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ISOPRENE PRODUCTION BY PYROLYSIS OF C_6 ALKYL ETHER

Joseph A. Verdol, Dolton, and Byron W. Turnquest, Chicago, Ill., assignors to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

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10 Claims. (Cl. 260—681)

This application is a continuation of application Serial No. 95,521, filed, March 14, 1961, now abandoned.

This invention relates to a process for the production of isoprene from petroleum refinery streams.

In view of the similarity of cis-polyisoprene (i.e. "synthetic natural" rubber) to natural rubber, the demand for isoprene is increasing. The availability and cost of isoprene present formidable barriers to the commercial production of "synthetic natural" rubber.

The methods presently known and/or used for producing isoprene from petroleum refinery streams involve procedures wherein selected C_5 saturated or unsaturated hydrocarbons (isopentane or isoamylenes) are removed from the refinery stream by extraction or distillation and catalytically dehydrogenated to afford a C_5 fraction containing isoprene. These processes, however, have disadvantages which limit their usefulness. For example, expensive catalysts are employed and substantial amounts of piperylene and other undesirable materials are formed. Furthermore, the concentration of isoprene in the C_5 fraction is low so that the purification of the former requires the use of expensive extractive distillation techniques.

We have now discovered a process for the production of isoprene from petroleum refinery streams which does not have the disadvantages of isoprene production from C_5 refinery streams. In its broadest aspect in the present invention, comprises thermally cracking in the presence of an inert gas one or more tertiary C_6 alkyl ethers having the structural formula:

$$R—O—R'$$

wherein R is a tertiary C_6 alkyl radical and R' is a primary or secondary lower alkyl radical say of 1 to 6 carbon atoms, to produce isoprene. A tertiary alkyl radical contains a tertiary carbon atom, i.e. a carbon atom bonded to three carbon atoms. The tertiary atom in the above structural formula is also bonded to the oxygen.

Any source and method known to the art can be utilized to obtain the tertiary C_6 alkyl ethers of the present invention. A suitable source is the tertiary C_6 mono-olefins contained in mixed hydrocarbon streams boiling in the C_6 range. A petroleum refinery mixed stream boiling in the C_6 range, for instance, usually contains about 5 to 95% tertiary alkenes, preferably, for purposes of this invention, 25 to 95%. Other hydrocarbons present are non-tertiary olefins, parafins or other hydrocarbons and their mixtures. A tertiary olefin contains a tertiary carbon atom, i.e. a carbon atom bonded to three other carbon atoms and connected to one of these atoms by a double bond.

It is preferred that of the C_6 tertiary olefins in the mixed feedstock greater than about 10% is 2-methyl-2-pentene-2 and greater than about 5% is 2-methyl-pentane-1, the percentage of these two C_6 olefins usually constituting between about 30 to 80 percent but no more than about 50 or 60 percent is 2-methyl-pentane-2, Generally, there is also present about 15 to 50% 3-methyl pentane-2, about 5–35%, 2,3-dimethyl butenes, and about 0.5 to 15% 2-ethyl-butene-1. C_6 refinery

streams containing the above proportions of tertiary olefins can be conveniently derived from thermal and catalytic cracking of heavier petroleum hydrocarbons such as gas oils. In accordance with the process of the present invention, the tertiary alkenes contained in a mixed hydrocarbon stream boiling in the C_6 range is caused to selectively react with an alcohol of up to about 6 carbon atoms and the corresponding tertiary hexyl-alkyl ether product is then thermally cracked to produce isoprene.

The etherification can be performed, for instance, by using an ion-exchange material in the hydrogen form and in an amount sufficient to catalyze the selective conversion to the tertiary alkyl ether. The ether thus formed can be easily separated from the reaction mixture by distillation after removing the unreacted alkanol by washing the reaction mixture with water.

The organic hydrogen ion exchange etherification catalysts useful in accordance with the present invention are relatively high molecular weight water-insoluble resins or carbonaceous materials containing an SO_3H functional group or a plurality of such groups. These catalysts are exemplified by the sulfonated coals (Zeo-Karb H, Nalcite K, and Nalcite AX) produced by the treatment of bituminous coals with sulfuric acid, and commercially marketed as zeolite water softeners or base exchangers. These materials are usually available in a neutralized form, and in this case must be activated to the hydrogen form by treatment with mineral acid, such as hydrochloric acid, and water washed to remove sodium and chloride ions prior to use. Sulfonated resin type catalysts include the reaction products of phenol-formaldehyde resins with sulfuric acid (Amberlite IR–1, Amberlite IR–100, and Nalcite MX). Also useful are the sulfonated resinuous polymers of courmarone-indene with cyclopentadiene, sulfonated polymers of courmarone-indene with furfural, sulfonated polymers of courmarone-indene with cyclopentadiene and furfural and sulfonated polymers of cyclopentadiene with furfural. The preferred cationic exchange resin is a strongly acidic exchange resin consisting essentially of a sulfonated polystyrene resin, for instance a divinylbenzene cross-linked polystyrene matrix having about 0.5 to 20 percent, preferably about 4 to 16%, divinylbenzene therein to which are attached ionizeable or functional nuclear sulfonic acid groups. This resin is manufactured and sold commercially under various tradenames, e.g. Dowex 50, Nalcite HCR. This resin, as commercially obtained, has a moisture content of about 50% and it can be used in this form or it can be dried and then used with little or no differences in results ascertainable. The resin can be dried as by heating at a temperature of about 212° F. for 12 to 24 hours or the free water can be removed as by refluxing with benzene or similar solvents and then filtering.

The resin particle size is chosen with a view to the manipulative advantages associated with any particular range of sizes. Although a small size (200–400 mesh) is frequently employed in autoclave runs, a mesh size of 20–50 or larger seems more favorable for use in fixed bed or slurry reactors. The catalyst concentration range should be sufficient to provide the desired catalytic effect, e.g. between about 0.5 and 50 percent (dry basis) by weight of the reactants, with the preferred range being between about 5 to 25 percent (dry basis), for example, 10 percent.

In a continuous reactor the catalyst concentration is better defined by weight hourly space velocity; that is to say, the weight of feed processed per weight of catalyst per hour. A weight hourly space velocity of about 1 to 8 (based on hydrocarbon feed) and up to about 17 based on total hydrocarbon and alcohol feed may be used with

advantage. The WHSV can be about 0.1 to 100 based on hydrocarbon feed only, with the preferred WHSV being about 2 and 20.

The ether is formed by reacting the tertiary olefin in the hydrocarbon mixture with a primary alcohol, whether mono- or polyfunctional. A ratio of about 0.1 to 100 moles of primary alcohol (or polyol containing primary hydroxyl groups) per mole of tertiary olefin may be used in the etherification with the usual amount being between about 1 and 10 moles of primary alcohol per mole of tertiary olefin, preferably about 5 to 10 moles of the alcohol. A high ratio of alcohol to t-olefin increases the amount of olefin taken from the mixed hydrocarbon feed stream.

Primary alcohols, whether mono- or polyfunctional are effective in the etherification step of this process. Although secondary alcohols do react with tertiary olefins, the conversion rate is too low for practical purposes. Economy and ease of volatilization during the decomposition step generally dictate the use of alcohols of 1 to 6 carbon atoms, and in general, ethanol and methanol are preferred because of economy and, usually, they afford higher conversion rates.

The etherification temperature range is about 100–350° F., with the preferred limit being from about 100–225° F. The lower temperature range is preferred, since the formation of the tertiary ether is favored, and the formation of dialkyl ether (dimethyl ether in the case of methanol being used as the alcohol reactant) is not significant at lower temperatures. Runs performed at autogeneous pressures and others performed under nitrogen pressure of 400–500 p.s.i.g. showed that pressure has no significant effect upon the reaction. The pressure may range from about atmospheric pressure to about 5000 p.s.i.g. or more, with the preferred limits being between about atmospheric pressure and about 600 p.s.i.g. Pressures above atmospheric pressure may be required to maintain the reactants in the liquid phase; however, the reaction can be carried out at autogeneous pressure in a continuous system, which is preferred for commercial operation. Batchwise reaction in an autoclave is feasible.

The thermal cracking or pyrolysis of the mixed tertiary alkyl ethers is usually conducted in the presence of an inert gaseous diluent at a temperature of about 1000 to 1600° F., preferably 1250 to 1500 F. in the vapor phase for a contact time sufficient to provide isoprene. Ordinarily a contact time of 0.001 to 10 or more seconds is employed, preferably about 0.01 to 1.0 second. Operating conditions are usually adjusted to give a total hydrocarbon partial pressure of about .005 to 0.5 atmosphere, preferably about .01 to .04 atmosphere. The total pressure can be about 0.1 to 10 atmospheres, preferably about 0.5 to 1.5 atmospheres.

As aforementioned, the thermocracking operation is conducted in the presence of an inert gaseous diluent such as steam, nitrogen, carbon dioxide etc., and the inert gas will generally be present in a molar ratio of about 10–200 or more moles per mole of olefin feed, preferably about 5–100 moles per mole of the feed. If desired, the inert gas can be employed as the heating medium to bring the feedstock rapidly to the cracking temperatures. This can conveniently be done by heating the inert gas to a temperature above that desired for conducting the cracking operation, generally at least 75° F. higher than the actual temperature and not above say about 400° F. of the reaction temperature. The inert gas is then quickly mixed with the hydrocarbon which is at a temperature below that which any reaction would occur. The temperature to which the gas can be heated can be readily determined from the specific heat of the gas, the molar ratios involved, etc. Any of the heating means known to the art can also be utilized, the means chosen being in some cases a matter of economics. The product from the thermal-cracking step can be quenched as with water, for instance, at a temperature below about 500° F. and fractionated in ordinary fractionating equipment to obtain substantially pure isoprene.

The following examples will serve to better illustrate the present invention.

Example I

A fluid catalytically cracked gasoline was distilled to obtain a C_6 fraction boiling at 130–163° F. Analysis of the stream shows that it contained a total olefin content of 62 percent. A mixture comprised of equal volumes of the C_6 gasoline fraction and methanol was made. This mixture was pumped through a continuous flow reactor packed with Dowex 50X–8 catalyst (20–50 mesh) at a total weight hourly space velocity of about 10. The reactor was maintained at 200° F. and a pressure of 400–500 p.s.i.g. with nitrogen. According to gas chromotographic analysis, approximately 36 percent of the C_6 olefins in the refinery stream were converted to tertiary ethers. The ethers were isolated from the mixture by washing out the unreacted methanol with water and distilling the residue. The resulting mixed tertiary hexylmethyl ethers were collected at 105–111° C.

The ethers were converted to isoprene by passing them through a reactor about 15 cm. in length and 1.7 cm. in diameter packed with ceramic beads. Steam was passed into the reactor system from a preheater section of the reactor. The table below summarizes the results of two runs which were conducted at temperatures from 1292–1400° F. The conversion of the ethers varied from 70–99%. The contact time in each run was about 0.05 second.

Run	1148-54	1148-55
Water (Moles/hr.)	11.9	11.7
Ether (Moles/hr.)	0.17	0.22
Mole Ratio, Water/Ether	70	53
Temperature, °F.:		
Outlet	1334	1439
Inlet	1312	1432
Water Preheat	1312	1446
Pressure, mm. Hg	784	774
Contact Time, sec.	0.05	0.05
Relative Yields of Hydrocarbons, Wt. Percent:		
C_1–C_2	8.9	17.8
Propylene	1.7	3.6
Butenes	3.4	9.7
Amylenes	14.4	15.0
Isoprene	5.8	16.4
Hexenes	71.4	37.8
Conversion of C_6-Methyl Ethers	70	99

We claim:

1. A process for the production of isoprene which comprises subjecting a tertiary C_6 alkyl ether having the structural formula:

$$R—O—R'$$

wherein R is a tertiary C_6 radical and R′ is a lower alkyl radical, to thermal pyrolysis in the absence of a catalyst at a temperature of about 1000 to 1600° F. and in the presence of an inert gaseous diluent to produce isoprene.

2. The process of claim **1** wherein R′ is a methyl radical.

3. The process of claim **1** wherein the thermal pyrolysis is at a temperature of about 1300 to 1450° F. and the inert gaseous diluent is steam.

4. A process for the production of isoprene which comprises reacting the tertiary C_6 monoalkenes in a mixed hydrocarbon fraction boiling in the C_6 range containing said monoalkenes and other C_6 hydrocarbons, with an alcohol of 1 to 6 carbon atoms to obtain the corresponding tertiary hexyl alkyl ethers, said monoalkenes consisting essentially of 10% to 60% 2-methylpentene-2, greater than about 5% 2-methylpentene-1, about 15 to 50% 3-methylpenetene-2, about 5% to 35% 2,3-dimethylbutenes and about 0.5 to 15% 2-ethylbutene-1, the percentages of said 2-methylpentene-2 and 2-methylpentene-1 constituting about 30–80% of the C_6 hydrocarbon fraction and subjecting said tertiary hexyl alkyl ethers to thermal

pyrolysis in the absence of a catalyst at a temperature of 1000 to 1600° F. and in the presence of an inert gaseous diluent to produce isoprene.

5. A process for the production of isoprene which comprises subjecting a tertiary C_6 alkyl ether having the structural formula:

$$R—O—R'$$

wherein R is a tertiary C_6 radical and R' is a lower alkyl radical, to thermal pyrolysis in the absence of a catalyst at a temperature of about 1300 to 1450° F. and in the presence of an inert gaseous diluent to produce isoprene.

6. The process of claim 5 wherein R' is a methyl radical.

7. The process of claim 5 wherein the inert gaseous diluent is steam.

8. A process for the production of isoprene which comprises reacting the tertiary C_6 monoalkenes in a mixed hydrocarbon fraction boiling in the C_6 range containing said monoalkenes and other C_6 hydrocarbons, with an alcohol of 1 to 6 carbon atoms to obtain the corresponding tertiary hexyl alkyl ethers, said monoalkenes consisting essentially of 10% to 60% 2-methylpentene-2, greater than about 5% 2-methylpentene-1, about 15 to 50% 3-methylpentene-2, about 5% to 35% 2,3-dimethylbutenes and about 0.5 to 15% 2-ethylbutene-1, the percentages of said 2-methylpentene-2 and 2-methylpentene-1 constituting about 30–80% of the C_6 hydrocarbon fraction and subjecting said tertiary hexyl alkyl ethers to thermal pyrolysis in the absence of a catalyst at a temperature of 1300 to 1450° F. and in the presence of an inert gaseous diluent to produce isoprene.

9. A process for the production of isoprene which comprises subjecting the tertiary hexyl alkyl ethers of a mixture of tertiary C_6 monoalkenes consisting essentially of 10 to 60% 2-methylpentene-2, greater than 5% 2-methylpentene-1, about 15 to 50% 3-methylpentene-2, about 5 to 35% 2,3-dimethylbutenes and about 0.5 to 15% 2-ethylbutene, the percentages of said 2-methylpentene-2 and 2-methylpentene-1 constituting about 30 to 80% of the total mixture to thermal pyrolysis in the absence of a catalyst at a temperature of 1000 to 1600° F. and in the presence of an inert gaseous diluent to produce isoprene.

10. A process for the production of isoprene which comprises subjecting the tertiary hexyl alkyl ethers of a mixture of tertiary C_6 monoalkenes consisting essentially of 10 to 60% 2-methylpentene-2, greater than 5% 2-methylpentene-1, about 15 to 50% 3-methylpentene-2, about 5 to 35% 2,3-dimethylbutenes and about 0.5 to 15% 2-ethylbutene, the percentages of said 2-methylpentene-2 and 2-methylpentene-1 constituting about 30 to 80% of the total mixture to thermal pyrolysis in the absence of a catalyst at a temperature of 1300 to 1450° F. and in the presence of an inert gaseous diluent to produce isoprene.

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DELBERT E. GANTZ, *Primary Examiner.*

G. E. SCHMITKONS, *Assistant Examiner.*