

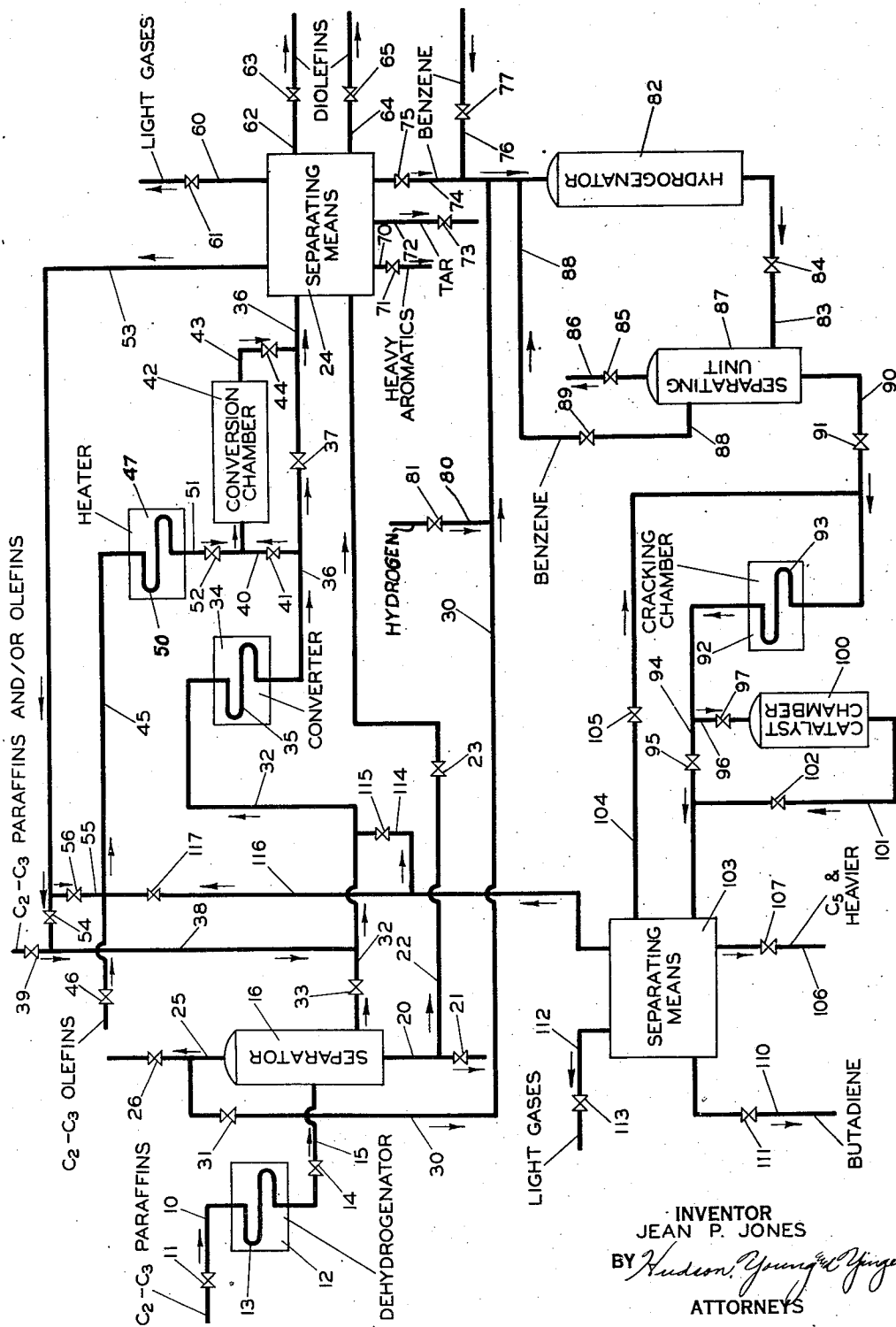
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PRODUCTION OF DIOLEFINS

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PRODUCTION OF DIOLEFINS

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This invention relates to the production of diolefin hydrocarbons from hydrocarbons heavier than methane. More particularly it relates to the production of diolefin hydrocarbons, such as butadiene and pentadiene, from aliphatic hydrocarbons having two and three carbon atoms per molecule. It also relates to the production of such diolefins from benzene and the like.

An appreciable number of diolefins such as butadiene and pentadiene have been known to the art for a number of years. These have been produced in a number of ways which have included cracking of heavier oils, the interreaction of acetylene and ethylene to form butadiene, catalytic or thermal conversion of alcohols, both of the same number of carbon atoms per molecule as the desired diolefin and of a fewer number of carbon atoms per molecule, as well as the dehydrogenation of the corresponding olefins which in turn may have been produced by the dehydrogenation of the corresponding paraffins. Diolefins have also been reported as being present in the pyrolysis products of light hydrocarbons, including even methane. There are enormous quantities of such lighter hydrocarbons which are potentially available for the production of diolefin hydrocarbons but apparently most of the commercial installations and processes to date have been one of the more involved types previously mentioned rather than the direct conversion of cheap and abundant light hydrocarbons to diolefins.

I have found that I can successfully produce substantial yields of low-boiling diolefins of the type mentioned from lighter gaseous hydrocarbons by a suitable combination of high-temperature conversion steps, to be more fully disclosed hereinafter, with certain steps for the conversion of aromatic hydrocarbons, such as benzene, to diolefin hydrocarbons.

In one modification of my invention an ethane-propane fraction is converted at an elevated temperature to produce an optimum yield of unsaturated hydrocarbons of low molecular weight, the effluent is passed to a separating means wherein an unsaturate-containing C₂—C₃ fraction is separated from a heavier hydrocarbon fraction which may contain some diolefin hydrocarbons and from a lighter fraction which contains hydrogen, the unsaturate-containing C₂—C₃ fraction is passed to a second conversion step at an elevated temperature and low pressure to form an optimum yield of diolefin hydrocarbons, benzene which is inherently produced in said second conversion is separated from the effluent thereof, hydrogenated

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with hydrogen produced in the first conversion step to cyclohexane and cyclohexane so produced cracked to low-boiling diolefin hydrocarbons, and diolefins, particularly butadiene, are recovered from the effluent of the last step.

In another modification of my invention benzene from an outside source is hydrogenated to cyclohexane and cyclohexane cracked to butadiene and a lighter hydrocarbon fraction. Such lighter hydrocarbon fraction comprises substantial quantities of C₂ and C₃ hydrocarbons which are separated therefrom and subsequently passed to a conversion step for production of additional butadiene.

It is an object of my invention to convert aliphatic low-boiling non-diolefinic hydrocarbons into low-boiling diolefin hydrocarbons.

Another object of my invention is to convert cyclic hydrocarbons into low-boiling diolefin hydrocarbons.

Another object of my invention is to convert aliphatic hydrocarbons of two and three carbon atoms per molecule to diolefin hydrocarbons.

A further object of my invention is to convert ethane and propane to butadiene.

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

The features of my invention will now be disclosed and discussed in connection with the accompanying drawing, which illustrates diagrammatically by way of a flow sheet the manner of practicing my invention, together with auxiliary steps which may be incorporated with various modifications of it, and which serves to exemplify my invention.

In one modification of my invention a light gaseous hydrocarbon material, such as a mixture comprising ethane and propane, is passed from any suitable source through conduit 10, controlled by valve 11, to a dehydrogenator 12, which will generally be a cracking and dehydrogenating furnace. This mixture is heated and cracked in coil 13 at a low pressure of the order of 5 to 50 pounds per square inch absolute and at a temperature of 1300 to 1600° F. for a time sufficient to form an optimum amount of ethylene and propylene with only minor amounts of light oils. When desirable, a suitable dehydrogenating catalyst, not shown, may be used in place of or along with the non-catalytic cracking operation, especially when a heavier stock is being dehydrogenated to produce higher boiling unsaturates, but for the charge stocks here specifically described the simple non-catalytic cracking and

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dehydrogenation is adequate, and generally less expensive.

The dehydrogenated material is passed through conduit 15, controlled by valve 14, to separator 16 wherein a light fraction, containing essentially hydrogen and minor amounts of methane, is separated from higher boiling unsaturated hydrocarbon material. The light fraction containing hydrogen is removed from separator 16 through conduit 25 and may be removed from the process through valve 26. However, a major portion of said light fraction is preferably passed through conduit 30 and valve 31 to be used in a subsequent hydrogenation step of my process described hereinafter.

A light oil fraction containing hydrocarbons of more than three carbon atoms per molecule may be removed from my process through conduit 20, controlled by valve 21. Usually, hydrocarbon material passed through conduit 20 contains recoverable amounts of diolefin hydrocarbons, in which case I prefer to pass such material through conduit 22, controlled by valve 23, to separating means 24 in which diolefin hydrocarbons, such as butadiene and pentadiene, are separated and can be recovered through conduits 62 and 64, respectively.

A light hydrocarbon fraction containing essentially C_2 - C_3 unsaturated hydrocarbons is removed from separator 16 through conduit 32, controlled by valve 33. Such low-boiling unsaturated hydrocarbons are passed to the heating and/or conversion zone 35 represented by a tube coil in a suitable heating unit 34. The material charge to the conversion zone 35 may be augmented by similar low-boiling unsaturated hydrocarbons introduced from any suitable outside source through conduit 38, controlled by valve 39, which may at times constitute the sole charge to the process. In one modification the zone 35 is primarily a heating zone operated in conjunction with a conversion chamber 42 to which it is joined by conduits 36 and 40 controlled by valve 41. When using such a conversion chamber, the material passing through conduit 32 is rapidly heated in zone 35 to a temperature only sufficient to initiate an uncatalyzed reaction, which takes place in conversion chamber 42. This chamber is preferably insulated to preclude substantial heat transfer through the walls thereof, and the inlet conduit 40 and the outlet conduit 43 are preferably so placed that a direct passage of the contents from the inlet to the outlet is not favored but rather so that a dilution and mixing of the chamber contents with the incoming mixture is favored. Reaction effluents from chamber 42 are passed through conduit 43 controlled by valve 44 to a suitable separation means 24 by means of conduit 36. When the conversion chamber 42 is not used and the desired extent of conversion is effected in zone 35, effluents therefrom may be passed directly through conduit 36 and valve 37 to the separating means 24 by closing valve 41 in conduit 40. When conversion chamber 42 is used valve 37 in conduit 36 remains closed.

The conversion effected in zone 35 and/or 42 is such as to produce from low-boiling unsaturated hydrocarbons charged through conduit 32 an optimum yield of low-boiling diolefin hydrocarbons of the nature of butadiene, pentadiene, and cyclopentadiene. Optimum conditions for such a reaction exist when the conversion is conducted in a temperature range suitable for the production of low-boiling aromatic hydrocarbons for a period of time such that only a minor portion of

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such aromatics are produced. More specifically I prefer to operate within a range of about 1300 to 1700° F., preferably between about 1375 and 1550° F. for a period of time such that the effluent contains not more than about 10% by weight of C_4 and heavier hydrocarbons which are a result of synthesis reactions. However, of course, an appreciable amount of C_4 and heavier hydrocarbons will be produced by such synthesis reactions, and it has been found that the diolefin content does not approach a desirable value until at least about 3% by weight of the effluent consists of such synthetic C_4 and heavier hydrocarbons. The overall synthesis reactions are exothermic with highly unsaturated charge stocks and endothermic when the charge contains relatively large amounts of saturated hydrocarbons, and suitable means for removing or adding heat may be provided to maintain a fairly uniform reaction temperature.

In the conversion zone 35 and/or 42 the pressure should be low throughout the reaction, generally not in excess of about 50 pounds per square inch absolute and may be subatmospheric although pressures lower than about 1.5 pounds per square inch absolute are generally not practical. With some relatively more unsaturated charge stocks, the formation of butadiene, and the like, will result to a substantial extent from polymerization-type reactions, and pressures as high as 100 pounds per square inch may be employed. However, such pressures also tend to promote formation of other and less desired products of higher molecular weight. With such pressures, the throughput per unit of time is also increased. With relatively less unsaturated charge stocks, lower pressures are more desirable. Low partial pressures with the total pressure somewhat above atmospheric, may be readily employed by using diluent gases, which may be gases such as nitrogen, methane or other suitable gases which are substantially unreactive under the conversion conditions, or which may be in part or entirely gases such as steam carbon dioxide, which are not strictly reactants but whose presence appears to suppress or compensate for undesired side reactions such as the formation of tar and heavy carbonaceous material. When such diluents are used, the extent of conversion discussed above should be calculated on a basis free of such diluent, or of compounds formed from it.

Mention has been made of the fact that low-boiling unsaturated hydrocarbons from an outside source may be charged to conversion zones 35 and/or 42 by means of conduit 38 controlled by valve 39. Material charged through conduit 38 may contain essentially C_2 - C_3 olefin hydrocarbons although it usually also contains substantial amounts of C_2 - C_3 paraffin hydrocarbons. When an essentially unsaturated hydrocarbon material from an outside source is converted to diolefins according to my process I prefer to pass such material through conduit 45 controlled by valve 46 to heating coil 50 in furnace 47. Conditions in heating coil 50 are similar to those discussed in connection with coil 35 when the latter is used to heat hydrocarbon material passed through conduit 32 and such heated material is subsequently converted in conversion chamber 42. Low boiling unsaturated hydrocarbons so heated in coil 50 are passed through conduit 51 controlled by valve 52 and through conduit 40 to conversion chamber 42 wherein conditions are such as have been discussed in connection with material charged thereto through conduit 40 from heating

coil 35 when little or no conversion occurs in coil 35.

Reaction effluents passing through conduit 36 to separating means 24 are treated therein in such a manner that various types of hydrocarbons are segregated. In one preferred manner of practicing my invention, a substantial portion of the C_2 and C_3 hydrocarbons are separated in means 24 and returned to heating and/or conversion zone 35 by means of conduits 53, 38 and 32 when valve 54 is open. In some instances such material may be passed to heating zone 50 through conduits 53, 55 and 45 when valve 56 is open and valve 54 is partly or entirely closed. This is particularly true when such material contains essentially unreacted unsaturated hydrocarbons. In other cases when the material in conduit 53 contains essentially ethane and propane in combination with only relatively small amounts of corresponding olefins, such material is preferably returned to cracking coil 13 through conduit 10 by means not shown in the drawing.

Light gases, although present in small quantities in separating means 24 and containing hydrogen and methane, are removed from separating means 24 through conduit 60 controlled by valve 61. When desirable such light gases are admixed with the light gases in conduit 30 which are ultimately charged to hydrogenator 82.

Diolefin hydrocarbons which comprise essentially C_4 and C_5 diolefins as produced according to my process are removed from separating means 24 through conduits 62 and 64, respectively, controlled by valves 63 and 65, respectively. Aromatic hydrocarbons inherently produced in heating and/or conversion coil 35 or conversion chamber 42, when operating according to the conditions disclosed herein for the production of diolefins, are separated in means 24 into a benzene fraction and a heavier aromatics fraction. A fraction containing still heavier material and comprising essentially tar is removed from separating means 24 through conduit 72 controlled by valve 73. A hydrocarbon fraction containing essentially aromatic hydrocarbons having higher boiling points than benzene is removed from separating means 24 through conduit 70 controlled by valve 71 and an aromatic hydrocarbon fraction containing essentially benzene is removed from separating means 24 through conduit 74 controlled by valve 75.

The aromatic hydrocarbon fraction containing essentially benzene is passed via conduit 74 to hydrogenator 82 wherein benzene is converted to cyclohexane by treatment under non-destructive hydrogenation conditions with a hydrogen-rich material produced in dehydrogenation and cracking coil 13 and passed to hydrogenator 82 from separator 16 by means of conduits 25 and 30 and valve 31. When the hydrogen supplied from coil 13 is insufficient for carrying out the necessary hydrogenation or when dehydrogenation, such as would be carried out in coil 13, is omitted from my process hydrogen from some convenient outside source may be supplied to hydrogenator 82 through conduit 80 controlled by valve 81.

When the benzene fraction recovered from separating means 24 through conduit 74 contains impurities which would be deleterious to a hydrogenation catalyst if allowed to come in contact therewith, such impurities are preferably removed from said benzene fraction before being passed to hydrogenator 82 in equipment

and means not shown in the drawing. Such impurities can be removed from the benzene fraction by suitable fractional distillation, treatment with an aluminum halide type of compound, caustic washing, and/or water washing such as would be obvious to any skilled operator in the art.

At times it may be desirable to admix benzene from an outside source with the benzene fraction recovered from separating means 24. Such additional benzene is conveniently added to my process through valve 77 and conduit 76. When more benzene is produced by my process than can be suitably hydrogenated, valve 77 may be operated in such a manner that it can also be used as an outlet valve for said excess benzene.

The conversion effected in hydrogenator 82 is such as to produce an optimum yield of cyclohexane from benzene by utilizing hydrogen and benzene produced in previous conversion steps. Such a reaction is preferably conducted in the presence of a hydrogenation catalyst with a charge stock that is substantially free from material which would tend to poison the hydrogenation catalyst as has been discussed herein. In the presence of a nickel-alumina-copper catalyst similar to that described in U. S. Patent 2,242,627; optimum conditions for such a catalytic reaction exist when the conversion is conducted in a temperature range between 200 and 600° F. and preferably between about 250 and 500° F. at flow rates between about 0.5 to 10 volumes of fresh charge stock per volume of catalyst per hour and preferably at flow rates of 1.0 to 5.0 volumes of fresh charge stock per volume of catalyst per hour when the conversion is effected in the preferred temperature range. Pressures in the hydrogenator 82 should be relatively high since the hydrogenation reaction is favored by high pressures. Pressures as high as 2000 to 3000 pounds per square inch gage have been found advantageous in some cases. Also, pressures as low as 50 to 100 pounds per square inch gage have been observed to be sufficiently high to produce substantial amounts of hydrogenation. I prefer, however, to operate at pressures between 450 and 1000 pounds per square inch gage in the preferred temperature and flow rate ranges mentioned.

The amount of hydrogen admixed with the hydrocarbon charge passed to hydrogenator 82 will be such that the hydrocarbon effluent consists primarily of cyclohexane, with little unreacted benzene. I prefer to conduct the hydrogenation by recycling cyclohexane so that the combined hydrocarbon charge to the catalyst chamber 82 contains 10 to 50 per cent benzene, and with a substantial amount, 10 to 50 mol per cent, of unreacted hydrogen in the effluent.

Effluent from hydrogenator 82 passes through conduit 83 controlled by valve 84 to separating unit 87. Separating unit 87 may comprise simple means for separating hydrocarbon material, cyclohexane, from light gases when the conversion to cyclohexane is substantially complete. It is desired not to include any appreciable amounts of benzene with the cyclohexane charged to the subsequent conversion step, and when incomplete conversion of benzene to cyclohexane is effected, separating unit 87 will comprise any combination of means for the separation of an aromatic hydrocarbon fraction from a naphthenic hydrocarbon fraction, in this instance, specifically benzene from cyclohexane. Such a separation is usually brought about by selective sol-

vent extraction methods which are well known to the art. Separating unit 87 will include absorbers and strippers to bring about the desired separation and will generally not be a single piece of equipment as represented in the drawing. Benzene separated in unit 87 is removed therefrom through conduit 88 controlled by valve 89 and returned to conduit 76 and hydrogenator 82 for further conversion to cyclohexane. When cyclohexane is recycled, as mentioned previously, this may be done through conduit 88. The light gases separated in unit 87 are withdrawn via line 86 and valve 85. Cyclohexane produced in my process is removed from separating unit 87 through conduit 90 controlled by valve 91 and passed through the conversion coil 93 in cracking chamber 92.

In coil 93 conditions are such that an optimum yield of butadiene is produced. Effluent from the hydrogenator 82 charged to coil 93 through conduit 90 may contain appreciable amounts of cyclohexene and cyclohexadiene and/or other partially hydrogenated aromatic hydrocarbons, such as methylcyclohexene particularly when the benzene fraction from separating means 24 contains substantial amounts of toluene. The production of butadiene in coil 93, therefore, may not only be from the conversion of cyclohexane but also from the conversion of partially hydrogenated aromatics, such as cyclohexene, methylcyclohexene, and cyclohexadienes, for example.

The conversion of hydroaromatics to diolefins may be either catalytic or noncatalytic and I have found that in the preparation of diolefins from cyclohexane, for example, the conversion is preferably carried out in the presence of a catalyst although it is entirely within the scope of my invention to convert hydroaromatics to diolefins by means of noncatalytic conditions. When noncatalytic conversion is employed I prefer to operate coil 93 under conditions of low pressure such as between about 1.5 and 100 pounds per square inch absolute and preferably below atmospheric pressure and at a temperature between 1050 and 1550° F. and preferably between about 1200 and 1450° F. The time of reaction will vary with the extent of conversion desired. Under any given condition of temperature and pressure within the preferred range of operation, long contact time usually results in a greater extent of conversion than shorter contact times. In some instances I have found that the presence of extraneous material, such as steam, enhances the desired conversion to diolefins.

I prefer however to convert cyclohexane or any other hydrogenated aromatic hydrocarbon to a diolefin in the presence of a catalyst, such as a difficultly reducible metal oxide, for example, oxides of the alkali metals or alkaline-earth metals or the vanadate, uranate, phosphate, aluminate, chromate, or tungstate salts of these metals. Also, oxides of scandium, zirconium, titanium, tungsten, yttrium, lanthanum, molybdenum, thorium or uranium are suitable for use according to the present invention for the conversion of hydrogenated aromatic hydrocarbons to diolefin hydrocarbons. The temperature employed for the catalytic reaction should be at least 1000° F. and preferably not greater than 1500° F. The preferred temperature range is between 1100 and 1400° F. Pressures similar to those discussed in connection with the preparation of diolefins from hydroaromatics in the noncatalytic conversion step are employed in said catalytic step. Contact times are such that be-

tween about 20 and 60 per cent of the cyclohydrocarbon is converted per pass. As high as 85 per cent of the theoretical of diolefins are produced from the hydroaromatics undergoing conversion.

When the catalytic conversion is employed, coil 93 is a heating coil and a major portion of the conversion occurs in catalyst chamber 100 containing material which acts as a catalyst for said conversion. Hydroaromatics heated to a catalytic reaction temperature pass through conduits 94 and 96, controlled by valve 97, to catalyst chamber 100. After being subjected therein to conditions as discussed for the catalytic step, effluent therefrom, containing the desired diolefins, is passed through conduit 101 controlled by valve 102 to conduit 94 and thence to separating means 103. When only noncatalytic conversion is employed, valve 97 is closed and effluent from coil 93 passes through conduit 94 and valve 95 directly to separating means 103.

Separating means 103 will comprise a number of individual separating units from which desired fractions are segregated. Light gas undesirable for further treatment in my process, such as methane, is recovered from means 103 through conduit 112 and valve 113. When such gas contains larger amounts of hydrogen, said hydrogen may be passed to hydrogenator 82 by means not shown and employed therein as discussed.

A normally gaseous hydrocarbon fraction comprising essentially ethylene is removed from means 103 through conduit 116 and may be passed either by lines 114 and 32 to coil 35 or by line 45 to coil 50 by suitable control of valves 115 and 117 in conduits 114 and 116, respectively, to be treated in either or both of said coils under conditions as hereinbefore discussed. Unconverted cyclohexane or other hydroaromatic may be returned to coil 93 through conduit 104 controlled by valve 105 as recycle stock. Butadiene is removed as a product of the process from separating means 103 through conduit 110 controlled by valve 111. C₅ diolefins and heavier aliphatic hydrocarbons may be removed from means 103 through conduit 106 controlled by valve 107 and subsequently treated as may appear desirable, such as by the separation of C₅ diolefins from heavier aliphatics.

I claim:

1. The process of converting a hydrocarbon charge consisting essentially of C₂ to C₃ paraffins to butadiene which comprises converting said charge to C₂ to C₃ olefins by dehydrogenating same at an elevated temperature and a low pressure, separating from the effluent a light gaseous fraction containing essentially hydrogen and also a fraction containing essentially C₂ to C₃ olefins, converting said last-named fraction to butadiene and benzene by subjecting it to an elevated temperature and a low pressure for a time such that at least 3% and not more than 10% by weight of C₄ and heavier hydrocarbons based on the weight of the resulting effluent are synthesized, separating from the effluent from the last-named converting step the butadiene content thereof and also a fraction containing essentially said benzene formed in said last-named converting step, hydrogenating said benzene fraction with said hydrogen-containing fraction separated from the effluent of said first converting step to convert said benzene to cyclohexane, separating cyclohexane from the hydrogenation effluent, converting said cyclohexane to butadiene and ethylene

by subjecting it to an elevated temperature and low pressure, recovering butadiene from the resulting effluent and also a fraction containing essentially said ethylene formed in said last converting step, and feeding said ethylene fraction to said second converting step in admixture with said C₂ to C₃ olefin fraction recovered from the effluent of said first-named converting step.

2. The process of converting a hydrocarbon charge consisting essentially of C₂ to C₃ paraffins to butadiene which comprises converting said charge to C₂ to C₃ olefins by dehydrogenating the same at a temperature of from 1300 to 1600° F. and at a pressure of from 5 to 50 pounds per square inch absolute, separating from the effluent a light gaseous fraction containing essentially hydrogen and also a light hydrocarbon fraction containing essentially C₂ to C₃ olefins, converting said last-named fraction to butadiene and benzene by subjecting it to a temperature of from 1300 to 1700° F. and a low pressure for a time such that at least 3% and not more than 10% by weight of C₄ and heavier hydrocarbons based on the weight of the resulting effluent are synthesized, separating from the effluent from the last-named converting step the butadiene content thereof and also a fraction containing essentially said benzene, hydrogenating said benzene fraction with said hydrogen-containing fraction separated from the effluent of said first converting step to convert said benzene to cyclohexane, separating cyclohexane from the hydrogenation effluent, converting said cyclohexane to butadiene and ethylene by subjecting it to a temperature between 1050 and 1550° F. and a low pressure, recovering butadiene from the resulting effluent and also a fraction containing essentially

said ethylene formed in said last converting step, and feeding said ethylene fraction to said second converting step in admixture with said C₂ to C₃ olefin fraction recovered from the effluent of said first converting step.

3. A process for converting ethane to butadiene, which comprises converting ethane by dehydrogenating same at an elevated temperature and a low pressure to form ethylene and free hydrogen, separating from effluents of said dehydrogenation a gaseous fraction containing free hydrogen so produced and a normally gaseous hydrocarbon fraction containing ethylene so produced, converting said ethylene-containing hydrocarbon fraction together with ethylene from a subsequent cyclohexane conversion hereinafter specified at an elevated temperature and a low pressure to produce an optimum yield of butadiene together with a substantial amount of benzene, recovering from effluents of said conversion butadiene so produced as a product of the process, recovering also from effluents of said conversion benzene incidentally produced, hydrogenating said benzene with free hydrogen from said gaseous hydrogen-containing fraction to produce cyclohexane, converting said cyclohexane at an elevated temperature and low pressure to produce an optimum yield of butadiene together with a substantial amount of ethylene, recovering from effluents of said conversion butadiene so produced as a product of the process, recovering also from effluents of said conversion ethylene incidentally produced, and admixing said ethylene with the aforesaid normally gaseous hydrocarbon fraction containing ethylene to form the feed to second-named converting step.

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