Patented Oct. 8, 1946 2,408,922

UNITED STATES PATENT OFFICE

2,408,922

SEPARATION OF DIOLEFINS BY AZEOTROPIC DISTILLATION

Theodore W. Evans, Oakland, Rupert C. Morris, Berkeley, and Edward C. Shokal, Oakland, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application April 30, 1942, Serial No. 441,246

8 Claims. (Cl. 202—42)

1

This invention relates to the separation of a component of a fluid mixture and particularly to the separation of a component of a mixture whose components possess little difference in vapor pressure so that practical separation by ordinary fractional distillation is very difficult, if not impossible. The invention more especially pertains to a practical and economical method for effecting the separation of acyclic diolefins of at least five carbon atoms from mixtures thereof with compounds of a lesser degree of unsaturation and/or saturated compounds having the same number of carbon atoms.

The pyrolysis or cracking of petroleum or petroleum fractions such as naphtha, kerosene, stove oil, gasoline and the like, gives rise to many valuable compounds useful in a variety of industries. Piperylene (pentadiene-1,3) and isoprene (2-methyl-butadiene-1,3) are examples of such valuable compounds. In addition to many other uses, both of these products of the pyrolysis of petroleum are applicable to the preparation of resins and other polymerization products.

While it is practically impossible to effect the separation of isoprene or piperylene from hydrocarbon mixtures resulting from the pyrolysis of petroleum or petroleum fractions by ordinary fractional distillation, it is relatively easy to fractionally distill such mixtures to obtain a fraction consisting of or predominating in hydrocarbons having five carbon atoms and to thereby materially increase the concentration of these acyclic diolefins. The following is a list of most of the hydrocarbons of five carbon atoms, all of which may be present in such a fraction, together with their boiling points:

	°C.
3-methyl-butene-1	20.1
Pentene-1	30.1
2-methyl-butene-1	30.05
2-methyl-butadiene-1,3 (isoprene)	34.07
Pentene-2	36.4
2-methyl-butene-2	38.4
Cyclopentadiene	41.0
Pentadiene-1,3 (piperylene)	42.5
Pentane	36
Cyclopentane	44

The applicability of ordinary fractional distillation to the separation of isoprene and piperylene from among the reaction products obtained by the pyrolysis of petroleum does not end with the isolation of a fraction consisting of or predominating in hydrocarbons of five carbon atoms as it is also economically practicable to fractionally distill this fraction to obtain two relatively narrow boiling cuts or fractions, one consisting chiefly of isoprene and mono-olefins having boiling temperatures in the close vicinity of the boiling temperature of this diolefin, the other predominating in piperylene and mono-olefins boiling close thereto. It is to the treatment of these last-mentioned relatively narrow boiling fractions that the process of the present invention is most particularly directed.

2

An object of the present invention, therefore, is to provide an efficient and easily executed process for effecting the separation of isoprene and piperylene from relatively narrow boiling hydrocarbon fractions wherein they are contained.

The process of the invention, whereby the foregoing and other objects are accomplished, comprises fractionally distilling a mixture containing an acyclic diolefin of at least five carbon atoms and one or a plurality of mono-olefins and/or one or a plurality of saturated hydrocarbons having a like number of carbon atoms in the presence of a compound which has a preferential solvent power for the acyclic diolefin and which is capable of forming constant boiling azeotropes with each of the components of the mixture, including the acyclic diolefin, the azeotrope of the diolefin and the azeotrope-forming compound being higher boiling than the other azeotropes. According to a preferred mode of executing the process, the components of the mixture other than the diolefin or, more accurately, the major portions thereof, are distilled off in the form of their azeotropes with the azeotrope-forming compound which has been added in a quantity only sufficient to form these azeotropes, the acyclic diolefin being thereby concentrated in the distillation kettle. In a second and more preferred method of executing the process of the invention, the azeotrope-forming compound is added in a quantity greater than is required to form azeotropes with the said other components of the mixture, whereby increased advantage is taken of the preferential solvent power of the azeotrope-forming compound for the diolefin and more complete concentration thereof attained. By means of the process of the invention, a hydrocarbon mixture containing less than 12 weight per cent of diolefin was concentrated in a single treatment to over 70 weight per cent, whereas by ordinary fractional distillation of a mixture much richer in original diene (34.3 mol per cent) the best concentration which could be achieved was 52.6 mol per cent.

As indicated, the process of the invention is most preferably applied to preliminarily fractionated materials, that is, to relatively narrow boiling mixtures containing either isoprene or piperylene to the substantial exclusion of the other. However, the process is not to be construed as so limited. It may, for example, be applied to a mixture comprising all of the above listed five carbon atom hydrocarbons, rather than to isoprene or piperylene fractions separated from such mixtures in which event the separation is between

the acylic diolefins on the one hand, the mono-olefins and paraffins on the other. It may be here parenthetically noted that where the treated hydrocarbon mixture has been obtained by the pyrolysis of petroleum it will consist in the main of unsaturated compounds, paraffins being present only to a minor extent.

The presence of cyclopentadiene in a fraction subjected to treatment according to the present process is not detrimental to the efficient concentration or separation of the acyclic diolefin or diolefins contained therein, but since this compound is easily removed, prior separation thereof is recommended. Cyclopentadiene polymerizes to dicyclopentadiene in the presence of other five-carbon hydrocarbons upon the application of mild heat, and since the dimeric material has a boiling point greatly in excess of that of any hydrocarbon of five carbon atoms, the other components of the mixture are easily distilled off overhead. If it is desired to later employ the cyclopentadiene as such, care should be exercised to apply only moderate temperatures in heating the mixture under treatment, as excessive heat, particularly if prolonged for any appreciable period, results in the formation of more complex polymers, such as tetra- and penta-cyclopentadiene which are a great deal more difficult to depolymerize without excessive decomposition. It has been found that the formation of these higher polymers can be prevented and conversely that the formation of the easily depolymerized dimer can be selectively accomplished in the presence of other hydrocarbons of five carbon atoms if the temperature applied to the treated mixture is not permitted to substantially exceed 100° C. At this temperature, a conversion of 95% of the monomer to the dimer has been achieved without the aid of a catalyst.

Returning now more specifically to the azeotropic distillation which constitutes the present process, a compound which has been found particularly adapted to the formation of constant boiling azeotropic mixtures of the required character with hydrocarbons of at least five carbon atoms is isopropylamine. By azeotropic mixtures of the required character is meant azeotropic mixtures, the boiling ranges of which enable more efficient and complete concentration of acyclic diolefins of at least five carbon atoms as contained in mixtures with mono-olefins and/or paraffin hydrocarbons of similar vapor pressures than is practicable by ordinary fractional distillation. The azeotropic mixtures which isopropylamine forms with hydrocarbons of at least five carbon atoms are minimum boiling. In other words, isopropylamine in effect causes a lowering of the effective distillation temperatures of the constituents of a mixture of hydrocarbons of at least five carbon atoms. The drop in distillation temperature, however, is not uniform for the different components, isopropylamine lowering the distillation temperatures of five-carbon acyclic diolefins to a lesser extent than it lowers the distillation temperatures of five-carbon mono-olefins and paraffins. Therefore, the azeotropes of the mono-olefins and/or paraffins of the mixture boil before the azeotropes of the acyclic diolefins and thus an economical, efficient and ready method for the separation or concentration of the latter is provided.

In general it is preferable to employ the isopropylamine in a quantity sufficient to form azeotropes with each and every hydrocarbon present in the mixture treated, but greater or lesser amounts may be used. The amount of amine added to the mixture to be treated should not, however, be less than the amount required to form azeotropes with all of the components of the mixture other than the diolefin, as this practice greatly reduces the efficiency of the process. When a quantity of amine is used which is not sufficient to form the azeotrope with the diolefin, but which is sufficient to form the azeotropes with the other components of the mixture, by fractionally distilling off the azeotropes of the other components, a high concentration of diolefin in the distillation kettle is achieved. While this method of executing the process of the invention is convenient, superior results are attained by using an amount of amine adequate to form the azeotrope with the diolefin as well as the other azeotropes. Isopropylamine has a preferential solvent power for acyclic diolefins of at least five carbon atoms present in mixtures with mono-olefins and/or paraffins of similar vapor pressures which is naturally exerted the more strongly the greater the concentration of the amine in the treated mixture. Even an excess of amine over that required to form azeotropes with all of the hydrocarbons of the treated mixture is without harmful effect.

When the mixture distilled comprises the most preferred quantity of amine, that is, not less than the amount required to form azeotropes with all of the components of the mixture, the quantity of diolefin leaving the still with the azeotropes of the other components is materially less than when the treated mixture contains a lesser amount of amine; hence, for the same result, towers of fewer plates may be used which is distinctly advantageous. The distillation as executed with the preferred amount of amine is preferably carried to completion, the recovered fractions becoming progressively richer in diolefin.

The azeotropic distillation constituting the present invention may be conducted at superatmospheric or subatmospheric pressures, but operation at atmospheric pressure is preferred. It must be noted that varying the pressure may change the ratio of the compounds in the azeotropic mixtures, as well as the distillation temperatures of these mixtures.

The following example is introduced to illustrate a mode of executing the invention and the results thereby attained. The invention is not to be considered as limited either to the specific fraction treated or the particular aliphatic amine employed, or to the conditions of operation disclosed.

Example

An isoprene fraction (boiling range 30° C.–38° C.) was fractionated from a mixture resulting from the pyrolysis of second cut straight run gasoline. The fraction analyzed 42.5 mol per cent (41.6 weight per cent) dienes, 97.0 mol per cent total unsaturates. About 230 grams of the separated isoprene fraction was charged to a distillation unit together with approximately 460 grams of isopropylamine. The distillation unit included a helix-packed tower of 15 to 18 theoretical plates, an automatic reflux controller, and a condenser. The mixture was then subjected to distillation at atmospheric pressure and at a reflux ratio of 10 to 1, the overhead condensate being collected in a plurality of containers to determine the diolefinic content of each of the fractions or cuts thus obtained. In all, seven cuts were taken, the most concentrated containing

72.4 weight per cent diene. The complete data covering the run are given in the following table:

Analysis of cuts

Cut No.	Wt., g.	Boiling range, ° C.	Wt. per cent hydrocarbon	Wt. per cent solvent	Solvent free hydrocarbon, wt. per cent dienes
1	78	26.5 to 28.2	50.7	49.3	20.9
2	80	28.2 to 29.5	49.0	51	28.0
3	109	29.5 to 29.5	35.3	64.7	43.2
4	82	29.5 to 29.8	42.5	57.5	39.3
5	84	29.8 to 30	37.5	62.5	50.2
6	86	30 to 30.5	31.4	68.6	62.4
7	96	30.5 to 31.2	15.6	84.4	72.4

The separation of the isopropylamine from the various fractions obtained as above may be effected, by means of cooling, addition of water, or by treatment of the azeotropic mixtures in any other convenient manner known to those skilled in the art.

Although by the procedure of the example, the diolefin is merely concentrated, it will be understood that any one or more of the fractions obtained may be resubjected to distillation according to the process of the invention until actual separation is achieved. When the treated mixture comprises both isoprene and piperylene, their separate fractionation from the fraction or fractions wherein they are obtained together may be effected either in the presence or absence of the azeotrope-forming agent, but preferably the isopropylamine is first removed.

The invention claimed is:

1. A process for separating isoprene from mixtures thereof with one or more compounds from the class consisting of mono-olefins and paraffins having vapor pressures close to that of isoprene which comprises adding isopropylamine to the mixture in a quantity adequate to form constant boiling azeotropes with each of the components thereof, subjecting the resulting mixture to fractional distillation to distill off an azeotropic fraction the hydrocarbon content of which is made up principally of the components of the original mixture other than the isoprene, continuing the distillation at a higher still head temperature to obtain an azeotropic fraction the hydrocarbon content of which predominates in isoprene, and separating the isoprene from said last mentioned fraction.

2. A process for separating piperylene from mixtures thereof with one or more compounds from the class consisting of mono-olefins and paraffins having vapor pressures close to that of piperylene which comprises adding isopropylamine to the mixture in a quantity adequate to form constant boiling azeotropes with each of the components thereof, subjecting the resulting mixture to fractional distillation to distill off an azeotropic fraction the hydrocarbon content of which is made up principally of the components of the original mixture other than the piperylene, continuing the distillation at a higher still head temperature to obtain an azeotropic fraction the hydrocarbon content of which predominates in piperylene, and separating the piperylene from said last mentioned fraction.

3. A process for separating isoprene from mixtures thereof with one or more compounds from the class consisting of mono-olefins and paraffins having vapor pressures close to that of isoprene which comprises adding isopropylamine to the mixture in an amount only sufficient to form constant boiling azeotropes with the components of the mixture other than the isoprene, and subjecting the resulting mixture to fractional distillation to attain a residue the hydrocarbon content of which predominates in isoprene.

4. A process for separating piperylene from mixures thereof with compounds of the class consisting of mono-olefins and paraffins having vapor pressures close to that of piperylene which comprises adding isopropylamine to the mixture in an amount only sufficient to form constant boiling azeotropes with the components of the mixture other than the piperylene, and subjecting the resulting mixture to fractional distillation to attain a residue the hydrocarbon content of which predominates in piperylene.

5. A process for separating an acyclic diolefin of five carbon atoms from mixtures thereof with one or more compounds from the class consisting of mono-olefins and paraffins having vapor pressures close to that of the acyclic diolefin which comprises adding isopropylamine to the mixture in an amount adequate to form constant boiling azeotropes with each of the components thereof, subjecting the resulting mixture to fractional distillation to distill off an azeotropic fraction the hydrocarbon content of which is made up principally of the components of the original mixture other than the acyclic diolefin, and continuing the distillation at a higher still head temperature to obtain an azeotropic fraction the hydrocarbon content of which predominates in the acyclic diolefin.

6. A process for separating an acyclic diolefin of five carbon atoms from mixtures thereof with one or more compounds from the class consisting of mono-olefins and paraffins, the vapor pressures of which are close to that of the acyclic diolefin, which comprises adding isopropylamine to the mixture in an amount only sufficient to form constant boiling azeotropes with the components of the mixture other than the acyclic diolefin, and subjecting the resulting mixture to fractional distillation to attain a residue the hydrocarbon content of which predominates in the acyclic diolefin.

7. A process for concentrating acyclic diolefins of five carbon atoms as contained in mixtures with one or more compounds from the class consisting of mono-olefins and paraffins, the vapor pressures of which closely approach the vapor pressures of the acyclic diolefins which comprises adding isopropylamine to the mixture in an amount at least sufficient to form minimum-boiling azeotropic mixtures with each of the components thereof and subjecting the resulting mixture to fractional distillation to obtain a plurality of overhead fractions progressively richer in the acyclic diolefins.

8. A process for concentrating acyclic diolefins of five carbon atoms as contained in mixtures with one or more compounds from the class consisting of mono-olefins and paraffins the vapor pressures of which closely approach the vapor pressures of the acyclic diolefins which comprises adding isopropylamine to the mixture in an amount only sufficient to form minimum boiling azeotropes with the components thereof other than the acyclic diolefins and subjecting the resulting mixture to fractional distillation to obtain a residue the hydrocarbon content of which predominates in the acyclic diolefins.

THEODORE W. EVANS.
RUPERT C. MORRIS.
EDWARD C. SHOKAL.