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PROCESS FOR THE DEHYDROGENATION OF HYDROCARBONS

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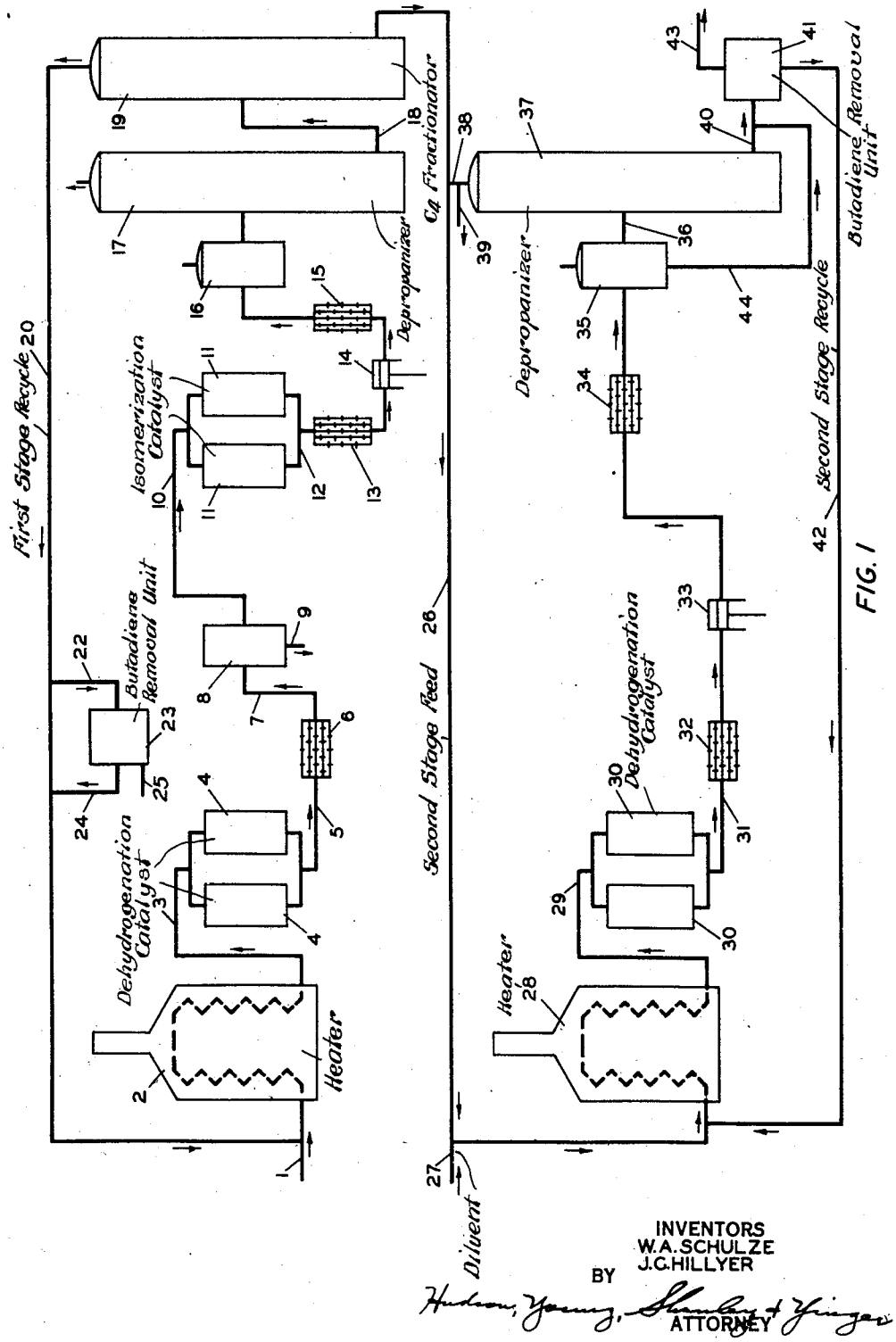


FIG. 1

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PROCESS FOR THE DEHYDROGENATION OF HYDROCARBONS

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2 Claims. (Cl. 260—680)

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-2 obtained as one of the products from the catalytic dehydrogenation of normal butane or of the C_4 fraction of thermally cracked 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 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 as 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 re-resulting yields of butenes were not commercially 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 by catalytic dehydrogenation but also includes the segregation of butene-2 as charge to a second dehydrogenation treatment to produce butadiene. By the practice of our invention we have further discovered that the equilibrium concentrations of butene-1 and butene-2 in the effluent from the dehydrogenation of n-butane can be adjusted by isomerization to increase the concentrations of butene-2 prior to fractionation, thus increasing the per pass recovery of substantially pure butene-2 by fractional distillation while butene-1 and n-butane together with a portion of the butene-2 are recycled to the dehydrogenation catalyst. It is therefore an object of this invention to convert normal butane to butadiene in two stages of dehydrogenation using a stream of substantially pure butene-2 separated after isomerization of 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 the boiling points of the components are as follows: (from—Physical Constants of Hydrocarbons, volume I—Egloff—Reinhold Publishing Company, 1939).

	°F.
Butene-1	20
Butadiene	23
n-Butane	31
Trans-butene-2	33
Cis-butene-2	39

It has already been proposed in copending application Serial No. 352,787 filed August 15, 1940, to separate butene-1 from this mixture by fractional distillation. However, the equilibrium concentrations established at dehydrogenation temperatures are such that of the total butenes produced, the predominant percentage is the 2-isomer. The following tabulation shows equilibrium concentrations of butene-1, trans butene-2, and cis butene-2 over a wide range of temperatures.

Temperature, °F.	Concentrations in mol per cent of total butenes		
	Butene-1	Trans butene-2	Cis butene-2
80	2.9	75.6	21.5
260	7.7	63.8	28.5
440	13.7	55.8	30.5
980	30.3	40.9	28.8
1,160	34.9	36.6	28.5

It is thus seen from the above tabulation that while the dehydrogenation of normal butane in the temperature range of 900 to 1200° F. yields high concentrations of butene-1 this represents only about one-third of the total butenes, the remaining two-thirds being cis and trans isomers of butene-2.

It may be seen also, in the above tabulation that at low temperatures the equilibrium concentration ranges up to more than 97 per cent of

butene-2. We have now discovered that the rapid attainment of the low-temperature equilibrium concentrations of butene-2 is possible by passage of the partially cooled effluents from the first catalytic dehydrogenation step through active isomerization catalysts at temperatures in the range of 250–500° F. Even lower temperatures may sometimes be used in this isomerization step. We have found it possible to convert nearly all of the butene-1 present in a C_4 hydrocarbon mixture of the type described above into the higher-boiling butene-2 isomers, thereby concentrating the butenes on the higher-boiling side of normal butane.

We have found that after the application of this step of catalytic isomerization at the proper temperature levels to the partially cooled vapors from the dehydrogenation of normal butane we are able to secure a satisfactory separation between normal butane and the butene-2 isomers by means of ordinary fractional distillation. Although clean separation between normal butane and trans butene-2 can be obtained only with columns employing somewhat more than 100 plates, we do not normally attempt to clean separation but conduct the fractionation in such manner that the bottoms product is composed predominately of butene-2. By our process, the overhead fraction comprising unconverted butene-1, normal butane, and a little trans butene-2 is recycled to the initial dehydrogenation step, while the bottoms fraction comprising the butene-2 rich fraction is the charge for the second dehydrogenation step to produce butadiene. Operating costs are extremely low due to (1) the catalytic isomerization step is performed on the effluents from the dehydrogenation step during the normal cooling operation in such manner that no additional heat input is required and (2) the fractionation step has been greatly simplified by concentrating the butenes on the higher-boiling side of normal butane.

In our process the recycled butene-1 does not build up in the system because the amount recycled is far below the equilibrium concentration at dehydrogenation temperatures and further conversion of normal butane reestablishes the equilibrium.

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) catalytic isomerization of the effluents from (1) to increase the concentration of butene-2 therein; (3) separation of the effluent from (2) by fractional distillation into an overhead fraction comprising butene-1, trans butene-2 and n-butane and a bottoms fraction comprising cis and trans butene-2 with some n-butane; (4) continuously recycling the overhead fraction to the initial dehydrogenation step along with fresh butane feed; (5) subjecting the bottoms fraction to a second catalytic dehydrogenation to effect a considerable conversion to butadiene; and (6) recycling the unconverted effluents of (5) after separation of butadiene to the second dehydrogenation step. In the practice of this invention, any butadiene formed in step (1) will distill overhead along with the butene-1 and n-butane fraction. If the quantity thus formed is large enough to make a recovery step feasible, the butadiene may be absorbed from the recycle material prior to re-introduction into the first dehydrogenation step.

If we use the C_4 fraction from refinery cracked gases instead of n-butane in our process the steps are not materially altered. In such a fraction comprising n-butane and butenes, the butene concentration is not usually great enough to justify the segregation of butene-2 prior to dehydrogenation, and the entire stock may be dehydrogenated according to the first step of the process. Obviously, if such a C_4 fraction contains normal butenes in concentrations equal to or greater than those produced by the first dehydrogenation operation, the raw feed may be charged directly to the second step of our process. Any isobutene present in the stocks mentioned above may be removed or utilized as desired prior to treatment by our process.

In order that the invention may be more clearly understood, reference will be made to the figure which is a flow diagram of the steps of the process.

In the figure the raw n-butane or suitable C_4 hydrocarbon feed comprising butane and butenes enters by line 1 into heater 2 where the feed is raised to the desired temperature. The hot vapors then pass by line 3 into catalyst cases 4 containing a suitable dehydrogenation catalyst. From 4 the treated vapors pass through line 5 to cooler 6 where the vapor temperature is lowered to the range desired for isomerization. The partially cooled vapors then pass by line 7 through polymer separator 8 wherein any heavy material is removed through line 9. The vapors then pass through line 10 into catalyst chambers 11 containing an isomerization catalyst. The effluents from 11 pass through line 12 and in turn through cooler 13, compressor 14, cooler 15 and into accumulator 16. From 16 the condensate passes to fractionator or depropanizer 17 for the separation of propane and lighter material overhead while the bottoms comprising C_3 and C_4 material passes through line 18 to fractionator 19. In fractionator 19 an overhead fraction predominantly lower boiling than trans butene-2 and comprising butene-1, n-butane and some trans butene-2 is taken overhead while cis and trans butene-2 and some n-butane constitute the bottoms fraction predominantly higher boiling than trans butene-2. The overhead fraction is recycled to the dehydrogenation step through line 20. If butadiene removal is desirable the recycle material passes through line 22 into absorption unit 23 and by line 24 back into the recycle line 20. Refrigeration (not shown) may be required. The butadiene addition product is removed by line 25. The conventional auxiliary equipment for fractionators 17 and 19 including heat exchangers, condensers, reflux accumulator and the like is familiar to the art and thus is not shown in this flow diagram.

The butene-2 concentrate, namely the bottoms fraction from 19, passes through line 26 and together with a diluent which may be added through line 27 enters heater 28 where the stream is heated to dehydrogenation temperatures. The hot vapors then pass through line 29 into catalyst chambers 30 containing a dehydrogenation catalyst. The dehydrogenated vapors leave through line 31 and then pass in turn through cooler 32, compressor 33, and cooler 34 into accumulator 35 where propane and heavier material are condensed and lighter material is vented. The liquid from 35 may pass through line 36 into fractionator or depropanizer 37. In 37, propane and lighter material is taken overhead and may enter line 26 through line 38 and serve as diluent gas or alternately may be vented through line 39.

The C_4 fraction from the bottom of fractionator **37** passes through line **40** to butadiene absorption unit **41**. The C_4 residuum from the butadiene absorption passes through line **42** and is recycled to the dehydrogenation step. The butadiene in combination with the absorption medium is taken to a suitable desorption or recovery unit (not shown) through line **43**.

Alternately, the C_3–C_4 liquid from accumulator **35** may pass with suitable refrigeration (not shown) directly to the butadiene absorption unit **41** through lines **44** and **40**. In this case, butadiene is absorbed from the total condensate without fractionation and the C_3–C_4 residuum passes as recycle to the catalyst through line **42**. The propane thus included may serve as diluent in the dehydrogenation to replace all or a part of the diluent indicated as added through lines **27** and **38**.

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 portion thereof may be recycled with the fresh feed vapors through the catalyst chambers. Some additional heat may be applied 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 catalyst to be used in each step 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 in the two dehydrogenation steps of our process. Among the types suggested are metals, metallic oxides, particularly difficult reducible oxides, but including oxides, of metals in groups II to VIII inclusive of the periodic system, activated or lustrous carbon, clays, some silicates and many others. The great variety of oxide catalysts makes them of the most importance.

For the isomerization step, catalysts active in relatively low temperature ranges are preferred. These include catalysts of an acidic nature; either mineral materials containing acidic substances such as certain clays and natural silicates, acidic salts such as aluminum phosphate and the like or strong mineral acid catalysts are useful. Other types of catalysts may be used under substantially anhydrous conditions, including alkali and alkaline earth metal oxides, but the acidic catalysts are generally more uniform and more active.

In the practice of our invention the charging stock to the initial dehydrogenation operation is usually heated to temperatures in the range of 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. Low superatmospheric pressures of about 5 to about 50 pounds gage are normally used, although higher pressures up to 200 or 300 pounds gage may be used if desired. Conditions of operation are selected with reference to economic and technical factors in any given installation.

In the isomerization step of our process the effluent vapors from the initial dehydrogenation are cooled and any heavy polymer formed may be separated prior to passage in vapor phase over the isomerization catalyst at temperatures within the range of 200 to 600° F. The temperature is maintained at the lowest level which will give rapid isomerization and a minimum of polymerization reactions since the equilibrium favors butene-2 at lower temperatures. Low superatmospheric pressures of 5 to 50 pounds gage are suitable in the isomerization reaction, and flow rates equivalent to 0.5 to 5 liquid volumes of charge per hour volume of catalyst are usually satisfactory. The effluents from the isomerization step are further cooled, compressed, and partially condensed prior to the fractionation for separation of butene-2 for the second dehydrogenation operation.

In the second dehydrogenation step, the charge stock is heated sufficiently to maintain temperatures between about 1050 and 1350° F. in the catalyst chambers. The catalysts used may be those which give a suitable degree of conversion of butene-2 to butadiene and which do not induce excessive polymerization and cracking reactions. Further, it is usually desirable to maintain low partial pressure of butene-2 in the charge to the second dehydrogenation step, for example by addition of an inert diluent, in order to suppress deleterious side reactions involving the unsaturated hydrocarbons.

Ordinarily two or more catalyst chambers would be provided for each catalytic step. Those chambers not in service would be under preparation for subsequent use, either by replacement or spent catalyst or by regeneration. Regeneration is contemplated for the dehydrogenation catalysts 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 gauge. 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 cooled quickly to about 450° F. and passed over an aluminum phosphate catalyst to isomerize butene-1 to butene-2. The vapors emerging from this tower had approximately the equilibrium concentration, or about 14 per cent of the butene content as butene-1 and 86 per cent as butene-2.

The effluents from this tower were depropanized and submitted to fractionation in the highly efficient tower diagrammed. The cut was made in the trans butene-2 fraction, separating as bottoms

cis butene-2 and part of the trans butene-2 together with some butane. The light gases were separated from the butane-butene-1 overhead and the latter was recycled. When the recycle stream of butane and butene-1 had been admitted and a steady state of dehydrogenation-isomerization had been established, hydrogen and light gases separated accounted for about three per cent by weight of the charge. Butene-2 separated from the bottom of the tower accounted for 21 per cent of the total charge to the heater with which additional butene equivalent to 2 per cent of the charge was associated. The butene-1 and trans butene-2 recycled amounted to 24 per cent of the charge, while the butane recycled was 50 per cent and fresh added butane was 26 per cent of the charge. Thus an ultimate yield of about 81 per cent of the butane charged to the first dehydrogenation was obtained as butene-2 in the charge to the second dehydrogenation.

The butene-2-butane fraction was then charged to the second dehydrogenaton step shown in the drawing, with sufficient volume of substantially inert diluent gas to reduce the partial pressure of butenes to 25 per cent of the total pressure. This stock was processed at a pressure of 5 pounds gage and at a temperature of 1125–1130° F. over bauxite catalyst. A space velocity of 1400 volumes per hour was employed. About 28 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 C_4 fraction after removal of fixed gases and the extraction of the butadiene 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 gases 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 obtained by its use might be multiplied greatly, the scope of the invention is limited only by the following claims.

We claim:

1. A process for preparing butadiene from n-butane which comprises treating said n-butane with a dehydrogenating catalyst under suitable conditions to produce a mixture comprising butadiene, butene-1, butene-2, and butane, passing said mixture over an isomerization catalyst under conditions suitable to promote the conversion of butene-1 to butene-2, fractionating the effluent from the isomerization step to produce an overhead fraction predominantly lower-boiling than trans butene-2 and a bottoms fraction comprising essentially cis and trans butene-2, recycling said overhead fraction after absorption of butadiene therefrom to the initial dehydrogenation step along with fresh butane feed, treating said bottoms fraction in a second dehydrogenation step to convert a substantial proportion of the butene-2 to butadiene, separating the butadiene from the products of the second dehydrogenation step prior to recycling the unconverted C_4 material therefrom to the second dehydrogenation step along with fresh added butene-2 stock and finally combining the butadiene so recovered from the two dehydrogenation steps.

2. A process for preparing butadiene from hydrocarbon mixtures containing major proportions of n-butane which comprises catalytically dehydrogenating said mixture under suitable conditions to convert a substantial portion of the n-butane to butenes-1 and 2 with the simultaneous production of some butadiene, catalytically isomerizing the butene-1 in the dehydrogenated material to butene-2 as the principal reaction to increase the butene-2/butene-1 ratio, fractionating the isomerized material to produce a fraction predominantly lower boiling than trans butene-2 and a fraction comprising cis and trans butene-2, removing butadiene from said lower boiling fraction and recycling the remainder of the lower boiling fraction along with fresh feed to the first dehydrogenation catalyst, catalytically dehydrogenating the butene-2 rich fraction in a second dehydrogenation step under suitable conditions to convert a portion of the butene-2 to butadiene, extracting the butadiene so produced and recycling to the second dehydrogenation step the unconverted butene stock along with fresh added butene-2 feed.

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