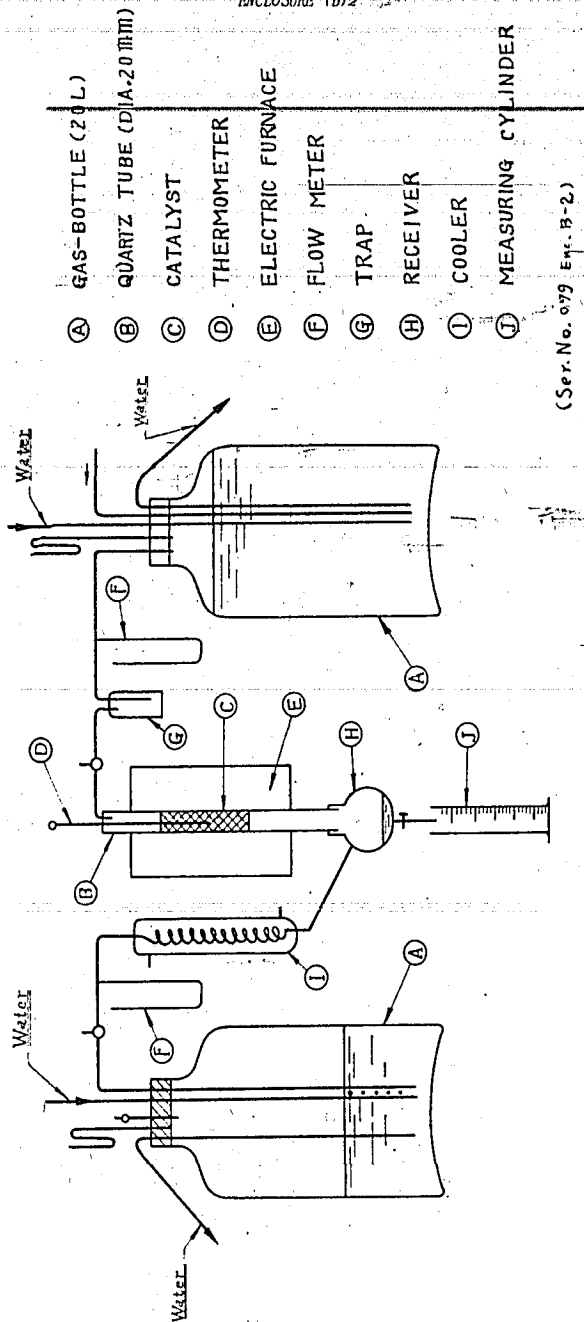


Figure 2(B)₂
APPARATUS FOR POLYMERIZATION OF BUTENE