

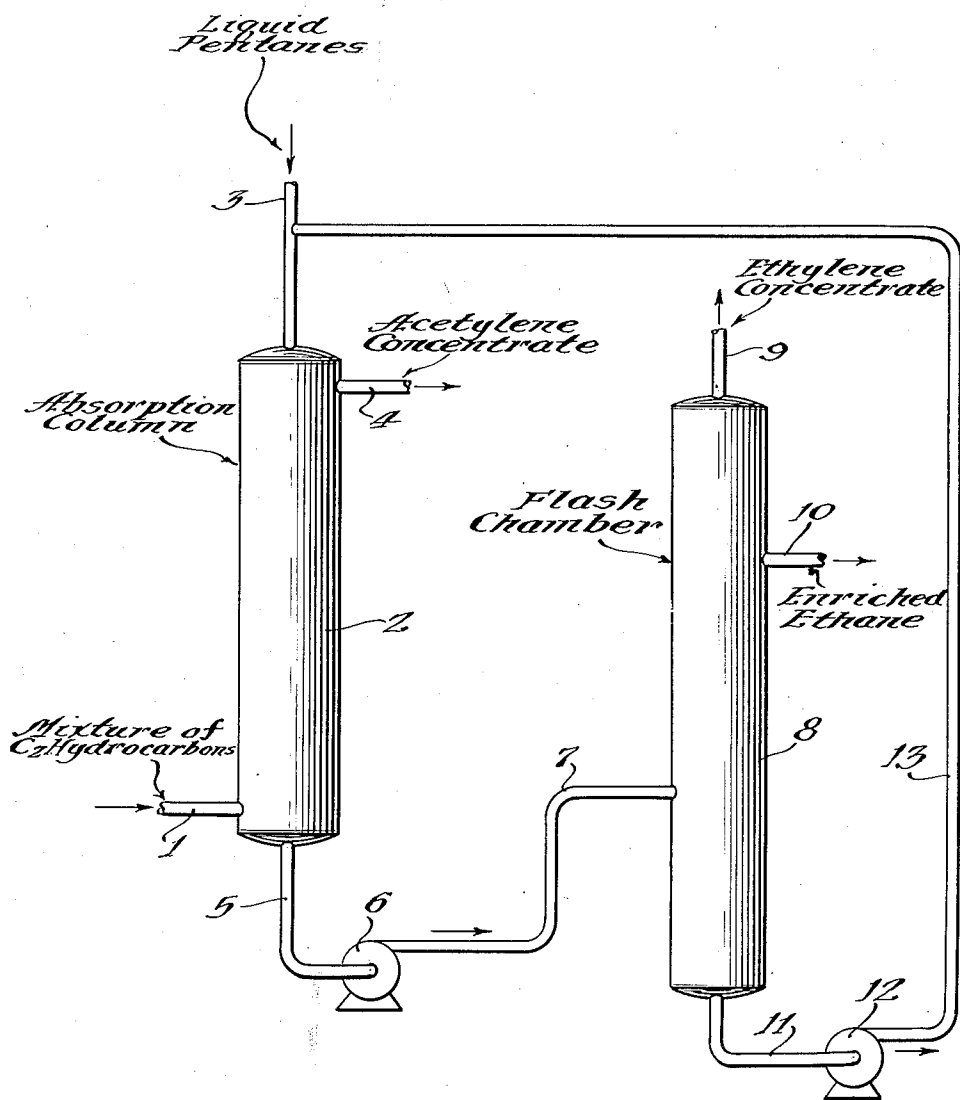
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PROCESS FOR SEPARATION OF HYDROCARBONS

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PROCESS FOR SEPARATION OF
HYDROCARBONS

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This invention relates to a process for concentrating and separating unsaturated aliphatic hydrocarbons from hydrocarbon mixtures containing the same and is particularly applicable to the separation of unsaturated aliphatic hydrocarbons containing from 2 to 4 carbon atoms per molecule from saturated aliphatic hydrocarbons of the same carbon atom content by a method involving preferential dissolution of the more saturated component of the hydrocarbon mixture in a liquefied paraffinic solvent.

It is the principal object of this invention to separate a mixture of saturated and unsaturated aliphatic hydrocarbons of the same carbon atom content within the range of from 2 to 4 carbon atoms per molecule which are not conveniently separable by ordinary fractional distillation.

It is an object of this invention to provide a satisfactory and economical process for concentrating acetylene from a mixture of C_2 hydrocarbons which do not readily separate by simple fractional distillation.

Another object of the present invention is to separate normally gaseous hydrocarbon mixtures containing components of the same carbon atom content of both saturated and unsaturated structures by utilizing a method which does not depend upon utilization of low temperatures involving expensive and complex refrigeration apparatus or involved extraction procedures for effecting the separation.

Still another object of the invention is to provide a process involving a selective solvent which may be continuously recycled in the separation process without consumption or deterioration of the solvent.

Hydrocarbon mixtures of the type utilized as charging stocks in the present process are formed in various hydrocarbon conversion processes such as hydrocarbon dehydrogenation processes and petroleum cracking operations where said hydrocarbon mixtures are formed as the gaseous effluent of the operation, the latter containing an admixture of the paraffinic, olefinic, and in many cases, the acetylenic hydrocarbons, especially when the operation involves a dehydrogenation stage wherein both cracking and dehydrogenation take place to form a mixture of the aliphatic saturated and unsaturated gaseous hydrocarbons. The mixture of hydrocarbons ordinarily obtained as the gaseous effluent of a hydrocarbon conversion process may be desirably fractionated to separate a fraction containing hydrocarbons of the same carbon atom content prior to being subjected to the separation process of this invention.

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The present process is particularly applicable to the separation of the various C_2 hydrocarbons, such as the separation of acetylene and/or ethylene from ethane. The process is also applicable to the separation of the saturated components from the unsaturated components of hydrocarbon mixtures containing the same number of carbon atoms. Thus propane may be separated from propene and/or propene and the various butanes from the corresponding C_4 olefins, diolefins or acetylenic derivatives.

Although mixtures of the above type are separable by methods heretofore known, such as by fractional distillation, such methods are ordinarily limited in their application to the separation of components varying rather widely in molecular weight or boiling points such as distillation into fractions consisting of hydrocarbons of the same number of carbon atoms per molecule; the further separation of such fractions, however, by means of fractional distillation into relatively pure species (as for example, olefins from paraffins of the same number of carbon atoms) is of considerable difficulty by conventional simple fractionation due to the close proximity of the boiling points of the various types of hydrocarbons having the same number of carbon atoms.

Known methods of separating hydrocarbon mixtures containing components having from 2 to 4 carbon atoms per molecule in which the components have different degrees of unsaturation almost without exception involve either an extraction procedure in which liquid-liquid or liquid-vapor contacting techniques between the charge stock and a selective solvent for one or more of the components are employed and in such methods, refrigeration is usually an essential factor in the separation. In contradistinction to the complex and expensively operated processes of the prior art, the present method involves a simple procedure in which the charging stock comprising normally gaseous hydrocarbons of the same carbon atom content is compressed to a superatmospheric pressure and contacted at said pressure with a liquefied paraffinic hydrocarbon containing from 3 to 6 carbon atoms per molecule and having at least the same carbon atom content as the hydrocarbon mixture being separated. The solvent utilized in the present invention as the absorbing medium for the saturated component of the hydrocarbon mixture charged to the process is preferably a C_4 or C_5 paraffin, although the process is also operable when utilizing respectively lighter or heavier paraffins as the absorbent. It is also within con-

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templation of the present process to utilize mixtures of paraffinic hydrocarbons, such as a mixture containing one or more of the butanes with one or more of the pentanes. In the case of propane and the butanes as the solvent utilized for the separation, superatmospheric pressures and/or a subnormal temperature (i. e., below about 0° C.) are utilized such that the solvent remains in liquid phase during the separation process. In the presence of the above solvents in the liquid state, it has been observed that the solvent selectively dissolves the saturated component of a mixture of hydrocarbons to be separated while the vapor phase above the solvent becomes enriched in the unsaturated component or components of the hydrocarbon mixture charged. A physical or manual separation of the liquid and vapor phases while the charge and solvent are under the pressures specified herein, will effect a separation of the hydrocarbon components of the mixture charged. It is on the basis of the latter observation that the present process operates to effect the separation herein provided.

In accordance with one of its embodiments, the invention relates to a process for separating a mixture of aliphatic hydrocarbons of the same carbon atom content per molecule within the range of from 2 to 4 carbon atoms and having varying degrees of saturation which comprises contacting said mixture with a solvent comprising a liquefied paraffinic hydrocarbon containing at least the same number of carbon atoms per molecule as the components of the mixture being separated within the range of from 3 to 6 carbon atoms at a superatmospheric pressure thereby effecting selective absorption of the more saturated hydrocarbons of said mixtures in the paraffinic solvent and separating the resultant liquid phase containing the more saturated hydrocarbons of said mixture from the resultant gaseous phase containing the less saturated hydrocarbons of the mixture charge.

A specific embodiment of the invention relates to a process for concentrating acetylene from a mixture of hydrocarbons also containing ethane and ethylene by contacting the mixture with a liquefied paraffinic hydrocarbon solvent containing from 3 to 6 carbon atoms per molecule at a superatmospheric pressure above about 2 atmospheres, at a temperature below the critical temperature of the paraffinic solvent to thereby selectively absorb ethane in the solvent, and separating the resulting liquid phase from the resulting gaseous phase containing acetylene.

Other embodiments relating to specific absorbents, to the separation of specific hydrocarbon mixtures and to other variables associated with the process of this invention will hereinafter be described in greater detail.

The present process may be operated either on a batch or continuous basis. In a typical batch operation, the hydrocarbon mixture to the separated is charged into a pressure vessel containing the paraffinic hydrocarbon absorbent until the pressure above the surface of the liquid absorbent has reached the desired value, above about 2 atmospheres and usually below about 100 atmospheres, with suitable economically operable pressures being from about 10 atmospheres to about 60 atmospheres. The volume of liquid absorbent required in the pressure vessel depends upon the ultimate pressure attained in the separation; for the above specified range of from about 10 to about 60 atmospheres pressure, the ratio of the volume of liquid paraffinic solvent to

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the volume of gaseous hydrocarbon charge to be separated is from about 0.01 to about 1, where the volume of gaseous hydrocarbon charge is based upon normal conditions (i. e. at 0° C. and atmospheric pressure). The gaseous phase above the liquid absorbent will then be found to be enriched in the unsaturated component of the hydrocarbon mixture charged while substantially greater proportions of the saturated component of said mixture will be dissolved in the paraffinic liquid absorbent. The saturated hydrocarbon dissolved in the absorbent may be recovered therefrom by applying heat to the liquid phase, by reducing the pressure above the paraffinic absorbent thereby vaporizing the dissolved saturated gaseous hydrocarbon therefrom or by any other suitable method for separating a volatile hydrocarbon from a solution of the same in a relatively non-volatile hydrocarbon. In order to obtain more complete separation of the hydrocarbon mixture charged, the above operation may be repeated on either the gaseous phase recovered from the separation process or the volatilized gas recovered from the paraffinic absorbent.

As heretofore indicated, the present process may be operated on a continuous basis. A suitable procedure for continuous separation of the hydrocarbon mixture involves, for example, contacting the hydrocarbon mixture to be separated at the desired pressure with a stream of the paraffinic liquid absorbent flowing, preferably, countercurrent to the flow of the gaseous hydrocarbon mixture, effecting the contact between the gaseous and liquid phases by any suitable means known to the art. One method of effecting continuous contact of the gaseous and liquid hydrocarbon phase is represented by an operation, for example, in which the gaseous mixture is charged into the bottom of a packed or bubble plate absorption column while the liquid paraffinic hydrocarbon is charged into the top of the column. As the solvent flows downwardly it scrubs the up-flowing stream of hydrocarbon gases, absorbing from the latter the more soluble saturated component of the gas mixture. The solvent accumulating in the kettle attached to the column may be treated in any manner desirable to remove the dissolved component of the hydrocarbon mixture, as for example, by flashing the liquid into a low-pressure chamber to vaporize the dissolved hydrocarbon therefrom. The solvent recovered from the flashing operation denuded of the dissolved saturated hydrocarbon of the original mixture may be recycled to the absorption column. The unsaturated components of the original mixture (as, for example, acetylene, and to some extent, ethylene) which do not readily dissolve in flowing upwardly through the absorption column may be withdrawn from the top of the column and subjected to further extraction treatments in a subsequent series of absorption towers if additional purification is desired. The completeness of separation and the purity of the respective saturated and unsaturated fractions recovered from the absorption column is dependent upon not only the ratio of solvent to hydrocarbon mixture charged to the column, but also on the number of theoretical plates in the absorption column. Instead of the conventional bubble cap design for the contacting means between the gaseous and liquid phases within the absorption column, desirable contact between the phases may be obtained by utilizing a packing material in the column such as berl saddles, quartz chips,

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or other means known to the prior art to effect liquid vapor-contact.

The temperature and pressure conditions utilized for effecting the present absorption and separation depend upon the composition of the hydrocarbon mixture charged to the process. It is essential in the operation of the present process that the absorbent remain in substantially liquid phase during the process and to maintain this condition, the temperature utilized is below the critical temperature for the particular paraffinic solvent utilized as absorbent. The pressure condition maintained in the column during absorption is desirably sufficiently superatmospheric to maintain liquid phase without resorting to refrigeration of the solvent, although refrigeration is not necessarily excluded. Thus, it is usually desirable to maintain temperatures of from about 0° to about 100° C. and pressures above about 2 atmospheres, preferably from about 10 to about 60 atmospheres, although in general it is preferred to operate at higher temperatures as the molecular weight of the hydrocarbons to be separated increases. Thus, temperatures for separating a C₄ mixture are higher than for a C₃ mixture.

A suitable apparatus and arrangement thereof for the separation of a mixture of C₂ hydrocarbons utilizing a liquefied mixture of pentanes as the selective solvent for the unsaturated components of the mixture is illustrated diagrammatically in the accompanying drawing which is illustrative only of one species of charging stock and solvent utilizable in the present separation process. Referring to the diagram, the charging stock consisting of a mixture of C₂ hydrocarbons and containing any given proportion of ethane, ethylene and acetylene is charged through line 1 into any suitable absorption column, such as countercurrent extraction column 2 which may be packed with a suitable granular packing material or may be designed for vapor-liquid contact through a series of horizontally disposed bubble cap trays within column 2. The solvent comprising liquid pentanes is introduced into the top of absorption column 2 through line 3 and is allowed to flow downwardly through column 2 in countercurrent contact with the gaseous mixture of C₂ hydrocarbons introduced into the lower portion of column 2. The solvent may consist of a single liquid C₅ hydrocarbon or a mixture of various C₅ isomers and may, in addition, contain minor amounts of unsaturated C₅ hydrocarbons, such as the C₅ fraction of a cracked petroleum fraction. The gaseous phase which becomes progressively enriched in the acetylene component of the charging stock mixture and denuded of ethane and/or ethylene percolates upwardly through column 2 and is ultimately withdrawn therefrom through line 4 which may lead to additional absorption columns or to other separating means for effecting further purification of the acetylene. The liquid pentane absorbent phase which gravitates downwardly through column 2 is removed therefrom through line 5, transferred by means of pump 6 and line 7 into flash chamber 8 for separating the absorbed C₂ hydrocarbons from the pentane solvent, the distillation obtained in flash chamber 8 merely being one means of many for separating the dissolved C₂ hydrocarbons from the liquid pentane extract phase. In order to obtain a flash vaporization of the dissolved C₂ components from the pentane solvent, the pressure on the extract may be reduced and/or its

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temperature increased to a level at which the dissolved ethylene, ethane and to a lesser extent, acetylene, spontaneously vaporize from the extract. The ethylene component which boils at the lowest temperature is recovered from flash chamber 8 through line 9 and may be diverted to additional absorption columns in series, not shown on the accompanying diagram, for further purification of the ethylene concentrate. Ethane, and/or acetylene, if any, which boil at a somewhat higher temperature than ethylene, may be removed from flash chamber 8 through line 10 and may be diverted into additional absorption columns for further purification, if desired. The liquid pentane solvent is removed from the bottom of chamber 8 through line 11 and is preferably transferred by means of pump 12 into recycle line 13 which connects with the pentane solvent charging line 3. The liquid pentane absorbent thus recovered may be recycled indefinitely in the system and may be brought to the proper operating temperatures by means of refrigerating apparatus not illustrated, although atmospheric temperatures and pressures are generally preferred.

The present process is further illustrated in the following examples which indicate merely some of the variable factors encountered in the operation of the process; however, said examples are not introduced with the intention of limiting the generally broad scope of the invention in accordance thereto.

Example I

In a typical batch operation, 300 ml. of n-pentane was sealed into a pressure autoclave of 850 ml. capacity. This was pressured with equal quantities of acetylene, ethylene and ethane until the pressure was 500 p. s. i. gauge. The autoclave was then shaken and rotated to obtain intimate contact between the vapor and liquid phases present in the autoclave. The final pressure after mixing was 185 p. s. i. gauge and the temperature essentially room temperature (30° C.). The distribution of the three added gases in the liquid pentane and gaseous phase was:

	C ₂ H ₂ , per cent	C ₂ H ₄ , per cent	C ₂ H ₆ , per cent
Gas phase.....	38	33	29
Liquid phase.....	21	31	48

Pressure was released from the autoclave until the pressure was reduced to 80 p. s. i. gauge. The distribution of the three gases in the gaseous phase was then:

	C ₂ H ₂ , per cent	C ₂ H ₄ , per cent	C ₂ H ₆ , per cent
Gas phase.....	32	34	34

Pressure was further released from the autoclave until a valve pressure of 20 p. s. i. was obtained. The gas phase at this pressure contained the following distribution of gases.

	C ₂ H ₂ , per cent	C ₂ H ₄ , per cent	C ₂ H ₆ , per cent
Gas phase.....	25	33	42

From the above data it is readily apparent that were the respective liquid and gaseous phases separated after mixing at 185 p. s. i. gauge pres-

sure, a concentration of the acetylene component of the mixture in the gaseous phase could be obtained while the liquid pentane phase would contain a relatively larger proportion of ethane than was present in the original mixture of gases charged.

Example II

A similar batch procedure as that employed in Example I, except that n-butane was utilized as the absorbent produced the following gaseous and liquid phases at a final pressure, after mixing, of 220 p. s. i. gauge and at a temperature of 0° C.:

	C ₂ H ₂ , per	C ₂ H ₄ , per	C ₂ H ₆ , per
Gas phase.....	52	33	15
Liquid phase.....	15	31	54

The analysis of the gas phase indicates that n-butane may be utilized as a somewhat more selective adsorbent at lower temperatures.

Example III

A hydrocarbon fraction containing butanes, butenes, butynes and butadienes was charged to a contactor containing n-pentane at 125° C. The butanes were mostly concentrated in the pentane phase; the olefins were about equally distributed between the gaseous and liquid phases; the butynes and butadienes were found mainly in the gaseous phase.

I claim:

1. A process for separating acetylene from a mixture thereof with more saturated C₂ hydrocarbons which comprises contacting said mixture with a paraffinic hydrocarbon solvent, said paraffin having from 3 to 6 carbon atoms per molecule, at a superatmospheric pressure of at least about 10 atmospheres to thereby effect selective absorption of the more saturated hydrocarbon components of said mixture in said solvent and separating the resulting liquid phase containing said more saturated hydrocarbon components from the resulting gaseous phase containing acetylene.

2. The process of claim 1 further characterized in that said mixture of hydrocarbons having varying degrees of saturation is contacted with said paraffinic hydrocarbon solvent at a temperature below the critical temperature of said paraffinic solvent.

3. A process for separating acetylene from ethane which comprises contacting a mixture of acetylene and ethane with a liquefied paraffinic hydrocarbon containing from 3 to 6 carbon atoms per molecule at a superatmospheric pressure of at least about 10 atmospheres to thereby effect selective absorption of said ethane in said solvent and separating the resulting liquid phase from the resulting gaseous phase.

4. A process for removing ethane from a mixture of C₂ hydrocarbons containing acetylene which comprises contacting said mixture with a liquefied paraffinic solvent containing from 3 to 6 carbon atoms per molecule at a superatmospheric pressure of at least about 10 atmospheres and at a temperature below the critical temperature of said paraffinic solvent to thereby effect selective absorption of said ethane in said solvent and separating the resulting liquid phase containing said ethane from the resulting gaseous phase containing said acetylene.

5. The process of claim 4 further characterized in that said solvent comprises a C₄ paraffin.

6. The process of claim 4 further characterized in that said solvent comprises a C₅ paraffin.

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