Jan. 16, 1945. W. A. SCHULZE ET AL 2,367,622

PROCESS FOR DEHYDROGENATION OF HYDROCARBONS

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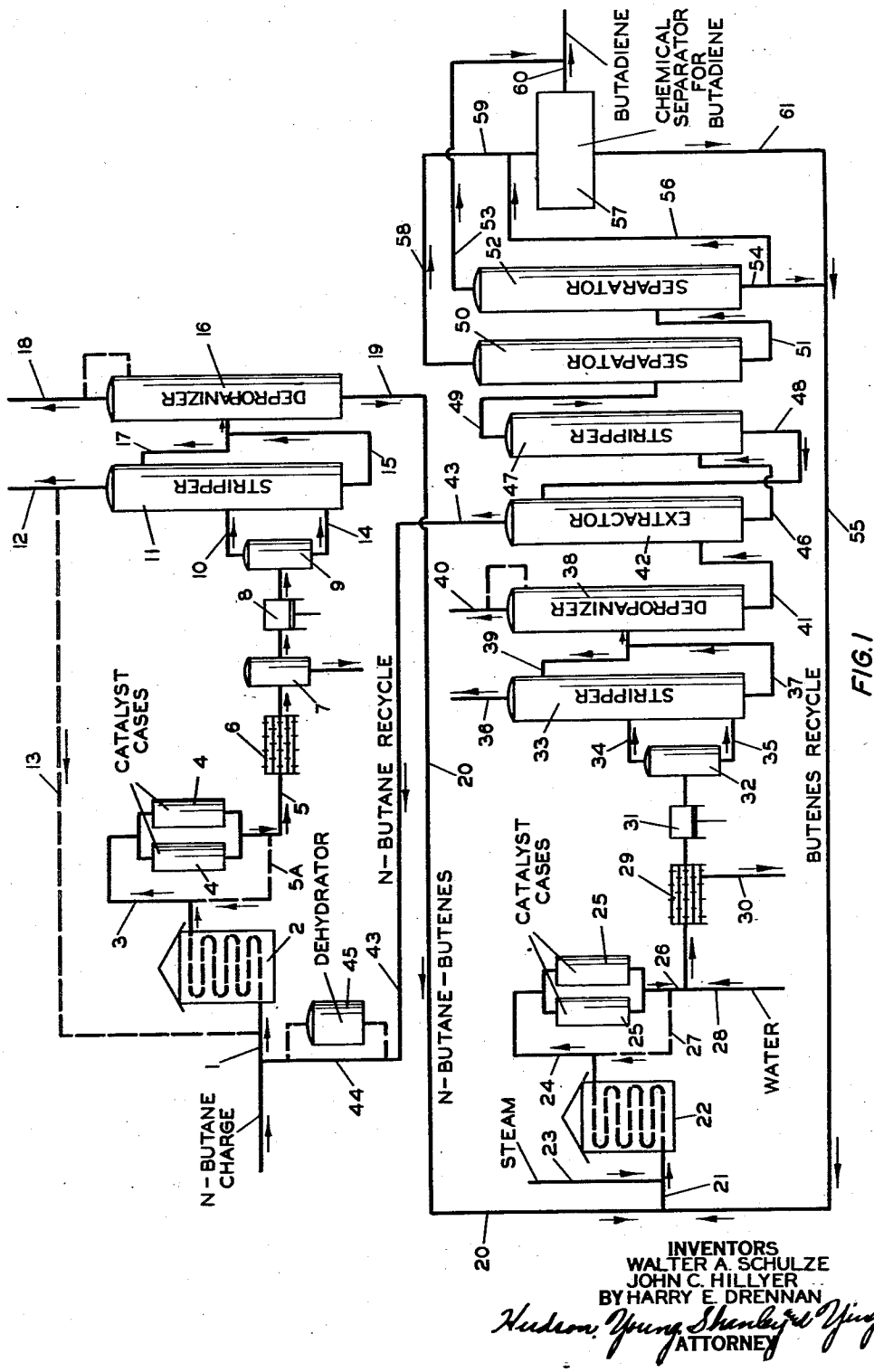


FIG. 1

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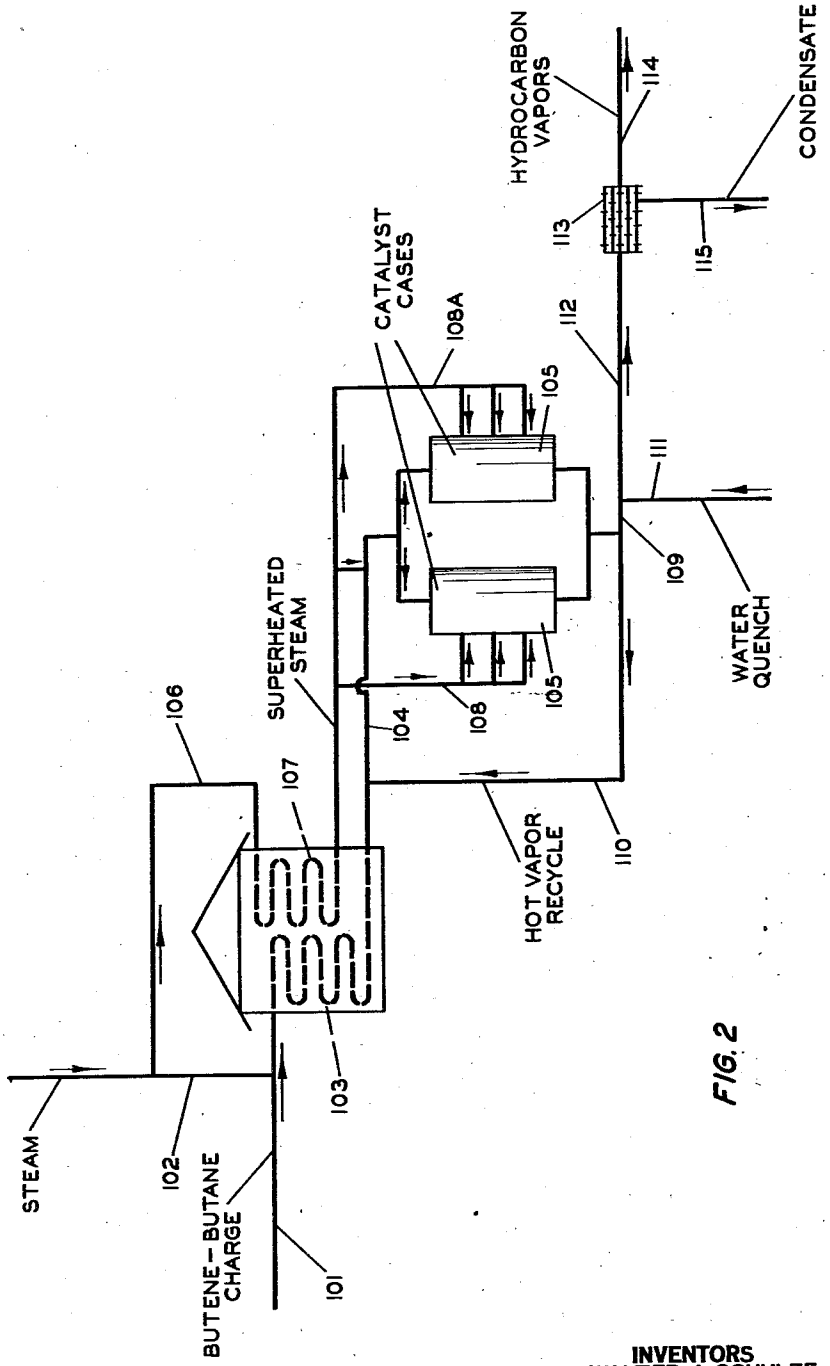


FIG. 2

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PROCESS FOR DEHYDROGENATION OF HYDROCARBONS

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Application September 27, 1941, Serial No. 412,636

3 Claims. (Cl. 260—680)

This invention relates to the catalytic dehydrogenation of hydrocarbons to produce olefins and diolefins. It relates more specifically to an improved process for the dehydrogenation of paraffin and/or olefin hydrocarbons to produce diolefins and has particular application to the production of diolefins from low boiling aliphatic hydrocarbons of said classes.

In the preparation of valuable diolefins by catalytic dehydrogenation, the corresponding olefins may be treated to yield diolefins directly, or the corresponding paraffins may be the starting material for a two-stage dehydrogenation treatment in which olefins are an intermediate product of the initial dehydrogenation. In the latter instance the olefins may or may not be segregated prior to conversion to diolefins. The combination of the dehydrogenation treatment into a single operating stage wherein the paraffin-olefin and olefin-diolefin conversions are concurrent, has been described. However, such combinations of the concurrent reactions have usually encountered serious difficulties due to the fact that optimum conversion conditions are quite different for the two dehydrogenation reactions. Thus the conditions of temperature, flow rate, catalyst activity and the like which promote satisfactory conversions of olefins have previously caused over-conversion of paraffins with consequent losses due to cracking, carbon formation and the ensuing complications due to side reactions and curtailed catalyst life.

An alternative procedure starting with low-boiling paraffins such as normal butane has involved the separation of the two dehydrogenation reactions into two operating stages whereby the olefins formed under optimum conditions for paraffin dehydrogenation are segregated and used as the feed stock for a second conversion step to produce the diolefin. This procedure has been based on the necessity of having low concentrations of paraffins present during olefin dehydrogenation. Conversely, low concentrations of olefins are desirable in the paraffin dehydrogenation step. This procedure introduces a difficult and relatively expensive operation to segregate the paraffin and olefin stocks, but is often justified on the basis of improved yields and operation.

Because of the relatively higher conversion temperatures, the large concentrations of unsaturated hydrocarbons, and the instability of the reaction products, the dehydrogenation of olefins is carried out at low partial pressures of reactants. In this manner excessive decomposition of both olefins and diolefins is avoided. One expedient for obtaining the necessary low partial pressures of olefins during conversion is the inclusion of a suitably inert diluent gas to reduce the partial pressure of olefins to values varying with the total system pressure, but usually below .05 atmosphere. On the other hand, the dehydrogenation of paraffins such as normal butane may be conducted in the absence of a diluent with principal attention being devoted to an efficient separation of olefin products from the paraffins feed stock.

The application of catalytic dehydrogenation to the low-boiling paraffins and to the corresponding olefins has developed certain novel operating methods and processes which have been disclosed in co-pending applications Serial Numbers 352,786, 352,787, 353,961, 353,962, and 355,710. Said disclosures have dealt with the preferred catalysts, methods of obtaining feed stocks, and the operating conditions for the dehydrogenation of low-boiling paraffins and olefins respectively. In general, the use of extremely acting catalysts at relatively low temperatures for normal butane dehydrogenation has been disclosed. Further, the use of higher temperatures and catalysts of lower but maintained and specific activity have been designated for the dehydrogenation of butenes. The use of certain C_3 hydrocarbon diluents in the olefin dehydrogenation has also been disclosed on the basis of a two-stage operation. In co-pending application Serial No. 353,962 there is disclosed a method of operation in which a predominantly unsaturated C_3 fraction formed in the dehydrogenation of normal butane step or secured from other sources is used as the diluent in the dehydrogenation of butenes. This process provides certain advantages in the physical and chemical characteristics of the C_3 hydrocarbon diluent, but the handling and recycling of large amounts of C_3 hydrocarbons represents a larger item in plant investment and operating costs.

It is an object of this invention to describe an improved method for the production of diolefins from corresponding paraffins. More particularly, it is an object of this invention to produce lower boiling aliphatic diolefins such as butadiene from corresponding paraffins, such as butane.

One of the specific objects of this invention is to provide an efficient process for producing diolefins such as butadiene by a two-stage dehydrogenation of paraffins such as butane in which different catalytic and other conditions

are utilized in each stage, said catalysts and the condtions of their use being adapted to produce optimum results in each stage and in the combination of steps hereinafter more fully described.

We have noted that from the standpoint of chemical and physical characteristics, the most promising diluent for olefin dehydrogenation is water vapor. This diluent may be cheaply provided in any desired amounts and may be removed from the hydrocarbon stream by simple condensation, thereby eliminating a large part of the compression and fractionation equipment necessary when other diluents are used. However, the use of water vapor has previously been condemned in the art because of its deleterious effects on the activity of conventional dehydrogenation catalysts and hence on the conversions obtained by the use of said catalysts in prior dehydrogenation processes.

By extensive investigation we have determined the extent to which substantially all suggested dehydrogenation catalysts are susceptible to deterioration and loss of activity by water vapor, and the conditions which govern the use of water vapor in hydrocarbon conversions. We have discovered certain new catalysts, furthermore, which are water-resistant and which may be satisfactorily employed in dehydrogenation reactions in a manner hereinafter described. The application of our discoveries to the dehydrogenation of both paraffins and olefins and the improved dehydrogenation process thereby evolved are described below in detail.

The conversion of paraffin hydrocarbons such as n-butane to olefins is promoted by dehydrogenation catalysts operating with maximum activity at temperatures below those causing excessive thermal or catalytic rupture of the carbon chain. Said catalysts often exhibit suitable activity in the temperature range of 850 to 1150° F. and produce substantially equilibrium conversion with moderate contact times. Said catalysts, however, are characterized by inhibition of activity in the presence of water vapor so that even relatively minor amounts of steam inhibit conversion. We prefer, therefore, to perform the paraffin-olefin conversion in the presence of a highly active although water-sensitive dehydrogenation catalyst and in the substantial absence of water vapor.

In the dehydrogenation of olefins to diolefins, however, we have found that at the temperatures of about 1100 to 1300° F. desirable for conversion, the presence of water vapor does not inhibit conversion when the catalyst is water-resistant either inherently or by reason of a modifying pre-treatment. Said water-resistant properties are obtained by experimental selection or by pre-treatment of certain catalytic materials to impart water-resistance. In fact, we have discovered that the quality of water-resistance may be imparted in certain instances by treatments designed to produce stability at high temperatures and specific activity in certain valuable catalytic materials. We have further discovered that in the presence of water vapor and a water-resistant catalyst, the dehydrogenation reaction is specific for olefins to the extent that the corresponding paraffins if present in normal concentrations are substantially unconverted. This discovery makes possible the dehydrogenation of butenes, for example, in the presence of relatively large amounts of n-butane with excellent yields of butadiene and negligible conversion of the paraffin hydrocarbon. In such an operation the mixture of C_4 paraffin and olefins is diluted with water vapor and treated over a water-resistant catalyst. This process for conversion of olefins to diolefins is described in our co-pending application Serial No. 412,637, filed Sept. 27, 1941.

The present invention is directed to a two-stage process for the stepwise dehydrogenation first of paraffins in the absence of water and using a water sensitive catalyst, and second, of olefins in the manner described in our co-pending application Serial No. 412,637, filed Sept. 27, 1941. By means of this combination of steps, an effective method for the conversion of butane to butadiene is described, in which the first stage of dehydrogenation produces a feed particularly suitable for the second stage of dehydrogenation and in which conditions in each stage are effective for maximum operating efficiency, the combination of steps thus giving optimum results. By the use of our invention, the necessity or desirability of segregating olefins from paraffins prior to dehydrogenation is wholly or partially eliminated with consequent savings and simplification in operations: Also, the use of the steam diluent in olefin dehydrogenation tends to reduce the rate and amount of deposition of carbonaceous material on the catalyst. This effect results in increased operating cycles for the catalyst as well as a reduction in the time required for reactivation. These and other advantages of our process will be apparent from the following disclosure.

In a more specific embodiment, our process may include the following steps: (1) dehydrogenation of n-butane over a water-sensitive catalyst in the substantial absence of water vapor to produce substantially equilibrium conversion to n-butenes; (2) treatment of the products from (1) to remove lower-boiling material from the C_4 fraction comprising substantially butenes and unconverted butane; (3) charging the C_4 fraction from (2) diluted with steam to a second dehydrogenation stage using a water-resistant catalyst to produce butadiene; (4) treatment of products from (3) to segregate a C_4 fraction comprising butadiene, butenes and n-butane; (5) removing the butadiene from the C_4 fraction of step (4) and returning the butenes and n-butane to the first and/or the second dehydrogenation stage for further conversion.

The process may be illustrated by reference to Figure 1 which is a flow diagram of one arrangement of conventional equipment for application of our invention to normal butane.

Figure 2 is a flow diagram of an alternative manner of performing the second stage dehydrogenation.

In Figure 1 the fresh n-butane feed enters by line 1 and passes to heater 2 where the charge is heated to reaction temperature. The hot vapors then pass by line 3 to catalyst cases 4 containing a water-sensitive dehydrogenation catalyst, and the treated vapors exit through line 5 to cooler 6. A portion of the effluent vapors may be recycled through line 5A to the inlet of the catalyst cases. The cooled vapors from 6 pass through polymer separator 7 in which minor amounts of heavy material are removed, then are compressed in unit 8, and pass to accumulator 9. The compressed gas then passes by line 10 to stripper column 11 where C_2 and lighter material is removed by line 12. A portion of this latter stream which contains hydrogen may be returned to the feed line 1 through line 13 if

desired. The accumulator liquid from 9 passes to column 11 through line 14, while the liquid from column 11 is taken through line 15 to column 16, a portion being returned through line 17 to column 11 as absorbent. Column 16 operates to remove C_3 and lighter hydrocarbons from the C_4 mixture and the former material is removed through line 18. The C_4 mixture which is the bottoms fraction from column 16 is taken through line 19 to line 20 as fresh feed to the second-dehydrogenation stage.

The second stage feed enters the heater 22 through lines 20 and 21 together with steam from line 23 and recycled material from line 55. The butene-butane-steam mixture is heated to reaction temperature and passes through line 24 to catalyst cases 25 filled with a water-resistant catalyst. The treated effluents exit by line 26. and a portion thereof may be returned to the catalyst case inlet through line 27.

The hot vapors passing through line 26 are chilled by water injection through line 28, and pass to condenser 29 wherein water vapor is condensed and condensate removed through line 30. The hydrocarbon vapors then pass to compressor 31 and accumulator 32. The material from accumulator 32 enters column 33 through lines 34 and 35, and said column operates to remove C_2 hydrocarbons and lighter material overhead through line 36. The liquid from column 33 is taken through line 37 to column 38 or partly as absorbent through line 39 to column 33. Column 38 operates to remove C_3 and lighter material overhead through line 40, while the depropanized liquid is taken through line 41 to solvent extraction unit 42.

In unit 42 a separation is made by a selective solvent between the n-butane and the unsaturated C_4 hydrocarbons. The n-butane which is not dissolved passes through line 43 and may be returned through line 44, and if necessary through dehydrator 45, to the first dehydrogenation stage. The solvent passes from unit 42 through line 46 to stripper 47 where the C_4 unsaturates are separated, and the solvent is returned to unit 42 through line 48. The butenes-butadiene mixture thus substantially freed of n-butane then is taken through line 49 and fractionated in column 50 to separate butene-1 as an overhead product. The bottoms fraction comprising butenes-2 and butadiene is withdrawn through line 51 to fractionator 52, where substantially pure butadiene is taken overhead through line 53 to storage and butenes-2 pass through line 54 to recycle line 55 or through line 56 to chemical extraction unit 57. The butene-1 stream passing from column 50 through lines 58 and 59 is treated in chemical extraction unit 57 for the separation of the relatively low percentages of butadiene present in the butene-1. The butadiene recovered therein from either or both of the butene streams is removed through line 60 and the butenes pass through line 61 to recycle line 55. The recycle material from line 55 is returned to the second dehydrogenation stage for further conversion to butadiene.

Various modifications of the process outlined in Figure 1 will be obvious from our disclosure and no attempt will be made to discuss all the possibilities within the scope of our invention. For example, the separation of C_3 and lighter material from the products of dehydrogenation in both stages may be performed in a single fractionation or with other auxiliary operations such as refrigeration and the like. Similarly other methods for separating butadiene from the second stage total C_4 mixture may be utilized without departing from the present disclosure.

Certain devices for obtaining essentially adiabatic reaction conditions in the second stage catalyst cases may be employed particularly well with steam diluent, such as the multi-point injection of steam into different sections of the catalyst cases. In this arrangement the steam may be superheated to or above reaction temperatures in a separate furnace coil and injected into the catalyst bed to offset falling temperatures due to endothermal heat of reaction.

This last-named arrangement is illustrated by the flow diagram of Figure 2. This shows the paraffin-olefin charge passing through line 101 and admixed with steam from line 102 prior to entering heating coil 103. The mixture is heated to reaction temperature, and passes through line 104 to catalyst cases 105. The concentration of the pre-mixed steam from line 102 is adjusted somewhat below the desired eventual steam concentration. Additional steam from line 106 passes through auxiliary heating coil 107 and then after being heated up to or somewhat above the reaction temperature attained by the vapors in line 104 is injected into the transfer line 104 and/or the catalyst cases as indicated through lines 108 and 108A at a plurality of points. The effluent vapors may be divided at the exit of the catalyst cases 105 with a portion being recycled to line 104 through line 110. The remainder passes through line 109 into which cooling water may be injected from line 111, and thence through line 112, condenser 113 and line 114 to further processing for the recovery of butadiene as illustrated in Figure 1. The condensed water is withdrawn through line 115.

In the first stage of our process, the dehydrogenation to produce olefins is desirably performed on substantially dry feed stocks at pressures of about atmospheric to 100 pounds gage. Temperatures and pressures are selected within a range suitable for the catalyst used, and temperatures within the range of 850 to 1150° F. are ordinarily employed. At these conditions flow rates of the order of 1 to 10 liquid volumes of hydrocarbons per hour per volume of catalyst are usually maintained. Particular conditions of flow rate, temperature and pressure are usually chosen to conform to the characteristics of the specific catalyst used.

The water-sensitive catalysts which are useful in the first stage of our process are those having suitable activity at temperatures below those causing excessive cracking of the paraffin hydrocarbons and capable of promoting substantially equilibrium conversion under the designated conditions. Said catalysts include the conventional high-activity dehydrogenation catalysts such as metals, metal oxides or composites thereof alone or supported on suitable carriers. Of particular value are the oxides of aluminum and magnesium which possess considerable activity in themselves, and are preferably promoted with more or less minor quantities of oxides of metals of Groups IV, V, and VI of the Periodic Table. Specific examples are alumina catalysts promoted with the oxides of chromium and zirconium. Also of particular value are certain active chromium oxide catalysts with or without carriers. Another class of valuable water-sensitive catalysts are the natural mineral ores such as bauxite and activated clays promoted with chromium or other metal oxides or salts.

These catalysts are characterized by loss of ac-

tivity due to the presence in the hydrocarbon vapors of water vapor, even in relatively minor quantities at temperatures corresponding to the range of optimum activtiy. However, for the paraffin-olefin dehydrogenation, said catalysts are preferred because of their high activity and satisfactory yields of olefins without excessive loss of charge stock or olefinic products through carbon and fixed gas formation and/or polymerization reactions.

The effluent vapors from the first stage of our process are processed to separate any high-boiling material formed by the catalytic treatment, and to remove propane and lower-boiling gaseous products. The separation of light gases is indicated in two stages, and the gas from the deethanizing column containing hydrogen may be partly returned to the feed stock vapors ahead of the catalyst to reduce the rate of catalyst poisoning. Precautions are observed in such an operation to avoid building up concentrations of hydrogen which will suppress the dehydrogenation reaction.

The completeness with which C_3 hydrocarbons are separated from the first stage effluents may vary somewhat, and the retention of a propylene-propane mixture in the charge to the second stage may not be undesirable since said gases are essentially diluents in the second stage dehydrogenation. Further, the propylene is a potential hydrogen acceptor capable of promoting dehydrogenation. In fact, the depropanizing step may be omitted following our first stage if desired, and the separation of C_3 hydrocarbons performed following the second stage. Our purpose is to remove the C_3 hydrocarbons at at least one point in the system to prevent the pyramiding and recirculation of this relatively inert material which increases the compression requirements of the process. Also, the substantially complete separation of propane is desirable ahead of the diolefin purification steps indicated in our second stage.

In the operation of the second dehydrogenation step, the charge stock is prepared in such proportions that the partial pressure of olefins is less than one atmosphere and ordinarily in the range of 0.2 to 0.5 atmosphere. The other constituents of the mixture are principally unconverted paraffins and steam together with any C_3 hydrocarbons remaining in the product from the first stage. After steady state conditions are obtained in an integrated operation, the relative proportions of paraffins and steam will only slightly vary according to the composition of the product. Thus with a vapor mixture charge to said second stage containing 20 to 30 or more volume per cent of olefins, the paraffinic hydrocarbon content may vary between 20 and 30 volume per cent while the steam component amounts to 40 to 60 volume per cent. These exemplary volume ratios, however, may be varied with specific operations on different low-boiling paraffin feed stocks and within the terms of our disclosure.

The vapor effluents from the second catalytic treatment are cooled to condense and separate water and any high-boiling polymer or tar. The method of cooling may be designed to provide an extremely rapid reduction of temperature such as the introduction of a quenching medium. After separation of the condensate, the hydrocarbon vapors are compressed and processed to remove C_3 and lower-boiling hydrocarbons and other gases in one or a series of stripping and/or fractionation operations.

In the treatment of butane-butene-butadiene mixtures these operations produce a substantially propane-free mixture which may then be treated by solvent extraction, azeotropic distillation or the like to produce the desired degree of separation and recovery of the paraffinic hydrocarbons. In many cases it is desirable to segregate a butadiene-containing fraction substantially free of butane and for economic reasons, the butane concentrate returned to the first stage is ordinarily substantially denuded of butadiene. The recycled butane concentrate may contain varying amounts of butenes and, although we usually prefer to maintain a relatively low degree of unsaturation in the feed to the first stage, the dehydrogenation will proceed as long as equilibrium concentrations are not exceeded.

The recovery of diolefin from the resulting unsaturated hydrocarbon mixture may be effected by the methods illustrated or by other known processes which produce substantially equivalent results. Thus, the first operation on a butenes-butadiene mixture may be a fractionation to separate a bottoms fraction comprising butenes-2 and butadiene and an overhead fraction comprising principally butene-1 with minor amounts of butadiene. This overhead fraction may then be treated by a chemical extraction process for the removal of butadiene, and the butene-1 returned to the second stage of dehydrogenation.

The bottoms product is then fractionated to produce substantially pure butadiene as the overhead product, while the butenes-2 bottoms fraction is returned to the second stage catalyst along with the above-mentioned butene-1. Or, if desired, the butene streams may be combined ahead of the chemical extraction step to effect more complete recovery of butadiene.

In certain instances it may be desirable to treat the entire C_4 mixture from the second dehydrogenation stage, without preliminary fractionation, in a chemical extraction unit for the recovery of butadiene. In this embodiment the residue from the chemical separation unit comprises butenes and n-butane which may be recycled to either or both of the catalytic treatments for further conversion, with precautions being observed to avoid pyramiding of n-butane in the second stage.

The second stage of dehydrogenation is operated at low pressures of about atmospheric to 100 pounds gage. Low total pressures are desirable to increase the yield of diolefin. Also, since the partial pressure of olefins in the charge is ordinarily below 0.5 atmosphere, it is desirable to operate at low total pressures in order to have maximum volume concentrations of this component.

Higher temperatures are usually employed in the second stage dehydrogenation than in the first stage. Thus, in order to obtain satisfactory conversion of butenes to butadiene, temperatures of about 1100 to 1300° F. are ordinarily employed. Flow rates used are between 1 and 10 liquid volumes of hydrocarbon charge per hour per volume of catalyst. In terms of the total vapor mixture charged to the catalyst, space velocities of 500 to 5000 are satisfactory under proper conditions. The particular combination of flow rate and temperature for a specific operation will depend on the catalyst employed, the composition of the charge, and on the degree of conversion desired.

The catalysts used in the second stage are those of satisfactory activity in promoting selec-

tive olefin dehydrogenation at temperatures in the range of 1100° to 1300° F. and in the presence of water vapor. Of the greatest value are catalysts prepared by the treatment of bauxite with the hydroxides or oxides of barium and/or strontium in such a manner that the adsorbent mineral ore is impregnated with the metal compound. Such a catalyst and methods for manufacturing it have been disclosed in our co-pending application Serial No. 353,961 filed August 23, 1940. In the prior disclosure the application of the catalysts to butene dehydrogenation is described, but the present invention embodies a valuable additional development in the use of same in general olefin dehydrogenation, particularly in view of the property of water-resistance disclosed herein.

The oxides of aluminum and magnesium have been found to give especially satisfactory catalysts, as have also those of zirconium and titanium. Both synthetic preparations of the substantially pure oxides, hydrated oxides, or hydroxides, and also natural mineral ores comprising these oxides, can yield satisfactory catalysts. High porosity, or specific surface, and other qualifications of good catalysts are desirable in these materials, both before and after treatment to impart water-resistant qualities.

We have found that various alkaline materials added to the untreated catalysts in such a manner as to impregnate the catalyst thoroughly, serve to impart the qualities of water resistance and selective olefin dehydrogenation to a varying degree. While catalysts can be prepared by impregnating with alkali oxides, we have found the specific alkaline earth oxides and/or hydroxides of barium and strontium to be most satisfactory.

Catalysts prepared by impregnating bauxite with barium or strontium hydroxides and/or oxides are water-resistant and do not lose activity in contact with steam at elevated temperatures. Further, these catalysts promote selective dehydrogenation in the presence of steam to such an extent that the butane in a butane-butene mixed charge is relatively unconverted while excellent conversion of butenes to butadiene is obtained. Said catalysts are also deactivated with respect to cracking and/or polymerization reactions involving the hydrocarbon reactants or products.

In the catalytic dehydrogenation of butenes over the above-mentioned catalysts certain benefits have been noted from the use of water vapor as diluent. Thus, while the dehydrogenation of butenes proceeds with good conversion to butadiene, butane present in the mixture is relatively unconverted although operating temperatures are usually over 100° F. higher than those used for butane conversion in our first stage. Also, a prolonged period of maximum catalyst activity for butene dehydrogenation is obtained when the preferred conditions are maintained. These benefits apparently are due to the use of steam in conjunction with water-resistant qualities of our preferred catalysts and to the function of the water vapor in reducing tar and/or coke deposition on the catalysts during the hydrocarbon conversion. This latter effect is responsible both for prolonged operating cycles and greatly reduced time requirements for reactivation.

The following examples will further illustrate specific applications of our process, without implying any particular limitations thereto.

Example I

Normal butane was dehydrogenated over a bauxite-chromium oxide catalyst containing 10 weight per cent of chromium oxide. The dehydrogenation was carried out at a temperature of 1100° F. and 25 pounds gage pressure. At a flow rate of one liquid volume of charge per hour per volume of catalyst, conversion amounted to 35 per cent per pass of the n-butane with an efficiency of about 80 per cent based on the butenes produced. The effluent vapors from this first dehydrogenation stage were cooled, compressed and fractionated to produce a C_4 fraction containing about 30 mol per cent of butenes and about 70 mol per cent of n-butane with minor amounts of C_3 hydrocarbons and butadiene.

This mixture which constituted make-up feed to a second dehydrogenation stage was combined with a recycle stream predominantly comprising butenes from said second stage and diluted with steam to reduce the total butenes content to 30 volume per cent. The charge composition under recycle conditions was approximately as follows:

	Volume per cent
Butenes	30
n-Butane	21
Steam	49

This charge was heated to 1185° F. and passed over a water-resistant catalyst consisting of bauxite impregnated with 4.5 weight per cent of barium hydroxide at a space velocity of 1150 and a pressure of 5 pounds gage. The effluents were cooled by direct water injection and the steam was condensed and separated. The hydrocarbon vapors were processed to separate material lower-boiling than C_4 hydrocarbons, and the C_4 fraction represented a volume yield of about 95 per cent based on the C_4 content of the charge. The product had the following approximate vapor composition:

	Volume per cent
Butadiene	9–10
Butenes	45–46
n-Butane	45

The product represented approximately 30 per cent per pass conversion of the butenes charged and about 50 per cent efficiency in the conversion to butadiene.

The C_4 fraction was then submitted to selective solvent extraction for the separation of the n-butane, and the butenes-butadiene mixture was fractionated to separate overhead first butene-1 and finally substantially pure butadiene. The butene-1 fraction contained some butadiene which was recovered by a chemical separation process utilizing a cuprous chloride reagent.

The butene-1 and the butenes-2 bottoms from the final fractionation were combined as the recycle stream to the second dehydrogenation stage, while the n-butane previously separated was dehydrated and returned to the first dehydrogenation stage. The make-up n-butane for the first stage amounted to a little more than 35 per cent of the total charge to that unit since there was substantially no loss or conversion of n-butane in the second stage. The two-stage process as operated produced a 40 per cent yield of butadiene based on make-up n-butane feed or a 50 per cent yield based on the butenes charge to the second stage.

Example II

A C_4 fraction produced by the dehydrogenation of n-butane and containing about 30 volume per cent of butenes, 69 volume per cent n-butane and the balance C_3 hydrocarbons was mixed with recycled butenes from the treatment to be described and charged to a dehydrogenation catalyst consisting of bauxite impregnated with 5 weight per cent of barium hydroxide to produce butadiene. Steam was added to the charge vapors at the inlet of a pre-heating furnace to produce a charge of the following composition:

	Volume per cent
Butenes	36
Butane	25
Steam	39

This charge left the preheater at 1185° F. and at the inlet to the catalyst chamber steam at 1200° F. was injected, in an amount equal to about 10 volume per cent of the resulting total mixture. This addition offset a slight drop in temperature in the transfer line and permitted correspondingly lower temperature in the preheater to produce an initial reaction temperature of 1185° F. at the point of entry to the catalyst case. Without steam addition at this point, the catalyst inlet temperature was about 1180° F.

During the passage of the vapors through the catalyst, an additional volume of steam at 1200° F. was injected at several points in the catalyst bed. The volume added amounted to about 7 volume per cent of the resulting total vapor mixture. The exit temperature of the vapors was 1150° F. whereas without steam injection and at equivalent space velocity the exit temperature was 1140° F. The higher average temperature throughout the bed produced a higher conversion of butenes to butadiene, and the additional incremental dilution of the effluents increased the recovery of the diolefin without adversely affecting the equilibrium in the olefin-diolefin conversion reaction.

After processing the vapors to segregate n-butane for recycle to the first stage and a butenes-butadiene fraction, the latter fraction was treated by the scheme outlined in Example 1, except that both the butene-1 overhead fraction and the butenes-2 bottoms fraction from the last two fractionation steps were combined ahead of the chemical extraction unit and treated for the recovery of butadiene. The butadiene yield was 55 volume per cent based on the butenes charged to the second dehydrogenation catalyst.

While the foregoing examples have served to illustrate specific applications of our invention, other modifications will be obvious and within the scope of our disclosure.

Butadiene separation may be carried out as indicated or by any satisfactory method or combination of methods such as the use of cuprous or other metal salt reagents and/or extraction by sulfur dioxide, or by other selective solvents. Further, although we usually prefer to utilize a clean-up extraction on recycle streams to the olefin dehydrogenation step, small amounts of butadiene may be returned with said recycle streams.

The water resistant catalysts prepared and/or selected by the methods described may be reactivated over long periods of use by treatment with oxidizing gases to burn out carbonaceous residues responsible for decreased activity. In this connection it has been noted that in the reactivation of our preferred water-resistant catalysts, neither relatively high temperatures during reactivation nor the presence of relatively large amounts of water vapor in the reactivating gas streams cause any appreciable deterioration in the properties of the catalyst. The water-sensitive catalysts, on the other hand, ordinarily require essentially dry reactivating gases and more rigid temperature control during reactivation to avoid serious deterioration.

The terms "water-sensitive" and "water-resistant" as applied to the dehydrogenation catalysts described herein are intended to indicate the degree to which said catalysts become poisoned and/or inactive due to the presence of more than a trace of water vapor in the hydrocarbons undergoing the specified conversions.

While the foregoing disclosure has been relatively specific to the treatment of C_4 hydrocarbons for the production of butadiene, we have found that equivalent results may be obtained from the application of our process to higher boiling paraffins of five or six or more carbon atoms for the production of diolefins.

We claim:

1. A pressure for the production of butadiene from normal butane which comprises contacting said normal butane with a dehydrogenation catalyst under conditions effecting conversion of a portion of said normal butane to normal butenes, and passing the C_4 hydrocarbon content of the resulting effluent, without separation into its components, in admixture with steam into contact with a catalyst consisting of bauxite rendered water resistant by incorporation of a minor proportion of a compound selected from the group consisting of the oxides and hydroxides of barium and strontium, under conditions effecting conversion of normal butenes to butadiene as the principal reaction without substantial conversion of normal butane.

2. A process for the production of butadiene from normal butane which comprises contacting said normal butane with a dehydrogenation catalyst under conditions effecting conversion of a portion of said normal butane to normal butenes, and passing the C_4 hydrocarbon content of the resulting effluent, without separation into its components, in admixture with steam into contact with a catalyst consisting of bauxite rendered water resistant by incorporation of a minor proportion of barium hydroxide, under conditions effecting conversion of normal butenes to butadiene as the principal reaction without substantial conversion of normal butane.

3. A process for the production of butadiene from normal butane which comprises contacting said normal butane with a dehydrogenation catalyst under conditions effecting conversion of a portion of said normal butane to normal butenes, and passing the C_4 hydrocarbon content of the resulting effluent, without separation into its components, in admixture with steam in amount sufficient to reduce the partial pressure of the butenes in the mixture to from 0.2 to 0.5 atmosphere into contact with a catalyst consisting of bauxite rendered water resistant by incorporation of a minor proportion of a compound selected from the group consisting of the oxides and hydroxides of barium and strontium, under conditions effecting conversion of normal butenes to butadiene as the principal reaction without substantial conversion of normal butane.

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CERTIFICATE OF CORRECTION.

Patent No. 2,367,622. January 16, 1945.

WALTER A. SCHULZE, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 7, for ".05 atmosphere" read --0.5 atmosphere--; line 24, for "acting" read --active--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of April, A. D. 1945.

Leslie Frazer

(Seal) Acting Commissioner of Patents.