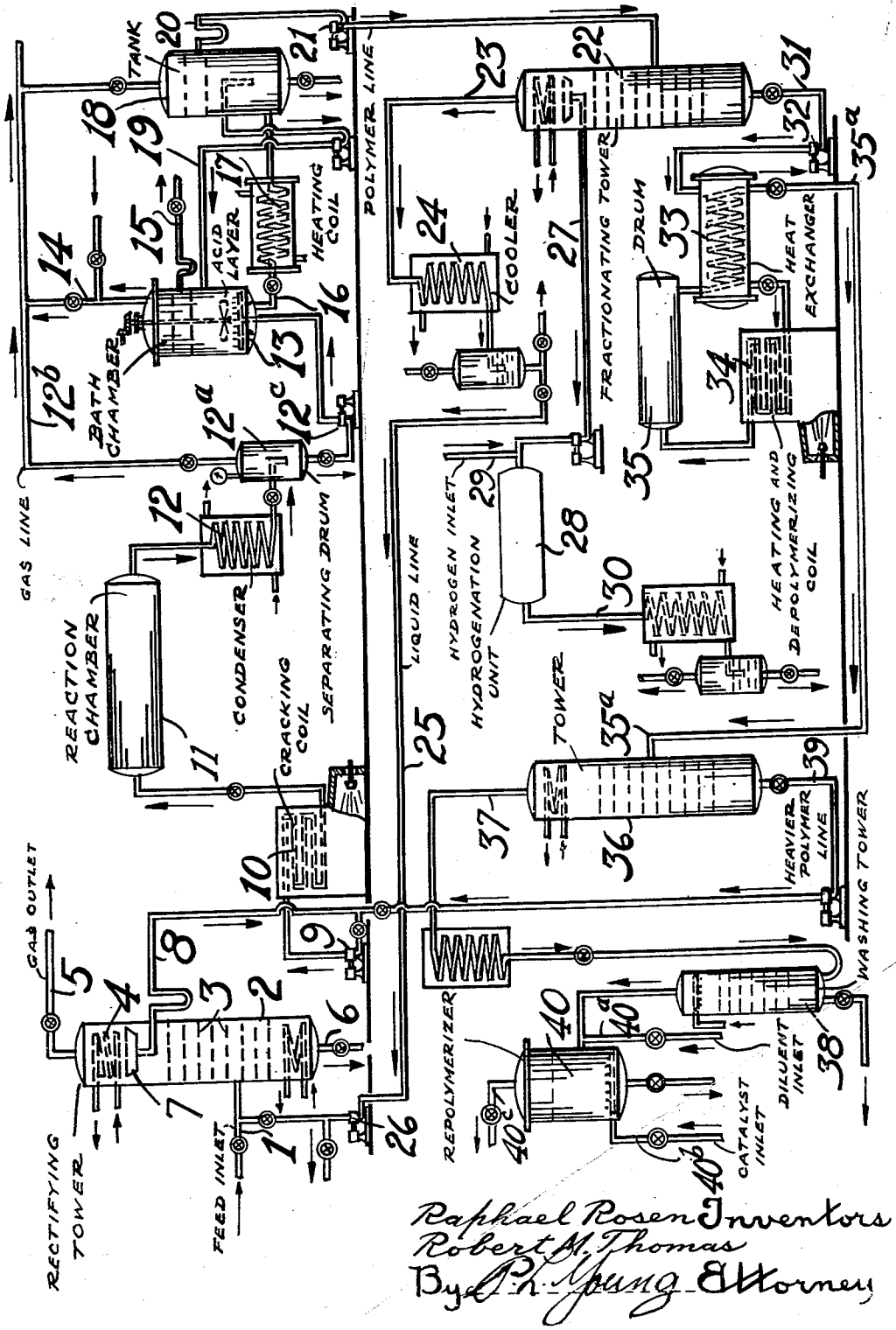
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Raphael Rosen Inventors
Robert M. Thomas
By P. K. Young Attorney

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PROCESS FOR PRODUCING VALUABLE POLYMERS FROM HYDROCARBON GASES

Raphael Rosen, Elizabeth, and Robert M. Thomas, Union, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

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The present invention relates to an improved process for obtaining valuable products from hydrocarbon gases and more specifically for obtaining valuable polymers. The invention will be fully understood from the following description and the drawing.

The drawing is a diagrammatic view in elevation showing the apparatus for use in carrying out the process and indicates the flow of material.

Within recent years much attention has been given to polymerization of normally gaseous olefins for the production of more valuable products; for example, of fuels or fuel blending fractions of high anti-detonation quality, also of lubricants and viscous to solid polymers of even higher molecular weight suitable as addition agents to lubricating oils to improve their temperature-viscosity characteristics and for other purposes. Polymers of molecular weight even higher than can be used for this latter purpose may also be made.

It also appears that among the normally gaseous hydrocarbons, isobutylene is preferred to any other olefin in the production of the various types of polymers mentioned above, and it is necessary for the refiners to carefully adapt their processes so as to make the best use of the limited amount of this particular raw material.

One object of the present invention is to present a method by which large yields of naphtha of high anti-detonation quality can be prepared while at the same time a good grade of high molecular weight polymer may also be produced. Economically and practically it is necessary that these two processes be connected since they use the same raw material, and the following specification discloses a method by which the hydrocarbon gases of the types available to refiners can be best utilized for producing anti-knock polymers and at the same time high molecular weight polymers, and describes methods by which the amount of either the one or the other type of polymer can be increased or decreased according to demand.

Referring to the drawing, the reference numeral 1 denotes a pipe by which light hydrocarbon fractions are fed to the system, preferably at least partially in liquid condition. The raw material may consist of gases and light liquids produced by cracking or similar light hydrocarbons obtained from crude stills. These gases are very largely saturated although they contain olefins and range from say methane to pentane. Pipe 1 discharges into a rectifying tower 2 which is fitted with the usual fractionation plates 3 and a reflux coil 4. The lighter fractions, essentially permanent gases such as methane and ethane, are allowed to pass overhead by a pipe 5, while pentane and any higher hydrocarbons are removed from the tower by a pipe 6. The lighter hydrocarbons may be used for fuel at the refinery or otherwise, and the heavier ones may be mixed with the regular production gasoline. An intermediate cut consisting essentially of butane and butylenes with or without propane and propylene is withdrawn from the tower by means of a pipe 8 connected to a pan 7, which is provided in the tower under the refluxing coil. As stated above, this intermediate cut consists essentially of butane, but propane may be included if desired. Otherwise, the propane is allowed to pass overhead through the pipe 5. The tower is preferably operated at elevated pressure, say in excess of 100 or 200 lbs. per square inch, in order to provide a refluxing temperature at the top of the tower 2 which can be obtained without refrigeration. It will be understood, however, that the tower can be operated at lower pressure if desired.

A pump 9 passes the intermediate cut which is in liquid condition through a heating and/or cracking coil 10, in which the hydrocarbons are raised to an elevated temperature of 1100 to 1600° F., and the cracking is accomplished or completed in a reaction chamber 11. The splitting reaction may be accomplished at ordinary or elevated pressures, either without catalyst or in the presence of suitable catalytic agents, particularly those promoting dehydrogenation in preference to breaking of the carbon bonds, such as clays, or catalysts containing the sixth group metals especially on aluminous or silicous supports.

The cracked product is cooled and preferably liquefied in the condenser 12. Gases, such as methane, ethane, ethylene, and hydrogen are separated in the drum 12*a* by line 12*b*, and the liquefied products are then passed by pump 12*c* into an acid absorption and/or polymerization bath 13. The acid is of suitable strength to selectively absorb and/or polymerize the olefins of four carbon atoms. The conditions and the results obtained will be specified more clearly below, but it is sufficient here to say that any olefins below butylene are not substantially affected and the polymer is essentially or principally a complex mixture of di- and tributylenes.

The temperature is preferably sufficiently high

in the acid bath to allow vaporization of any propane, propylene and other lighter hydrocarbons which pass off in vapor form through the pipe 14. These gases may be used as seems advisable, for example, converted into alcohols, ethers, or esters by known means, either along with the gases in pipe 12b or separately in an apparatus of a known type not shown.

The fractions dissolved by the acid consist chiefly of the various butylenes, while the saturated hydrocarbons collect in a layer above the acid. The upper layer may be withdrawn by a pipe 15, and used for whatever purpose desired, while the acid layer, containing the dissolved butylenes, is taken off by pipe 16, heated by rapid passage through heating coil 17 to effect polymerization, and is then discharged into a tank 18. The polymer separates from the acid in this tank and the acid which forms the lower layer is returned to tank 13 by pipe 19. The separated polymer is then withdrawn by pipe 20. If desired, a single absorption and polymerizing step may be substituted for the two-step process illustrated above.

Pump 21 forces the polymer withdrawn by pipe 20 into a fractionating tower 22, but it is preferable to wash the polymer so as to remove all acid prior to fractionation. Vapor is removed from fractionating tower 22 by pipe 23, and consists mainly of unconverted butane and butylene which are condensed in a cooler 24, from which the liquid is conveyed by pipe 25 and pump 26, out of the system for use elsewhere, or preferably, it is returned to pipe 1 for recirculation.

The butylene dimer cut is collected as an intermediate fraction and is removed from tower 22 by pipe 27. It may be used as such for gasoline or for other purposes, but is preferably hydrogenated which increases its anti-detonation value. The apparatus for hydrogenation is shown generally at 28 and may be in any desired form. Hydrogen is introduced by pipe 29 and the products removed by pipe 30. Some of the trimer may also be included and hydrogenated along with the dimer.

The unvaporized fractions of the polymer, consisting of the trimers and higher polymers, are drawn off by the pipe 31 and are forced by a pump 32 through a heat exchanger 33, and thence through a heating and depolymerizing coil 34. If desired, a drum 35 may also be included, but is ordinarily not required. The temperature in this coil is carefully adjusted so as to bring about only a partial depolymerization which is effective only on the polymers of isobutylene, that is to say, the polymers which are formed by the union of 3 or more molecules of isobutylene. The so-called co-polymers or mixed polymers formed by the union of one molecule of isobutylene with two or more of normal butylene, or the polymers of the normal butylenes, are found to be more staple and are substantially unaffected. The drum 35 discharges through line 35a into a fractionating tower 36, from which the isobutylene produced by depolymerization is withdrawn by a vapor pipe 37, cooled and condensed. It may be utilized as such but it is preferred to wash the product with soda or doctor solution or with other reagents to remove sulfur and sulfur compounds. This washing step is shown at 38. The heavier polymer remaining is collected as a residue and may be depolymerized in a second unit, but it is found most convenient to force this material through a pipe 39 to pipe 8 and thence into the heating coil 10 which will serve that purpose. In this way the regenerated butylenes are automatically recirculated to the process.

The isobutylene obtained by depolymerization is repolymerized in an apparatus shown generally at 40. Any desired form of the apparatus can be used for this purpose. A liquefied normally gaseous hydrocarbon diluent such as propane, ethane or ethylene may be added to the polymerizing vessel by a pipe 40a, and catalyst may be introduced by the pipe 40b. A low temperature, ranging from −10 to −100° C. may be maintained in the polymerization zone by any suitable means; for example, by allowing a portion of the solvent to vaporize by pipe 40c under an adjusted pressure.

In the present process, the acid polymerization is preferably conducted with sulfuric acid of a strength ranging from 60 to 75%. The olefins are introduced below the acid and preferably in liquid form in a fine state of sub-division which may be obtained by the use of a suitable nozzle, spray or other known device. The temperature for absorption is low, for example about room temperature. Polymerization is effected by heating to 150 to 200° F. for a short time, 1 second usually being sufficient. The polymerization unit is preferably held under pressure of say 100 to 200 lbs. per square inch or higher. The acid is not consumed in the reaction but losses occur which must be made up from time to time. Suitable agitation may be provided in the absorption zone and suitable settling space is also provided to allow complete separation for collection of the polymer. If a single zone for absorption and polymerization is used, the temperature should be from 150 to 300° F. and preferably a higher pressure, say, 400 lbs. per square inch, is employed. Yield and quality of the polymer depend to some extent on the nature of the raw material, the ratio of butylene to isobutylene, strength of acid and temperature. These factors should, of course, be inter-adjusted so as to obtain the best yield of polymer of the particular quality desired. The dimer formed by the union of two molecules of isobutylene is superior in some respects to a polymer formed by the union of a molecule of isobutylene and one of normal butylene, but the difference in quality is not very great, and by producing the copolymer it is possible to greatly increase the yield of naphtha. The above polymers are much superior to the dimers of normal butylenes and the process may be operated so as to give increased yield of less valuable dimer or decreased yield of superior products as the demand varies.

The polymers thus obtained do not consist entirely of dimer but of trimer and higher polymers are formed as well, for example 60–70% dimer, 20–30% trimer and 5–10% higher. These trimers and higher boiling polymers are, like the dimers, of several different types. The one is formed by the union of three or more molecules of isobutylene. Another type is formed by the union of isobutylene with one or more mols of normal butylenes. A third type is formed by the union of several mols of normal butylene.

One of the most important features of the present invention is the discovery that of all these various types of higher polymers, the first produced by the union of isobutylene molecules exclusively is the most readily depolymerized by heat, and that if conditions of depolymerization are properly conducted, the depolymerized product may consist substantially entirely of isobutylene. Depolymerization should be accomplished

at temperatures from about 650 to 950° F., but preferably 650 to 850° F., either in the absence of catalysts or in their presence, and if they are used, the preferred ones are the clays, silica, alumina and the like.

It should be understood that all of the polymers will eventually depolymerize under high temperatures if a sufficiently long time is employed, but it has been found that by limiting the duration of the reaction the depolymerized fraction may be substantially limited to the isobutylene. The time of reaction depends upon the temperature and the composition of the particular polymer treated. If the proportion of the true isobutylene is large, then a longer time can be employed under the same temperature conditions. In any case, the time is a matter of a few minutes only at temperatures of the range given above, and it is desirable to provide sufficient time to permit only depolymerization of from 65 to 85% of the polymer treated, especially in the case of the types of polymers obtained from the gases available to petroleum refiners, and the type of polymer produced by the acid treatment described hereinbefore. If this is exceeded to any substantial extent, the amount of normal butylenes becomes appreciable and does not permit a proper repolymerization of the isobutylene, as will be described below. Using a good clay catalyst at temperatures of 800 to 850° F. at 5 pounds per square inch gage pressure, yields of 70 to 80% isobutylene are obtained at the rate of 1 to 2 volumes per volume of catalyst per hour.

By properly selecting the low temperature of depolymerization and limiting the time, the depolymerized fractions, as noted above, are practically pure isobutylene and polymer fractions which can be separated by distillation. The isobutylene is separated as stated above and may then be repolymerized to produce high molecular weight polymers which are desirable for blending with lubricating oils and for other purposes. This reploymerization, as stated above, is accomplished at temperatures below −5° F. and preferably much lower temperatures of the order of −40° F. to −150° F., preferably in liquid phase, using catalysts of the active halide type, and particularly aluminum chloride, boron fluoride and titanium fluoride, although others are suitable as well as double halides of these materials and organo-complexes. The temperature must be held down during the reaction, and strong cooling or refrigeration is necessary because the heat of reaction is quite large. The isobutylene may be diluted prior to polymerization, preferably with saturated hydrocarbon gases or with ethylene. The lower the temperature used, the higher molecular weight of the polymer is recovered. In this way polymers ranging from 2000 to 10,000 may be readily produced at relatively low temperatures, −5 to −40° F., while polymers of the range of 50,000, 100,000 to 200,000 can be produced at extremely low temperatures of the order of −100° F. or below.

The following examples may be taken as illustrative of the nature of my process and the results obtained with it:

A mixture containing 10% of isobutylene, 25% of normal butylene and the balance made up of saturated hydrocarbons, is brought into contact with 65% sulfuric acid at room temperature. The undissolved portion of the hydrocarbon mixture is drawn off and the acid containing dissolved portion is heated by rapid passage through coil to polymerizing temperature of about 200° F. The polymer thus prepared is separated from the acid and is found on fractionation to consist of 60 to 70% dimer, 20 to 30% trimer and 5 to 10% of a somewhat heavier polymer.

The trimer cut was then separated into different portions which were cracked under different conditions, using in each case the same clay catalyst. The depolymerized product is repolymerized in each case, using boron fluoride as a catalyst at a temperature of −150° F., approximately. Care was taken during the polymerization to have the conditions as closely the same as possible. The following table shows the results of the runs:

Run No.	Feed	Cracking conditions: Temperature	Cracking conditions: Feed rate	Cracking conditions: Percent conversion of polymer	Molecular weight of the repolymerized product
		°F.			
1	Unwashed trimer	842	2	90.2	39,000
2	do	662	4	75.0	56,000
3	Trimer washed to remove sulfur	842	2	91.7	93,000
4	do	662	4	76.3	180,000
5	Trimer single step polymerization	842	2	77.0	31,000
6	do	662	4	44.6	51,000

The above runs clearly show that there is a profound influence in the molecular weight of the polymers produced, depending on the conditions of cracking. In runs 1 and 2, by lowering the temperature of cracking and by increasing the rate of flow, it was possible to obtain a selective cracking of the various polymers, so that the repolymerized product has substantially higher molecular weight than was obtained under conditions of non-selective cracking.

Run 3 and 4 show substantially the same thing. They also show the effect of removing sulfur compounds prior to repolymerization. The molecular weights obtained in 3 and 4 are substantially greater than those obtained in 1 and 2, and the effect of the cracking is even more pronounced in this pair of runs. It will be noted under the selective conditions a polymer of almost twice the molecular weight was obtained than could be obtained under non-selective cracking.

Runs 5 and 6, included in the above table, show the same general result but in this case, the original acid polymerization was carried out in a different manner. Here the acid polymerization was conducted in a single step at a temperature between 200 and 250° F. with 68% acid and at a pressure of about 400 lbs. per square inch. It will be noted also that the conversions are smaller in runs 5 and 6 than are obtained in previous runs. The reason for this appears to be that this method of acid polymerization gives a larger percentage of co-polymers than is produced in the two-stage process.

The present invention is not to be limited to any theory on the reactions involved or to any specific methods of polymerization or depolymerization, nor to materials drawn from any particular source, but only by the following claims in which it is desired to claim all novelty inherent in the invention.

We claim:

1. An improved process for preparing polymers of isobutylene, comprising selectively depolymer-

izing a mixture of polymers of isobutylene exclusively, polymers of normal butylene and copolymers of normal butylene with isobutylene, said mixture consisting substantially of trimers of the butylenes, by passing said mixture rapidly through a heated reaction zone at a depolymerization temperature of the order of 650 to 950° F. and providing sufficient time for depolymerization substantially only of the said polymers of isobutylene exclusively, whereby the depolymerized reaction product is substantially pure isobutylene, separating the isobutylene from the undepolymerized polymers, and repolymerizing the separated isobutylene.

2. An improved process for preparing polymers of isobutylene, comprising selectively depolymerizing a mixture of polymers of isobutylene exclusively, polymers of normal butylene and copolymers of normal butylene with isobutylene, said mixture consisting substantially of trimers of the butylenes, by passing said mixture rapidly through a heated reaction zone and at a depolymerization temperature of the order of 650 to 950° F., and providing sufficient time only for depolymerization to the extent of about 60 to 80%, whereby the depolymerized reaction product is substantially pure isobutylene, separating the isobutylene from the undepolymerized polymers, and repolymerizing the separated isobutylene.

3. An improved process for obtaining valuable polymers of isobutylene from hydrocarbon gases containing normal butylene and isobutylene, comprising first polymerizing said butylenes under conditions suitable for producing the maximum yield of polymers of said butylenes in the range of dimers and trimers, said polymers comprising a mixture of polymers of isobutylene exclusively, polymers of normal butylene and copolymers of isobutylene with normal butylene, separating said dimers from said trimers, then selectively depolymerizing said trimers by heating them at a temperature of the order of 650 to 950° F. and providing sufficient time for depolymerization substantially only of the said polymers of isobutylene exclusively, whereby the depolymerized reaction product is substantially pure isobutylene, separating the isobutylene from the undepolymerized polymers, and repolymerizing the separated isobutylene.

4. An improved process for obtaining valuable polymers from refinery gases rich in isobutylene and normal butylene, comprising first polymerizing such refinery gases in the presence of sulfuric acid of 60 to 70% strength at a temperature from about 150 to 300° F., whereby a substantial portion of the said butylenes is converted into a mixture of polymers in the range of dimers and trimers, comprising polymers of isobutylene exclusively, polymers of normal butylene and copolymers of isobutylene with normal butylene, separating said dimers from said trimers and higher polymers, then selectively depolymerizing said trimers by heating them at a temperature of the order of 650 to 950° F. and providing sufficient time for depolymerization substantially only of the said polymers of isobutylene exclusively, whereby the depolymerized reaction product is substantially pure isobutylene, separating the isobutylene from the undepolymerized polymers, and repolymerizing the separated isobutylene to polymers of high molecular weight.

5. Process according to claim 4 in which the polymers of higher molecular weight than the said trimers are separated from the said trimers prior to the said depolymerizing treatment.

6. A process according to claim 3 in which the first polymerizing step is brought about by contact with sulfuric acid of 60–70% strength at a temperature between 150 and 300° F.

7. A process according to claim 3 in which the first polymerizing step is brought about by contact with 60–75% sulfuric acid, under superatmospheric pressure sufficient to maintain the hydrocarbon in liquid phase, and a temperature of 150 to 300° F.

8. A process according to claim 4 in which the polymer remaining after the selective depolymerization is depolymerized in a separate step and recirculated to the acid polymerization step.

9. A process according to claim 4 in which the isobutylene obtained from the selective depolymerization step is repolymerized at a temperature below —5° F. in the presence of an active halide catalyst to a molecular weight in excess of 2000.

RAPHAEL ROSEN.
ROBERT M. THOMAS.