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EXTRACTIVE DISTILLATION OF HYDROCARBON MIXTURES USING HYDROCARBON SOLVENTS

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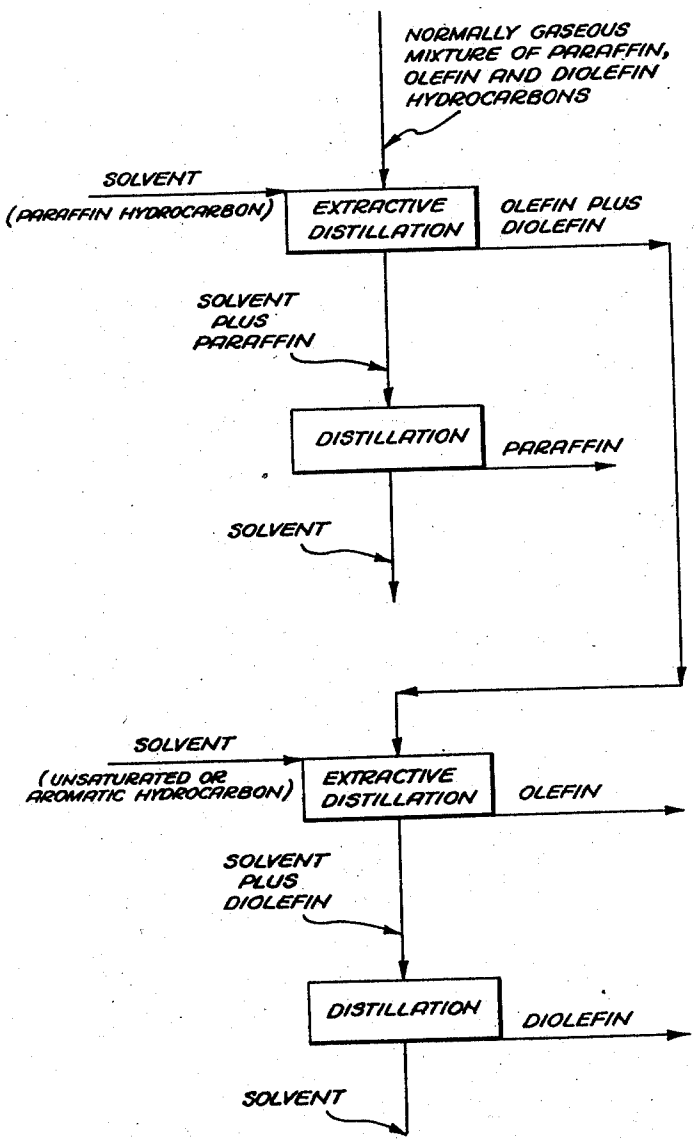

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EXTRACTIVE DISTILLATION OF HYDROCARBON MIXTURES USING HYDROCARBON SOLVENTS

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1

This invention relates to the preparation of pure hydrocarbons from hydrocarbon fractions or, more particularly, from narrow boiling hydrocarbon fractions. More specifically it relates to a method of treatment of a complex hydrocarbon mixture to cause the separation of relatively unsaturated or olefinic hydrocarbons or of aromatic hydrocarbons from relatively saturated or paraffinic hydrocarbons or naphthenic hydrocarbons.

An object of this invention is to provide a means of separating individual hydrocarbons from hydrocarbon mixtures having boiling points so close as to prevent separation by means of ordinary distillation processes. The method is less complex and involves fewer steps than chemical methods of separation and yields a purer product than that obtained by processes involving solvent extraction.

Another object of the invention is to separate relatively olefinic hydrocarbons from relatively non-olefinic hydrocarbons having approximately the same boiling point range and particularly to separate the diolefins from monoolefins and paraffins in the case of relatively narrow boiling fractions containing these hydrocarbons, said fractions being those such as may be obtained by the fractional distillation of the products of petroleum cracking or dehydrogenation processes.

It is also an object of my invention to separate mixtures of two or more hydrocarbons which form minimum boiling point azeotropes thus preventing separation by ordinary fractional distillation processes.

The difficulty in separating hydrocarbons having similar boiling points is well recognized and many methods for effecting such separations have been suggested including chemical processes, highly efficient fractional distillation processes, solvent extraction processes, and combinations of solvent extraction and distillation processes which, in many instances, may be described as extractive distillation processes and also azeotropic distillation processes. Some of these processes, particularly azeotropic distillation processes and extractive distillation processes have resulted in the separation of relatively pure hydrocarbons with high yields although the types of compounds used as azeotrope formers in the azeotropic distillation processes and as solvents in the extractive distillation processes are often costly, undesirably chemically reactive and difficult to separate from the hydrocarbons after the treatment. The present invention relates to an improvement in an extractive distillation process.

2

The drawing shows a flow sheet of the process.

According to my invention the separation of a specific hydrocarbon from a mixture of hydrocarbons or a hydrocarbon fraction whose components have substantially the same boiling points as said specific hydrocarbon is accomplished by extractive distillation using as a solvent a hydrocarbon or relatively narrow boiling hydrocarbon mixture having a boiling point or boiling point range higher than the boiling point or boiling point range of the mixture of hydrocarbons being treated. The addition of the higher boiling hydrocarbon or hydrocarbon mixture to the hydrocarbon fraction to be treated has the effect of changing the relative vapor pressures of the hydrocarbon components of the hydrocarbon fraction, the extent of the change in vapor pressure of each component of said hydrocarbon fraction being dependent upon the relative saturation or unsaturation of the particular component as defined hereinbelow. Thus the effect of adding the solvent is to change the relative boiling points of the hydrocarbons present in the hydrocarbon fraction thereby allowing separation of the hydrocarbons by controlled fractional distillation.

The extractive distillation may be effected at any desired pressure, the particular pressure employed in any given case being dependent in part upon the boiling range of the complex hydrocarbon fraction being treated. Thus when extractively distilling complex hydrocarbon fractions comprising C_4 hydrocarbons it is usually desirable to operate under pressures in the order of about 80 to 100 pounds per square inch gage and in some instances even much higher pressures are employed such as for example about 300 pounds per square inch, although when treating complex hydrocarbon fractions comprising C_5 hydrocarbons it is usually preferred to operate at ordinary atmospheric pressures.

Solvents which may be employed in the extractive distillation process may be classified into first, those which have the effect of depressing the vapor pressure of the relatively saturated hydrocarbons to a greater extent than the relatively unsaturated hydrocarbons and, second, those solvents which act in the opposite manner and depress the vapor pressure of the relatively unsaturated hydrocarbons to a greater extent than the saturated hydrocarbons. For the purposes of this description, by the term relatively saturated hydrocarbons is meant those hydrocarbons having relatively high hydrogen to carbon ratios, and specifically those having the general formula C_nH_{2n+2} or the paraffins and C_nH_{2n}

or the monoolefins and the naphthenes. Moreover, by the term relatively unsaturated hydrocarbons is meant those hydrocarbons having relatively low hydrogen to carbon ratios and specifically those having the general formula C_nH_{2n-2} or diolefins, and C_nH_{2n-6} or aromatics. Solvents of the first type include the saturated straight and branched chain paraffin hydrocarbons having three or more carbon atoms per molecule, as for example, propane, butane, isobutane, normal and isomeric pentanes, hexanes, heptanes, etc., up to those hydrocarbons containing about 30 carbon atoms per molecule, or mixtures of two or more of these paraffin hydrocarbons, also relatively narrow boiling hydrocarbon fractions comprising paraffin hydrocarbons. Solvents of the second type include olefin and diolefin hydrocarbons having three or more carbon atoms per molecule, such as propene, propadiene, the butenes and butadienes, pentenes and pentadienes, etc., and also aromatic hydrocarbons, such as benzene, toluene, xylene and higher homologs of benzene, naphthalene, and the various alkyl substituted naphthalenes, such as methyl naphthalene, ethyl naphthalene, etc.

The selection of a solvent in any case will depend upon the hydrocarbon fraction being treated and upon the particular hydrocarbon or hydrocarbon component which is to be separated from said hydrocarbon fraction. In general, the solvent will be selected upon the basis of its boiling point or boiling point range. The boiling point of the hydrocarbon or the initial boiling point of the hydrocarbon fraction used as solvent should be at least 25° F. and preferably 50° F. or more above the maximum boiling point of the hydrocarbon fraction being treated. Solvents of the first type disclosed above will be used in those cases in which it is desired to vaporize and distill overhead the relatively unsaturated hydrocarbons leaving the relatively saturated hydrocarbons as a residue and solvents of the second type will be selected when it is desired to vaporize the relatively saturated hydrocarbons and leave the relatively unsaturated hydrocarbons as a residue.

The advantages which may be gained by using hydrocarbon solvents as above disclosed are manifold. These solvents are in general chemically stable, low in cost, particularly because narrow boiling range mixtures of hydrocarbons or hydrocarbon fractions may be successfully employed, they are readily separated from the hydrocarbon being treated, and, due to their relatively low viscosities, the plate efficiency in fractionating columns operating on mixtures of hydrocarbons containing the hydrocarbon solvents is particularly high.

The amount of solvent to be employed in any case will be dependent upon the particular hydrocarbon fraction being treated, upon the hydrocarbon or hydrocarbon fraction used as the extractive solvent and upon the efficiency of the fractionating equipment in which the extractive distillation is carried out. Generally, as the ratio of solvent to hydrocarbon fraction being treated is increased the efficiency of the extractive distillation increases although at the same time the effective capacity of the fractionating equipment decreases. Thus in any given case there is an ideal ratio of solvent to hydrocarbon fraction, smaller ratios producing less efficient separation and larger ratios being less economical. While I may use any ratio of solvent to hydrocarbon fraction which is great enough to produce the desired separation I prefer to employ weight ratios of about 2:1 to about 25:1, respectively.

In separating relatively olefinic hydrocarbons, such as diolefins from relatively non-olefinic hydrocarbons, a narrow boiling point range mixture of these hydrocarbons to which is added an appropriate amount of a solvent which, in this case may be a paraffin hydrocarbon, is extractively distilled. The relatively olefinic hydrocarbons are vaporized and distilled thereby leaving the relatively non-olefinic hydrocarbons together with the solvent as a distillation residue. More specifically in separating, for example diolefins from monoolefins and paraffins, an appropriate amount of a suitable paraffin hydrocarbon is added to the mixture of diolefins, olefins and paraffins and upon extractive fractional distillation the diolefins vaporize at temperatures lower than those required to distill the monoolefins and paraffins and are obtained as an overhead distillate, the mixture of monoolefins, paraffins and solvent being obtained as a residue substantially completely separated from the diolefin hydrocarbons. This distillation residue may then be distilled to separate the monoolefins and paraffins from the higher boiling paraffin used as a solvent in the above extractive distillation.

It is possible to segregate hydrocarbons or hydrocarbon components by adding a solvent, as defined hereinabove, to a mixture of hydrocarbons and distilling the resulting mixture batchwise, however, in this method of operation the solvent remains as a liquid and comes into contact with the unvaporized hydrocarbons only, and not with the vaporized hydrocarbons. The desirable effect of the solvent is greatly increased by effecting the distillation in such a manner that the liquid solvent contacts and scrubs the vapors of the hydrocarbon mixture being treated. This effect is realized to some extent in the case of a flash-type distillation in which the mixture of solvent and hydrocarbon is passed through a heated zone where it is substantially completely vaporized and the vapors are lead into a fractionating column which is maintained at a temperature such that the solvent and some of the higher boiling hydrocarbons of the vaporized mixture are condensed and flow downward through the column and the lower boiling hydrocarbons remain as vapor and ascend the column. The temperature in the column may be controlled by regulating the temperature of the feed to the column or by using a reboiler at the bottom of the column or both. In this type of distillation the solvent, due to its appreciably higher boiling point, condenses first and the thus formed liquid solvent contacts the vapors of the hydrocarbon mixture being treated.

The preferred method of extractive distillation, which is more efficient than either of the above described methods comprises passing the hydrocarbon mixture, as a liquid or as a vapor, into a fractionating column at a point below about the middle of the column and passing the liquid solvent into the same column at a point above the point of entry of the hydrocarbon mixture and preferably at a point near the top of the column. Heat is supplied to the column by means of heating the incoming hydrocarbon stream and/or by means of a reboiler at the base of the column, the temperature being maintained at such a level that at least one hydrocarbon is vaporized and distills overhead from the column. The solvent flows downward through the column contacting and scrubbing the ascend-

ing hydrocarbon vapors carrying with it those hydrocarbons present in the hydrocarbon mixture which have the lowest vapor pressure in the presence of the solvent. This mixture of solvent and hydrocarbons is withdrawn from the bottom of the column and transferred to a second column where it is distilled at a somewhat higher temperature to vaporize the hydrocarbons thereby leaving the solvent as a distillation residue. This solvent may be recycled to the extractive distillation column.

In some cases it is preferable to employ a two stage extractive distillation process using one type of solvent, as disclosed hereinabove, in the first stage and the other type of solvent in the second stage. This two stage extractive distillation process is of particular value in those instances in which the hydrocarbon fraction being treated has a relatively wide boiling point range or where large number of hydrocarbons or hydrocarbon components are present in the hydrocarbon mixture. Thus the hydrocarbon fraction may be distilled in the presence of a solvent of the first type, the distillation temperature being maintained at such a point that the hydrocarbon which is to be separated from the complex hydrocarbon mixture just distills. For the purpose of this description the hydrocarbon or hydrocarbon component which is to be separated will be referred to as component A. At the distillation temperature employed, some of the other hydrocarbons originally present in the complex mixture, i. e., those which vaporize at the temperature employed in this extractive distillation process, such hydrocarbons being referred to as component B, will distill together with component A. The residue will consist of component C and solvent, where component C comprises those hydrocarbons which do not vaporize at the temperature employed in this distillation. This residue may be separately distilled at a somewhat higher temperature to vaporize component C leaving solvent as the distillation residue. The overhead distillate from the first extractive distillation stage, comprising components A and B, is then extractively distilled using a solvent of the second type and maintaining a distillation temperature such that component B vaporizes and distills leaving component A together with solvent as a residue. This residue is separately distilled at a somewhat higher temperature to vaporize component A leaving solvent as the distillation residue.

Treatment of the overhead distillate from the first extractive distillation stage comprising components A and B for the separation of component A may in some instances be effected by careful fractional distillation since in the absence of solvent the relative vapor pressures of components A and B are changed in a manner favorable to such separation, that is, the spread between the boiling points of component A and component B is wider in the absence of solvent.

The process of my invention is shown diagrammatically in the drawing.

The following specific examples serve to illustrate further the invention, but they are not to be taken as in any way limiting the invention.

Example I

To 100 parts by weight of a mixture comprising 80 parts by weight of butadiene and 20 parts by weight of n-butane is added 1500 parts by weight of n-pentane and the mixture is distilled at a pressure of 80 pounds per square inch gage.

Distillation is effected by vaporizing the mixture of solvent and hydrocarbons at a temperature of about 195° F. and passing the vapor into a fractionating column at a point near the middle of the column. The fractionating column is maintained at such a temperature that the vapor outlet temperature is about 125° F. Butadiene distills and is obtained as an overhead product from the fractionating column and a mixture of n-butane and n-pentane is obtained as a bottoms fraction. This bottoms is transferred to a second column maintained at the same pressure and at a somewhat higher temperature (stillhead temperature of about 130° F.) where the n-butane is vaporized leaving n-pentane as a residue.

Example II

A mixture of C_4 hydrocarbons comprising about 50 parts by weight of butadiene, 20 parts by weight of n-butane, 15 parts by weight of butene-1 and 15 parts by weight of isobutene is heated and passed into an extractive distillation column at a point near the bottom of the column, and n-pentane is passed into the same column at a point near the top of the column at the rate of 10 parts by weight of the n-pentane to 1 part by weight of the C_4 hydrocarbon mixture. The column is maintained at a pressure of 80 pounds per square inch absolute and a top or vapor outlet temperature of about 125° F. Under these conditions the overhead distillate is a mixture comprising butadiene, butene-1 and isobutene, while n-butane together with n-pentane is obtained as a distillation residue, substantially completely separated from butadiene, butene-1, and isobutene.

The overhead distillate from this extractive distillation is passed to a second extractive distillation column maintained at the same pressure where it enters at a point near the bottom and benzene, which is used as the extractive solvent, is pumped into the column at a point near the top of the column at a rate of 5 parts of benzene to 1 part of the C_4 hydrocarbon mixture. The distillation temperature (vapor temperature) is maintained at about 122° F. and the butene-1 and isobutene vaporize and distill overhead leaving butadiene and benzene as a distillation residue. The mixture of butadiene and benzene is fractionally distilled in a third fractionating column to vaporize the butadiene and leave benzene as a residue.

The foregoing description of my invention is not to be taken as in any way limiting but merely illustrative of my invention for many variations may be made by those skilled in the art without departing from the spirit or scope of the following claims.

I claim:

1. A method for the treatment of a mixture of normally gaseous hydrocarbons comprising paraffin, monoolefin and diolefin hydrocarbons to separate said mixture of hydrocarbons into its components which comprises extractively distilling said mixture in the presence of a solvent comprising a paraffin hydrocarbon boiling at least 25° F. above the boiling point of said hydrocarbon mixture to reduce the vapor pressure of the paraffin contained in said hydrocarbon mixture to a greater extent than the vapor pressure of the monoolefin and diolefin is reduced, thereby permitting the vaporization of said monoolefin and diolefin thereby leaving said paraffin together with said solvent as a distillation residue sub-

stantially completely separated from monoolefin and diolefin, separately distilling said residue to vaporize said paraffin thereby leaving said solvent in the residue; separately extractively distilling said vaporized monoolefin and diolefin in the presence of a sufficient amount of a second solvent selected from the class consisting of unsaturated hydrocarbons and aromatic hydrocarbons, said second solvent boiling at least 25° F. above the maximum boiling point of said vaporized mixture of monoolefin and diolefin, to reduce the vapor pressure of said diolefin to a greater extent than the vapor pressure of the monoolefin is reduced, to vaporize said monoolefin thereby leaving diolefin together with said second solvent in the residue, and separately distilling said last named residue to vaporize said diolefin thereby leaving said second solvent in the residue.

2. A method for the treatment of a mixture of C_4 hydrocarbons comprising butadiene, butane and butenes to separate butadiene therefrom which comprises extractively distilling said mixture of C_4 hydrocarbons in the presence of a sufficient amount of a solvent comprising a paraffin hydrocarbon boiling at least 25° F. above the boiling point of said mixture of C_4 hydrocarbons to reduce the vapor pressure of said butane to a greater extent than the vapor pressure of butadiene and butenes is reduced, thereby permitting the vaporization of said butadiene and said butenes thereby leaving said butane together with said solvent as a distillation residue substantially completely separated from butadiene and butenes; separately distilling said residue to vaporize butane thereby leaving said solvent in the residue; and separately extractively distilling said vaporized butadiene and butenes in the presence of a sufficient quantity of a second solvent selected from the class consisting of unsaturated and aromatic hydrocarbons and having a boiling point at least 25° F. above the boiling point of said butadiene and butenes to reduce the vapor pressure of the butadiene to a greater extent than the vapor pressure of the butenes is reduced, to vaporize said butene thereby leaving butadiene together with said second solvent in the residue and separately distilling said last named residue to vaporize butadiene thereby leaving said second solvent in the residue.

3. A method as in claim 1 wherein said solvent comprising a paraffin hydrocarbon is normal pentane.

4. A method as in claim 1 wherein said solvent comprising a paraffin hydrocarbon is normal hexane.

5. A method as in claim 1 wherein said second solvent is benzene.

6. A method as in claim 1 wherein said solvent comprising a paraffin hydrocarbon is normal pentane and said second solvent is benzene.

7. A method for the treatment of a mixture of C_4 hydrocarbons comprising butadiene, normal butane and butenes to separate butadiene therefrom which comprises extractively distilling said mixture of C_4 hydrocarbons in the presence of a sufficient amount of normal pentane to reduce the vapor pressure of said normal butane to a greater extent than the vapor pressure of butadiene and butenes is reduced thereby permitting the vaporization of said butadiene and said butenes thereby leaving said normal butane together with said normal pentane as a distillation residue substantially completely separated from butadiene and butenes, separately distilling said residue to vaporize normal butane thereby leaving normal pentane in the residue and separately extractively distilling said vaporized butadiene and butenes in the presence of a sufficient quantity of benzene to reduce the vapor pressure of the butadiene to a greater extent than the vapor pressure of the butenes to vaporize said butene: thereby leaving butadiene and benzene in the residue and separately distilling said residue to vaporize butadiene thereby leaving benzene in the residue.

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