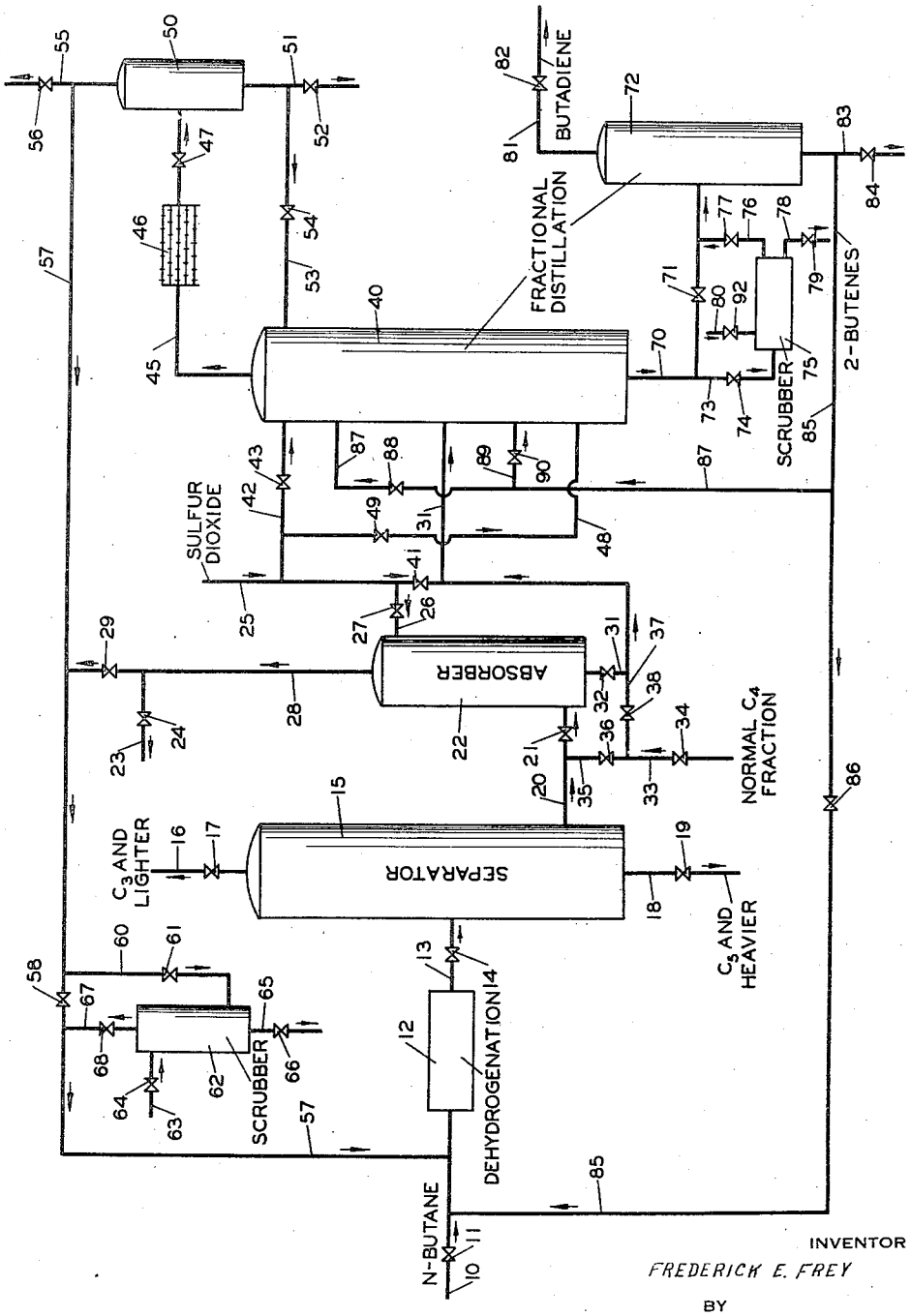
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PRODUCTION OF BUTADIENE

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PRODUCTION OF BUTADIENE

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This invention relates to the concentration of diolefin hydrocarbons. It relates further to the concentration of low boiling diolefins, more particularly butadiene, from mixtures containing other hydrocarbons of closely adjacent boiling points. As one modification, it relates to the production of a normal C_4 hydrocarbon mixture by the dehydrogenation of normal butane and the separation of a butadiene concentrate therefrom. This application is a division of my copending application Serial No. 383,235, filed March 13, 1941, and also is a continuation-in-part of my copending application Serial No. 354,890, filed August 30, 1940.

Diolefins are produced in a number of ways which include cracking of heavier oils, pyrolysis of gaseous hydrocarbons other than methane, the copolymerization of acetylene and ethylene to form butadiene, catalytic and 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, and other more or less involved chemical processes, as well as the dehydrogenation of the corresponding olefins which in turn may have been produced by the dehydrogenation of the corresponding paraffins. Although this latter procedure is one of the more direct ways of producing diolefins it has not yet found very extensive commercial application, and one of the obstacles in its commercial development has been the difficulty of effecting separation of olefins and diolefins from each other and from mixtures containing the corresponding paraffins.

In my aforementioned copending application of which this is a continuation-in-part, I have disclosed a process of producing low boiling diolefins from the corresponding paraffins in which a single dehydrogenation step is employed. As discussed therein, this dehydrogenation step apparently does not form the major part of the diolefin product by a dehydrogenation of a paraffin directly to a diolefin with no intermediate reactions, but apparently cooperates with the rest of the process to effect a dehydrogenation of paraffins to olefins and concomitantly a dehydrogenation of olefins to diolefins, the latter being produced in substantial quantities. In this process the dehydrogenation effluent will contain predominantly free hydrogen, and olefin and diolefin hydrocarbons corresponding to the paraffin hydrocarbon charged to the process, as well as quantities of such paraffin hydrocarbons which are unreacted. In this process unreacted paraffins and corresponding olefins are separated from the other products and are returned to the dehydrogenation along with fresh paraffin hydrocarbon material.

I have now found that efficient separation of butadiene from a C_4 fraction of the effluent of such a dehydrogenation process can be readily carried out, and the butadiene recovered in a state of high purity, by a series of fractional distillation steps, in the first of which sulfur dioxide is present in a limited amount, and in the second of which essentially no sulfur dioxide is present. While my separation step is quite advantageously combined with a step for the dehydrogenation of normal butane to produce butadiene such as is disclosed in my copending application, it is understood that in its broadest modification my separation step can operate on any C_4 fraction which contains butadiene and other C_4 hydrocarbons which are difficult to remove therefrom.

It has been disclosed in U. S. 2,186,524, of which I am a coinventor, that sulfur dioxide forms minimum-boiling azeotropic mixtures with each of the butanes and butenes. I have now found that if a C_4 fraction containing butadiene together with normal butane and normal butenes is fractionally distilled in the presence of sulfur dioxide, the amount of sulfur dioxide can be so limited that the overhead fraction contains substantially all the normal butane, 1-butene and sulfur dioxide charged to the distillation, the kettle product will then contain 2-butenes and substantially all the butadiene charged to the process, and butadiene can be separated in a state of high concentration from this kettle product by subsequent fractional distillation in the absence of sulfur dioxide. In the presence of actinic light and of certain catalysts butenes and butadiene form sulfones and/or heteropolymeric compounds of extremely high molecular weight. Such reactions are not desirable in connection with my process, and are to be avoided.

It is an object of my invention to produce low boiling diolefins in high concentration.

Another object of my invention is to obtain a butadiene fraction of high concentration from the dehydrogenation of normal butane.

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

My invention will now be more specifically described in connection with the accompanying drawing which shows diagrammatically by way of a flow sheet an arrangement of apparatus for practicing one modification of my invention. In this modification the invention will be described

in connection with a dehydrogenation step for producing butadiene from normal butane.

Referring now to the drawing, a paraffin hydrocarbon material comprising essentially normal butane enters the system through pipe 10 and valve 11 and is passed at a relatively low pressure to dehydrogenation unit 12. The dehydrogenation unit 12 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. The hydrocarbons charged to the process may be joined by recycled normal butane and normal butenes which will be passed to the pipe 10 through pipes 57 and/or 85. The dehydrogenation is conducted to effect a dehydrogenation both of normal butane and normal butenes to form butenes and butadiene respectively, along with free hydrogen. When a steady state of operation is reached only a limited amount of dehydrogenation per pass will actually take place, since the net reaction will be the dehydrogenation of a small amount of butane to form butenes, and of butenes to form a corresponding amount of butadiene, and a large substantially adiabatic catalyst chamber may be used with adequate heating of the stream charged to such chamber. The resultant products pass through pipe 13 and valve 14 to the separating means 15. In separating means 15, C_3 and lighter material including free hydrogen is separated from the C_4 hydrocarbons and removed through pipe 16 and valve 17. If any C_5 and heavier material is present in the effluent of the dehydrogenation, this material should also be removed, as through pipe 18 and valve 19.

A resulting C_4 hydrocarbon fraction is passed from separating means 15 through pipe 20 and may be passed through valve 21 to an absorption unit 22. The absorption unit 22 is used to effect a preliminary concentration of butenes and butadiene, which may be done by using any suitable absorption operation, but which is more advantageously accomplished in combination with the present invention by using a liquid sulfur dioxide as a selective absorbent. In such a case sulfur dioxide is passed through pipe 25 and through pipe 26 and valve 27 to a high point of absorber 22 and therein is passed countercurrent as a liquid to a hydrocarbon stream, introduced through valve 21 as previously described, also in liquid phase, although it may in some instances be in vapor phase. Unabsorbed butane is removed through pipe 23 and may be discharged from the system through pipe 23 and valve 24 or, if desired, may be passed through valve 29 to pipe 57 for recycle within the system, as will be discussed hereinafter.

In the absorption unit 22 liquid sulfur dioxide selectively dissolves normal butenes and butadiene and will also take up a certain amount of normal butane. The rich absorption liquid is passed through pipe 31 and valve 32 to a fractional distillation unit 40.

When a normal C_4 fraction is available from any suitable source, such as a fraction obtained from the gases resulting from the cracking of heavier oils or in the cracking of light gases to form normally gaseous olefins, such a material may be charged to the process through pipe 33 and valve 34 and may join a C_4 fraction passing from the separating unit 15 through pipe 20 or, if desired, it may constitute the sole hydrocarbon material charged to the process. If the absorption unit 22 is employed as just discussed, such a C_4 fraction may be passed through pipe 35 and valve 36 to pipe 20. However, if it is not desired to use such an absorption means for concentrating the unsaturated hydrocarbons, the C_4 fraction may be passed from pipe 33 through pipe 37 and valve 38 to pipe 31 and on to the fraction distillation unit 40. In many instances when the dehydrogenation unit 12 is used to produce all or part of the butadiene, it will not be necessary to use the absorption unit 22 and the C_4 fraction from separating means 15 may be passed directly through pipe 20, pipe 35 and pipe 37 to pipe 31 and the fractional distillation unit 40, as will be readily appreciated.

In fractional distillation unit 40, which is illustrated diagrammatically as a single fractionating column, a distillation of the C_4 hydrocarbons takes place in the presence of sulfur dioxide, which is added in amount sufficient to form azeotropic mixtures with substantially all of the normal butane and 1-butene fraction and in an amount so limited that little if any of the 2-butenes or butadiene are included. Sulfur dioxide for this purpose may either enter the distillation column along with the hydrocarbons through pipe 31 from absorption unit 22, or may be introduced separately at one or more other points along the line of the distillation column through pipe 42 and valve 43 and/or at some other part of the column as through pipe 48 and valve 49. When it is desired to add sulfur dioxide to the material passing through pipe 31 this may be accomplished by suitable control of valve 41 in pipe 25.

A low boiling mixture containing sulfur dioxide, normal butane and 1-butene is passed from the top of the fractionating column 40 through pipe 45, cooling and condensing coil 46 and valve 47 to a suitable separating means such as separator 50. In this separating means a suitable separation may be effected between sulfur dioxide and hydrocarbon constituents passing with it through pipe 45. This may be accomplished by suitable condensation and subatmospheric cooling to temperatures within the range of about +20 to −100° F., or by a further azeotropic distillation such as is disclosed in U. S. Patent 2,186,524, or by other suitable operations. A sulfur dioxide-rich material is passed from separator 50 through pipe 51 and may be discharged from the process entirely or in part through valve 52. Generally, however, a substantial portion thereof will be returned to the fractionating column 40 through pipe 53 and valve 54 as a liquid reflux. If the olefin content of this stream tends to build up too high a value, such material may be removed through valve 52 for a further separation of more or less pure sulfur dioxide which may be reintroduced in the system through pipe 25.

Hydrocarbon material separated from sulfur dioxide in separator 50 may be removed through pipe 55 and may be passed entirely or in part from the system through valve 56. However, when dehydrogenation unit 12 is a part of the process, it will generally be desirable to recycle all or a part of the hydrocarbons contained in this material to this dehydrogenation, and this may be effected by passing any desired portion of the stream from pipe 55 through pipe 57 and through valve 58 to pipe 10. If this stream contains an appreciable proportion of sulfur dioxide, this

should be removed before the material is passed to the dehydrogenation unit. Such removal may if desired be effected by passing the stream through pipe **60** and valve **61** to a scrubber **62** and passing purified hydrocarbons from the scrubber **62** through pipe **67** and valve **68** back to pipe **57** with valve **58** being closed. A suitable scrubbing agent such as water or an alkali solution such as sodium hydroxide or sodium carbonate may be passed to the scrubber through pipe **63** and valve **64** to effect the removal of sulfur dioxide from the hydrocarbons treated therein and the contaminated scrubbing medium may be removed through pipe **65** and valve **66** for regeneration or such other treatment as may seem desirable. Other suitable means for separating hydrocarbons from sulfur dioxide may be used, as may seem desirable or expedient.

From the bottom of fractional distillation means **40** a kettle product, which will comprise essentially 2-butenes and butadiene and which should be substantially free of sulfur dioxide, is passed through pipe **70** and valve **71** to a second fractional distillation means **72**. If there is sufficient sulfur dioxide in this material to require its removal, this may be accomplished by passing the stream from pipe **70** through pipe **73** and valve **74** for suitable purification as by treatment with a suitable scrubbing medium in scrubber **75**. A suitable scrubbing medium may be added through pipe **80** and valve **92**, and the spent scrubbing medium may be removed from the system through pipe **78** and valve **79**. The purified hydrocarbon material is passed through pipe **76** and valve **77** back to pipe **70** and fractional distillation means **72**, valve **71** being closed.

The fractional distillation unit **72** is so operated as to effect a separation of a substantially pure butadiene fraction, which should generally contain more than 90 per cent butadiene and preferably more than 95 per cent butadiene, although a purity greater than about 98 per cent will generally not be necessary. This fraction is removed as an overhead product through pipe **81** and valve **82** for whatever subsequent use may be desired. The kettle product, which will contain substantial quantities of 2-butenes, is removed through pipe **83** and may be discharged from the system through valve **84**. In one modification of my process it may be desirable to pass a portion of this kettle product back to the fractional distillation unit **40**, and this may be accomplished by passing the desired portion through pipe **85**, pipe **87** and valve **88** to a point in the upper portion of the fractional distillation unit **40**, or as may be found more desirable in some particular instance, it may be passed from pipe **87** through pipe **89** and valve **90** to a point in the lower part of this fractional distillation unit. When the dehydrogenation unit **12** is a part of my process and this kettle product does not contain too high a concentration of butadiene, a portion of it may be passed through valve **86** in a continuation of pipe **85** to pipe **10**.

While fractional distillation units **40** and **72** have been shown as single units, it is to be understood that this is merely diagrammatic and either one or both of them may comprise two or more fractional distillation columns, each with suitable bubble trays or packing not shown, to afford intimate contact by the reflux liquid and ascending vapors with suitable heating means for the kettle, and cooling means for the top, reflux accumulators and reflux lines and the like as will be readily understood by one skilled in the art. It will be desirable that the butadiene-containing material, especially when the butadiene is in a somewhat concentrated state, should not be heated to too high a temperature since this material polymerizes somewhat readily. It is well known that sulfur dioxide forms sulfones and high molecular weight heteropolymeric compounds with butenes and butadiene. Such chemical reactions take place in the presence of actinic light and also in the presence of certain catalysts and are to be avoided. In some instances it may be necessary to add materials to inhibit the formation of such compounds, such as phenyl-beta-naphthylamine, pyrogallic acid, hydroquinone, catechol, resorcinol, cresols and similar phenolic compounds. Any iso-C_4 hydrocarbons present in the charge to fractionating means **40** will be removed therefrom in the overhead product, and may be discharged from the system through valves **52** and/or **56**. Some or all of any iso-C_4's present in the material charged to separating means **15** may be removed, as a part of the C_3 and lighter material, through pipe **16**.

Although it is desirable that the major part of the 2-butenes be separated along with the butadiene as a kettle product, at times a better separation can be effected if a small portion of the 2-butenes, especially the trans-isomer, is permitted to pass from the distillation column **40** through pipe **45** as a part of the overhead product.

As an example of my process, a C_4 hydrocarbon fraction containing about 7 per cent butadiene, 25 per cent normal butenes of which about one-fourth is 1-butene and three-fourths 2-butenes, and 68 per cent normal butane may be passed as a liquid to a fractional distillation column of 100 plates and in two sections operated under a total column pressure of about 120 pounds per square inch. Sulfur dioxide is introduced to the column in two places, the major part being returned as reflux at a point near the top, with sufficient "make-up" being added along with the C_4 stream to give a total amount of sulfur dioxide introduced equal to about 10 per cent in excess of that required to form azeotropic mixtures with the normal butane and 1-butene introduced, under the conditions existing at the top of the column. Under these conditions a small amount of 2-butene, primarily the trans-isomer, is included in the overhead product. A sulfur dioxide-rich fraction is separated from the overhead product and returned to the column as a liquid reflux, thereby controlling the top temperature and furnishing sulfur dioxide for the azeotropic distillation. A kettle product comprising primarily 2-butenes and butadiene is freed from traces of sulfur dioxide and passed to a second fractional distillation column, containing 120 plates in three sections. This column is operated at a pressure of about 75 pounds per square inch, the overhead fraction contains butadiene of about 98 per cent purity of which a portion is continuously returned as liquid reflux, another being a product of the process. The kettle product contains only a small amount of butadiene and comprises primarily 2-butenes.

I claim:

1. In a process for the production of butadiene from normal butane, which comprises dehydrogenating normal butane together with recycled C_4 hydrocarbons in a single dehydrogenation step under conditions effecting dehydrogenation of normal butane to normal butenes including 1-butene and 2-butenes and simultaneous dehydrogenation of normal butenes to butadiene, the im-

provement which comprises subjecting effluents of said dehydrogenation to selective solvent extraction with liquid sulfur dioxide to effect a preliminary concentration of butenes and butadiene, passing the resulting solution of hydrocarbons and sulfur dioxide to a first fractional distillation and removing an overhead fraction comprising azeotropes of sulfur dioxide with 1-butene and normal butane, removing a liquid kettle product consisting essentially of 2-butenes and butadiene, subjecting said product to a second fractional distillation in the absence of sulfur dioxide, removing therefrom as a gaseous overhead product a butadiene concentrate as a product of the process, removing also therefrom a liquid kettle product substantially free of butadiene and comprising essentially 2-butenes and passing same to said dehydrogenation as at least a part of said recycled C_4 hydrocarbons.

2. In a process for the production of butadiene from normal butane which comprises dehydrogenating normal butane in admixture with recycled normal butane and butenes under conditions effecting conversion of normal butane to normal butenes including 1-butene and 2-butenes and simultaneous conversion of normal butenes to butadiene, the improvement which comprises treating the resulting effluent to segregate a fraction consisting essentially of the C_4 hydrocarbon content thereof, extracting said C_4 hydrocarbon fraction with liquid sulfur dioxide as a selective solvent and thereby effecting selective dissolution of the normal butenes and butadiene content thereof while allowing most of the normal butane to remain undissolved, recycling said undissolved normal butane to the dehydrogenating step, passing the rich solvent from said extracting step to a first fractional distillation zone and there fractionally distilling same in the presence of sulfur dioxide in amount sufficient to form minimum-boiling azeotropes with all of the normal butane and 1-butene contained therein but insufficient to form an azeotrope with the major portion of the 2-butenes contained therein, removing as an overhead all of said azeotropes of sulfur dioxide with normal butane and 1-butene, treating the overhead to effect separation thereof into a sulfur dioxide-rich liquid fraction and a fraction of normal butane and 1-butene, refluxing said distillation zone with at least a part of said sulfur dioxide-rich liquid fraction, recycling said fraction of normal butane and 1-butene to said dehydrogenating step, removing from said distillation zone a kettle product consisting essentially of 2-butenes and butadiene and substantially free of sulfur dioxide and passing same to a second fractional distillation zone and there fractionally distilling same in the absence of sulfur dioxide to produce an overhead product consisting essentially of butadiene as the product of the process and a kettle product consisting essentially of 2-butenes, and recycling said 2-butenes kettle product to said dehydrogenating step.

3. The process for the recovery of substantially pure butadiene from a C_4 hydrocarbon fraction containing the same in admixture with 1-butene, 2-butenes and normal butane which comprises extracting said fraction with liquid sulfur dioxide as a selective solvent and thereby effecting selective dissolution of the normal butenes and butadiene content thereof while allowing most of the normal butane to pass through undissolved, passing the resulting rich solvent to a first fractional distillation zone and there fractionally distilling same in the presence of sulfur dioxide in amount sufficient to form minimum-boiling azeotropes with all of the normal butane and 1-butene contained therein but insufficient to form an azeotrope with the major portion of the 2-butenes contained therein, removing as an overhead all of said azeotropes of sulfur dioxide with normal butane and 1-butene, treating the overhead to effect separation thereof into a sulfur dioxide-rich liquid fraction and a fraction of normal butane and 1-butene, refluxing said distillation zone with at least a part of said sulfur dioxide-rich liquid fraction, removing from said distillation zone a kettle product consisting essentially of 2-butenes and butadiene and substantially free of sulfur dioxide and passing same to a second fractional distillation zone and there fractionally distilling same in the absence of sulfur dioxide to produce an overhead product of substantially pure butadiene and a kettle product consisting essentially of 2-butenes.

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