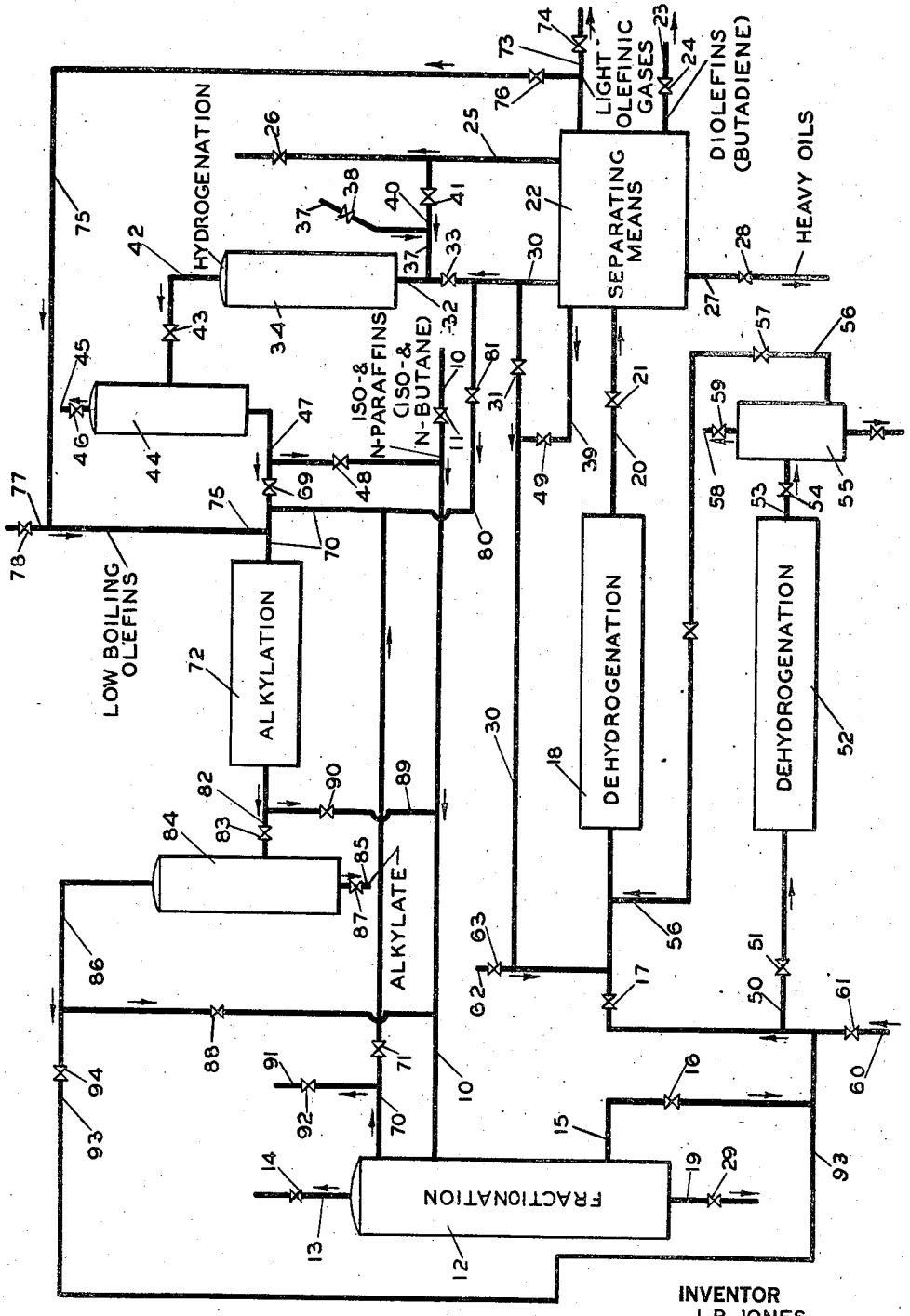
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MANUFACTURE OF DIOLEFINS

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MANUFACTURE OF DIOLEFINS

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This invention relates to the production of diolefin hydrocarbons from paraffin hydrocarbons by dehydrogenation. It relates more particularly to the production of such diolefins by means of catalytic dehydrogenation wherein unreacted hydrocarbons comprising paraffins and olefins are recycled to a dehydrogenation step. The invention has particular reference to the production of diolefins such as butadiene and pentadiene from the corresponding paraffin hydrocarbons, preferably by means of catalytic dehydrogenation. This application is a continuation-in-part of my copending application, Serial No. 404,420, filed January 28, 1941.

It has been proposed to produce diolefins by dehydrogenation in a single step wherein a paraffin hydrocarbon such as normal butane is charged to the dehydrogenation step, a diolefin such as butadiene is recovered from the dehydrogenation effluent, and a hydrocarbon fraction containing unreacted hydrocarbons, such as normal butane and butenes, are separated from the effluent and returned to the dehydrogenation step. It has also been proposed to produce diolefins from paraffin hydrocarbons by the use of at least two dehydrogenation steps in the first of which paraffins are dehydrogenated to olefins and in the second of which olefins are dehydrogenated to diolefins. In such a process there is generally a recycle of unreacted hydrocarbons to one or more of the dehydrogenation steps. In preparing the charge to such dehydrogenation processes it is impossible from a practical point of view to separate a hydrocarbon material such as normal butane in a state of high purity, and in most instances when the particular desired hydrocarbon is present in a concentration of about 95 per cent or more, it is considered to be in a sufficiently high state of purity for practical operations. At times the concentration may even be somewhat lower than 95 per cent although generally it will not be appreciably lower than about 90 per cent. Also in such dehydrogenations there is a tendency for isomeric forms of the hydrocarbons being treated to be formed as by-products in the dehydrogenation step. Thus, in the dehydrogenation of normal butane and/or normal butenes to form butadiene, there is a tendency for small amounts of isobutene and isobutane to be formed. When a hydrocarbon fraction containing unreacted hydrocarbons is recycled to the dehydrogenation step, it will contain such isomeric hydrocarbons in either case, and as a result after a steady state of operation has been reached, the total charge to a dehydrogenation step will contain a substantial amount of such isomeric hydrocarbons which do not contribute directly to the production of the desired diolefins which not only decrease capacity of the dehydrogenation units but also tend to enter into undesired side reactions.

I have now found that this tendency for isomeric hydrocarbons to build up in such a dehydrogenation system may be effectively kept under control and limited to any desired extent by removing a portion of the recycled hydrocarbon fraction, separating such isomeric hydrocarbons from this removed portion of this hydrocarbon fraction, and returning unseparated hydrocarbons to the dehydrogenation system. In one specific form of my invention this is accomplished by subjecting a fraction containing branched chain aliphatic hydrocarbons separated from effluents of the dehydrogenation system to non-destructive hydrogenation to form a fraction comprising isoparaffins and subjecting such isoparaffins to alkylation to form higher-boiling paraffins. I have found that generally in producing butadiene and the like, sufficient lower-boiling olefins are formed by side reactions to react with such isoparaffins so that the charge to the alkylation system can come entirely from effluents of the dehydrogenation system for producing diolefins. This procedure may be followed either when the undesired isomeric hydrocarbons are present as a result of formation within the dehydrogenation system or when they are present as a result of being included as impurities as a charge to the dehydrogenation system or for any other reason.

An object of my invention is to produce diolefin hydrocarbons.

It is an object of my invention to produce low-boiling diolefin hydrocarbons from paraffin hydrocarbons of the same number of carbon atoms per molecule.

It is a further object of my invention to produce diolefin hydrocarbons by means of catalytic dehydrogenation of more saturated hydrocarbons under conditions such that there is a minimum formation of undesired by-products.

Further objects and advantages of this invention will become apparent from the accompanying disclosure and discussion.

My invention will now be described in connection with the accompanying drawing which shows diagrammatically by way of a flow sheet an arrangement of apparatus for practicing my invention together with certain modifications thereof. The description of my invention in connection with the drawing will also serve to exemplify the same.

Referring now to the drawing, a suitable hydrocarbon material enters the system through a pipe 10 controlled by a valve 11 and is passed to a separating means illustrated by the fractionating column 12. Preferably such a hydrocarbon mixture will comprise predominantly hydrocarbons of a single number of carbon atoms per molecule such as a butane fraction comprising both normal butane and isobutane, or a pentane fraction comprising both normal pentane and isopentane. For purposes of illustration it will be considered that the material charged through pipe 10 will be a butane fraction. The fractionating column 12 is so operated as to separate a normal butane fraction from other hydrocarbons contained in the material charged. Undesired low-boiling hydrocarbons are discharged from the system through a pipe 13 controlled by a valve 14, and any undesired high-boiling material is discharged through a pipe 19, controlled by valve 29. A normal butane fraction of as high a purity as is practical, and preferably containing normal butane as at least 95 per cent of the mixture, is removed through a pipe 15 controlled by a valve 16 and may be passed through a valve 17 directly to a single dehydrogenation unit 18. The dehydrogenation unit 18 is comprised of suitable heating units or furnaces, catalyst chambers and the like known to the art for effecting and maintaining catalytic nondestructive dehydrogenation of low-boiling hydrocarbons. The catalyst chambers may be so arranged that heat is supplied to the catalyst body or bodies and to the reacting mixture. When a single dehydrogenation unit is used, the dehydrogenation is conducted to effect a dehydrogenation both of paraffins and of olefins to form olefins and diolefins, respectively, along with free hydrogen. The resulting products pass through a pipe 20 controlled by a valve 21 to separating means 22. Separating means 22 will include suitable fractionating columns, condensing units, heat exchangers, solvent extraction units and the like suitable for effecting a separation of the material charged into the desired fractions as will be discussed. A diolefin fraction, in this case containing a high concentration of butadiene, is recovered as a product of the process from separating means 22 through a pipe 23 controlled by a valve 24. A fraction containing light gases with a high concentration of free hydrogen formed by the dehydrogenation is removed from separating means 22 through a pipe 25 and may be discharged at least in part from the system through a valve 26. Any undesired heavy material may be discharged from the system through a pipe 27 controlled by a valve 28. A normally gaseous fraction comprising olefin hydrocarbons produced by side reactions in the dehydrogenation system and having a fewer number of carbon atoms per molecule than the desired diolefin may be separated from the system through pipe 73. Although such olefins may be discharged through valve 74, I prefer to pass them from pipe 73 through valve 76 and pipes 75 and 70 to alkylation unit 72 as will be more fully discussed hereinafter. A recycle fraction, which in this case will comprise predominantly normal butane and normal butenes, is removed from separating means 22 through a pipe 30 and a substantial portion thereof, preferably a predominant portion, may be passed through valve 31 to be returned to the dehydrogenation unit 18. As discussed, this recycle fraction wil contain appreciable amounts of isomeric hydrocarbons, in this case isobutane and isobutene. In accordance with the invention a portion of the recycle material passing through pipe 30 is passed therefrom through a pipe 32 and is passed through valve 33 to a hydrogenation unit 34. Hydrogen in an amount sufficient to effect a substantially complete saturation of unsaturated material charged to hydrogenation unit 34 is added to the system through a pipe 37. This hydrogen may be added entirely or in part through a valve 38, but generally there will be more than sufficient hydrogen in the stream discharged through pipe 25 to suffice for this operation, and any desired portion of this stream may be passed from pipe 25 through a pipe 40 controlled by a valve 41 to pipe 37 and hydrogenation unit 34.

In some instances it may be found more desirable to operate separating means 22 so as to separate a fraction containing isobutane and isobutene in higher concentration than would otherwise be present in the recycle stream passing through valve 31 back to the dehydrogenation system. Such a fraction can then be passed to hydrogenation unit 34, and a recycle stream with a depleted amount of isobutane and isobutene, or substantially free of these hydrocarbons, is passed to the dehydrogenation system as by being removed from separating means 22 through pipe 39 and valve 49.

The hydrogenation in unit 34 will be one of simple nondestructive substantially complete saturation of unsaturated hydrocarbons charged thereto and may be carried out in the presence of an active hydrogenation catalyst, such as finely divided nickel on an inert support such as pumice, silica gel, or the like, under a suitable pressure and temperature. Such temperature and pressure will generally not need to be greatly elevated and conditions for any particular stock being treated may be readily determined by trial by one skilled in the art. The effluent of the hydrogenation is passed from unit 34 through a pipe 42 controlled by a valve 43 to a separating means 44. Any undesired low-boiling material such as unreacted free hydrogen and hydrocarbons of a fewer number of carbon atoms than the material treated in the dehydrogenation unit 18 may be discharged from the system through a pipe 45 controlled by a valve 46. A paraffin hydrocarbon fraction preferably predominately of a single number of carbon atoms per molecule, in this case a butane fraction, is recovered through a pipe 47 and may be passed through valve 48 directly to pipe 10 and fractionating unit 12. When the content of isoparaffin is sufficiently high in the stream passing through pipe 47, it may be passed directly to pipe 70 and alkylation unit 72 through valve 69.

From fractionating unit 12 an isobutane fraction is removed through pipe 70 and is passed through valve 71 to alkylation unit 72. If such an isobutane fraction is present in excess, a portion of it may be discharged from the system through pipe 91 controlled by valve 92. In alkylation unit 72 isobutane is reacted with low-boiling olefins such as ethylene, propylene, and isobutylene to produce higher-boiling paraffins which will generally be in the motor fuel boiling range, and which are suitable as blending stocks for premium motor fuels. I prefer that such olefins be those which have been formed as by-products in the dehydrogenation system which is operated primarily to produce diolefins and which may be passed from separating means through pipes 73, 75 and 70 to alkylation unit 72. In case there is not a sufficient supply of olefins to react with all the isoparaffin

charged to alkylation unit 72, olefins from any suitable outside source may be introduced to the process through pipe 77 controlled by valve 78. In some instances, particularly when separating means 22 is so operated as to discharge a fraction with a high concentration of branched chain hydrocarbons through pipe 30, a portion of these may be passed to pipe 80 controlled by valve 81 to pipe 70 and alkylation unit 72 while a further portion is passed through valve 33 to hydrogenation unit 34 as has been discussed.

The alkylation in unit 72 may be conducted either in the presence or in the absence of a catalyst, but I prefer to conduct the operation in the presence of a suitable alkylation catalyst. Such a catalyst may be concentrated hydrofluoric acid promoted with a small amount of boron fluoride, particularly when ethylene is one of the olefin alkylating reactants, concentrated sulfuric acid, an active metal halide, preferably activated with a corresponding hydrogen halide, or one of numerous others known to the art. A reaction temperature may be between about 30 and 200° F. as may be found suitable in any particular case with sufficient pressure to maintain at least a substantial part of hydrocarbon material in liquid phase. Preferably the olefin alkylating reactant is introduced to the alkylation step in a manner such that its concentration in the reaction zone is maintained at a low value, as by successive addition at several points along the length of a reaction zone or at a single point with recycling of a substantial portion of the reaction mixture without immediate fractionation, or the like as is well known in the art. Alkylation catalyst may be admitted to the alkylation unit 72 by means not shown or it may be admitted in admixture with reactant hydrocarbons. Alkylation unit 72 will also comprise suitable equipment for separating alkylation catalyst from hydrocarbons effluent from the alkylation reaction zone and for discharging spent catalyst from the system together with necessary associated equipment, as will be understood by those skilled in the art. When it is found necessary to react individual olefins under individual reaction conditions, alkylation unit 72 may comprise several alkylation reaction zones.

A hydrocarbon material effluent from alkylation unit 72 is passed through pipe 82 and valve 83 to separating means 84. This hydrocarbon material will comprise primarily alkylate and unreacted normal butane. The alkylate may be recovered through pipe 85 controlled by valve 87 and unreacted normal butane is passed through pipe 86 and valve 88 to pipe 10 and fractionation unit 12. If this normal butane fraction has a sufficiently high purity to be suitable for charging directly to the dehydrogenation system, it may be passed from pipe 86 through pipe 93 controlled by valve 94 and introduced to the dehydrogenation system through pipe 60. In some instances it may be found desirable to employ fractionation unit 12 to separate alkylate and unreacted normal butane, in which case, the hydrocarbon material is passed from pipe 82 through pipe 89 and valve 90 to pipe 10 and fractionation unit 12.

In some instances it may be desired to conduct the dehydrogenation operation in two or more steps; in such an event the stream passing through pipe 15 will be passed therefrom through pipe 50 controlled by a valve 51 to a dehydrogenation unit 52 which as in the case of dehydrogenation unit 18 is comprised of suitable heating units or furnaces, catalyst chambers and the like known to the art for effecting and maintaining catalytic non-destructive dehydrogenation of low-boiling hydrocarbons. The material charged to dehydrogenation unit 52 should be predominately paraffinic, and the dehydrogenation conditions should be such that there is an optimum formation of mono-olefins of the same number of carbon atoms per molecule as the paraffins charged. The dehydrogenation effluent is passed through the pipe 53 controlled by valve 54 to separating means 55. A fraction containing the desired olefins produced by the dehydrogenation is removed from separating means 55 through a pipe 56 controlled by a valve 57 and is passed back to pipe 15 for introduction to dehydrogenation unit 18. With such an operation valve 17 in pipe 15 will be closed. Undesired low-boiling materials, including free hydrogen produced by the dehydrogenation may be discharged from the system through pipe 58 controlled by a valve 59 passing from separating means 55. Free hydrogen contained in this stream may be used in the hydrogenation unit 34, and if such use is desired the hydrogen may be introduced through valve 38 as will be readily appreciated. In some instances the material passing through pipe 56 will contain substantially all of the unreacted paraffin charged to dehydrogenation unit 52, in which case separating means 55 can be operated simply to separate a hydrocarbon fraction such as a butane-butene fraction from lower boiling material. However, in some instances it may be found desirable to have a high concentration of olefins in the material charged to dehydrogenation unit 18. In such a case separating means 55 will also include suitable equipment for separating olefins from paraffins, such as selective solvent extraction equipment as will be readily appreciated by those skilled in the art. Paraffin hydrocarbons separated in such a manner may be returned to dehydrogenation unit 52 as through pipe 60 controlled by a valve 61. In some instances with either modification of the dehydrogenation system, material charged through pipe 60 may contain substantially only hydrocarbons of a single carbon atom skeleton structure and may in such a case constitute the sole charge to the process. When a fraction containing a high proportion of olefins suitable for dehydrogenation into diolefins is available from any outside source such a material may be charged to the system through pipe 60 when dehydrogenation unit 18 is the only part of the dehydrogenation system. When such a charge is available and a dehydrogenation system includes both units 52 and 18, such an olefin-containing charge may be introduced to the process through pipe 62 controlled by a valve 63 passing into pipes 30 and 15 directly to dehydrogenation unit 18, and in some instances material charged through pipe 62 may constitute the sole charge to the process.

It has previously been mentioned that the dehydrogenation carried out in units 18 and/or 52 will be conducted under conditions known to the art and will generally be conducted under a relatively low pressure with or without the presence of diluent material such as hydrocarbons inert under the dehydrogenation conditions, nitrogen, steam, carbon dioxide and the like. Sometimes introduction of small amounts of free hydrogen along with the charge to a catalyst bed has a beneficial effect, especially upon the initial portion of a catalyst bed before hydrogen is produced by dehydrogenation, and the presence of such added hydrogen does not retard unduly or upset the dehydrogenation reaction. Such introduction can be made for example, through pipe 60 and/or pipe 62. Any of various dehydrogenation catalysts may

be used, among which the more preferred are alumina and/or chromium oxide catalysts, such as bauxite, bauxite treated with other materials such as an alkali or alkaline earth oxide, as barium oxide, unglowed chromium oxide, alone or in admixture with other oxides, and prepared from a gelatinous chromium hydroxide, from carefully controlled low temperature decomposition of an ammonium chromate, and the like. Suitable dehydrogenation temperatures will generally be found in the range of 800 to 1300° F. A single stage dehydrogenation, as first described in connection with dehydrogenation unit 18, is preferably carried out with a catalyst comprising chromium oxide, or chromium oxide and alumina, chromium oxide and zirconite, etc., at a temperature in the range of 950 to 1100° F., while a two-stage operation may be carried out with a similar catalyst under slightly less drastic time-temperature conditions in dehydrogenation unit 52, with subsequent dehydrogenation of resultant olefins at a higher temperature, such as within the range of 1050 to 1250° F., using a catalyst such as bauxite treated with barium hydroxide, or temperature-stabilized chromium oxide, with or without the presence of steam, or the like, as diluent. In all such dehydrogenation steps low pressures, which may be subatmospheric but which generally will be slightly above atmospheric, are preferred. The above conditions are particularly suitable for treating C_4 hydrocarbons; the treatments of C_5 hydrocarbons are substantially within the same ranges, with slightly lower temperatures in otherwise comparable cases.

The amount of the paraffin-olefin mixture which, in any particular case, is removed and passed to the hydrogenation unit 34 will depend on the degree of purity of the stock charged to the dehydrogenation unit or units, and on the isomerizing characteristics of the dehydrogenation conditions. With less pure stocks and/or appreciable tendencies to form isomeric hydrocarbons, a larger portion will need to be passed to the hydrogenation step than with more favorable conditions. Generally the amount so treated will be at least about 5 per cent of the total recycle stream, and while it may be as high as about 25 per cent, it will generally be more economical to modify other conditions to obtain more favorable operation than to operate so that more than about 15 per cent is so treated. Suitable ratios in any particular case can be readily determined by one skilled in the art.

Pumps or compressors for the various streams in connection with the drawing have not been shown; general flow of the various streams, however, has been indicated and discussed, and suitable mechanical equipment for desired treatment of this material can be readily supplied, as required in any particular modification of my invention, by one skilled in the art. Similarly other units of equipment have been shown only diagrammatically but their functions have been described and explained so as to serve as suitable guides for adaption of suitable specific equipment for specific installations. It will be obvious to those skilled in the art that various modifications of my invention may be practiced as being included in the spirit of the disclosure and in the scope of the claims. In the present specification and claims when it is stated that a portion of a stream is removed therefrom, the term portion shall be understood to mean an unfractionated part which has the same composition as the stream from which it is removed.

I claim:

1. A process for the production of butadiene which comprises catalytically dehydrogenating normal butane to form a dehydrogenation effluent containing butadiene and a substantial amount of iso-C_4 hydrocarbon including isobutylene, treating said effluent to separately recover a fraction of butadiene, a normally gaseous fraction comprising olefin hydrocarbons having less than four carbon atoms per molecule, and a recycle fraction comprising normal butane and normal butenes and said iso-C_4 hydrocarbon including isobutylene, recycling a major portion of said recycle fraction to said dehydrogenating step, passing the balance of said recycle fraction to a hydrogenation step and there non-destructively hydrogenating same to effect substantially complete saturation of the unsaturated hydrocarbons contained therein and thereby converting the isobutylene content thereof to isobutane, passing the isobutane-containing C_4 hydrocarbon content of the hydrogenation effluent directly to a catalytic alkylation step and there alkylating the isobutane content thereof with the olefins contained in said normally gaseous fraction comprising olefin hydrocarbons having less than four carbon atoms per molecule, treating the alkylation effluent to separately recover an alkylate fraction and an unreacted normal butane fraction, and returning said normal butane fraction to the dehydrogenation step, the proportion of said recycle fraction passed to said hydrogenation step and thence to said alkylation step being such as to prevent iso-C_4 hydrocarbon from building up to an objectionable extent in the dehydrogenation step.

2. A process for the production of piperylene which comprises catalytically dehydrogenating normal pentane to form a dehydrogenation effluent containing piperylene and a substantial amount of iso-C_5 hydrocarbon including isopentylene, treating said effluent to separately recover a fraction of piperylene, a normally gaseous fraction comprising olefin hydrocarbons having less than five carbon atoms per molecule, and a recycle fraction comprising normal pentane and normal pentenes and said iso-C_5 hydrocarbon including iso-pentylene, recycling a major portion of said recycle fraction to said dehydrogenating step, passing the balance of said recycle fraction to a hydrogenation step and there non-destructively hydrogenating same to effect substantially complete saturation of the unsaturated hydrocarbons contained therein and thereby converting the iso-pentylene content thereof to iso-pentane, passing the iso-pentane-containing C_5 hydrocarbon content of the hydrogenation effluent directly to a catalytic alkylation step and there alkylating the iso-pentane content thereof with the olefins contained in said normally gaseous fraction comprising olefin hydrocarbons having less than five carbon atoms per molecule, treating the alkylation effluent to separately recover an alkylate fraction and an unreacted normal pentane fraction, and returning said normal pentane fraction to the dehydrogenation step, the proportion of said recycle fraction passed to said hydrogenation step and thence to said alkylation step being such as to prevent iso-C_5 hydrocarbon from building up to an objectionable extent in the dehydrogenation step.

3. A process for the production of a normal diolefin having from 4 to 5 carbon atoms per molecule which comprises catalytically dehydrogenating a normal paraffin hydrocarbon having from 4 to 5 carbon atoms per molecule to form a dehydrogenation effluent containing the corresponding

normal diolefin and a substantial amount of the corresponding iso-hydrocarbons including the corresponding iso-olefin, treating said effluent to separately recover a fraction of said normal diolefin, a normally gaseous fraction comprising olefin hydrocarbons having fewer carbon atoms per molecule than said normal paraffin, and a recycle fraction comprising the normal paraffin and the corresponding normal olefin and said iso-hydrocarbon including said corresponding iso-olefin, recycling a major portion of said recycle fraction to said dehydrogenating step, passing the balance of said recycle fraction to a hydrogenation step and there non-destructively hydrogenating same to effect substantially complete saturation of the unsaturated hydrocarbons contained therein and thereby converting the iso-olefin content thereof to the corresponding iso-paraffin, passing the iso-paraffin-containing hydrocarbon content of the hydrogenation effluent directly to a catalytic alkylation step and there alkylating the iso-paraffin content thereof with the olefins contained in said normally gaseous fraction comprising olefin hydrocarbons having fewer carbon atoms per molecule than said normal paraffin, treating the alkylation effluent to separately recover an alkylate fraction and an unreacted normal paraffin fraction, and returning said normal paraffin fraction to the dehydrogenation step, the proportion of said recycle fraction passed to said hydrogenation step and thence to said alkylation step being such as to prevent iso-hydrocarbon corresponding to said normal paraffin from building up to an objectionable extent in the dehydrogenation step.

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