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PROCESS FOR SEPARATING HYDROCARBONS

Filed June 4, 1942

2 Sheets-Sheet 1

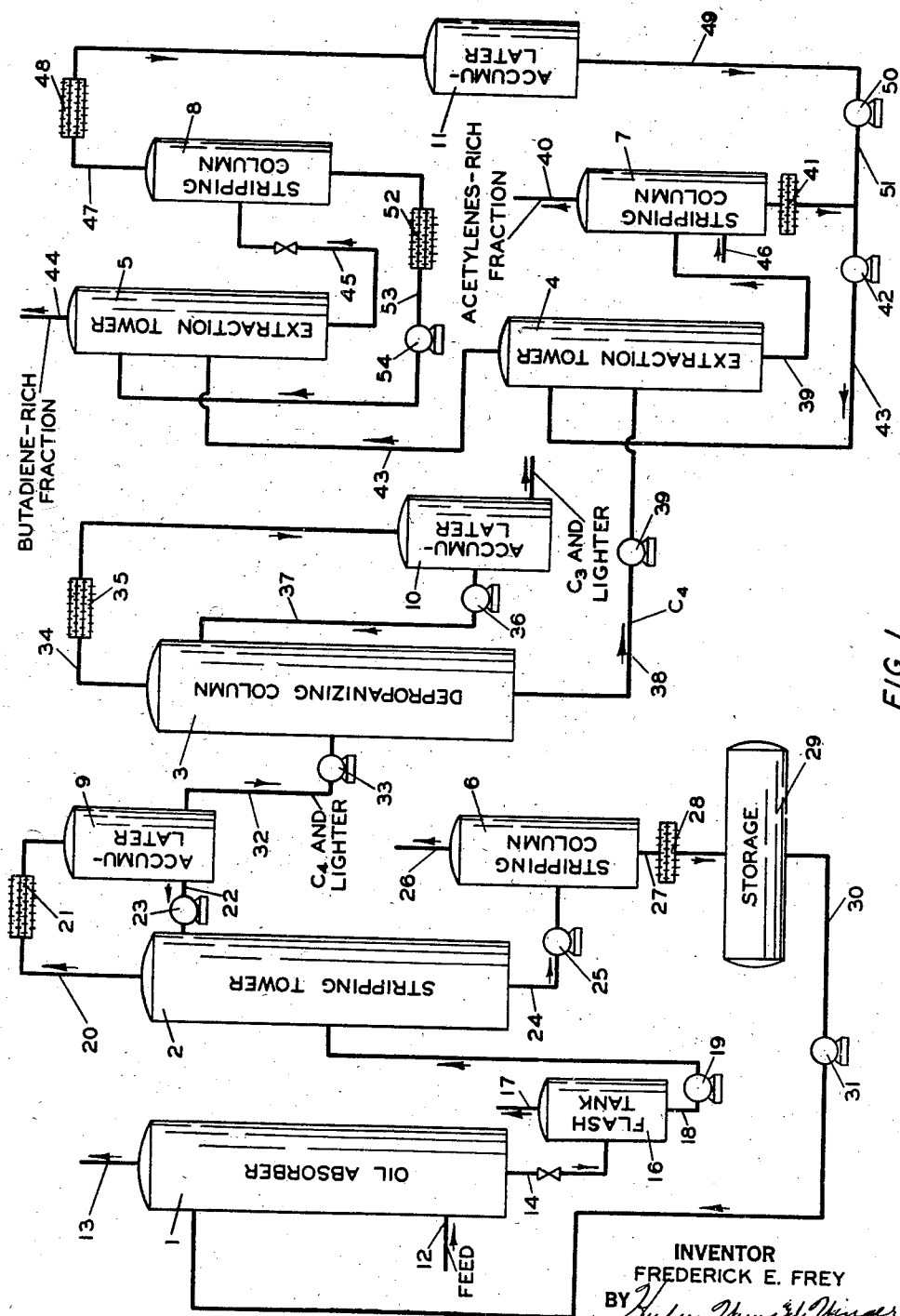


FIG. 1

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Aug. 29, 1944.

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PROCESS FOR SEPARATING HYDROCARBONS

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2 Sheets-Sheet 2

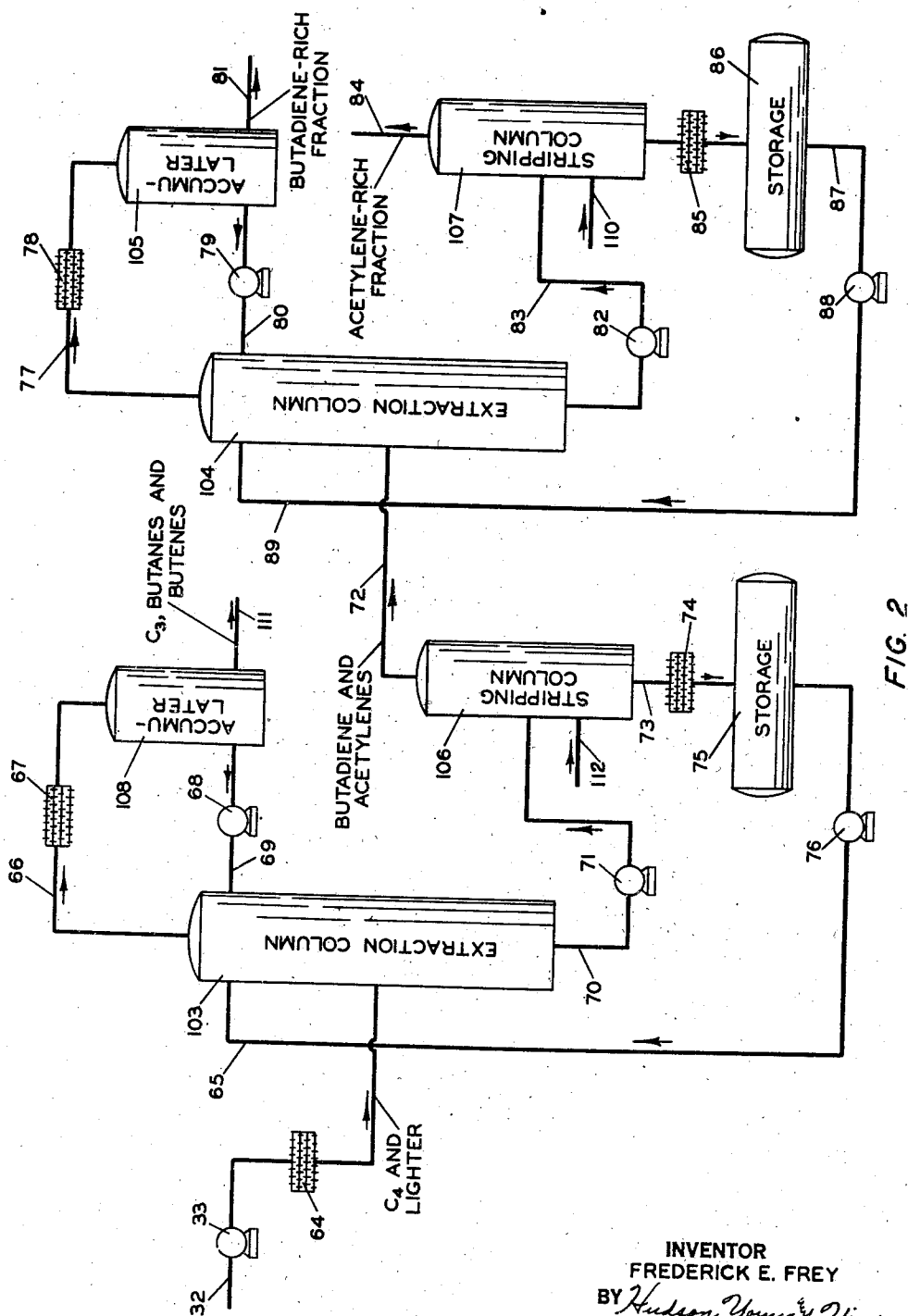


FIG. 2

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PROCESS FOR SEPARATING HYDRO-CARBONS

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5 Claims. (Cl. 183—115)

This invention relates to an improved process for the separation into two fractions of a mixture of hydrocarbons containing four carbon atoms per molecule, the separation being of such a nature as to produce a relatively butadiene-rich fraction and a fraction relatively rich in compounds containing an acetylenic linkage.

There are commercially important gas mixtures, produced by thermal cracking of low-molecular-weight hydrocarbons or in other ways, that contain the valuable hydrocarbon butadiene and various other saturated and unsaturated four-carbon-atom hydrocarbons which have boiling points quite close to that of butadiene. Separation and purification of butadiene from gas mixtures is ordinarily necessary in order to utilize the butadiene, as for the production of rubbery polymers or the like. As is known in the art, hydrocarbons containing an acetylenic linkage are particularly undesirable impurities in butadiene that is to be used for chemical synthesis. Examples of acetylenic compounds that have four carbon atoms per molecule and that boil relatively near to butadiene are ethyl acetylene and vinyl acetylene. The production of butadiene free from such undesirable impurities, notably vinyl acetylene, is quite difficult and costly by known methods of fractional distillation because of such factors as the relatively small boiling point differences that are involved, the tendency for azeotropic, constant-boiling mixtures of hydrocarbons of different types to be formed and to interfere with the fractionation, and the large energy requirements of complicated distillation procedures.

It is an object of my invention to provide a process whereby a gaseous mixture of light hydrocarbons containing butadiene and acetylenic hydrocarbons of four carbon atoms per molecule may be separated into fractions rich in butadiene and in acetylenes, respectively, by treating the gaseous hydrocarbon mixture with suitable solvents.

It is a further object of my invention to provide a process whereby substantially pure butadiene may be recovered from a gaseous mixture of light hydrocarbons containing butadiene and acetylenic hydrocarbons of four carbon atoms per molecule.

Other objects and advantages will be apparent from the following description, the accompanying drawings, and/or the appended claims.

In brief, my invention consists in contacting, preferably in countercurrent fashion, the gaseous hydrocarbon mixture with a selective solvent at

a suitable temperature and pressure. I have found that, under suitable conditions, the four-carbon-atom acetylenes tend to selectively dissolve in, and to be carried away by, the solvent, whereas the remaining gaseous phase is enriched in butadiene and is impoverished in acetylenic constituents.

I may apply my process in treating hydrocarbon mixtures that contain substantial amounts of hydrocarbons of molecular weight lower than that of four-carbon hydrocarbons. My process is likewise applicable in treating hydrocarbon mixtures containing minor amounts of materials heavier than four-carbon hydrocarbons.

An advantage of my process resides in the fact that it is particularly well adapted to treating, at low cost, large volumes of hydrocarbons that contain only small amounts of the objectionable acetylenic compounds. In such cases the acetylenic compounds may be absorbed by quite limited amounts of solvent, and economies in the size of equipment and heat requirements are realized as compared with known methods of fractional distillation.

A further advantage of my process over known methods of fractional distillation is found in instances in which butene-2 is a component of the hydrocarbon mixture to be treated. In such cases, by application of my process in one form, I can, if desired, separate the hydrocarbon mixture into a fraction rich in vinyl and ethyl acetylenes and into a fraction rich in butadiene, and this latter fraction will also contain substantially all of the butene-2 that was in the original mixture. When a similar separation is attempted by conventional fractionation, it is found that the tendency of butene-2 and vinyl acetylene to form a minimum-boiling constant-boiling mixture causes difficulty and, in consequence, in order to make sure the butadiene-rich fraction is freed of acetylenes, it becomes necessary to regulate the fractionation so that only a part, if any, of the butene-2 is incorporated into the butadiene-rich fraction, while producing an acetylene-rich fraction that contains most, if not all, of the butene-2.

In some cases, when treating hydrocarbon mixtures according to my process, I have found it desirable to subject the butadiene-rich gas fraction that is produced to further treatment in order to recover the small quantity of primary selective solvent that is lost to the gas stream because of the vapor pressure that the solvent exerts under the conditions of the extraction. In order to effect such recovery of primary solvent

vapor from the hydrocarbon mixture, I have found that I may pass the gaseous mixture countercurrently to a relatively small liquid stream of a suitable secondary solvent which serves to extract vapor of the primary solvent from the gaseous mixture. This secondary solvent should be of such a nature that the primary solvent may be separated from it in some fashion, as by distillation. It will normally be desirable to employ as a secondary solvent a material with a boiling point approximately 100° C. higher than the boiling point of the primary solvent.

In accordance with my invention, I take a stream consisting essentially of C₄ hydrocarbons including the butadiene and the alkyl and alkenyl acetylenes to be separated and usually substantial amounts of butanes and/or butenes, and occasionally also containing some C₅ hydrocarbons of the same general type. This stream may be already available or may be prepared from available hydrocarbon streams in any desired manner. This stream is selectively extracted in the gaseous phase with a primary solvent which is selective for the acetylenes in preference to the butadiene under conditions including temperature, pressure, etc. causing the acetylenes to be selectively dissolved in the solvent.

If desired, and usually it will be preferable, the butadiene-rich residual gas fraction may be contacted with a secondary selective solvent for the primary solvent and essentially a non-solvent for butadiene, in order to recover any traces of the primary solvent from the residual gas. This secondary solvent should be one which is readily separable from the primary solvent in any suitable manner for example by fractional distillation, and to this end should boil at least 100° C. above the primary solvent.

In one embodiment, my invention may involve taking a stream containing the C₄ hydrocarbons mentioned above, namely the butadiene and the alkenyl and alkyl acetylenes and butanes and/or butenes, with or without corresponding C₅ hydrocarbons, and containing in addition C₃ hydrocarbons, and treating this stream preliminarily with a selective solvent such that and under conditions such that the butadiene and the C₄ acetylenes are dissolved therein in preference to the butanes, butenes and C₃ hydrocarbons, following which the dissolved butadiene and acetylenes mixture may be treated in accordance with the foregoing to effect resolution into a butadiene-rich fraction on the one hand and an acetylene-rich fraction on the other hand. Some C₅ hydrocarbons including any C₅ diolefins and C₅ acetylenes may be dissolved in the solvent along with the butadiene and the C₄ acetylenes. This preliminary selective solvent extraction may be brought about by suitable adjustment of the extraction conditions in a manner which will be obvious to those skilled in the art in the light of this disclosure.

In the accompanying drawings, Figure 1 and Figure 2 are schematic flow-diagrams of specific embodiments that exemplify the practice of this invention.

In Figure 1, the gaseous hydrocarbon mixture to be treated is assumed to be that produced by low pressure cracking of propane or of a mixture of light paraffinic hydrocarbons with an average molecular weight about that of propane. The cracked gas so produced is assumed to have been passed through a tar trap and subjected to one or two stages of compression. The cracked gas,

after compression, is introduced by line 12 into oil absorption tower 1, down which flows mineral seal oil in countercurrent contact with the cracked gas. The least soluble components of the cracked gas issue from the top of the tower through line 13. The rich oil, containing relatively soluble components of the cracked gas, is passed from the bottom of tower 1 through line 14 into flash tank 16, where the most volatile hydrocarbons dissolved in the rich oil are allowed to flash off and where some reduction in temperature occurs. The light hydrocarbons so flashed from the oil are withdrawn through line 17, and the oil proceeds by line 18 and pump 19 into column 2, where further stripping of the oil occurs. Column 2 is operated to produce a mixture of four-carbon and lighter hydrocarbons issuing overhead from the column through line 20 into condenser 21, where they are condensed; the condensate passes to accumulator 9. A portion of the condensate from accumulator 9 is returned as reflux to column 2, as through line 22 and pump 23. The absorption oil reaching the kettle of column 2 passes through line 24 and pump 25 into column 6, where all remaining absorbed materials, consisting of five-carbon and heavier hydrocarbons, are stripped from the oil and are removed through line 26. The stripped oil is conducted from column 6 to cooler 28 by line 27 and thence to storage tank 29. Oil from storage tank 29 is recycled by means of line 30 and pump 31 to column 1.

Condensate from accumulator 9, containing four-carbon, three-carbon, and small amounts of lighter hydrocarbons, is passed by line 32 and pump 33 into column 3. In column 3 a depropanizing operation is carried out so that overhead product reaching accumulator 10 through line 34 and condenser 35 contains mainly three-carbon and any lighter hydrocarbons present in the feed to column 3. Reflux is provided for column 3 by pumping a portion of the condensate in accumulator 10 back into the top of the column by means of pump 36 and line 37. It may be noted that in some cases only a very rough depropanization may be required, since rather considerable amounts of lighter-than-four-carbon materials may be tolerated in the subsequent extraction step.

The four-carbon fraction obtained as kettle product from column 3 is conducted through line 38 and pump 39 into absorption tower 4, where countercurrent contacting of the vapors with a primary selective solvent effects absorption of four-carbon acetylenes, so that butadiene-rich vapor passes overhead whereas vinyl and ethyl acetylenes are removed in the selective solvent. Selective solvent containing dissolved hydrocarbons proceeds from the kettle of absorption tower 4 through line 39 into stripping column 7, where the dissolved hydrocarbons are stripped from the solvent; the vapors so produced are removed through line 40 as a fraction rich in acetylenic constituents. Stripped solvent passes from the kettle of column 7 to cooler 41, from whence it is recycled through pump 42 and line 43 to absorption tower 4.

The butadiene-rich four-carbon fraction produced as overhead from absorption tower 4 contains a certain amount of primary solvent vapor; in order to prevent loss of solvent, as well as contamination of the hydrocarbon stream, this fraction in gaseous form is conducted by line 44 into extraction tower 5, where a countercurrent contacting with a secondary selective solvent is car-

ried on. The butadiene-rich fraction, after being stripped of primary solvent vapor, passes overhead from extraction tower 5 through line 44 to storage or to equipment for further processing, not shown. The secondary solvent removed from the kettle of extraction tower 5 contains dissolved primary solvent and is passed through line 45 into stripping column 8, where primary solvent is distilled from the secondary solvent. If desired, the fractionation may be conducted at atmospheric or subatmospheric pressure. The primary solvent vapor produced as overhead in column 8 passes by line 47 to condenser 48 and thence to accumulator 11. Condensate is recycled from accumulator 11 to absorption tower 4 as by means of line 49 and pump 50 and through line 51, pump 42, and line 43. If desired, provision may be made for returning a part of the condensate from condenser 48 as reflux to the top of stripping column 8. The stripped secondary solvent from the kettle of stripping column 8 passes to cooler 52, and thence by line 53 and pump 54 is recycled to extraction tower 5.

It is to be understood that in each of the towers or columns there are provided suitable means for ensuring countercurrent gas-liquid contacting, such as trays with bubble caps, packing, or the like.

The amount of primary selective solvent required per unit quantity of hydrocarbon mixture treated is, as will be recognized by those skilled in the art, dependent upon such factors as the particular solvent utilized, the percentage of acetylenic compounds present in the hydrocarbon mixture, the extent to which these are to be removed, the temperature and the pressure at which the process is operated, and the efficiency of the equipment employed to contact solvent and gaseous hydrocarbons.

In cases in which the acetylenic compounds to be removed are present in relatively minor quantities, that is, under 5 to 10 per cent, then with furfural as the primary selective solvent, preferred operating conditions are: (1) solvent rate in the range of 0.1 to 3 moles solvent per mole of hydrocarbons treated; (2) pressure in the extraction column in the range of about 50 to 100 pounds per square inch; and (3) temperature within the column so adjusted as to maintain the desired pressure. In the stripping of dissolved acetylenes from the rich solvent, somewhat lower pressure and higher temperature than those prevailing in the extraction column are desirable. In case a primary solvent is chosen from the group including furfural, nitrobenzene, dichlorodiethyl ether, dimethyl formamide, methyl levulinate, glycol diacetate, diethyl acetamide, pyridine, phenol, phenol plus water (containing 1-20% of water), and benzyl alcohol, both the extraction and the stripping may preferably be carried out at somewhat lower pressure or at higher temperature than in the case of furfural.

In connection with the stripping of rich solvent, it is to be noted that the hydrocarbons evolved may be rich in vinyl acetylene. This compound exhibits a strong polymerizing tendency when in high concentration, and under some conditions difficulty soluble polymers may be formed. In order to avoid difficulties from this source, provision may be made for passing a stream of relatively insoluble, inert, non-condensable, diluent gas, such as nitrogen, methane, or the like, into the stripping column 7 via line 46 at a point below the point of introduction of rich solvent. In this manner the rate of polymerization of

vinyl acetylene may be greatly reduced, and thus a valuable material is recovered in better yield and with decreased danger of resinous deposits being formed in the equipment. This feature may be employed wherever a stream comprising alkenyl acetylene is stripped, i. e., in the stripping of the primary or of the preliminary rich solvent.

I may choose a secondary selective solvent from a large group of quite high boiling organic materials that are somewhat polar in nature and that preferably exhibit reasonably good thermal stability. Some individual members of this group are: diphenyl amine, ditolyl amine, esters of phthalic acid, nitrogen bases such as quinoline, and ethyl sebacate.

Quite a wide range of operating conditions and gas-to-secondary solvent ratios may be used satisfactorily in the recovery of primary solvent vapor. In most cases satisfactory operation will be had at pressures of 50 to 100 pounds per square inch and at temperatures slightly above the dew point temperature for the gaseous mixture being treated. Only limited volumes of secondary solvent, of the order of 0.01 to 0.2 mole per mole of gas to be treated, are required.

In Figure 2, the initial steps of oil absorption, stripping, and the like are substantially the same as in the process of Figure 1, and are omitted for sake of simplicity since the description of them made hereinbefore in connection with Figure 1 is believed to be sufficient. Subsequent steps are carried out as follows:

Condensate from accumulator 9, containing three- and four-carbon hydrocarbons and small amounts of lighter hydrocarbons, is passed by line 32 and pump 33 through vaporizer 64 into extraction column 103. A stream of a selective solvent, such as furfural, is introduced into column 103 through line 55 in such fashion as to bring about countercurrent extraction of these hydrocarbons. Column 103 is operated under such conditions of temperature, pressure, and volumes of solvent and hydrocarbon feed as to effect extraction of butadiene and four-carbon acetylenes by the solvent. Undissolved hydrocarbons pass overhead from column 103 via line 66 and condenser 67 to accumulator 102. Reflux liquid may be returned to column 103 from accumulator 102 by means of line 68 and pump 68. The hydrocarbons produced overhead from column 103 may be withdrawn from the system by line 111 and may comprise three-carbon and lighter hydrocarbons together with butanes and butenes. Solvent containing dissolved butadiene and four-carbon acetylenes together with minor amounts of less soluble hydrocarbons and possibly some five-carbon hydrocarbons is passed from column 103 through line 70 and pump 71 into stripping column 106. By application of heat and/or by reduction of pressure the dissolved hydrocarbons are stripped from the solvent in column 106 and pass overhead and through line 72 into extraction column 104. The denuded solvent passes from the kettle of column 106 through line 73 and cooler 74 to storage tank 75. From storage tank 75 solvent may be recycled through pump 76 and line 65 to extraction column 103.

The hydrocarbons passing overhead from stripping column 106 through line 72 into column 104 are there subjected to countercurrent vapor-liquid extraction under such conditions of temperature, pressure, and volumes of solvent and hydrocarbon feed that a separation of butadiene

from the four-carbon acetylenes is effected. Selective solvent is introduced by line 89 into column 104. A butadiene-rich fraction is taken off overhead from column 104 by line 77 into condenser 78 and thence to accumulator 105. If desired, liquid from accumulator 105 may be returned as reflux liquid to the top of column 104 by means of pump 79 and line 80. The butadiene concentrate produced is withdrawn from accumulator 105 through line 81 to storage or subsequent processing steps, not shown. Solvent containing dissolved hydrocarbons, largely four-carbon acetylenes, is passed from the kettle of column 104 through pump 82 and line 83 into solvent stripping column 107. In column 107 the solvent is freed of dissolved hydrocarbons, which pass overhead and are removed from the system through line 84. Stripped solvent is passed from the kettle of column 107 through cooler 85 to storage tank 86. Solvent is recycled to column 104 from tank 86 via line 87, pump 88, and line 89.

The separation effected in extraction column 103 is made by taking advantage of the fact that both butadiene and four-carbon acetylenes are more soluble in certain selective solvents than are butanes, butenes, and three-carbon hydrocarbons. Because the butadiene and the four-carbon acetylenes are more soluble in the solvent, they are withdrawn from the kettle of column 103 as solute in the solvent, while the above-named less soluble hydrocarbons pass overhead from the column in vaporous form. As will be recognized by those skilled in the art, the exact conditions of temperature, pressure, internal reflux in the column, and relative volume of solvent to be employed will depend upon the particular solvent, the exact composition of the feed stock, and the completeness of separation that is to be realized. When furfural is used as the selective solvent, the operating pressure preferably lies in the range of two to ten atmospheres with temperatures within the column so adjusted as to maintain the desired pressure. In cases in which the butadiene plus four-carbon acetylenes amount to only a few per cent of the hydrocarbon feed, the preferred solvent rates lie in the range of 2 to 20 moles solvent per mole of hydrocarbon feed. For any particular application, optimum conditions may be readily determined by trial. In the operation of stripping the rich solvent of dissolved butadiene and acetylenes, somewhat lower pressure and higher temperature than those prevailing in the extraction column are desirable.

Alternatively to furfural, suitable selective solvents for separation of butadiene plus four-carbon acetylenes from butanes, butenes, and lighter hydrocarbons may be chosen from the group of primary solvents indicated hereinbefore.

The separation effected in extraction column 104 is made by taking advantage of my discovery that four-carbon-atom acetylenes tend to be dissolved selectively by certain solvents when a gaseous mixture comprising said acetylenes and butadiene is contacted with solvent. The same considerations as to operating conditions and choice of solvent apply to the separation effected by extraction column 104 as have been indicated hereinbefore for absorption tower 4 of Figure 1.

In order to prevent or minimize polymerization of the vinyl acetylene, a stream of diluent gas of the type described above may be introduced via line 110 into primary stripping column 107. If desired a similar stream may be introduced

via line 112 into preliminary stripping column 108.

Because the invention may be practiced otherwise than as specifically shown herein, and because many modifications and variations of it will be obvious to those skilled in the art, it should not be restricted except as specifically indicated in the appended claims.

I claim:

1. The process of effecting resolution of a mixture of butadiene and at least one four carbon atom acetylene into a fraction rich in butadiene and essentially free from four carbon atom acetylene and a fraction rich in the four carbon atom acetylene content of said mixture which comprises extracting said mixture in gaseous form with an organic liquid selective solvent for the four carbon atom acetylene content thereof and thereby effecting preferential solution of said four carbon atom acetylene in said solvent while causing the butadiene to pass through undissolved in gaseous phase and essentially free from four carbon atom acetylene, and separating the resulting solvent enriched in four carbon atom acetylene from the resulting butadiene-enriched gaseous phase essentially free from four carbon atom acetylene.
2. The process of effecting resolution of a mixture of butadiene and ethyl acetylene into a fraction rich in butadiene and essentially free from ethyl acetylene and a fraction rich in ethyl acetylene which comprises extracting said mixture in gaseous form with an organic liquid selective solvent for the ethyl acetylene and thereby effecting preferential solution of said ethyl acetylene in said solvent while causing the butadiene to pass through undissolved in gaseous phase and essentially free from ethyl acetylene, and separating the resulting solvent enriched in ethyl acetylene from the resulting butadiene-enriched gaseous phase essentially free from ethyl acetylene.
3. The process of effecting resolution of a mixture of butadiene and at least one four carbon atom acetylene into a fraction rich in butadiene and essentially free from four carbon atom acetylene and a fraction rich in the four carbon atom acetylene content of said mixture which comprises extracting said mixture in gaseous form with furfural and thereby effecting preferential solution of said four carbon atom acetylene in said furfural while causing the butadiene to pass through undissolved in gaseous phase and essentially free from four carbon atom acetylene, and separating the resulting furfural enriched in four carbon atom acetylene from the resulting butadiene-enriched gaseous phase essentially free from four carbon atom acetylene.
4. The process of effecting separate recovery of four carbon atom acetylene and butadiene essentially free of four carbon atom acetylenes from a hydrocarbon stream containing the same and also containing other more saturated C₄ hydrocarbons which comprises contacting said stream in the gaseous form with an organic liquid selective solvent and thereby effecting preferential dissolution therein of the four carbon atom acetylene and butadiene content of said stream while allowing at least a major proportion of said other hydrocarbons to pass through undissolved in gaseous phase, separating the rich solvent from the residual undissolved gas, stripping said dissolved four carbon atom acetylene and butadiene content from said rich solvent, contacting said stripped four carbon atom acetylene and buta-

diene in the gaseous phase with an organic liquid selective solvent and thereby effecting preferential dissolution therein of said four carbon atom acetylene content while leaving the butadiene undissolved and essentially free from four carbon atom acetylenes and in the gaseous phase, and separating the resulting four carbon atom

acetylene-enriched solvent from the resulting butadiene-enriched gaseous phase essentially free from four carbon atom acetylenes.

5. The process of claim 4 wherein the said selective solvent used in both of said contacting steps is furfural.

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