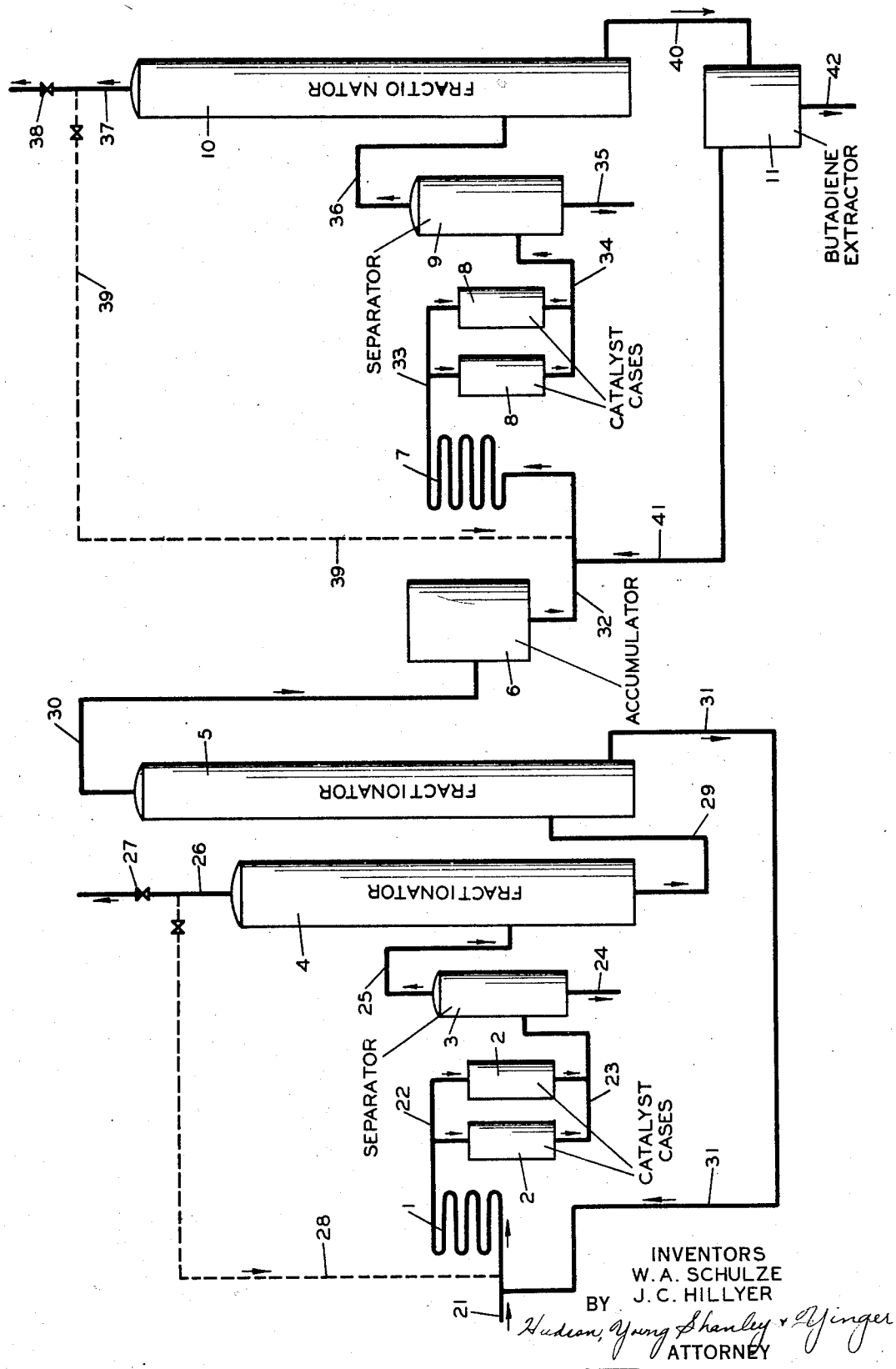
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PROCESS FOR THE DEHYDROGENATION OF HYDROCARBONS

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PROCESS FOR THE DEHYDROGENATION OF HYDROCARBONS

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This invention relates to the production of the valuable diolefinic hydrocarbon butadiene from suitable four-carbon-atom hydrocarbons. It relates more particularly to the process of dehydrogenating normal butane in successive stages to produce successively butenes and butadiene.

In a more specific sense this invention is concerned with a new and improved process in which the mono-olefin butene-1, obtained as one of the products from the catalytic dehydrogenation of normal butane or of the C_4 fraction of thermally cracked hydrocarbon gases is separated by fractional distillation and is subsequently dehydrogenated in a second catalytic step to produce a good yield of butadiene.

It has already been proposed to produce butadiene by the catalytic treatment of the total butene mixture resulting from the dehydrogenation of normal butane. However, it has been the practice of those attempting to carry out such a process to first dehydrogenate butane to produce mixed butenes and to recycle the treated vapors until the desired concentration of butenes was reached or the desired percentage of the butane charge had been converted. Because of the limitations imposed by thermodynamic equilibrium, it has not been possible to secure satisfactorily pure mixed butenes by this procedure without resorting to such severe conditions and excessive recycling that considerable quantities of the butane and butenes were decomposed, and the resulting yields of butenes were commercially not feasible.

Also attempts have been made to produce mixed butenes by dehydrogenating normal butane and separating the resulting butenes after each passage over the catalyst for further dehydrogenation. Such attempts have involved various complex solvent extraction and chemical separation methods which have proved expensive and generally unsatisfactory.

We have now discovered a novel process for the production of butadiene which eliminates the unsatisfactory practices of the art to date. Our invention not only provides for the economical production of butenes from normal butane by catalytic dehydrogenation but also includes the segregation from said butenes of butene-1 as the most suitable charge to a second dehydrogenation treatment to produce butadiene. By the practice of our invention we have further discovered that the dehydrogenation of normal butane over suitable catalysts may be operated to yield larger amounts of butene-1 when butene-2 is recycled to the catalyst along with unconverted butane. Thus, it is an object of this invention to convert normal butane to butadiene in two stages of dehydrogenation using a stream of substantially pure butene-1 separated from the products of the first dehydrogenation step as a charge to the second dehydrogenation step.

In a mixture of C_4 hydrocarbons such as is produced by dehydrogenating normal butane and comprising butene-1, butene-2 (in both cis and trans forms) and normal butane, the boiling points at 760 mm. are 20° F. for butene-1, 33° F. for trans butene-2, 39° F. for cis butene-2 and 31° F. for n-butane. Up to the present, most attention has been centered on separating unconverted n-butane from the butene mixture, and even the very efficient commercial fractionating equipment available is not satisfactory for separating n-butane from trans butene-2 in such a mixture. For this reason the above-mentioned solvent extraction and chemical separation processes for the segregation of butenes have been attempted in spite of obvious disadvantages. However, we have discovered that a highly satisfactory fractional distillation may be conducted to separate butene-1 from the C_4 hydrocarbon mixture produced by the dehydrogenation of n-butane. By our process the C_4 hydrocarbons remaining after the separation of butene-1 and comprising butene-2 and unconverted n-butane are returned to the first dehydrogenation step for further conversion to butene-1.

We have further discovered that the efficiency of our process based on the segregation of butene-1 is not impaired by the continuous recycling of butene-2, but that the concentration of butene-2 in the effluents from the first dehydrogenation step does not at any time exceed the equilibrium value at any given temperature of dehydrogenation. This has been found to be due to the isomerization of butene-2 during the catalytic treatment to produce substantially the ratio of the isomeric butenes produced by dehydrogenation of pure n-butane regardless of the amount of butene-2 in the charge. This isomerization accompanying dehydrogenation enhances the value of our process by promoting the ultimate conversion of substantially all the C_4 hydrocarbons in our raw feed stock, and by assuring a feed of substantially constant butene-1 content for our fractional distillation step.

In its broader aspects, our invention comprises conducting the conversion of n-butane to butadiene by a series of steps listed below in the order employed: (1) catalytic dehydrogenation of n-butane; (2) separation of the C_4 hydrocarbon

mixture so produced by means of fractional distillation into an overhead fraction comprising substantially pure butene-1 and a bottoms fraction comprising butene-2 and n-butane; (3) continuously recycling the bottoms fraction to the initial dehydrogenating unit, together with fresh n-butane, and producing thereby additional butene-1, both by dehydrogenation of n-butane and by isomerization of butene-2; (4) subjecting the overhead fraction comprising butene-1 to a second catalytic treatment under suitable conditions to effect a considerable dehydrogenation to butadiene; (5) separating the butadiene so produced by any convenient means; and (6) recycling the unconverted butenes remaining after separation of the butadiene to either of the dehydrogenation steps as may be convenient. In the practice of this invention, any traces of butadiene formed directly in step (1) will of course distill over with the butene-1, and thus be recovered along with the butadiene from the second dehydrogenation.

If we use the C_4 fraction from refinery cracked gases instead of n-butane in our process, the steps of our invention are not materially altered. In such a fraction comprising n-butane and butenes, the butene concentration usually is not great enough to justify preliminary fractionation for the segregation of butene-1, and the entire stock is then dehydrogenated by the first step of our process to produce additional butenes prior to the separation of the butene-1 fraction. Obviously, if such a C_4 fraction is rich enough in butenes to approximate or exceed the butene content resulting from the initial dehydrogenation step we may first separate butene-1 by fractional distillation, and then return the butene-2 and n-butane as charge to the initial dehydrogenation operation. Any isobutene present in the stocks mentioned above may be removed or utilized as desired prior to treatment of said stocks by our process.

In order that the invention may be more clearly understood, reference will be made to the drawing, which is a flow diagram according to which the steps of the invention may be carried out.

In the drawing, the raw n-butane or suitable C_4 hydrocarbon feed comprising n-butane and butenes enters by line **21** into heater **1** where the feed stream is raised to the desired temperature. The hot vapors then pass by line **22** into catalyst cases **2**. These cases contain a catalyst capable of effecting the desired degree of dehydrogenation of n-butane to yield butenes. From **2**, the treated vapors pass with some cooling (not shown) through line **23** into polymer separator **3** where small amounts of heavy material are removed by line **24**. From **3** the vapors pass with required compression and/or cooling (not shown) into fractionating column **4**. In **4** a fractionation is effected to remove hydrogen and C_3 and lighter hydrocarbons overhead while the C_4 hydrocarbons constitute the bottoms fraction. The overhead fraction leaving by line **26** may be sent to further processing units through valve **27**, or a portion may be returned by line **28** into the raw butane stream ahead of the heater, providing the quantity of hydrogen gas thus returned is not allowed to pyramid in a fashion unfavorable to the dehydrogenation reaction. The C_4 fraction leaves column **4** by line **29** and is passed to fractionating column **5** wherein a fraction distillation is carried out to take butene-1 and butadiene overhead, while butene-2 and n-butane are removed from the kettel by line **31** and recycled to the raw feed stream ahead of the heater. The butene-1 fraction is collected in storage **6**, by means of line **30**. The auxiliary equipment for columns **4** and **5**, including heat exchangers, condensers, reflux accumulators and the like is familiar to the art, and thus is not shown in this flow diagram.

From storage **6** the butene-1 concentrate passes by line **32** into a heater **7**, where the stream is heated to the temperature required for the second dehydrogenation. The heated vapors pass by line **33** to catalyst cases **8** containing a suitable dehydrogenation catalyst. The treated vapors exit through line **34** with some cooling, and into polymer separator **9**, wherein small amounts of heavy material are removed through line **35**. From **9**, the stream passes through line **36** into fractionating column **10** after suitable compression and cooling (not shown). In column **10**, hydrogen and hydrocarbons including propane and lighter are removed overhead while C_4 hydrocarbons constitute the kettle product. The overhead product from **10** may be passed to further processing units through valve **38**, or optionally a portion or a component thereof may be sent through line **39** to the feed stream ahead of heater **7** to serve as a diluent. In the latter operation, the quantity of hydrogen gas recycled is regulated so as not to influence the reaction unfavorably. The C_4 fraction from column **10** passes through line **40** to the butadiene extractor **11** where butadiene is removed by suitable reagents. The unconverted mono-olefin leaves the extractor through line **41** and is recycled to the second dehydrogenation step into line **32** ahead of the heater **7**. The butadiene in combination with the extracting medium is taken through line **42** to a suitable desorbing or recovery unit (not shown).

In the operation of the first dehydrogenation step, the hydrocarbon vapors may be subjected to two or more successive treatments with dehydrogenation catalyst in a series of catalyst chambers, or the vapors or any fraction thereof may be recycled with the fresh feed vapors through the catalyst chamber. This may be accomplished, if desired, by splitting the stream of hot treated vapors leaving the catalyst tower with one part passing through a compressor or its equivalent wherein the pressure is raised enough to force the recycled vapors into the stream of heated vapors prior to passage into the catalyst tower. Some additional heat, also, may be supplied to the recycled vapors, if desired.

Other possible arrangements of the conventional equipment used in the practice of our invention will be apparent to those skilled in the art, and thus are held within the scope of our invention. Also, the conditions of temperature, pressure, flow rate and the like used in operating this equipment will depend largely on the selection of the catalyst to be used and on the desired degree of conversion, since each catalyst has a specific range of conditions within which it operates with maximum efficiency.

Many catalysts have been found for the dehydrogenation of hydrocarbons, and some of these may be used more or less successfully. Among the types suggested are metals, metallic oxides, particularly difficultly reducible oxides, but including oxides of metals in groups II to VIII inclusive of the periodic table, activated or lustrous carbon, clays, some silicates, and many others. The great variety of oxide catalysts makes them of the most importance.

In the practice of our invention the charging stock to the initial dehyrogenation operation is normally heated to temperatures in the range 850° to 1200° F. and passed over the catalyst at such velocities that contact time is quite short, of the order of 0.5 to 10 seconds. Pressures only slightly above atmospheric, from about 5 to 50 pounds are normally used, although higher pressures, up to 200 or 300 pounds gauge may be used, if desired. Conditions of operation are selected with reference to economic and technical factors in any given installation.

In the second dehydrogenation step of our process, the charge stock is heated sufficiently to maintain temperatures between about 1050 and 1350° F. in the catalyst cases. The catalysts used may be those which give a suitable degree of conversion of butene-1 to butadiene and do not induce excessive polymerization or cracking reactions. Further, it is usually desirable to maintain low partial pressure of butene-1 in the charge to the second dehydrogenation step, for example, by addition of an inert diluent in order to suppress deleterious side reactions involving butene-1.

Ordinarily two or more catalyst cases would be provided. Those cases not on stream will generally be under preparation for subsequent use, either by replacement of spent catalyst or by regeneration. Regeneration is contemplated whenever the activity has declined to any predetermined level. The regeneration may be carried out by means such as controlled treatment with an oxygen-containing gas.

The following example will serve to further illustrate one method of practicing our invention.

Example

Normal butane was charged to the system diagrammed in the drawing, operated at a pressure of 30 pounds per square inch gage. The heated vapors emerged from the furnace and entered the catalyst cases at 1120° F. The multiple cases were filled with calcined 6–14 mesh bauxite to such depth that the total pressure drop was of the order of five pounds or less, and the temperature of the entire bed maintained within the range of about 1100–1120° F. The butane was processed at a space velocity of 1000 volumes (STP) per hour per volume of catalyst, equivalent to a contact time of approximately 1.7 seconds. About 15 per cent of the butane charged was converted to butenes, and the run was continued for 24 hours before catalyst activity had declined to a point at which regeneration was necessary.

The effluents were subjected to fractionation employing two consecutive highly efficient fractionating towers. Hydrogen and light hydrocarbons separated in the first column accounted for about three per cent by weight of the charge. When the recycle stream of butene-2 had been admitted and a steady state of dehydrogenation-isomerization had been established the butene-1 taken overhead from the second column amounted to 15 per cent of the total charge to the heater. The butene-2 recycled was 30 per cent of the charge, butane recycled 52 per cent, and fresh butane added 18 per cent. Thus, an ultimate yield of about 83 per cent of the butane charged to the unit was obtained as butene-1.

The butene-1 was then charged to the second dehydrogenation step shown in the drawing, with three volumes of added substantially inert gas. It was processed at slightly above atmospheric pressure at a temperature of 1125–1130° F. over bauxite catalyst at a space velocity of 1400 volumes per hour. Twenty-eight per cent conversion per pass of the butene was obtained, of which 50 per cent was butadiene, and the remainder light gases, polymer, and coke. The remaining butene was recycled. A cycle of six hours operation followed by regeneration was used in this stage, the stream being changed to a fresh set of catalyst cases at the end of this period and the first catalyst regenerated by controlled combustion.

The foregoing specification and example have disclosed and illustrated the invention, but since it is of generally wide application and the number of examples of results obtainable by its use might be multiplied greatly, the scope of the invention is limited only by the following claims.

We claim:

1. In a process for preparing butadiene by a two-stage stepwise dehydrogenation of n-butane, the steps of separating by fractional distillation of the material resulting from the first dehydrogenation step an overhead fraction comprising chiefly butene-1 and a bottom fraction comprising essentially butene-2 and n-butane, recycling the bottom fraction to the first dehydrogenation step along with fresh n-butane, treating said overhead fraction in a second dehydrogenation step to convert a portion of said butene-1 to butadiene, separating the butadiene from the unconverted butene-1 and recycling the unconverted mono-olefin to the second dehydrogenation step.

2. A process for preparing butadiene from n-butane which comprises treating said n-butane with a dehydrogenating catalyst under suitable conditions to convert a substantial proportion to butenes, fractionating the resulting C_4 mixture comprising n-butane and butenes after the removal of heavy polymers and propane and lighter material therefrom to produce an overhead fraction comprising substantially butene-1 and a bottom fraction comprising essentially butene-2 and n-butane, continuously recycling said bottom fraction to the first dehydrogenation step along with fresh added n-butane feed, treating the butene-1 fraction with a dehydrogenating catalyst in a second step under suitable conditions to convert a substantial proportion of butene-1 to butadiene, treating the material from the second dehydrogenation step subsequent to the removal of heavy polymers and propane and lighter material therefrom to separate butadiene, and finally recycling the unconverted mono-olefin to the second dehydrogenation step along with fresh butene-1 feed.

3. A process of preparing butadiene from n-butane which comprises passing said n-butane over a dehydrogenation catalyst in a first dehydrogenation stage under such conditions as to produce a mixture comprising butene-1, butadiene, butene-2, and n-butane, fractionally distilling said mixture to produce an overhead fraction comprising said butene-1 predominantly and some butadiene and substantially free of n-butane and a bottom fraction comprising essentially said butene-2 and n-butane, continuously recycling said bottom fraction to said first dehydrogenation stage for further conversion along with said first-named n-butane under conditions such that isomerization of said recycled butene-2 to butene-1 and dehydrogenation of said recycled n-butane take place, and passing said overhead fraction over a dehydrogenation catalyst in a second dehydrogenation stage under such conditions as to produce butadiene.

4. The process of claim 3 wherein the effluent from said second dehydrogenation stage is treated to extract the butadiene content thereof, and the unconverted butene content thereof is continuously recycled to said second dehydrogenation stage for further conversion along with said overhead fraction.

5. A process of preparing butadiene from the C_4 fraction of cracked hydrocarbon gases containing n-butane and butenes which comprises passing said C_4 fraction over a dehydrogenation catalyst in a first dehydrogenation stage under such conditions as to produce a mixture containing additional butenes and comprising butene-1, butadiene, butene-2, and n-butane, fractionally distilling said mixture to produce an overhead fraction comprising said butene-1 predominantly and some butadiene and substantially free of n-butane and a bottom fraction comprising essentially said butene-2 and n-butane, continuously recycling said bottom fraction to said first dehydrogenation stage for further conversion along with said C_4 fraction under conditions such that isomerization of said recycled butene-2 to butene-1 and dehydrogenation of said recycled n-butane take place, passing said overhead fraction over a dehydrogenation catalyst in a second dehydrogenation stage under conditions such as to convert a portion of the butene-1 to butadiene, extracting the butadiene from the second stage dehydrogenation effluent, and continuously recycling the unconverted butene content of the effluent to said second dehydrogenation stage for further conversion along with said overhead fraction.

6. A process of preparing butadiene from n-butane which comprises passing said n-butane over a dehydrogenation catalyst in a first dehydrogenation stage under such conditions as to produce a mixture comprising butene-1, butadiene, butene-2, and n-butane, fractionally distilling said mixture to produce an overhead fraction comprising said butene-1 predominantly and some butadiene and a bottom fraction comprising essentially said butene-2 and n-butane, continuously recycling said bottom fraction to said first dehydrogenation stage for further conversion along with said first-named n-butane under conditions such that isomerization of said recycled butene-2 to butene-1 and dehydrogenation of said recycled n-butane take place, and passing said overhead fraction over a dehydrogenation catalyst in a second dehydrogenation stage under such conditions as to produce butadiene.

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