DEHYDROGENATION OF ISOPENTANE TO ISOPRENE

FIG. 2.
This invention relates to the dehydrogenation of isopentene to isoprene.

Hitherto, it has been proposed to form isoprene directly from isopentane by a single step dehydrogenation process. Considerable difficulty is encountered in obtaining adequate yields, and in making proper separations of the isoprene products resulting from the single step dehydrogenation.

I have discovered that isoprene can be manufactured on a commercial scale by a two-stage catalytic dehydrogenation process. In the first step, isopentane is dehydrogenated in the presence of an alumina or magnesia catalyst promoted with an oxide of a metal of group IV, V, or VI of the periodic table. The resulting methylbutene is, in turn, dehydrogenated in the presence of a catalyst composed of a major amount of a potassium compound, a minor amount of iron oxide, and a small amount of chromium oxide. In this manner, isoprene is formed in suitable yields by a commercially feasible process.

A marked contribution to successful commercial operation is made by the particular separation steps utilized. More particularly, the effluent from both dehydrogenation steps is combined, after removal of methane and light gases, and this combined product is fractionated to provide an overhead product containing a preponderance of the isopentane present together with isopentane, 3-methylbutene-1 and 2-methylbutene-1 together with a bottom product containing 2-methylbutene-2 and the remainder of the isoprene. The overhead product is fed to a second fractionation zone of the 3-methylbutene-1 is taken overhead, while the bottom product is passed to an absorber-stripper unit to separate isopentane, which is recycled, from a fraction consisting principally of 3-methylbutene and 2-methylbutene-1. The latter fraction is combined with the isopentane, 2-methylbutene-2 bottom product from the first fractionation zone and fed to an absorber-stripper unit from which an isoprene product together with any heavier materials present in the dehydrogenation effluent is produced, the isoprene product being readily separated from the heavier oils in a subsequent fractionation step. The overhead fraction consisting principally of 2-methylbutene-1 and 2-methylbutene-2 is recovered from the last-mentioned absorber, combined with the 3-methylbutene-1 fraction from the second fractionation zone and fed to the second dehydrogenation step wherein these methylbutenes are dehydrogenated to form isoprene. In some cases, it is advantageous to add a portion of the isoprene, 2-methylbutene-2 bottom product from the first fractionation zone to the feed to the olefin dehydrogenation step.

It is an object of the invention to provide an improved two-step dehydrogenation process to produce isoprene from isopentane.

It is a further object to provide improved fractionation and separation steps resulting in a commercially acceptable process for isoprene manufacture.

It is a still further object to provide a process which can be efficiently and economically carried out on a commercial scale to produce a valuable isoprene product. Various other objects, advantages and features of the invention will become apparent from the following detailed description taken in conjunction with the accompanying drawing in which the figure is a flow diagram of the dehydrogenation process of the invention.

Referring now to the drawing in detail, the isopentane feedstock is fed through a line 10 to an isopentane dehydrogenation zone 11 where it is contacted with a catalyst under conditions such that the major reaction is the conversion of isopentane to isomeric methylbutenes. In a broad aspect of the invention, the catalyst can be any high-activity metal or metal oxide dehydrogenation catalyst or composite, alone or supported on suitable carriers, which catalysts have suitable activity at temperatures below those causing excessive cracking of isopentane and capable of promoting equilibrium conversion under the designated conditions.

In a more specific aspect of the invention, the catalyst employed is magnesia, alumina, or a combination thereof promoted with up to 40 percent of an oxide of a metal of group IV, V and VI of the periodic table. Specific examples of such catalysts are alumina promoted with 40 percent chromium oxide, alumina promoted with 40 percent zirconium oxide, alumina promoted with 40 percent titanium oxide, alumina promoted with 40 percent tin oxide, magnesia promoted with 20 percent molybdenum oxide, magnesia promoted with 40 percent zirconium oxide, magnesia-alumina promoted with 20 percent vanadium oxide, and unsupported active chromium oxide. The temperatures and pressures are selected within a range suitable for the catalyst used.

For successful commercial operation, I utilize an alumina catalyst with 20 percent chromium oxide with the feed to the dehydrogenation step in dry conditions. Conversion temperatures range from 1000 to 1100°F. at a liquid hourly space velocity of 0.1 to 1.0. Pressure is not a critical variable, and the process can be suitably operated at atmospheric pressure. However, in both steps, use of sub-atmospheric pressure results in increased isoprene yield.

The effluent from the dehydrogenation step 11 is passed to a light gas removal column 12 wherein methane, hydrogen, and other light gases are taken overhead. The bottom product from the demethanizer column is fed to a fractionation zone 13.

In the zone 13 a cut is made at isoprene, thus providing an overhead fraction of 3-methylbutene-1, isopentane, 2-methylbutene-1 and most of the isoprene together with a bottom product of 2-methylbutene-2 and the rest of the isoprene.

The overhead product from the zone 13 is fed to a fractionation zone 14 whence 3-methylbutene-1 overhead product is withdrawn by a line 15. The bottom product from the fractionator zone 14 is fed to a unit consisting of an absorber 16 and a stripper 17. In this unit, the bottom product from the fractionator 14 is contacted with a suitable non-volatile absorptive material, for example, furfural. Many solvents can be used in this step in a broadly similar manner. For example, ethylene glycol, methyl carbitol, and methyl Cellosolve. An overhead isopentane product is obtained from the absorber 16 which is recycled through a line 18 to the feed condensate 34. The dehydrogenation product is withdrawn by a line 16 and fed to the absorber 19. This fraction is combined with the isoprene, 2-methylbutene-2 bottom product from the fractionation zone 13 and fed to a unit consisting of a stripper 20 and a stripper 21. In this unit, there is circulated a solvent
of the type previously described in connection with the
absorber-stripper unit 16, 17. An isoprene product con-
taining any heavier materials which may be present is
recovered from the stripper 21 and fed through a line 22
to an isoprene column 23. From this column, an isoprene
product is withdrawn overhead through a line 24
where the heavier oils are recovered as a bottom product.

The overhead product of the absorber 20, which con-
ists principally of 2-methyl-butene-1 and 2-methyl-but-
tene-2, is withdrawn through a line 26, combined with
the 3-methyl-butene-1 overhead product from the fractiona-
tion zone 13, and fed to an olefin dehydrogenation unit 27.
In some cases, it is desirable to combine a portion of the
bottom product from the fractionation zone 13 with the
feed to the dehydrogenation unit 27.

In the unit 27, the methylbutenes are dehydrogenated
to isoprene by contact with a catalyst under suitable con-
version conditions. As most catalysts of this type are
steam active, steam is mixed with the feed by a line 28.

In a broad aspect of the invention, any suitable olefin
dehydrogenation catalyst can be employed in the zone
27, such as a catalyst composed of 3 percent chromium
oxide, 50 percent potassium carbonate and the balance
iron oxide.

However, an outstanding catalyst for securing com-
mercially satisfactory yields of isoprene is a potassium base
material composed of 51 to 59 percent by weight potas-
sium carbonate, 39 to 47 percent by weight iron oxide and
1 to 10 percent by weight chromium oxide. With this particu-
lar catalyst, satisfactory conversion of methyl-
butenes to isoprene is obtained at temperature of 1100 to
1250° F., liquid hourly space velocities of 1 to 10 and a
steam to hydrocarbon ratio of 5:1 to 20:1. Pressure
is not critical where the steam dilution is employed, and
the process can be conveniently operated at atmospheric
pressure. Under these conditions, a highly satisfactory
conversion of methylbutenes to isoprene is attained in the
dehydrogenation zone 27.

The effluent from the zone 27 is fed to a light gas
removal zone 29 where methane, hydrogen and other light
gases are taken overhead, the bottom product being fed
through a line 30 to the fractionation zone 13 in combina-
tion with the bottom product from the zone 12. If
steam is fed to the reactor 27, a condenser and settler
for water should be interposed between the reactor and the
zone 29. Thus, it will be apparent that decided economies
in separation are achieved by the process of the invention
in that separate fractionation systems are not required
for the two dehydrogenation steps. Moreover, the separa-
tion process permits the recovery of substantially
pure isoprene together with recovery of isopentane and
methylbutenes of suitable purity for recycling to the
respective dehydrogenation zones 11 and 27. The key
separation is in the absorber column 20. At a tempera-
ture of 25° C., a water content of 16 percent by volume
and a hydrocarbon content of 6.2 weight percent in the
solvent phase, a relative volatility of 2-methyl-butene-2
to isoprene of 1.62 can be attained with furfural solvent
which contributed to the recovery of the pure isoprene
and separation of the methylbutenes in sufficient purity
to recycle. Many pieces of apparatus are thus eliminated
from the separation system without losing the function of
such apparatus.

Also, the two-stage dehydrogenation process of isopent-
ane to isoprene utilizing a chromium oxide catalyst sup-
ported on alumina for the first stage and the potassium
oxide base catalyst containing iron oxide and a small
amount of chromium oxide in the second dehydrogena-
tion stage has been found to provide economically suitable
results and yields for commercial operation.

The following is presented as a specific example of my
process on the basis of one containing 100 mols of isopentane.
The composition of the materials at different portions of
the flow was as follows:
A catalyst consisting of 20 percent by weight chromium oxide supported on alumina was utilized in the isopentane dehydrogenation zone 11, and a catalyst consisting of 52.2 weight percent potassium carbonate, 44.6 weight percent iron oxide and 3.2 weight percent chromium oxide was utilized in the olefin dehydrogenation zone 27.

Conditions in the dehydrogenation zones were as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Overhead Product of Absorber 20</th>
<th>Overhead Product of Stripper 21</th>
<th>Bottom Product of Absorber Column 23</th>
<th>Overhead Product of Olefins Column 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol Per cent</td>
<td>Mol Per cent</td>
<td>Mol Per cent</td>
<td>Mol Per cent</td>
<td>Mol Per cent</td>
</tr>
<tr>
<td>Isoprene</td>
<td>79.6</td>
<td>98.9</td>
<td>8.0</td>
<td>9.9</td>
</tr>
<tr>
<td>2-Methyl-butene-1</td>
<td>76.9</td>
<td>81.0</td>
<td>1.0</td>
<td>96.0</td>
</tr>
<tr>
<td>2-Methyl-butene-2</td>
<td>76.2</td>
<td>81.0</td>
<td>1.0</td>
<td>96.0</td>
</tr>
<tr>
<td>Oils</td>
<td>76.2</td>
<td>81.0</td>
<td>1.0</td>
<td>96.0</td>
</tr>
</tbody>
</table>

A yield of 79.6 mols of isoprene was obtained for each 100 mols of fresh isopentane charged.

Operating conditions for the various separation zones were as follows, furfural being used as the absorbent material:

<table>
<thead>
<tr>
<th>Separation Unit</th>
<th>Top Temperature, °F</th>
<th>Bottom Temperature, °F</th>
<th>Pressure, p.s.i.a.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractionation zone 13</td>
<td>130</td>
<td>130</td>
<td>54</td>
</tr>
<tr>
<td>Fractionation zone 14</td>
<td>130</td>
<td>130</td>
<td>30</td>
</tr>
<tr>
<td>Absorber 16</td>
<td>80</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>Stripper 17</td>
<td>70</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Absorber 20</td>
<td>80</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>Stripper 21</td>
<td>70</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Isoprene Column 23</td>
<td>130</td>
<td>130</td>
<td>30</td>
</tr>
</tbody>
</table>

Of course, depending upon the particular solvent used and on the stream composition, the temperatures and pressures utilized in the separation may vary to produce the desired overhead and bottom products previously described.

With respect to the isopentane dehydrogenation, no appreciable spooling of the catalyst is observed with pentane feed stock over extended periods of operation. Due to the conversion, a carbonaceous deposit accumulates on the catalyst and, when 2.0 to 2.5 weight percent of coke is present, the catalyst should be regenerated by burning the coke therefrom with combustion gases containing 3 to 5 percent oxygen. One hour process and one hour regeneration cycles are suitable for large scale production and, under the described conditions, average conversions as high as 33 percent can be readily obtained.

The resulting catalyst operating under the described conditions, the reaction is quite selective, yielding hydrogen and alkylbutanes plus isoprene with only minor amounts of C4 to C9 paraffins and olefins and only traces of products having 6 or more carbon atoms. Surprisingly, no straight chain methylbutenes are formed which would yield the straight chain diolefins piperylene rather than the desired product, isoprene. Infrared data indicate that no straight chain alkenes are formed, with the sensitivity of the instrument being 0.25 percent.

The following example indicates the products obtained and conversions at various reaction conditions in zone 11.

<table>
<thead>
<tr>
<th>Run</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F</td>
<td>1,000</td>
<td>1,025</td>
<td>1,050</td>
</tr>
<tr>
<td>Space Velocity</td>
<td>4.9</td>
<td>4.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Cycle Time, minutes</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Conversion, percent</td>
<td>27.1</td>
<td>31.3</td>
<td>33.4</td>
</tr>
<tr>
<td>Efficiency (Isopentene plus isoprene)</td>
<td>84.7</td>
<td>87.5</td>
<td>83.7</td>
</tr>
</tbody>
</table>

It will be noted that utilizing the described catalysts and conditions a yield of 79.6 mols of isoprene was obtained for each 100 mols of fresh isopentane charged.
With respect to the olefin dehydrogenation in zone 27, it is observed that isomerization activity of the catalyst for double bond shift is high, with a result that an equilibrium mixture of the 3-methylbutenes is actually converted regardless of the feed composition. This produces the surprising result, therefore, that conversion and yield are substantially unaffected by changes in feed composition. The conversions obtained are 7 to 11 percentage points higher than the conversions obtained in converting butene to butadiene with the same catalyst.

Following are data indicating the excellent conversions, yields, and efficiencies at various operating conditions:

### TABLE III

**Composition of products and yields**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Feed</th>
<th>Raffinate</th>
<th>Extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1,175</td>
<td>1,175</td>
<td>1,175</td>
</tr>
<tr>
<td>Liquid Hourly Space Velocity</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Steam to Hydrogen</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Conversion %</td>
<td>31.00</td>
<td>40.25</td>
<td>47.30</td>
</tr>
<tr>
<td>Yield, Mole %</td>
<td>20.10</td>
<td>22.60</td>
<td>62.10</td>
</tr>
<tr>
<td>Efficiency, Mole %</td>
<td>58.30</td>
<td>62.00</td>
<td>80.90</td>
</tr>
</tbody>
</table>

**Products:**

- **Hydrogen:** 31.24, 31.40, 34.72
- **Methane:** 1.8, 1.1, 1.68
- **Ethylene:** 1.8, 1.9, 2.9
- **Carbon Dioxide:** 5.2, 2.9, 6.8
- **Propylene:** 25.9, 21.2, 57.3
- **Iso and Butene-1:** 78.6, 78.6, 99.3
- **Butene-2:** 5.0, 5.0, 6.9
- **Butadiene-1:** 2.7, 2.7, 2.7
- **3-Methyl-butene-1:** 16.0, 16.0, 16.0
- **2-Methyl-butene-2:** 20.0, 20.0, 20.0
- **Isoprene:** 96.8, 96.8, 96.8

1 Composite analysis by mass spectrographic and gas chromatographic methods.

To further illustrate the broad aspects of the invention relating to the two-step dehydrogenation of isopentane to form isoprene, I have shown in Figure 2 a system where, in the dehydrogenation products are separated by liquid-liquid extraction, rather than by fractionation. In this modification, there is an isopentane dehydrogenation zone 31 corresponding to the zone 11 of Figure 1, an olefin dehydrogenation zone 32 corresponding to the zone 27 of Figure 1, and a light gas removal zone 33.

In the modification of Figure 2, the effluents from both dehydrogenation zones are combined and separated in a single zone, rather than in separate zones as in Figure 1.

In one specific embodiment of the invention, 4228 mols per hour of effluent from the zone 33 is passed to a liquid-liquid extraction column 34 where it is contacted with methyl carbol as a solvent. The solvent enters the column through a line 35 at the rate of 37,300 mols per hour, and contains 7.8 percent water. Raffinate is withdrawn from the top of the column 34 by line 36 and passed to a flash zone 37, 192.0 mols per hour of isopentane is withdrawn overhead from the flash zone 37 and passed through a recycle line 38 to the dehydrogenation zone 31. About 1 mol per hour of solvent passes from the flash zone 37 to the line 35 to recycle solvent.

The extract from the column 34 is passed through a line 39 to a stripping zone 40, from which solvent is recovered. It is then passed through a column 41 by line 42 as reflux, and 258.0 mols per hour passing through a line 43 to a second liquid-liquid extraction column 44.

In the specific embodiment described, the column 44 has 80 trays and is operated at a temperature of 81°F.

The material balance for the column is shown by the following table, the figures being expressed in mols per hour.

**Component Feed Raffinate Extract**

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed</th>
<th>Raffinate</th>
<th>Extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Methyl-butene-1</td>
<td>19.1</td>
<td>18.9</td>
<td>0.2</td>
</tr>
<tr>
<td>Isopentane</td>
<td>9.0</td>
<td>9.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2-Methyl-butene-1</td>
<td>82.3</td>
<td>82.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Isoprene</td>
<td>78.6</td>
<td>78.6</td>
<td>0.0</td>
</tr>
<tr>
<td>2-Methyl-butene-2</td>
<td>90.5</td>
<td>88.7</td>
<td>0.8</td>
</tr>
<tr>
<td>250.8</td>
<td>171.6</td>
<td>78.2</td>
<td></td>
</tr>
</tbody>
</table>

It will be apparent, therefore, that the products of my novel two-step isopentane dehydrogenation process can be separated by liquid-liquid extraction, as well as by the distillation system shown in Figure 1.

While the invention has been described in connection with a preferred embodiment thereof, it is to be understood that this description is illustrative only and is not intended to limit the invention.

I claim:

1. The method of producing isoprene which comprises contacting isopentane with a chromium-alumina catalyst at a temperature of 1000 to 1100°F, separating methane and light gases from the dehydrogenation effluent, fractionating the resulting material containing substantially all of the 5 carbon atom hydrocarbons contained in said dehydrogenation effluent to separate a first fraction consisting essentially of 3-methylbutene-1, isopentane, 2-methyl-butene-1 and isoprene together with a second fraction consisting essentially of isoprene and 2-methyl-butene-1 from the rich absorbent material, combining said second and fourth fractions and contacting them with an absorption medium in a second absorption zone, recovering a fifth fraction consisting essentially of 2-methyl-butene-1 and 2-methyl-butene-2 from said second absorption zone, stripping an isoprene fraction from the rich absorbent material in said second absorption zone, separating an isoprene product from heavy oils in said...
isoprene fraction, combining said fifth fraction with said 3-methyl-butene-1 fraction, contacting the last-mentioned fractions with a catalyst consisting essentially of 51 to 59 percent by weight potassium carbonate, 39 to 47 percent by weight iron oxide and 1 to 10 percent by weight chromium oxide at a temperature of 1100 to 1250°F, together with steam, separating methane and light gases from the effluent of the last-mentioned dehydrogenation zone, and passing the remainder of said effluent containing substantially all of the 5 carbon atom hydrocarbons contained in the effluent of said last-mentioned dehydrogenation zone to the first fractionation zone along with the demethanized effluent from the first dehydrogenation zone.

2. The method of producing isoprene which comprises contacting isopentane with a chromia-alumina catalyst comprising about 20 percent chromium oxide at a temperature of 1000 to 1100°F, separating methane and light gases from the dehydrogenation effluent, fractionating the resulting material containing substantially all of the 5 carbon atom hydrocarbons contained in said dehydrogenation effluent to separate a first fraction consisting essentially of 3-methyl-butene-1, isopentane, 2-methyl-butene-1 and isoprene together with a second fraction consisting essentially of isoprene and 2-methyl-butene-2, fractionating said first fraction to separate 3-methyl-butene-1 therefrom, contacting the remainder of the material with an absorption medium in a first absorption zone, recycling isopentane from said first absorption zone to the dehydrogenation step, stripping a fourth fraction consisting essentially of isoprene and 2-methyl-butene-1 from the rich absorbent material, combining said second and fourth fractions and contacting them with an absorption medium in a second absorption zone, recovering a fifth fraction consisting essentially of 2-methyl-butene-1 and 2-methyl-butene-2 from said second absorption zone, stripping an isoprene fraction from the rich absorbent material in said second absorption zone, separating an isoprene product from heavy oils in said isoprene fraction, combining said fifth fraction with said 3-methyl-butene-1 fraction contacting the last-mentioned fractions with a catalyst consisting of about 52 percent by weight potassium carbonate, about 45 percent by weight iron oxide and about 3 percent by weight chromium oxide at a temperature of 1100 to 1250°F, together with steam, separating methane and light gases from the effluent of the last-mentioned dehydrogenation zone, and passing the remainder of said effluent containing substantially all of the 5 carbon atom hydrocarbons contained in the effluent of said last-mentioned dehydrogenation zone to the first fractionation zone along with the demethanized effluent from the first dehydrogenation zone.

References Cited in the file of this patent

UNITED STATES PATENTS

4,144,585 Eggertsen et al. ............. Jan. 21, 1947
4,212,506 Jones ..................... June 3, 1947
4,750,435 Fetchin .................... June 12, 1956
2,866,790 Pitzer ..................... Dec. 30, 1958