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PROCESS FOR ISOMERIZING NORMAL BUTENES TO ISOBUTENE

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This invention relates particularly to the treatment of normal butenes to transform them into isobutene.

More specifically this invention comprises a novel process for accomplishing this particular isomerization reaction employing particular catalysts and conditions of operation. The butenes comprise the mono-olefins containing 4-carbon atoms per molecule. The names of these hydrocarbons, their structures, and boiling points are given in the following table for purposes of later reference:

Name	Structure	Boiling point, °C.
1-butene	$CH_3CH_2-CH=CH_2$	−5
2-butene, cis	$HC-CH_3$ ‖ $HC-CH_3$	+1-1.5
2-butene, trans	$H-C-CH_3$ ‖ CH_3-CH	+2.5
Iso-butene	CH_3 \ $C=CH_2$ / CH_3	−6

Recently the butenes have become of considerable importance to the petroleum industry as a result of the demand for high anti-knock fuel suitable for use in high compression aviation engines. They occur as constituents of cracked gases formed in plants operating primarily to produce gasoline and can also be produced by the catalytic dehydrogenation of butanes which occur in large quantities in wet natural gases and in still and tank gases of petroleum refineries. The butenes and butanes are utilizable as such only in limited quantities on account of their relatively high vapor pressures and at the present time there is considerable over-production of them so that processes are being developed for their more efficient utilization.

The steps in preparing octanes for use as high anti-knock saturated aviation motor fuel consists, at the present time, in first polymerizing butenes by either thermal or catalytic processes and then hydrogenating the resultant octene fractions. As a result of a large number of investigations it has been determined that the octanes having the highest anti-knock value are those which have the most compact molecules, or in other words the greatest branched-chain structure. Further, it has been shown that the dimers of isobutene, which correspond largely to 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene on hydrogenation yield octane fractions of considerably greater anti-knock value than do the dimers produced by the direct polymerization of the normal butenes, or by mixed polymerization of isobutene and normal butenes. In actual numerical values, using 2,2,4-trimethyl pentane as a standard of reference of 100 octane number, the hydrogenated dimers of isobutene have octane numbers of 97–100; those of normal butenes from 83 to 85, and hydrogenated mixed dimers from 90 to 97. These data are only approximate as it has been found that the actual values vary with the conditions of polymerization. It is obvious from the foregoing that any increase in the relative percentages of isobutene in hydrocarbon gas mixtures is very desirable and it is the object of the present invention to provide a process for accomplishing this object.

In one specific embodiment the present invention comprises treatment of normal butenes for the conversion thereof into isobutene by contacting said normal butenes at temperatures of the order of 600–1000° F., under substantially atmospheric or superatmospheric pressure, with activated bleaching clays comprising Tonsil, floridin, and the like.

The principal feature of the process of the present invention consists in the use of a definite type of catalyst (which is of proven value in polymerizing olefins) under modified conditions of operation so that normal butenes are isomerized to isobutene at a considerably higher rate than they are polymerized. In general, when using this type of catalyst, normal butenes, either alone or in gas mixtures, are best polymerized at temperatures within the approximate range of 300–600° F., under pressures in the order of 100–600 pounds per square inch and with relatively long times of contact.

According to the process of the present invention, the temperature is increased to some point within the range of 600–1000° F., the pressure is reduced to substantially atmospheric, or slightly sub- or super-atmospheric, and the time of contact with the catalyst is reduced markedly and is usually in the order of 0.1–4.0 seconds. Under these modified conditions isomerization reactions proceed with much greater rapidity than polymerization reactions and high yields of isobutene are formed which can be recovered as such from the products and later subjected to conditions suitable for the formation of dimers by using the same general type of catalyst, as well as the so-called "solid phosphoric acid catalyst," described in United States Patent No. 1,993,513, and others.

The catalysts which are used in the present connection comprise, generally, certain members of the class of aluminum silicates and include such naturally occurring substances as the various fuller's earths and clays, such as bentonite, Floridin, montmorillonite, etc. The class also includes certain artificially prepared aluminum silicates of which the product known as "Tonsil" is representative, this substance being in a sense a

purified aluminum silicate made by treating certain selected clays with hydrochloric or other mineral acids and washing out the soluble reaction products. Both the naturally occurring and acid-treated substances in this general class are characterized by a high adsorptive capacity which is particularly in evidence in the activated granular material prepared from these clays. Each substance which may be used alternatively will exert its own specific influence which will not necessarily be identical with that of the other members of the class.

For preparation of the preferred type of isomerization catalyst, the finely powdered clay is dried so as to remove the excess of adsorbent moisture and the powder is formed into grains by pressing hydraulically, or by suitable pelleting methods, to form pellets or granules of usable size. Shaped particles may be formed also by extrusion of the moistened and plastic clay. The pellets, or granules, are then dried and activated by heating in a current of dry air or other inert gas, at temperatures in the order of 600–1000° F., for an optimum time determined by trial. Such activation treatment displaces a substantial proportion of the adsorbed moisture from the particles of the bleaching clay, thereby increasing its adsorptive capacity.

In conducting the process for the isomerization of normal butenes the simplest mode of operation is to preheat the butenes, or gas mixture containing them, to a temperature in the desired approximate range during passage through some type of effective tubular heater, and then to introduce the preheated gas into a chamber containing a section, or a number of sections of the granular catalyst, in which the time of contact is so regulated that there is optimum production of isobutene. As will be shown in later examples, some polymerization is unavoidable and the next step in the process, after contacting with the catalyst, will be the separation of liquid polymers and the further segregation of the gaseous components so that the isobutene produced is available for selective polymerization under conditions most suitable for the formation of its dimers and the residual normal butenes may be recycled to further contact with the catalyst.

Since as a rule the normal butenes and isobutene in the resultant gas mixture will correspond to substantially a relatively constant proportion of these two components, a procedure is suggested which involves their mixed polymerization to form iso-octenes without attempting to separate the gaseous reaction products. This polymerization may be effected under revised conditions of operation using a suitable catalyst, such as solutions of sulfuric acid, metal phosphates as calcium and cadmium, the so-called "solid phosphoric acid catalyst," or the types of activated clays mentioned above, which involves preferably the segregation of the 4-carbon fraction from the light gases and any extremely heavy products and the subjection of the recovered intermediate butene-butane fractions to polymerization. Each polymerization catalyst, which may be used alternatively, will exert its own specific influence, will not be identical with that of other members of the class, and will require particular conditions for effecting optimum results.

Use of the solid phosphoric acid catalyst for such polymerization is preferably effected under what may be termed "critical" phase conditions; namely, pressures of approximately 500–700 pounds per square inch, temperatures of 225–325° F., and preferably a long time of contact in the order of 100–350 seconds. Under these conditions 4-carbon atom hydrocarbons may be considered to exist as extremely heavy vapors, and it has been found that mixed polymerization of isobutene and normal butene is favored so that properly proportioned mixtures are converted almost quantitatively into mixtures of iso-octenes, which are readily hydrogenatable, to a large extent, into 2,2,4-trimethylpentane, the standard of reference in anti-knock test work.

The activated clay type of catalyst for which butene isomerizing activity is apparently not dependent upon the presence of water, as is true with so-called "solid phosphoric acid catalysts," may be used at a relatively high temperature for long periods of time substantially without diminution in isomerizing activity. Such activity, which decreases probably because of carbon deposition, may be restored by heating the catalytic material in a current of air, or in large commercial installations in a flue gas mixture containing a controlled oxygen concentration, so as to burn off the carbonaceous deposit without overheating the catalyst. After such burning treatment, the catalyst is active and ready for use. Also the catalyst may be used on relatively dry butane-butene fraction rather than on a "B—B" fraction under conditions of carefully controlled humidity, which is necessary for obtaining optimum isomerization results using solid phosphoric acid catalyst. Obviously this preferred operation on relatively dry charging stock simplifies the plant construction and its operation.

While the chemical reactions involved in the isomerization of normal butenes into isobutene are not understood clearly or completely, the following is suggested as a mechanism of the reactions involved:

In contact with the activated clays the normal butenes may be considered to undergo polymerization reactions forming normally liquid products as octenes, together with trimers, tetramers, and higher polymers which later suffer so-called "Depolymerization" or catalytic splitting reactions producing isobutene, normal butenes, and liquid products of lower boiling points than the originally-formed polymers. In view of the complexity of such a combination of polymerization and splitting reactions, it is obvious that the above mechanistic concept may not express the exact course of the reactions involved; and, accordingly, the concept should not be misconstrued so as to limit the invention.

The following numerical data are introduced to indicate some of the results obtainable in isomerizing normal butenes by the present process, although it is not intended to limit the scope of the invention in strict accordance therewith:

Isomerization runs were made on a dry so-called "de-isobutenized" butane-butene fraction obtained as outlet gas from a selective polymerization process operated to produce iso-octenes from the isobutene and a substantial portion of the normal butenes present in a 4-carbon fraction of refinery gases. This charging stock, containing 1.6% isobutene, 19.4% normal butenes, 70.7% butane, 5% propene and propane, and 3.3% pentanes or higher hydrocarbons, was passed downwardly through a vertical, electrically heated tube containing 4–10 mesh particles of Tonsil bleaching clay, which had been activated by heating previously in a stream of air

at atmospheric pressure for 16 hours at a temperature of approximately 600° F. Before this activation treatment the particles or granules of the Tonsil clay had been formed by pressing the powdered clay into a hard cake, by means of an hydraulic press, and then crushing this cake and screening the granules to the desired mesh size.

Results obtained at intervals of 90° F., from 662° F. to 932° F., showed that the isomerization of normal butene into isobutene increased with temperature rise. It was found, also, that considerable polymerization occurred at low space velocities, but was avoided to a substantial degree at space velocities in the order of 470–500. Formation of propene and lighter gases, at the expense of the butenes, occurred to some extent when isomerizing butenes at relatively high temperatures using low space velocities. For convenience, the polymerizations and losses have been grouped together in Table 1 to include the conversions of butenes into heavier and lighter products.

In other runs normal butenes were isomerized partially into isobutene in the presence of activated Tonsil clay, floridin, and another clay known as "Filtrol", using the same procedure described above for the isomerizing treatment by Tonsil clay of normal butenes present in butane-butene fractions. At the relatively lower temperatures of 572–662° F., under atmospheric pressure, approximately 4–8% of the butene charged was isomerized into isobutene and a substantial amount of polymer was formed, especially at the relatively long contact times corresponding to the space velocity below approximately 200. In other runs it was observed that the presence of a diluent, such as butane, decreased the undesirable polymerization accompanying butene isomerization. Isobutene so produced by partial isomerization of normal butenes, and normal butenes in admixture with butane have been polymerized at temperatures of approximately 300–325° F., under pressures in the range of 500–700 pounds per square inch in the presence of a solid phosphoric acid catalyst to produce mixed polymers convertible by hydrogenation into paraffinic hydrocarbons containing substantial percentages of iso-octane fractions of 95 or higher octane number.

TABLE 1

Isomerization into isobutene of normal butenes present in "de-isobutenized B—B" using Tonsil bleaching clay catalyst under atmospheric pressure

Temp., °F.	Space velocity, vol./hr./vol. catalyst space	Contact time, seconds	Exit gas analysis, mole percent						Percent polymerization and loss	Percent isomerization
			C_3H_6	C_3H_8	iC_4H_8	nC_4H_8	C_4H_{10}	C_5+		
	Charging stock		0.4	4.6	1.6	19.4	70.7	3.3	----	----
662	235	3.5			3.6	11.0			28.2	9.5
664	470	1.7			4.4	14.6			8.8	14.1
752	251	3.3	1.4	4.3	4.4	11.5	75.7	2.7	22.8	13.5
752	490	1.6			5.1	15.9			0	18.1
842	235	3.0	1.2	3.6	5.4	10.6	75.6	2.7	21.9	18.0
842	470	1.5			5.2	15.4			1.9	18.5
932	235	2.8	1.1	3.8	5.8	11.3	75.9	2.1	17.7	20.6
932	470	1.4	0.8	4.2	5.7	15.8	72.8	0.5	0.0	21.1

After these runs, which lasted approximately 5 hours, the catalyst was still as hard as when charged but black with a carbonaceous deposit on both the exterior and interior of the particles. It was then reactivated by heating in a stream of dry air for 10 hours at temperatures increasing gradually from 260 to 900° F., followed by 8 hours at 900° F., after which the catalyst had regained its original buff color.

This reactivated catalyst was next subjected to a life test at 842° F., using a space velocity of approximately 210–240. As shown by the results in Table 2 the percentage isomerization started at 24%, dropped to 17.7% after 3 hours, and continued there for 14 hours more. From the 40th to 80th hour on test the isomerization varied from 12.4 to 13.4. The test was continued through 114 hours, after which the catalyst was reactivated at 900° F., as above described.

The foregoing specification and limited numerical data will serve to indicate the character of the process of the present invention and the nature of the results to be expected in its practice, although neither section is introduced with the idea of unduly limiting the invention's generally broad scope.

We claim as our invention:

1. A process for producing isobutene which comprises subjecting normal butene, at a temperature in the approximate range of 600–1000° F. and a contact time of about 0.1 to about 4 seconds, to the action of an acid treated clay which has been activated by heating in a stream

TABLE 2

Isomerization into isobutene of normal butenes present in "de-isobutenized B—B" using Tonsil bleaching clay catalyst at atmospheric pressure and 842° F.

Time on test, hrs.	Space velocity. vol./hr./vol. catalyst space	Contact time seconds	Exit gas analysis, mole percent						Percent Polymerization and loss	Percent isomerization
			C_3H_6	C_3H_8	iC_4H_8	nC_4H_8	C_4H_{10}	C_5+		
	Charging stock		0.4	4.6	1.6	19.4	70.7	3.3		
1	213	3.4			6.4	12.5			9.7	24.1
3–4	222	3.2	0.8	2.5	5.1	14.1	75.8	1.7	8.4	17.7
16–17	235	3.1	1.1	4.8	5.0	15.8	72.5	0.8	0.9	17.5
40–41	241	3.0	0.3	2.9	4.0	18.6	73.3	0.9	0	12.4
68–69	241	3.0	1.1	5.9	4.2	17.8	70.6	0.4	0	13.4
80–81	213	3.4	0.8	4.4	4.1	16.8	73.0	0.9	0	12.9
93–94	227	3.1	0.2	0.8	5.4	17.0	75.1	1.5	0	19.6

of dry air at a temperature of the order of 600–1000° F.

2. A process for producing isobutene which comprises subjecting a mixture of normal butenes and a saturated hydrocarbon diluent gas, at a temperature in the approximate range of 600–1000° F. and a contact time of about 0.1 to about 4 seconds, to the action of an acid-treated clay which has been activated by heating in a stream of dry air at a temperature of the order of 600–1000° F.

3. A process for producing isobutene which comprises subjecting a mixture of normal butenes and butane, at a temperature in the approximate range of 600–1000° F. and a contact time of about 0.1 to about 4 seconds, to the action of an acid-treated clay which has been activated by heating in a stream of dry air at a temperature of the order of 600–1000° F.

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