June 10, 1952 L. F. BROOKE 2,599,743

CONVERSION OF PROPYLENE POLYMERS

Filed June 4, 1949 3 Sheets-Sheet 1

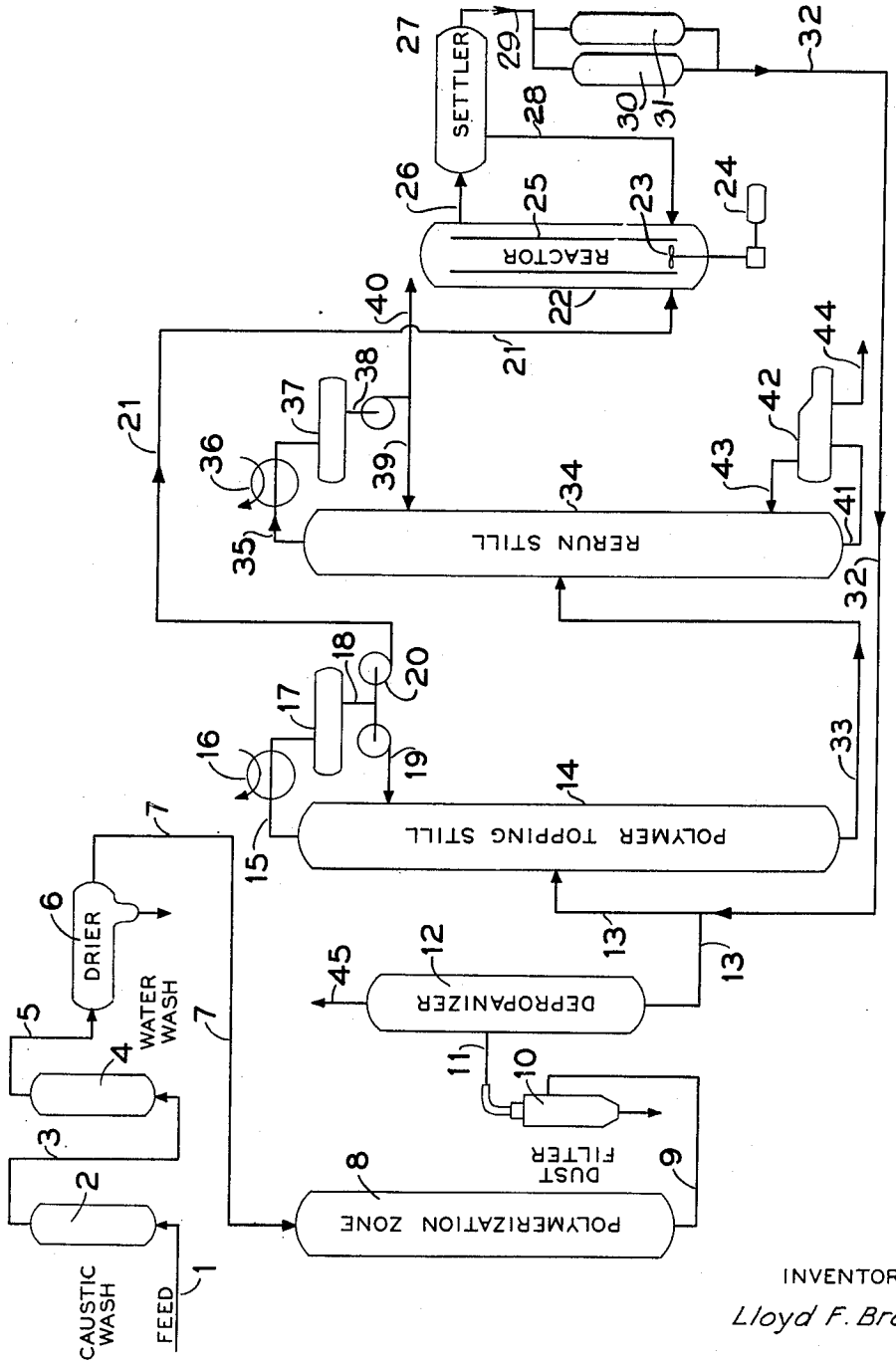



FIG. I

INVENTOR
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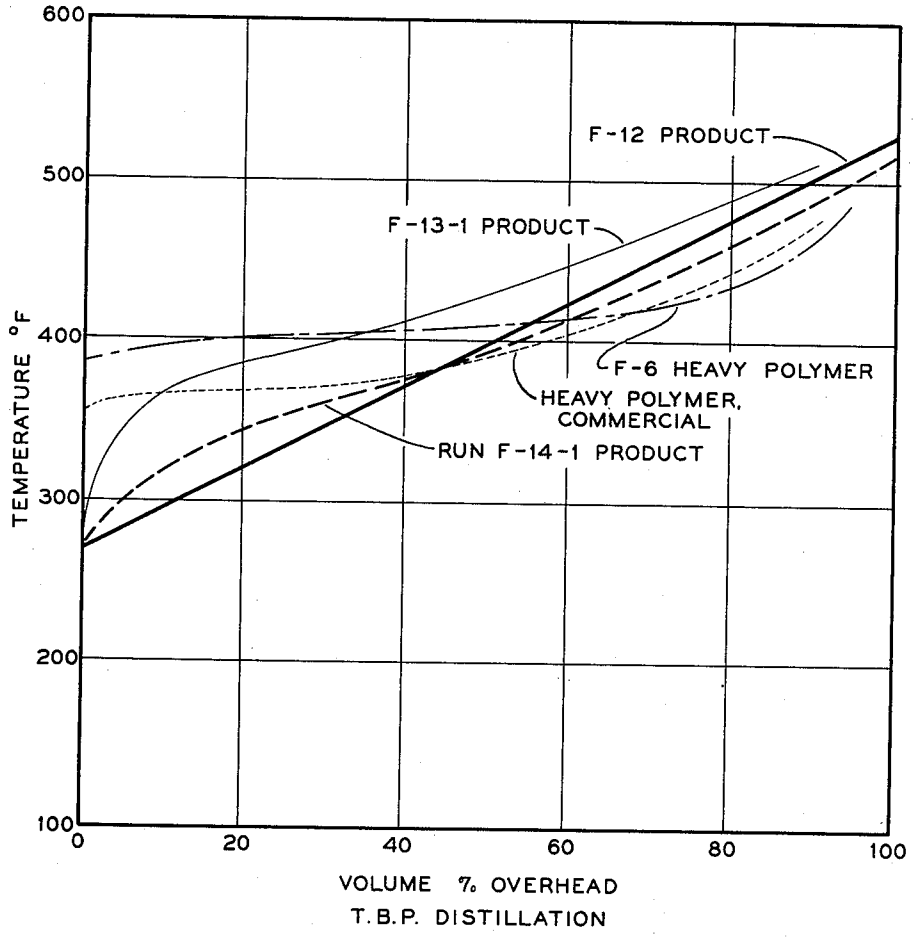



FIG. II

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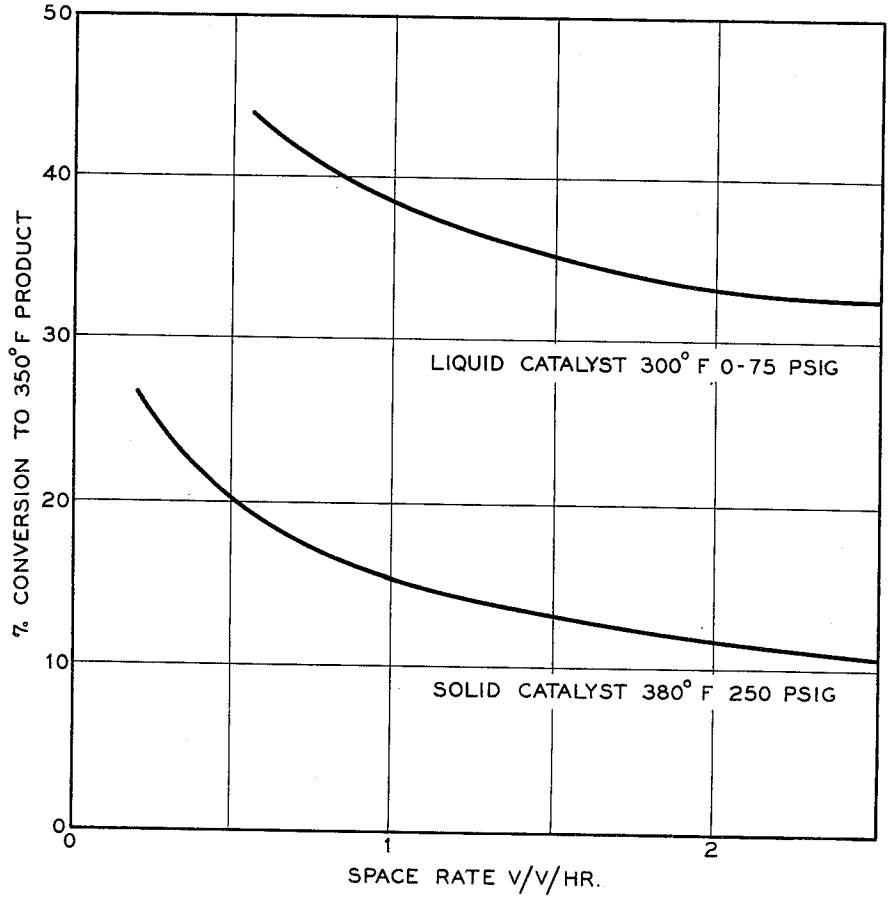



FIG. III

INVENTOR

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# UNITED STATES PATENT OFFICE

2,599,743

## CONVERSION OF PROPYLENE POLYMERS

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Application June 4, 1949, Serial No. 97,284

3 Claims. (Cl. 260—683.15)

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This invention relates to a process for the conversion of low boiling liquid hydrocarbons produced by polymerizing propylene to higher boiling olefinic hydrocarbons by contacting said low boiling hydrocarbons with concentrated liquid phosphoric acid in the absence of propylene.

In the past, propylene has been polymerized to produce liquid hydrocarbons boiling in the gasoline range for use as motor fuel. More recently, is has been found that the higher polymers of propylene, such as the tetramer and pentamer, may be used to alkylate benzene and that the reaction product may be sulfonated to produce a detergent of superior quality. This discovery has led to the practice of commercial polymerization of propylene directed to the production of the higher propylene polymers. In typical commercial operation a propylene containing hydrocarbon gas is polymerized by contact with a "solid phosphoric acid catalyst" at a temperature in the range of about 375° to 450° F. under pressure of at least 250 p. s. i. g. The reaction product is depropanized and separated into a fraction boiling below about 350° F. and a fraction boiling above about 350° F., which comprises the desired heavy propylene polymers. The lighter fraction boiling below 350° F. is recycled to the polymerization zone, together with fresh propylene feed. In the usual practice, a recycle ratio of light polymer to propylene of 4:1 to 6:1 or higher is required in order to obtain maximum yields of the desired heavy polymer.

This process has two serious disadvantages. First, the high temperature at which it is operated is not favorable to the production of the desired heavy polymer and, accordingly, the conversion per pass is low, hence, high recycle ratios are made necessary in order to obtain an acceptable overall conversion. Second, under the conditions of temperature and recycle ratio which are employed in the process, substantial quantities of saturated hydrocarbons are produced. These saturated hydrocarbons tend to accumulate in the recycle stream, and provision must be made for their rejection in order to permit sustained operation at reasonable conversion rates.

It is an object of this invention to effect the conversion of the lower boiling fraction separated from the product of a propylene polymerization to higher boiling olefinic hydrocarbons at low temperatures whereby higher conversion to the heavier hydrocarbons is obtained.

It is a further object of this invention to convert the lower boiling fraction separated from the product of a propylene polymerization to higher boiling olefinic hydrocarbons without any substantial simultaneous production of saturated hydrocarbons.

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In the practice of this invention the reaction product produced by catalytically polymerizing propylene is depropanized and then fractionally distilled to separate an overhead fraction boiling below about 350° F. This overhead fraction is then intimately contacted with concentrated liquid phosphoric acid at a temperature below 325° F. and usually in the range 225–325° F. to effect a substantial conversion of the overhead fraction to olefinic hydrocarbons boiling in the range 350°–500° F.

The process of this invention may be better understood by reference to Figure 1 of the appended drawings, which is a diagrammatic illustration of apparatus and a process flow suitable for the practice of the invention. A feed ordinarily containing above about 20% propylene and substantially free of hydrocarbons heavier than propane is treated by conventional methods to remove hydrogen sulfide. The feed is then passed through line 1 into caustic washer 2, where residual hydrogen sulfide and mercaptans are removed. The feed then is passed from caustic washer 2 through line 3 into water washer 4 and then through line 5 into drier 6, where water is removed. The feed is ordinarily dried to such a degree that its water content is sufficient to produce a water vapor pressure approximately equal to the water vapor pressure over the "solid phosphoric acid catalyst" with which it is subsequently contacted. The feed then passes from drier 6 through line 7 into polymerization zone 8. Polymerizattion zone 8 is packed with "solid phosphoric acid catalyst." The solid phosphoric acid catalysts are prepared by mixing liquid phosphoric acid with a siliceous adsorbent such as kieselguhr to form a paste which is then extruded, dried, calcined, and rehydrated to produce an extrudate having a dry appearance but having a substantial content of phosphoric acid. Preparation of such a catalyst is described in U. S. Patent 1,993,514. In polymerization zone 8 propylene is polymerized to form liquid polymers. The reaction product flows from polymerization zone 8 through line 9 into dust filter 10, where suspended particles of the solid catalyst are removed. The feed passes from filter 10 through line 11 into depropanizer 12, where propane and lighter hydrocarbons are removed overhead through line 45. The depropanized reaction

product is withdrawn from depropanizer 12 through line 13 and passed into topping still 14. A fraction boiling below about 350° F. is removed overhead through line 15 and passes through heat exchanger 16, where it is cooled and condensed, and then into reflux drum 17. A portion of the reflux condensate is withdrawn from reflux drum 17 through line 18 and returned to topping still 14 through line 19 as reflux. The remainder of the overhead fraction boiling below 350° F. is pumped by pump 20 through line 21 into reactor 22. Reactor 22 is charged with concentrated liquid phosphoric acid, the concentration being in the range 102–110% calculated as orthophosphoric acid. The hydrocarbons entering reactor 22 through line 21 and the liquid phosphoric acid are intimately mixed in reactor 22 by impeller 23, which is driven at a high rate of speed by motor 24. Reactor 22 is ordinarily provided with a draft tube 25, which is positioned in the reactor relative to the reactor walls and the impeller 23 to obtain maximum mixing efficiency. A mixture of hydrocarbon and acid is withdrawn from reactor 22 through line 26 and passed into settler 27, where the mixture separates into an upper hydrocarbon phase and a lower acid phase. The hydrocarbon phase consists in part of converted hydrocarbons boiling above 350° F. and in part of unconverted feed which is subsequently separated and recycled to reactor 22. The acid phase is withdrawn from settler 27 through line 28 and returned to reactor 22, where it is re-used. The hydrocarbon phase is withdrawn from settler 27 through line 29 and is passed through one of the two neutralizers 30 and 31. Neutralizers 30 and 31 are packed with an alkaline material such as limestone and are connected in parallel so that one may be on stream while the other is being recharged with alkaline material. The hydrocarbon flows from the neutralizers 30 and 31 through line 32 into line 13 and thence into polymer topping still 14. The bottoms fraction from topping still 14, which boils above about 350° F., is withdrawn from topping still 14 through line 33 and is passed into rerun still 34. An overhead fraction which boils usually in the range 350°–500° F. is withdrawn from rerun still 34 through line 35 and passes through heat exchanger 36, where it is condensed into reflux drum 37. A portion of the condensate is passed from reflux drum 37 through lines 38 and 39 into rerun still 34 as reflux, and the remainder of the condensate is withdrawn through line 40 as the final reaction product. A bottoms fraction from rerun still 34 is withdrawn through line 41 and passes into reboiler surge drum 42. A part of the bottoms product is returned from reboiler 42 through line 43 to rerun still 34 and a part of it is withdrawn from reboiler 42 through line 44 as a product. It is frequently desirable to return a bottoms fraction withdrawn at line 44 to polymerization zone 8, together with the fresh feed entering through line 7 in order to increase overall conversion.

When the process is conducted in the manner illustrated in Figure 1, there is no recycle of the lower boiling fraction of the propylene polymer to polymerization zone 8. The entire conversion of this low boiling fraction to the desired heavy polymer is effected in reactor 22, where the light fraction is contacted with concentrated liquid phosphoric acid in the absence of propylene. A single topping still serves to separate the products of both polymerization zone 8 and conversion zone 22, and the process flow is such that any of the light polymer which is not converted in conversion zone 22 to the desired heavy product is returned as overhead from topping still 14 to conversion zone 22.

The conversion of light polymer to heavy polymer may be practiced in the manner described in Figure 1, where the distillation equipment serves both polymerization zones or it may be practiced as a separate process in which light polymers are obtained from extraneous sources and converted to heavy polymer by contact with the concentrated liquid phosphoric acid.

The results which may be obtained by the process of the invention are illustrated by the following example. A gas containing 36% by volume of propylene was contacted with a solid phosphoric acid catalyst at a temperature of 441° F. and a pressure of 300 p. s. i. g. to polymerize the propylene. The reaction product was depropanized and distilled to separate a light polymer overhead which had the following inspections:

*Table I*

| | |
|---|---|
| A. P. I. gravity | 61.9 |
| Bromine No. | 144 |
| Average molecular weight | 118 |
| TBP distillation: | |
| Start 142° F.; 5%—160° F.; 10%—189° F.; 20%—218° F.; 50%—267° F.; 70%—278° F.; 90%—304° F.; 95%—311° F.; end point 311° F. | |

The body of liquid phosphoric acid having a concentration of 103.2% calculated as orthophosphoric acid was charged to a reactor corresponding to reactor 22 of Figure 1. The reactor employed was columnar in shape and had baffles extending from the column walls. A stirring shaft having mixing blades extending from the shaft and positioned opposite the baffles was centered in the column. The clearance between the mixing blades and baffles was approximately $\frac{1}{32}$ inch. The shaft was rotated at approximately 2000 R. P. M. during the reaction. The low boiling polymer product above described was charged to the reactor and intimately mixed with the concentrated phosphoric acid. The operation was conducted continuously for a period of 36.6 hours, during which time pressure and space velocity were varied. The conditions of the reaction and the results obtained are recorded in the following table:

*Table II*

| Run Number | F–13–1 | F–12 | F–13–2 |
|---|---|---|---|
| Hours Operation | 0–14 | 14–23 | 14–36.6 |
| Temperature, °F | 300 | 300 | 300 |
| Pressure, p. s. i. g | 75 | 0 | 75 |
| Titratable acidity, Final | | 99.7 | |
| Vol. Feed/Vol. Catalyst/hr | 0.58 | 0.7 | 0.49 |
| Recycle Ratio, Vol. Recycle/Vol. Feed | 0.84 | 1.2 | 2.4 |
| Vol. 350°F.+Product/Vol. Feed | 0.71 | 0.77 | 0.79 |
| Vol. 500°F.+Product/Vol. Feed | 0.12 | 0.14 | 0.13 |
| Vol. Saturates/Vol. Feed | 0.045 | 0.047 | 0.045 |
| Gas Produced | None | None | None |

During the runs summarized in the above table, topping still 14, rerun still 34, reactor 22, and settler 27 of Figure 1 constituted the entire process unit. The light polymer feed was introduced into the reactor from a storage tank rather than directly from polymer topping still 14, in order that conversion rates and recycle ratios might be accurately determined. It will be noted that the low boiling polymer feed to the reactor was converted to heavier olefinic product boiling above 350° F., with yields above 70%. The final titratable acidity was lower than the initial titratable

acidity as a result, mainly, of formation of phosphoric acid esters in the course of the reaction. A steady state titratable acidity somewhat lower than the initial titratable acidity is ordinarily established after several hours of operation. The production of very heavy polymer bottoms boiling above 500° F. was low, being on the order of 10%, and the production of saturates was very low, being below 5%. Production of saturates in an amount below 5% by the process of the invention contrasts sharply with the results obtained when the light polymer is recycled to the polymerization zone together with fresh feed in the current commercial operation, where saturate production on the order of 10–20% is common.

Such high saturate production requires that provision be made for rejection of saturates from the light polymer recycle stream. In the course of saturate rejection, olefin losses are usually sustained and the overall recovery of desired polymer is thus further reduced.

At lower temperatures, saturate formation is still further reduced and at 250° F. and below, it is eliminated. This is illustrated by the following results obtained in a run at 250° F. The charge was a light propylene polymer having an API gravity of 62 and an ASTM distillation as follows: Start 121° F.; 5%—146° F.; 10%—153° F.; 20%—166° F.; 30%—220° F.; 40%—254° F.; 50%—269° F.; 60%—273.5° F.; 70%—280° F.; 80%—285° F.; 90%—314° F.; 95%—353° F.; and end point with 97.4% over—359° F. The conditions and results of the run are shown in the following Table III:

*Table III*

| | |
|---|---|
| Run | F–47 |
| Temp., °F | 250 |
| Pressure | Atmospheric |
| Catalyst | 105.4% calculated as orthophosphoric acid |
| Vol. feed/vol. catalyst/hr. | 1.17 |
| Recycle ratio, vol. recycle/vol. feed | 2.85 |
| Volume 350° F.+ product/vol. feed | 0.32 |
| Volume 500° F.+ product/col. feed | 0.027 |
| Volume of saturates/vol. feed | 0.0 |
| Gas produced | None |

The reaction product had the following properties: A. P. I. gravity 47.6, A. S. T. M. distillation, start—278° F.; 5%—282° F.; 10%—328° F.; 20%—352° F.; 30%—366.5° F.; 40%—379° F.; 50%—397° F.; 60%—421° F.; 70%—443° F.; 80%—464° F.; 90%—488° F.; 95%—506° F.; end point with 97.3% overhead 512° F.

It was further determined that if the feed rate in the run summarized in Table III were reduced to 0.35 v./v./hr. and the other conditions were maintained constant, complete conversion of the light polymer feed to heavy polymer would be obtained.

From the runs recorded in the above tables and from further exploratory runs, it has been determined that the process may be conducted with the desired low saturate formation, low recycle rate, and high conversion at temperatures in the range 225°–325° F., and preferably in the range 250°–300° F. It has also been found that the concentration of the acid charged to the conversion zone should be in the range 102–110% in order to obtain the desired conversion, and that it is preferably in the range 103–107%, on the basis that the reaction proceeds satisfactorily, that corrosion rates are lower with the more concentrated acid and that if the acid concentration is about 107%, the formation of polymers boiling above 500° F. may be undesirably increased.

The reaction may be carried out at atmospheric pressure, but a moderately elevated presssure up to 200 p. s. i. may be employed advantageously. At superatmospheric pressures the light polymer feed may be maintained substantially completely in liquid phase, which facilitates the intimate mixing of the hydrocarbon and catalyst which is necessary to obtain high conversions. The space velocity should be maintained above about 0.2, since high conversions may be obtained at such space velocities and since lower space velocities result in longer contact times and tend to increase the production of undesirable saturated hydrocarbons.

In order to obtain high conversions, for example, above 70%, it is necessary that the catalyst and the hydrocarbon be subjected to very intimate mixing. It has been found that a high speed impeller mixer or turbo mixers available commercially will prdouce the necessary degree of mixing.

While liquid phosphoric acid is known to be a polymerization catalyst, it does not appear to function primarily as a polymerization catalyst in the process of this invention. An examination of the reaction product produced in the process of this invention indicates that the reaction which occurs when the light polymer feed is contacted with the liquid phosphoric acid catalyst in the conversion zone is not primarily polymerization, nor is it primarily a combination of depolymerization and polymerization, but rather it appears to be in the nature of disproportionation, molecular redistribution, and polymerization. It should be noted in this connection that essentially no gas is formed in the reaction and that the reaction product, when subjected to a true boiling point distillation, shows a uniform slope in a plot of distillation temperatures vs. per cent overhead. Such a uniform slope indicates that the hydrocarbons comprising the reaction product have varying molecular weights and that no particular molecular weight predominates in the product.

The manner in which the product of the reaction of the present invention contrasts with the products of a typical commercial polymerization reaction where recycle of the light polymer is employed is clearly shown by Figure 2 of the appended drawings. In Figure 2, the volume per cent overhead is plotted against the still temperature in a true boiling point distillation. The curves labelled "F–12 Product," "F–13–1 Product," and "F–14–1 Product," respectively, are the distillation curves for the heavy olefinic products obtained in runs F–12, F–13–1, and F–14–1 summarized in the foregoing tables. The curve labelled "F–6, Heavy Polymer" is the distillation curve for the heavy polymer produced in a run in which propylene is contacted with liquid phosphoric acid having a concentration of 103.5% calculated as orthophosphoric acid at a temperature of 300° F., a pressure of 350 p. s. i. g., and a space velocity of 0.95, and in which the light polymer product boiling below 350° F. was separated and recycled to the reaction zone together with the fresh propylene feed.

The curve labelled "Heavy Polymer, Commer-

cial" is the distillation curve of a commercial heavy polymer obtained by contacting propylene with a solid phosphoric acid catalyst at a temperature of 440° F., a pressure of 300–400 p. s. i. g., and a space velocity of 0.1 v./v./hr. In this run, the light polymer product boiling below 350° F. was separated and recycled into contact with the solid phosphoric acid catalyst, together with a fresh propylene feed. During this run the recycle ratio varied between 4:1 and 6:1, that is, 4 to 6 volumes of light polymer were recycled for each volume of liquid propylene charged as fresh feed. The curves of Figure 2 indicate that the F–6 Heavy Polymer and the Heavy Polymer, Commercial, are true polymers. Both curves show long plateaus in which a large proportion of the total polymer distilled in a narrow temperature range, which would indicate a uniform molecular weight of the overhead obtained across the plateau. In contrast to these curves, the curves for runs F–12, F–13–1, and F–14–1 conducted according to the process of this invention show no plateaus, but, rather, a uniform slope. The curve for run F–13–1 shows a sharp rise until the first 10% overhead has been removed, after which a uniform slope appears and persists throughout the distillation.

The product of the process of this invention characterized by uniform slope in the distillation curve as indicated in Figure 2 may be employed to considerable advantage in the preparation of alkyl aryl sulfonate detergents. When this reaction product is contacted with benzene in the presence of an alkylation catalyst under alkylation conditions and an alkylate is formed which is subsequently sulfonated to produce a detergent, the sulfonated product will show the same variety of molecular weights as that shown by the product of the process of the invention. The detergent thus prepared will contain hydrocarbon chains of varying lengths attached to the benzene ring. This characteristic in the detergent has been found to increase its efficiency. A good detergent appears to have two distinct characteristics. It has the ability to wet and remove dirt from a fabric and it has the ability to maintain the removed dirt in suspension so that it is not reabsorbed. It appears that the short chain alkyl aryl sulfonate detergents are more efficient in wetting the fabric and freeing the dirt from it, and that the long chain detergents are more efficient in maintaining the dirt in suspension. A detergent produced from the reaction product of the process of this invention shows both of these desirable characteristics.

It has been found that the liquid phosphoric acid here employed as the conversion catalyst is markedly superior to other polymerization catalysts which it might be attempted to employ for the same purpose. Comparative tests have been made in which both liquid phosphoric acid and a solid phosphoric acid catalyst were employed as the conversion catalyst to convert light propylene polymer to heavier olefinic hydrocarbons in the absence of propylene. The liquid phosphoric acid has been found to produce substantially higher conversion at lower temperatures. In Figure 3 of the appended drawings the per cent conversion of light propylene polymer to heavy olefinic hydrocarbons boiling above 350° F. has been plotted against space rate. Two curves are shown, one for liquid phosphoric acid at 300° F. and 0–75 p. s. i. g., and one for solid phosphoric acid catalyst at 380° F. and 250 p. s. i. g. It is seen from the curves that the conversion obtained with liquid phosphoric acid is somewhat more than twice the conversion obtained with the solid phosphoric acid catalyst. It should be noted that the temperature at which the solid phosphoric acid catalyst was employed is higher; however, this temperature was chosen because conversions obtained at lower temperatures were even less favorable.

I claim:

1. A continuous process for producing an olefinic hydrocarbon material characterized by a 5% point above 350° F. and a 90% point below 525° F. on a true boiling point distillation which comprises providing in a reaction zone a body of liquid phosphoric acid having a concentration in the range 103–110% calculated as orthophosphoric acid, intimately contacting with said acid a liquid olefinic hydrocarbon fraction separated from the reaction product of a catalytic polymerization of propylene, and boiling in a range below about 350° F., maintaining in the reaction zone a temperature below about 325° F. and contacting said hydrocarbon with said acid at a space velocity in excess of 0.2 volumes of hydrocarbon per volume of acid per hour.

2. A continuous process for the production of an olefinic hydrocarbon material having a boiling range extending substantially above 350° F. which comprises continuously introducing propylene polymers boiling below about 350° F. into a conversion zone, intimately mixing said polymers with liquid phosphoric acid having a concentration in the range 102–110% calculated as ortho-phosphoric acid in the conversion zone while maintaining therein a temperature below about 325° F., continuously withdrawing a mixture of acid and hydrocarbon from the conversion zone and settling it in a settling zone to separate an upper hydrocarbon layer and a lower acid layer, continuously returning the acid layer from the settling zone to the conversion zone and continuously withdrawing the hydrocarbon layer from the settling zone.

3. The method as defined in claim 2 wherein the hydrocarbon layer withdrawn from the settling zone is fractionally distilled to separate an overhead fraction boiling below about 350° F. and said overhead fraction is continuously recycled to the conversion zone.

LLOYD F. BROOKE.

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