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Catalytic Treatments of Gaseous Hydrocarbons with Special Reference to the Production of Motor Fuel.

By
Hirosi Ohtuka.

(Received October 1st, 1940.)

INTRODUCTION.

There are three processes now available on a commercial scale which produce motor fuel from gaseous hydrocarbons, viz., pyrolysis, polymerization and alkylation. "Pyrolysis" may be termed as the thermal reactions of hydrocarbons in which chemical degradation is predominant and the liquid products (if any) mainly consist of aromatics. "Polymerization" is the mutual combination of olefins producing large molecule olefins as primary products. "Alkylation" is, in a narrow meaning suitable to this case, the addition of olefins to paraffins which produces paraffins of iso-structure.

Pyrolysis processes have been adopted for the conversion of gaseous paraffins and olefins into liquid products boiling essentially in the gasoline range and of a pronounced aromatic character. Polymerization processes have been producing liquid hydrocarbons commercially from olefin gases for several years. The liquid products thus obtained, which are called "Polymer," are usually high octane motor fuels, or, in some cases, high V. I. lubricating oils. Alkylation processes have been established more recently for manufacturing high antiknock blending materials, such as isooctane and isohexane.

In the thermal processes for the polymerization of olefins, polymerization and pyrolysis occur, in most cases, either in sequence or simultaneously, though polymerization takes place as a major reaction and both reactions are conducted under the influence of heat and pressure. In the catalytic processes, polymerization reaction of olefins takes place in the presence of contact materials and under milder conditions of heat and pressure than those used in the thermal processes, Alkylation processes are also conducted both thermally and catalytically.

In this paper the catalytic polymerization of gaseous olefins is studied and discussed.

Part I. CATALYTIC POLYMERIZATION OF GASEOUS OLEFINS BY ACID CATALYSTS.

GENERAL DISCUSSION.

In general it may be said that the use of an efficient catalyst for the polymerization of olefins enables lower temperatures and pressures to be employed

than in the thermal processes, and often, as a result of this, secondary reactions by which the polymerized olefins are converted into non-olefinic hydrocarbons are suppressed. On the other hand, some catalysts have pronounced isomerization activity, and yield products which are predominantly saturated in character.

The active polymerization catalysts may be classified as follows:

(a) Adsorbents, e. g., floridin earth, active carbon, silica gel, silicious earth &c.,
(b) Metal halides,
(c) Inorganic acids, and inorganic acid salts.

Except the above-mentioned catalysts, certain metals, non-metals, metal oxides, metal sulfides and neutral salts are reported to promote the polymerization of olefins.

(a) Adsorbents.

The polymerizing activity of the common adsorbents is well known. The clay treatments of petroleum products, such as cracked gasoline, lubricating oil &c., are based on the polymerizing action of acid clay or floridin earth upon the unstable diolefin hydrocarbons in these products. Many investigators have studied the catalytic activity of adsorptive materials for the polymerization of olefin hydrocarbons. Among these, Gayer [1] has made an important contribution on the polymerization of propylene, in the presence of various adsorbents, to liquid hydrocarbons of gasoline boiling range, finding that at 350 deg. C. and atmospheric pressure dehydrated floridin possessed considerable catalytic power. The catalytic activity of floridin was found to increase after treatment with hydrochloric acid, and a precipitated porous silica containing adsorbed alumina on its surface was found 20 times more active than the best sample of activated floridin prepared. But each of the catalysts mentioned was less effective as compared with those now used commercially for producing motor fuel and each deteriorated rapidly in activity, though the useful life was extended by the addition of small quantities of hydrochloric acid to the olefin undergoing treatment.

To-day, some of these adsorbents are used commercially for the polymerization of olefins, not as catalysts but as suitable catalyst-carriers.

(b) Metal Halides.

The most important catalysts belonging to this group are aluminum chloride, zinc chloride and boron trifluoride. These are very vigorous in their action and catalyse many deep seated isomerization reactions, with the result that the products obtained are not true polymerization products.

Aluminum chloride has an extrordinary activity in promoting the polymerization of olefins. The reaction process is supposed to be another example of the Friedel-Crafts reaction so applied to olefin hydrocarbons. The most complete investigations on the polymerizing action of aluminum chloride are those

(1) F.H. Gayer, Ind. Eng. Chem., 1933, 25, 1122.

described by Stanley[2], and by Nash, Stanley, and Bowen[3]. With regard to the mechanism of the polymerization of olefins by aluminum chloride, Stanley believes that the production of the numerous and complex products formed by the action of aluminum chloride on olefins can be explained on the basis of three well-known processes, namely,

(1) polymerization to higher olefins,
(2) isomerization of the olefins to produce the corresponding cycloparaffins, and
(3) the splitting off of lower paraffin hydrocarbons under the influence of aluminum chloride with the simultaneous production of hydrocarbons of lower hydrogen content.

Of these three processes the first two can probably take place under the influence of aluminum chloride at quite low temperatures, whilst the third reaction becomes prominent at higher temperatures. Stanley considered that polymerization to form higher olefins is the first step in the process and that these combine with aluminum chloride as soon as they are formed to give complexes of the type $x(C_nH_{2n})\cdot yAlCl_3$. The next process is supposed to be the isomerization of the higher olefins into cycloparaffins. The cycloparaffin thus formed would be incapable of combination with the aluminum chloride, and therefore separates as free oil. On the other hand the aluminum chloride rendered free from combination by the loss of an olefin molecule would be free to effect the polymerization of more olefin to higher olefins, which themselves would be held in the form of an aluminum chloride complex.

Hunter and Yohe[4] also observed that aluminum chloride forms complex compounds with olefins which lead to the formation of olefin compounds. The use of these complex compounds as polymerizing agents is discussed, and a theory is advanced by them for the polymerization, based on the electronic structures of alminum chloride and olefins.

The polymerization of ethylene has been studied by Ipatieff and Grosse[5], who, for the most part, agree with the conclusions of Stanley. They investigated the polymerization at room temperature of ethylene under pressure in the presence of aluminum chloride using a glass-lined autoclave. It transpired that pure aluminum chloride did not react with pure ethylene under these conditions, and that traces of hydrogen chloride or moisture were necessary to cause reaction. It is suggested that the reaction mechanism is as follows:

$$\begin{array}{c} C_2H_4 + HCl \longrightarrow C_2H_5Cl \\ \uparrow \\ AlCl_3 \\ \downarrow \\ C_2H_5Cl + C_2H_4 \longrightarrow C_4H_8 + HCl \end{array}$$

Thus the HCl is regenerated continuously.

(2) H.M. Stanley, J.S.C.I., 1930, **49**, 349.
(3) A.W. Nash, H.M. Stanley & A.R. Bowen, J.I.P.T., 1930, **16**, 830.
(4) W.H. Hunter & R.V. Yohe, J.A.C.S., 1933, **55**, 1248.
(5) V.N. Ipatieff & A.V. Grosse, J.A.C.S., 1936, **58**, 915.

The mechanism of polymerization reactions induced by the other halides, e.g., zinc chloride, is similar to that in the case of aluminum chloride, but boron fluoride is reputed to bring about true polymerization in the presence of finely divided metals.

The action of anhydrous zinc chloride for the polymerization of propylene was observed by Brandes, Gruse and Lowry [6]. They obtained aromatic-free liquid polymer, though it contained considerable amounts of naphthene hydrocarbons in addition to olefin and paraffin hydrocarbons.

Many investigators are now dealing with the synthesis of lubricating oils from olefin hydrocarbons in the presence of aluminum chloride.

(c) Inorganic acids and acid salts.

The inorganic acids, sulfuric acid and phosphoric acids, and some of the acid salts, such as acid phosphates, have pronounced polymerization activity under certain conditions. This catalyser group is the most important and interesting for the commercial production of high octane gasoline from olefin-containing gases.

(i) Phosphoric acid as an olefin polymerization catalyst.

Phosphoric acid is one of the most successful polymerization catalysts yet developed, and is in commercial use on a large scale in the production of high octane polymer gasoline. The development has been carried out by Ipatieff and his co-workers of the Universal Oil Products Company[7], and also independently by Dunstan and his co-workers of the Anglo-Iranian Company [8].

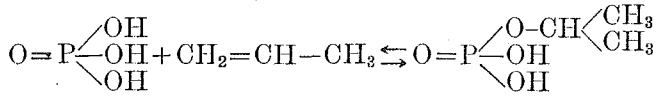
Ipatieff and Corson [7] observed the polymerization of propylene and butylenes under pressure in the presence of liquid phosphoric acid. Evidence is produced to show that polymerization occurs through the intermediate formation of alkyl phosphoric acid esters.

Under moderate polymerizing conditions, the olefins polymerize to liquids consisting almost entirely of monoolefins of isostructure, but, under more severe conditions, the polymerization reaction is followed by other reations, and the liquid products contain not only olefins, but naphthenes, paraffins, and aromatics. Ipatieff, with Pines [9], has also studied polymerization of ethylene in the presence and absence of phosphoric acid, and later, he conducted, with Corson,[10] the catalytic polymerization of ethylene in a small pilot plant using commercial "solid phosphoric acid" catalyst. The "solid phosphoric acid" is the catalyst mass developed by Ipatieff and his co-workers, which mainly consists of silicious earth impregnated with phosphoric acid and other additives.

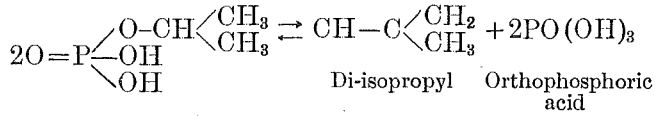
Based on the numerous experimental results, Ipatieff explained the reaction mechanism of olefin polymerization in the presence of phosphoric acid as following:

(6) O.L. Brandes, W.A Gruse & A. Lowry, Ind. Eng. Chem., 1936, 28, 554.
(7) V.N. Ipatieff & B.B. Corson, Ind. Eng. Chem., 1935, 27, 1067.
(8) A.E. Dunstan & A.D. Howes, J.I.P.T., 1936, 22, 347.
(9) V.N. Ipatieff & H. Pines, Ind. Eng. Chem., 1935, 27, 1364.
(10) V.N. Ipatieff & B.B. Corson, Ind. Eng. Chem., 1936, 28, 860.

In the case of propylene,



Which decomposes as follows:



Di-isopropyl Orthophosphoric acid

One of the exhaustive studies on the action of acid salts as polymerization catalysts was made by Dunstan and his colaborators[8]. They found that the acid phosphate of cadmium has pronounced activity for olefin polymerization. Phosphates of nickel, cobalt, copper and some rare earth elements are also reported to be effective catalysts for the same purpose.

(ii) Sulfuric acid as an olefin polymerization catalyst.

The polymerization of olefins in the presence of sulfuric acid is a recent development of considerable importance. Most olefins readily polymerize in the presence of sulfuric acid even at ordinary temperature and pressure.

Ipatieff and Pines[11] have investigated the effect of sulfuric acid on the polymerization of olefins at various conditions of temperature, concentrations of acid, and acid-olefin ratios. The results obtained from the treatment of olefins with concentrated sulfuric acid indicate that the following reactions occur: (1) polymerization, (2) depolymerization, (3) cyclization, (4) dehydrogenation, (5) hydrogenation and (6) isomerization. The term "conjunct polymerization" is used to describe the complex reaction which occurs on treatment of olefins with concentrated sulfuric acid, in order to differentiate this reaction from "true polymerization" which takes place when dilute acid is employed.

In the presence of concentrated sulfuric acid, lower olefins, with the exception of ethylene, not only readily react with each other, but react with considerable ease with isobutane to yield products consisting essentially of isoparaffins. Hence, sulfuric acid is used as "alkylation" catalyst, as well as polymerization catalyst.

(11) V.N. Ipatieff & H. Pines, J. Org. Chem., 1936, **1** (5), 464.

I. POLYMERIZATION OF PURE OLEFINS BY PHOSPHORIC ACID CATALYST UNDER ATMOSPHERIC PRESSURE.

1. INTRODUCTION.

In this paper, polymerization of propylene, normal butylene and isobutylene in the presence of phosphoric acid catalyst is studied under atmospheric pressure. From the results obtained, the reactivity of the individual olefins and catalytic power of the phosphoric acid catalyst are observed and discussed.

2. PREPARATION OF FEED STOCKS.

Propylene, butylene (mixture of 1- and 2-butylenes), and isobutylene were obtained by the dehydration of the corresponding alcohols in the presence of kaolin granules. All the sample olefins were purified by liquefaction followed by fractionation. But isobutylene sample always contained a very small amount of normal butylenes.

3. PREPARATION OF THE CATALYST.

The catalyst was phosphoric acid on silicious earth. Four parts of the acid and 1 part of the earth were thoroughly mixed and dried under a certain condition of temperature. The catalyst mass thus obtained was broken into pieces and stored in a closed vessel. The method of preparation of the catalyst will be fully discussed later.

4. APPARATUS AND PROCEDURE.

The apparatus used for the polymerization experiment was as shown in Fig. 1. The reaction tube was made of hard glass, 60 cm. long, and 3 cm. i.d., and was heated in an electric furnace (3) set in an inclined position lower to the outlet. Fifty gr. of the catalyst was used for each experiment. The sample olefin in the gas holder (1) was charged into the reaction furnace through a $CaCl_2$ -tube (2) at a constant rate of flow by means of the over-flow water feeder (8) and the screw cock (6). Liquid polymer obtained was collected in receivers (4), and unreacted gas in the gas holder (5).

The liquid polymers were fractionated and their important characteristics measured. The conversion per pass of the sample olefin and the yield of the liquid polymer were calculated by the following formulae.

$$\text{Conversion per pass} = \frac{\text{Reacted olefin volume at N.T.P.}}{\text{Sample olefin volume at N.T.P.}} \times 100.$$

$$\text{Polymer yield} = \frac{\text{Sp. gr. of the polymer} \times \text{polymer vol.}}{\text{Mol. wt. of sample olefin} / 22.4} \times 100.$$

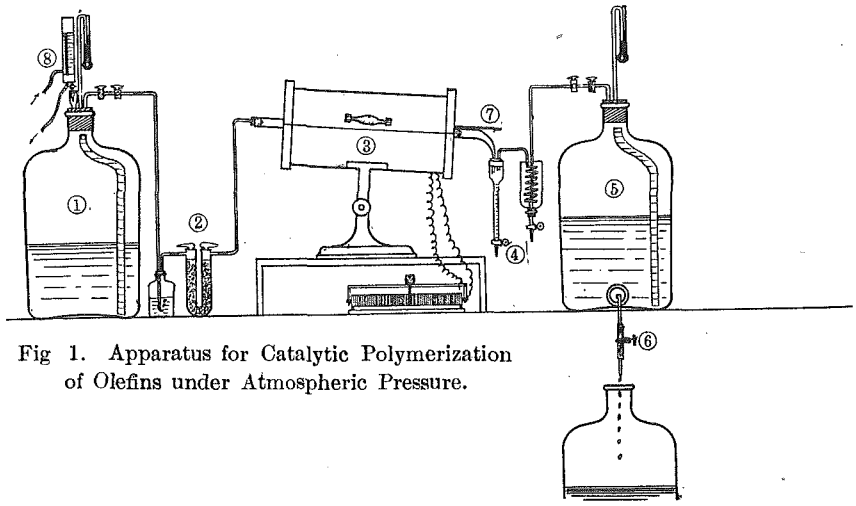


Fig 1. Apparatus for Catalytic Polymerization of Olefins under Atmospheric Pressure.

5. EXPERIMENTAL RESULTS.

The results of atmospheric polymerization of propylene, normal butylene and isobutylene with the phosphoric acid catalyst are summarized in the following tables.

(A) Polymerization of Pure Olefins.

(i) Polymerization of Propylene.

Exp. No.	SP—40	SP—51	SP—53	SP—54	SP—47
React. temp.	100°C.	125°C.	150°C.	175°C.	200°C.
Sample olefin vol. (N.T.P.)	9 88 l.	9.56 l.	9.67 l.	9.58 l.	9.37 l.
Reacted olefin vol. (N.T.P.)	2.29 l.	2.35 l.	2.55 l.	3.23 l.	6.02 l.
Conversion per pass	23.1%	24.6%	26.4%	33.7%	64.2%
Liquid polymer	0.5 c.c.	1.1 c.c.	1.2 c.c.	2.3 c.c.	9.1 c.c.
Polymer/1 l. Sample olefin	0.05 c.c.	0.1 c.c.	0.1 c.c.	0.2 c.c.	1.0 c.c.
Polymer/1 l. Reacted olefin	0.2 c.c.	0 5 c.c.	0.5 c.c.	0.7 c.c.	1.5 c.c.
Sp. gr. of polymer (D_{15}^{15})	—	—	—	—	0.7412
Polymer yield	—	—	—	—	59.4%

Exp. No.	SP—48	SP—46	SP—41	SP—44	SP—45
React. temp.	225°C.	250°C.	275°C.	300°C.	325°C.
Sample olefin vol. (N.T.P.)	9.57 l.	9.47 l.	9.67 l.	9.65 l.	9.59 l.
Reacted olefin vol. (N.T.P.)	7.83 l.	7.89 l.	7.46 l.	7.76 l.	7.35 l.
Conversion per pass	81.8%	83.3%	78.2%	80.4%	76.6%
Liquid polymer	13.4 c.c.	13.8 c.c.	12.6 c.c.	14.1 c.c.	12.4 c.c.
Polymer/1 l. Sample olefin	1.4 c.c.	1.5 c.c.	1.3 c.c.	1.5 c.c.	1.3 c.c.
Polymer/1 l. Reacted olefin	1.7 c.c.	1.8 c.c.	1.7 c.c.	1.8 c.c.	1.7 c.c.
Sp. gr. of polymer (D_{15}^{15})	0.7352	0.7252	0.7293	0.7183	0.7145
Polymer yield	67.3%	70.3%	66.4%	69.3%	65.0%

(ii) Polymerization of Normal butylene.

Exp. No.	SP—17	SP—20	SP—19	SP—21	SP—22
React. temp.	100°C.	125°C.	150°C.	175°C.	200°C.
Sample olefin vol. (N.T.P.)	10.17 l.	9.66 l.	10.10 l.	10.29 l.	9.33 l.
Reacted olefin vol. (N.T.P.)	3.30 l.	4.10 l.	5.86 l.	7.70 l.	8.02 l.
Conversion per pass	32.5%	42.4%	58.0%	74.8%	86.0%
Liquid polymer	4.6 c.c.	8.3 c.c.	13.8 c.c.	19.7 c.c.	21.3 c.c.
Polymer/1 l. Sample olefin	0.5 c.c.	0.9 c.c.	1.4 c.c.	1.9 c.c.	2 3 c.c.
Polymer/1 l Reacted olefin	1.4 c.c.	2.0 c.c.	2.4 c.c.	2 6 c.c.	2.7 c.c.
Sp. gr. of polymer (D_{15}^{15})	—	—	—	—	—
Polymer yield	—	—	—	—	—

Exp. No.	SP—23	SP—24	SP—25	SP—26	SP—13
React. temp.	225°C.	250°C.	275°C.	300°C.	325°C.
Sample olefin vol. (N.T.P.)	9.54 l.	9.18 l.	8.68 l.	9.84 l.	9.67 l.
Reacted olefin vol. (N.T.P.)	7.76 l.	7.05 l.	6.60 l.	7.75 l.	5.31 l.
Conversion per pass	81.3%	76.8%	76.0%	78.8%	75.6%
Liquid polymer	20.7 c.c.	19.3 c.c.	18.5 c.c.	17.0 c.c.	17.0 c.c.
Polymer/1 l. Sample olefin	2.2 c.c.	2.1 c.c.	2.1 c.c.	2.2 c.c.	1.8 c.c.
Polymer/1 l. Reacted olefin	2.7 c.c.	2.7 c.c.	2.8 c.c.	2.7 c.c.	2.3 c.c.
Sp. gr. of polymer (D_{15}^{15})	—	—	—	—	—
Polymer yield	—	—	—	—	—

(iii) Polymerization of Isobutylene.

Exp. No.	SP—62	SP—61	SP—60	SP—28	SP—29
React. temp.	25°C.	50°C.	75°C.	100°C.	125°C.
Sample olefin vol. (N.T.P.)	10.05 l.	9.91 l.	9.83 l.	9.70 l.	10.06 l.
Reacted olefin vol. (N.T.P.)	8.35 l.	8.96 l.	9.34 l.	9.12 l.	9.81 l.
Conversion per pass	83.1%	90.5%	94.1%	94.0%	97.5%
Liquid polymer	19.0 c.c.	21.9 c.c.	24.3 c.c.	23.7 c.c.	26.9 c.c.
Polymer/1 l. Sample olefin	1.9 c c.	2.2 c.c.	2.4 c.c.	2.4 c.c.	2.7 c.c.
Polymer/1 l. Reacted olefin	2.3 c.c.	2.5 c c.	2.6 c c.	2.6 c.c.	2.7 c.c.
Sp. gr. of polymer (D_{15}^{15})	0.7418	0.7453	0.7506	0.7403	0.7457
Polymer yield	68.3%	74.5%	79.0%	77.0%	81 8%

Exp. No.	SP—30	SP—31	SP—32	SP—33	SP—34
React. temp.	150°C.	175°C.	200°C.	250°C.	250°C.
Sample olefin vol. (N.T.P.)	9.92 l.	9.81 l.	9.61 l.	9.47 l.	9.68 l.
Reacted olefin vol. (N.T.P.)	9.64 l.	9.57 l.	9.05 l.	8.71 l.	8.73 l.
Conversion per pass	97.3%	97.5%	94.2%	92.0%	90.3%
Liquid polymer	27.2 c.c.	26.2 c.c.	22 8 c.c.	23.3 c.c.	23.6 c.c.
Polymer/1 l. Sample olefin	2.7 c.c.	2.7 c.c.	2.4 c.c.	2.5 c.c.	2.4 c.c.
Polymer/1 l. Reacted olefin	2.8 c.c.	2.8 c c.	2.5 c.c.	2.7 c.c.	2.7 c.c.
Sp. gr. of polymer (D_{15}^{15})	0.7315	0.7306	0.7225	0.7289	0.7121
Polymer yield	79.7%	80.1%	73.0%	77.9%	77.1%

Exp. No.	SP—42	SP—36	SP—39
React. temp.	275°C.	300°C.	325°C.
Sample olefin vol. (N.T.P.)	9.61 l.	9.79 l.	9.80 l.
Reacted olefin vol. (N.T.P.)	8.18 l.	8.13 l.	7.53 l.
Conversion per pass	85.1%	83.1%	76.9%

(iii) Polymerization of Isobutylene. (*Continued*)

Exp. No.	SP−42	SP−36	SP−39
Liquid polymer	23.3 c.c.	23.1 c.c.	21.1 c.c.
Polymer/1 l. Sample olefin	2.4 c.c.	2.4 c.c.	2.2 c.c.
Polymer/1 l. Reacted olefin	2.9 c.c.	2.8 c.c.	2.8 c.c.
Sp. gr. of polymer (D_{15}^{15})	0.7138	0.7157	0.7087
Polymer yield	81.3%	81.5%	79.6%

The conversion rates of the individual olefins at various temperatures are shown in Fig. 2.

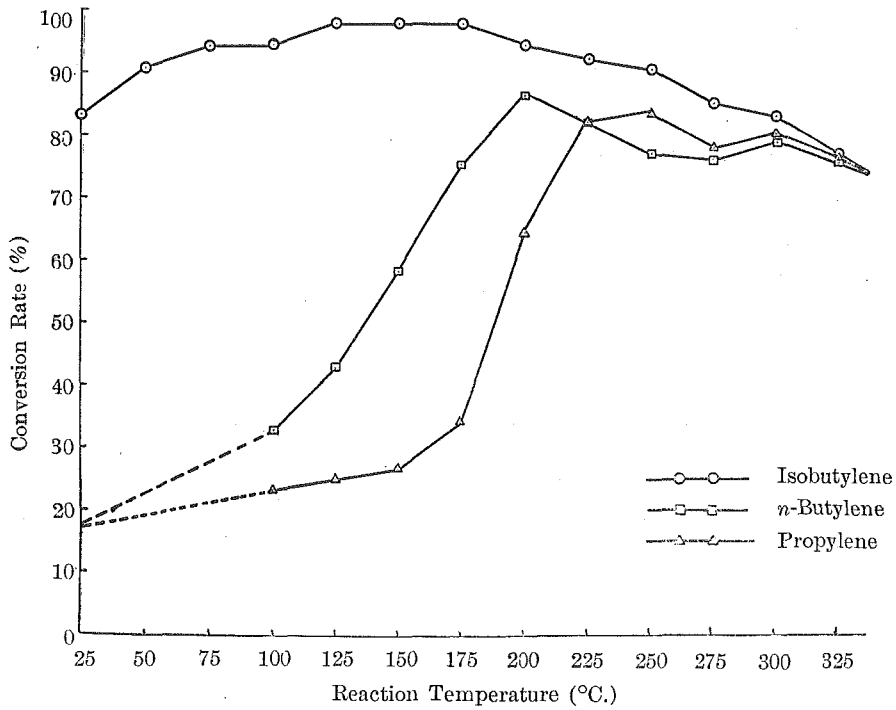


Fig. 2. Conversion Rate—Reaction Temperature Curve of Olefins.

(B) Characters and Compositions of the Liquid Polymers.

(i) Propylene Polymer.

React. temp. 250 °C. Rate of flow 5 l./hr.

(a) Distillation test.

Initial b. pt. 20.9 °C. Dry pt. 211.5 °C.

I. b. pt.~200°C. fraction 94.5% (D_{15}^{15} 0.7279)

200~Dry pt. fraction 4.1%

(b) Composition.

87% sulfuric acid soluble	75% by wt.
87% acid insoluble, 99% acid soluble	5%
99% acid insoluble	20%
Aniline pt. of the 99% acid insoluble	76.8°C.

(ii) Normal butylene polymer.
React. temp. 200°C. Rate of flow 5 l./hr.

(a) Distillation test.
Initial b. pt. 13°C. Dry pt. 247.0°C.
I. b. pt.~200°C. fraction 91.4% (D_{15}^{15} 0.7263)
200~Dry pt. fraction 7.1%

(b) Composition.

87% sulfuric acid soluble	77%
87% acid insoluble, 99% acid soluble	6%
99% acid insoluble	17%
Aniline pt. of the 99% acid insoluble	81.5°C.

(iii) Isobutylene Polymer.
React. temp. 150°C. Rate of flow 5 l./hr.

(a) Distillation test.
Inital b. pt. 18°C. Dry pt. 290°C.
I. b. pt.~200° fraction 97.4% (D_{15}^{15} 0.7384)

(b) Composition.

87% sulfuric acid soluble	85%
87% acid insoluble, 99% acid soluble	5%
99% acid insoluble	10%
Aniline pt. of the 99% acid insoluble	82.8°C.

The component distribution curves of the liquid polymers are shown in Fig. 3, 4 and 5.

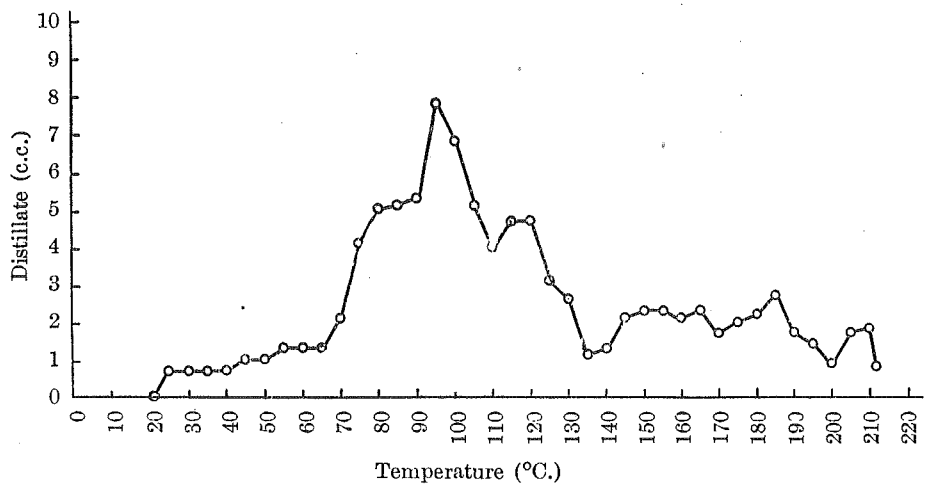


Fig. 3. Component Distribution Curve of Propylene.

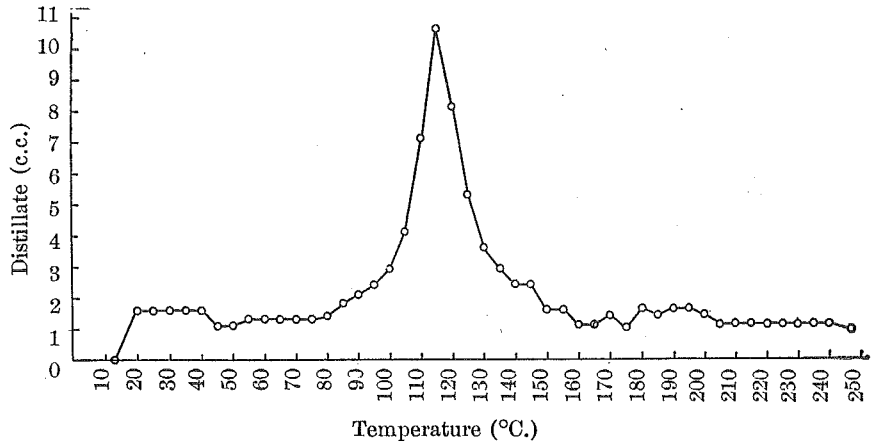


Fig. 4. Component Distribution Curve of *n*-Butylene.

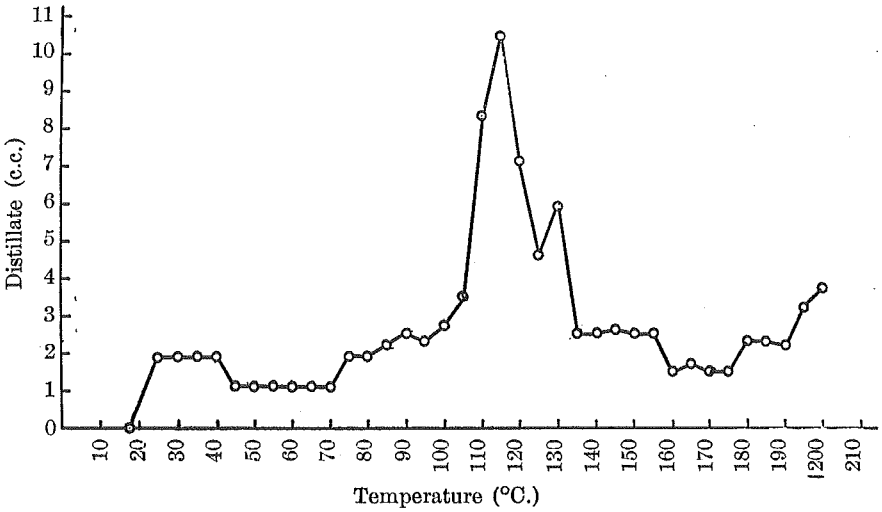


Fig. 5. Component Distribution Curve of *i*-Butylene.

6. DISCUSSION OF THE RESULTS.

(i) Composition of the Liquid Polymer.

According to the component analyses of the liquid polymers obtained, almost all parts of them were soluble in 87% sulfuric acid, that is to say, the unsaturated hydrocarbons. Each polymer also contained a small amount of 87% sulfuric acid insoluble and 99% acid soluble components. These components may be residual unsaturated hydrocarbons unabsorbed by 87% acid, though these are considered as aromatic hydrocarbons in conventional methods of hydrocarbon analysis.

Accordingly, all the liquid polymers produced by the action of the phosphoric acid catalyst consisted mainly of unsaturated hydrocarbons and also

contained a small amount of paraffin hydrocarbons. Considering from the component distribution curves of the polymers, the unsaturated components were mainly dimers of the sample olefins accompanied with small amounts of trimers and tetramers. (In the case of propylene, trimer was the main component.)

(ii) Influence of Reaction Temperature.

As shown in Fig. 2 (Conversion rate - Reaction Temperature Curve), isobutylene was by far more reactive as compared with other olefins and gave a good yield of liquid polymer even at room temperatures. Conversion rates of the olefins increased with reaction temperature to a certain maximum point, which was peculiar to the respective olefins, and then decreased. The optimum temperature of polymerization was, under our experimental conditions, 150 deg. C. for isobutylene, 200 deg. C. for normal butylene and 250 deg. C. for propylene. The optimum temperature range was comparatively wide (120~180 deg. C.) in the case of isobutylene, while that of normal butylene and propylene was confined to about ± 5 deg. C. Judging from the experimental results, temperatures below 275 deg. C. are recommendable for olefin polymerization with phosphoric acid catalyst even under atmospheric pressure.

By observing the reactivity for polymerization of individual olefins, it is possible to some degree to determine the operating conditions for selective or cross polymerization.

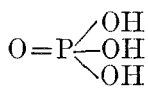
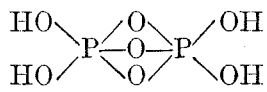
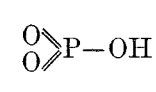
In considering the influence of reaction temperature, the question must be discussed whether the conversion rate of olefins is influenced by temperature alone or also influenced by some condition other than temperature. For instance, it is probable that the influence of degradation of the catalyst by temperature rise may superpose upon the temperature effect.

As for the phosporic acid catalyst prepared in our laboratory, the author believes that the effect of the catalyst deterioration is negligible at temperatures below 250 deg. C. Over that temperature deterioration of the catalyst becomes appreciable. The method of preparation of the phosphoric acid catalyst is discussed in the following paragraph.

7. PREPARATION OF THE PHOSPHORIC ACID CATALYST.

(i) Catalytic Power of Three Phosphoric Acids for Polymerization of Olefins.

There are three types of phosphoric acid as shown in the following:

Orthophosphoric acid	Pyrophosphoric acid	Metaphosphoric acid
H_3PO_4	$H_4P_2O_7$	HPO_3
$(P_2O_5 \cdot 3H_2O)$	$(P_2O_5 \cdot 2H_2O)$	$(P_2O_5 \cdot H_2O)$
		

Of the three phosphoric acids, ortho- and pyro-acid are effective catalysts for olefin polymerization, while meta-acid is inactive.

The results of the polymerization experiments with these three acids are summarized in the following tables.

(a) Polymerization with Liquid Phosphoric Acids.

In this series of experiments, isobutylene was bubbled into liquid phosphoric acid contained in the reaction vessel as shown in Fig. 6 at a constant rate of flow (5 l./hr.). A large portion of the liquid polymer produced stayed on the acid layer.

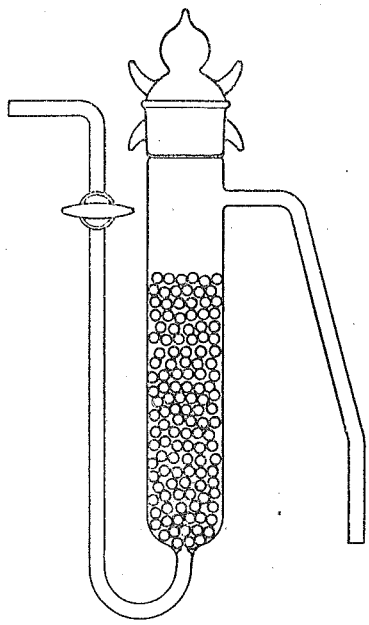


Fig. 6. Reaction Vessel for Olefin Polymerization with Liquid Acids.

Experiments with Pyro-acid.

React. temp.	50°C.	75°C.	100°C.
Sample olefin vol. (N.T.P.)	10.10 l.	9.80 l.	9.64 l.
Reacted olefin vol. (N.T.P.)	2.58 l.	3.12 l.	3.47 l.
Conversion per pass	25.7%	32.3%	36.0%
Liquid polymer	4.8 c.c.	7.2 c.c.	9.0 c.c.

Experiments with 90% Ortho-acid.

React. temp.	50°C.	75°C.	100°C.
Sample olefin vol. (N.T.P.)	9.74 l.	9.83 l.	9.47 l.
Reacted olefin vol. (N.T.P.)	1.00 l.	1.33 l.	1.51 l.
Conversion per pass	10.3%	13.5%	16.0%
Liquid polymer	0.4 c.c.	1.8 c.c.	3.7 c.c.

Experiments with Meta-acid.

No appreciable conversion of isobutylene was observed with metaphosphoric acid under the conditions of these experiments.

As shown above, pyrophosphoric acid was the best catalyst for olefin polymerization. As the activity of the 90% orthophosphoric acid might be weakened remarkably by the presence of water, the acid was heated at 75 deg. C. to expel water, and some of the concentrated acids thus produced were again tested as polymerization catalysts. The results were as follows:

Sample: Isobutylene. React. temp.: 75 deg. C. Rate of flow: 5 l./hr.

% of H_3PO_4	90.3%	93.2%	97.8%
Sample olefin vol. (N.T.P.)	9.83 l.	9.88 l.	9.69 l.
Reacted olefin vol. (N.T.P.)	1.33 l.	1.78 l.	2.38 l.
Conversion per pass	13.5%	18.0%	24.6%
Liquid polymer	1.8 c.c.	3.3 c.c.	5.6 c.c.

Judging from the above results, the catalytic activity of 100% ortho-acid was still weaker than that of pyro-acid, though the activity of the ortho-acid increased with acid concentration.

(b) Polymerization with Solid Phosphoric Acids.

The solid phosphoric acid catalysts were prepared from ortho-, pyro-, and meta-phosphoric acids and silicious earth by the following procedures.

Orthophosphoric acid-silicious earth catalyst.

Four parts of 90% ortho-acid and 1 part of silicious earth were well mixed, and dried over night at 75 deg. C. in a thin layer.

Pyrophosphoric acid-silicious earth catalyst.

Four parts of 90% ortho-acid were heated on a sand bath at ca. 200 deg. C. until all the ortho-acid converted into the pyro-form [see (ii) infra of this paragraph]. The pyro-acid thus produced was mixed with 1 part of silicious earth, and the mixture was dried over night at 150 deg. C. in a thin layer.

Metaphosphoric acid-silicious earth catalyst.

Four parts of meta-acid sticks were heated on a sand bath at ca. 250 deg. C., and 1 part of silicious earth was added to the molten acid. The mixture was dried over night at 150 deg. C. in a thin layer.

Comparison between the catalytic activities of the three solid phosphoric acids.

Sample: Isobutylene React. temp.: 50°C.

Expt. No.	SP—104	SP—105	SP—103
Catatyst	Ortho-	Pyro-	Meta-
Sample olefin vol. (N.T.P.)	9.42 l.	9.55 l.	9.54 l.
Reacted olefin vol. (N.T.P.)	3.74 l.	8.70 l.	1.89 l.
Conversion per pass	40.1%	91.1%	19.8%
Liquid polymer	6.4 c.c.	20.7 c.c.	trace

Of the three solid phosphoric acid catalysts the pyro-acid catalyst was the most effective.

From the results of (a) and (b), it is concluded that it is advisable and advantageous to use the phosphoric acid catalyst in the "pyro-form" for olefin polymerization.

(ii) The Action of Heat on Orthophosphoric Acid.

On heating orthophosphoric acid, it loses its intramolecular water and gradually changes into pyrophosporic acid. By further heating, the pyrophosphoric acid is converted slowly into metaphosphoric acid in the same manner.

Fifty gr. of 90% orthophosphoric acid was heated in a porcelain dish on a sand bath. The results observed were as follows:

Heating time	Temp.	Wt. of sample	Mol ratio (P_2O_5/H_2O)	Qualitative detection		
				ortho-	pyro-	meta-
0	20°C.	50.0 gr.	1 : 4.05	+	—	—
20 min.	98°C.	—	—	+	trace	—
1 hr.	179°C.	—	—	+	+	—
1½ hr.	210°C.	—	—	+	+	—
2 hr.	210°C.	42.9 gr.	1 : 2.30	—	+	—
3 hr.	210°C.	42.8 gr.	1 : 2.21	—	+	—
5½ hr.	210°C.	42.2 gr.	—	—	+	trace
6½ hr.	210°C.	42.2 gr.	1 : 2.12	—	+	trace
9½ hr.	210°C.	42.1 gr.	1 : 2.01	—	+	trace
19½ hr.	210°C.	42.1 gr.	1 : 2.01	—	+	trace
Temperature was then raised to 260 deg. C.						
1 hr.	260°C.	40.6 gr.	1 : 1.86	—	+	+

Weights and mol ratios of the sample at several heating stages are plotted in Fig. 7.

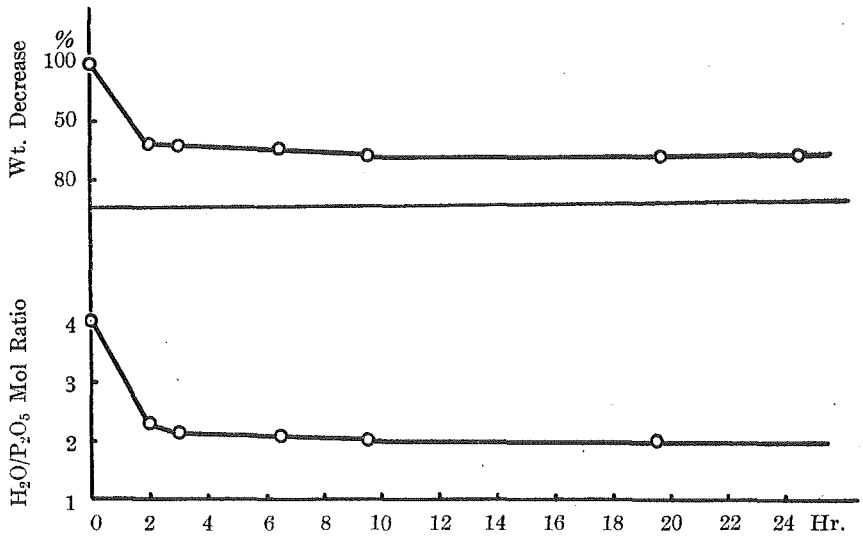


Fig. 7. Action of Heat on Orthophosphoric Acid.

Orthophosphoric acid was detected by silver nitrate or ammonium molybdate solution, and pyrophosphoric acid by silver nitrate or luteo cobalt chloride solution, and metaphosphoric acid by albumin (egg white).

P_2O_5 in the phosphoric acids was determined as magnesium pyrophosphate ($Mg_2P_2O_7$) by Schmitz's method (see Treadwell-Hall: Analytical Chemistry, 8 Ed., Vol II, p. 391). In the case of pyro- and meta-phosphoric acids, these acids were converted into orthophosphoric acid prior to the analysis by boiling the sample solutions for some time in the presence of nitric acid.

Changes of orthophosphoric acid by heating are summarized as following:

a) The formation of pyrophosphoric acid from orthophosphoric acid is recognized at comparatively low temperatures.

b) Not that the conversion of orthophosphoric acid into pyrophosphoric acid begins after all the adhesive water of orthophosphoric acid has expelled, but that it begins at earlier stages where the adhesive water still remains.

c) After heating at ca. 200 deg. C. for a few hours orthophosphoric acid changes perfectly into pyrophosphoric acid. But the pyrophosphoric acid is always accompanied with small amounts of adhesive water.

d) At temperatures up to ca. 200 deg. C. the formation of metaphosphoric acid is negligible.

e) At higher temperatures (250 deg. C. and over), the formation of metaphosphoric acid from pyrophosphoric acid becomes remarkable.

f) As pyrophosphoric acid is very stable at temperatures near 200 deg. C., appreciable weight decrease of the sample phosphoric acid by heating is not observed at these temperatures in spite of heating time. Hence, the weight of the sample phosphoric acid becomes almost constant for a while at this stage of heating.

(iii) Preparation of the Pyrophosphoric Acid - Silicious Earth Catalyst.

According to (ii), there may be two methods for the preparation of the most effective phosphoric acid catalyst (i.e., pyrophosphoric acid - silicious earth catalyst), Namely:

a) The mixture of orthophosphoric acid and silicious earth is dried in a thin layer at ca. 200 deg. C. until weight becomes constant. The weight of the catalyst mass at this stage is always about 80% of that of the original mixture.

b) Orthophosphoric acid is first heated on a sand bath at ca. 200 deg. C. until the perfect conversion into pyrophosphoric acid is achieved. Silicious earth is then added to the pyro-acid formed. The mixture is dried over night in a thin layer at ca. 150 deg. C.

The mixing ratio of 90% orthophosphoric acid and silicious earth was temporarily taken as 4 : 1 in weight. But this ratio may be changed, when the durability of the catalysts is taken into account.

Each method described above gave always an excellent catalyst having a high and constant catalytic power.

As shown in the following, the catalysts prepared by methods (a) and (b) respectively gave the same results when used for polymerization experiments.

Sample: Isobutylene, Rate of flow: 5 l./hr.

Expt. No.	SP−61	SP−105	SP−30	SP−107
React. temp.	50°C.	50°C.	150°C.	150°C.
Catalyst	(a)	(b)	(a)	(b)
Sample olefin vol. (N.T.P.)	9.91 l.	9.55 l.	9.92 l.	10.11 l.
Reacted olefin vol. (N.T.P.)	8.96 l.	8.70 l.	9.64 l.	9.93 l.
Conversion per pass	90.5%	91.1%	97.3%	97.5%
Liquid polymer	21.9 c.c.	20.7 c.c.	27.3 c.c.	27.7 c.c.

SUMMARY.

1. In the presence of phosphoric acid catalyst, polymerization of propylene, normal butylene and isobutylene was studied under atmospheric pressure. Tendency to polymerization of the individual olefin was observed at various reaction temperatures. The important characteristics of the liquid polymer of each olefin were investigated. These liquid polymers were found to consist mainly of dimers and trimers of mother olefins.
2. Catalytic activities of the three phosphoric acids (i.e., ortho-, pyro-, and meta-phosphoric acid) for olefin polymerization were compared. Pyrophosphoric acid was found to be the most effective and metaphosphoric acid almost inactive.
3. A method of preparation of a powerful solid phosphoric acid catalyst was proposed based on the investigation of the action of heat upon orthophosphoric acid. The recommended catalyst consisted of pyrophosphoric acid and silicious earth in the ratio of ca. 4 : 1, and possessed an excellent catalytic activity.

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