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SEPARATION OF CLOSE-BOILING NAPHTHENES BY AZEOTROPIC DISTILLATION

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1

The invention relates to a process of azeotropic distillation to prepare pure naphthenic hydrocarbons from mixtures thereof which naphthenes are difficult to separate by ordinary fractional distillation due to the deviation of naphthenic solutions from the ideal.

The process of separating one hydrocarbon component from another hydrocarbon component of substantially the same boiling point, contained in a complex hydrocarbon fraction, by azeotropic distillation is well known. This process consists of distilling the hydrocarbon fraction in the presence of an extraneous substance which has a preferential affinity for one of the hydrocarbon components contained in the fraction thus causing a disturbance of the vapor pressure equilibrium that formerly existed in the fraction in such a manner that the partial vapor pressure of fugacity of at least one component within the fraction is changed sufficiently to permit its separation by controlled fractional distillation. Such an azeotroping process has found wide spread usage in the treatment of hydrocarbon fractions for the separation of the relatively more paraffinic hydrocarbons from the relatively more aromatic hydrocarbons contained in the fraction. In most cases the azeotrope former employed has had the effect of increasing the vapor pressure of the relatively non-aromatic hydrocarbons in the fraction thus permitting their removal from the fraction as an overhead distillate together with the azeotrope former. In the present description of our invention the aforesaid type of distillation will hereinafter be referred to as azeotropic distillation, and the overhead product consisting of the azeotrope former together with the component or components most effected by said azeotrope former will hereinafter be referred to as the "azeotropic distillate," while the residue remaining as bottoms from the azeotropic distillation will hereinafter be referred to as the "azeotropic bottoms."

Heretofore the process of azeotropic distillation has been employed primarily for the separation of hydrocarbons of different structural type, that is paraffins, aromatics, naphthenes and the like, from hydrocarbon fractions in which they are contained which are difficult to separate from such a hydrocarbon fraction because of the small differences in boiling point exhibited between certain members of each of these series or types, or because of azeotropes existing between the members of these series within the fraction. A simple example of this usage of azeotropic distillation is in the separation of a naphthene from

2

an aromatic such as cyclohexane from benzene or of a paraffin fraction from an aromatic, or of a paraffin-naphthene mixture from an aromatic such as the separation of the paraffins and naphthenes boiling in the range of toluene from toluene by the addition to such a mixture of an azeotrope former having the effect of increasing the vapor pressure of the paraffins and naphthenes in the fraction whereby they may be separated more readily by a controlled distillation from the toluene in the fraction.

There are many cases, however, where it is desirable to improve the means of separation of two or more members of a homologous series such as for example two or more naphthenic hydrocarbons. It has been repeatedly observed in such mixtures that the relative ease of separation is not as closely correlated to the differences in boiling points existing between the members of the series as might be reasonably expected. For example, in a mixture of methylcyclopentane, boiling point 71.9° C., and cyclohexane, boiling point 80.8° C., it would be expected on the basis of an 8.9° C. difference in the boiling points of these two compounds that their separation by conventional fractional distillation could be readily accomplished. However, it appears that the binary mixture of methylcyclopentane and cyclohexane deviates sufficiently from an ideal solution to prevent their efficient separation. Thus, we have found that if an equal volume mixture of methylcyclopentane and cyclohexane is distilled under controlled conditions in a fractionating column of approximately 30 theoretical plates it is only possible to recover from about 50% to 55% of each of these components in the pure state. This difficulty appears to exist throughout the naphthenic hydrocarbon series and has been observed specifically in such mixtures as dimethylcyclopentanes, boiling point 90° C. to 99° C., and methylcyclohexane, boiling point 100.8° C., methylcyclohexane and ethylcyclopentane, boiling point 103.2° C., ethylcyclohexane, boiling point 130.4° C. and dimethylcyclohexane, boiling point 119° C. to 130° C., dimethylcyclohexane and propylcyclopentane, boiling point 130.8° C., and the like. Similarly, this difficulty of separation to a degree in excess of what might be expected from the differences in the boiling points of the naphthenic hydrocarbons has been observed between the members of the various isomeric forms of any particular naphthenes. For example, trans, 1,2-dimethylcyclopentane, boiling at approximately 92° C. is difficult to separate from the cis isomer boiling at approximately 99° C. and in

like manner the *cis* and *trans* forms of the dimethylcyclohexanes boiling from 4° C. to 5° C. apart are difficult to separate by ordinary fractional distillation. Still further, we have found that the naphthenic hydrocarbons differing from each other solely in the isomeric forms of the alkylating groups are more difficult to separate than would be expected from an observation of their boiling points. Thus, propyl cyclopentane, boiling at 130.8° C. and isopropyl cyclopentane, boiling at 126.4° C. are difficult to separate by ordinary fractional distillation as are mixtures of isobutyl cyclopentane, boiling at 108.3° C. and tertiary butyl cyclopentane, boiling at 145.2° C. These examples serve only to show the difficulty arising in the separation of the various forms of naphthenic hydrocarbons boiling from 3° C. to 10° C. apart, which difficulty apparently resides in the formation of a non-ideal solution between these naphthenic hydrocarbons.

It is an object of our invention to prepare hydrocarbons from hydrocarbon fractions which are difficult to separate by ordinary fractional distillation.

More specifically it is an object of our invention to prepare substantially pure naphthenic hydrocarbons from fractions thereof by means of azeotropic distillation employing the azeotrope formers hereinafter disclosed.

It is a further object of our invention to facilitate the separation of naphthenic hydrocarbons boiling from about 3° C. to about 10° C. apart, which are difficult to separate by conventional means due to the formation of a non-ideal solution.

Other objects and advantages of our invention will become apparent to those skilled in the art as the description thereof proceeds.

We have discovered that it is possible by employing azeotrope formers as hereinafter disclosed to improve the separation of naphthenic hydrocarbons. As azeotrope formers for this separation we have found the organic esters to be particularly effective. Esters are classified as the combination product of an alcohol and an acid in which water is eliminated between the two by combination of the OH group of the alcohol with a hydrogen of the acid. The preparation of esters is not confined to this reaction but the end product may be classified as such. In this group are included not only the esters of organic acids but of mineral acids as well and for convenience in this disclosure these will be divided into halogenides and oxygen esters to distinguish the esters of hydrogen halides from the esters of the oxygen-containing acids either organic or inorganic in nature. These halogenides and oxygen esters have the effect of forming with the lower boiling naphthenic hydrocarbon in the mixture a minimum boiling azeotrope which is more readily separated from the remaining naphthenic hydrocarbons by means of ordinary fractional distillation.

In this regard it appears that the azeotropic drop; that is, the difference in the boiling points of the azeotrope and of the lower boiling component of a binary mixture is of greater significance than would be expected.

It has been reported in the literature and is confirmed by our investigations that azeotropes of a given boiling point spread are in many cases more readily separated by fractional distillation than are two hydrocarbons of the same boiling point spread. Further an azeotrope with a given hydrocarbon boiling only slightly below the given

hydrocarbon is considerably more readily separated from a second hydrocarbon than is the given hydrocarbon itself. Thus we have found that the formation of an azeotrope between the lower boiling naphthenic hydrocarbon in a binary mixture and the azeotropic formers herein disclosed yielding an azeotropic drop of only a few degrees is considerably easier to separate from the higher boiling naphthene in the mixture by distillation than is the lower boiling naphthene itself. This we have found to be true throughout the range of naphthenic hydrocarbons and as a result have been able to separate these hydrocarbons by azeotropic distillation even in those cases where a large azeotropic drop is not obtained. However, it is to be understood that we prefer to employ those halogenides and esters which result in the greatest boiling point spread between the azeotrope of the lower boiling naphthene and the higher boiling naphthene or an azeotrope formed therewith.

We have found that in the separation of naphthenic hydrocarbons employing the esters and halogenides as azeotrope formers that it is necessary to employ the oxygenesters or the halogenides which boil at least 10° C. below the higher boiling naphthenic hydrocarbons, and not more than 15° C. below the lower boiling naphthenic hydrocarbons which are desired to be separated. As pointed out above it is not necessary in each case that the azeotrope former effect a spread in the boiling points of the two components inasmuch as azeotropes may be formed between each of the naphthenic hydrocarbons and the azeotrope former employed boiling the same distance apart or even slightly less distance apart than the naphthenic hydrocarbons themselves without defeating the purpose of our invention which is essentially to improve the separation of the various naphthenic hydrocarbons.

The oxygen esters which we may employ in the process of our invention are those organic esters in which the hydrocarbon radical is of comparatively low molecular weight and the ester group is selected or is derived from such acids as boric, nitric, formic, acetic, propionic, butyric, and the like. Thus we may employ such compounds as methyl borate, isobutyl nitrite, normal butyl formate, isobutyl formate, methyl acetate, ethyl propionate, and the like, providing such esters conform to the boiling point limitations established for the particular naphthenic hydrocarbon mixture to be separated. In like manner we may employ any halogenide conforming to the necessary boiling point specifications such as isobutyl chloride, chloroform, iodo ethane, 1-chloropropane, normal butyl chloride, 1-bromobutane, 1-fluoropentane, and the like.

Thus, for example in the separation of methylcyclopentane and cyclohexane we may use such esters as isobutyl nitrite and methyl borate; and such halogenides as isobutyl chloride and chloroform, and in the separation of methylcyclohexane from ethylcyclopentane we may use such esters as ethyl nitrate, and such halogenides as isopropyl iodide and the like and in the separation of dimethylcyclohexane from propyl cyclopentane we may use such esters as normal butyl formate, normal propyl nitrate and the like and such halogenides as normal amyl chloride and normal heptyl fluoride and the like.

In the application of our process the presence of hydrocarbons other than naphthenic hydrocarbons is immaterial to the effectiveness of the process inasmuch as these hydrocarbons when

present may be taken as overhead with the azeotrope or remain in the azeotropic residue depending upon the nature and relative boiling point, and may thereafter be separated from the corresponding naphthenic hydrocarbon by methods known in the art such as for example fractional distillation, azeotropic distillation, extractive distillation, solvent extraction and the like. Due to the difficulty of separating paraffins and naphthenes by these methods paraffins may remain as impurities in the naphthene fractions if their boiling points are too close. However, we have found that these extraneous hydrocarbons do not hinder the improved separation of the naphthenic hydrocarbons by our process.

It is within the scope of our invention to use any manner of separation of the azeotrope former from the naphthenic azeotrope after the separation of the azeotrope from the remaining naphthenic hydrocarbons such as for example secondary azeotropic distillation, solvent extraction, extractive distillation, or the like. The particular method employed for separating or breaking the azeotrope is a function of the particular azeotrope former employed, of the availability of solvents or secondary azeotrope formers and of the equipment available and is not a limiting factor in our invention.

The following examples of our process will serve to illustrate the advantages accruing from its usage.

Example I

A mixture of 50 volumes of cyclohexane and 50 volumes of methylcyclopentane was fractionated in a distillation column of approximately 30 theoretical plates with an internal reflux ratio of 20 to 1 in the absence of any azeotrope former resulting in the recovery of 27½ volumes of pure methylcyclopentane and of 27 volumes of pure cyclohexane, the remainder being a mixture of the two hydrocarbons. A second mixture of 100 volumes of methylcyclopentane, boiling point 71.9° C., and 100 volumes of cyclohexane, boiling point 80.8° C., and 200 volumes of methyl borate, boiling point 65° C., was fractionated in the same 30 theoretical plate column at an internal reflux ratio of 20 to 1. In this azeotropic distillation an initial fraction was taken overhead amounting to 57.3% of the original charge and comprising 100 volumes of methylcyclopentane, and 129 volumes of methyl borate at a vapor temperature of 64° C. A transition fraction was obtained boiling between 64° C. and 65° C. representing 17.7% of the original mixture and comprising 71 volumes of methyl borate. The azeotropic residue from this distillation consisted of essentially pure cyclohexane contaminated by only a trace of methyl borate. It is apparent from these data that an excess of methyl borate was employed over and above that necessary for effective separation of the naphthenes. Of still more importance is the fact that these data indicate that in this instance at least when the boiling point limitations established for the azeotrope formers are observed no azeotrope is formed with the higher boiling naphthene. Thus, methyl borate apparently does not form an azeotrope with the cyclohexane. It is evident from these two distillations that the azeotropic process of our invention results in a decided increase in the recovery of the pure naphthenic hydrocarbon.

Example II

Another azeotropic distillation was performed employing a halogenide as the azeotrope former

for the separation of methylcyclohexane and ethylcyclopentane. In this distillation 100 volumes of methylcyclohexane, boiling point 100.8° C., 100 volumes of ethylcyclopentane, boiling point 103.2° C., and 200 volumes of 2-iodo propane, boiling point 89.5° C. was distilled in a column of approximately 30 theoretical plates at an internal reflux ratio of 18 to 1. The initial fraction from this distillation representing 44% of the original mixture was obtained at a vapor temperature of 88° C. and comprised of 96 volumes of methylcyclohexane and 180 volumes of 2-iodo propane. A transition fraction representing 6.7% of the original fraction was obtained at a vapor temperature in the range of 88° C. to 90° C. and comprised of 20 volumes of 2-iodo propane, 3 volumes of ethylcyclopentane, and 4 volumes of ethylcyclohexane. The residue from this distillation amounted to 97 volumes of ethylcyclopentane contaminated by only slight traces of the azeotrope former.

The recoveries given in these examples are based on 100% recovery in the distillation, the 1% or 2% loss in the distillation is assumed to have been spread throughout.

Having described and illustrated our invention and realizing it is understood that we do not intend to be limited to the particular examples given inasmuch as our process is applicable over the range of naphthenic hydrocarbons and is limited only by the usage of such esters and halogenides as conform to the temperature limitations established for satisfactory azeotropy, we claim:

1. A process for the treatment of a complex hydrocarbon fraction to separate one naphthenic hydrocarbon from another close boiling naphthenic hydrocarbon contained therein which comprises azeotropically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an ester boiling at least 10° C. below the boiling point of the higher boiling naphthenic hydrocarbon in said complex hydrocarbon fraction and not more than 15° C. below the boiling point of the lower boiling naphthenic hydrocarbon in said fraction, said ester having the effect of forming a minimum boiling mixture with the lower boiling of said naphthenic hydrocarbons whereby said lower boiling naphthenic hydrocarbon is obtained in the azeotropic distillate and the higher boiling naphthenic hydrocarbon remains in the azeotropic bottoms.

2. A process for the treatment of a complex hydrocarbon fraction to separate one naphthenic hydrocarbon from another naphthenic hydrocarbon contained therein which naphthenic hydrocarbons have boiling points differing by not more than about 10° C., which process comprises azeotropically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an azeotropic former having a boiling point at least 10° C. below the higher boiling naphthenic hydrocarbon of said complex hydrocarbon fraction and not more than 15° C. below the lower boiling naphthenic hydrocarbon of said fraction, said azeotropic former being selected from the class of compounds consisting of the esters of organic and inorganic acids having the effect of forming a minimum boiling mixture with the lower boiling of said naphthenic hydrocarbons whereby said lower boiling naphthenic hydrocarbon is obtained in the azeotropic distillate and the higher boiling naphthenic hydrocarbon remains in the azeotropic bottoms.

3. A process for the treatment of a complex hydrocarbon fraction to separate one naphthenic

7

hydrocarbon from another naphthenic hydrocarbon contained therein which naphthenic hydrocarbons have boiling points differing by between about 3° and 10° C., which process comprises azeotropically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an ester of an oxygen-containing acid which boils at least 10° C. below the boiling point of the higher boiling naphthenic hydrocarbon in said fraction and not more than 15° C. below the boiling point of the lower boiling naphthenic hydrocarbon in said fraction which ester has the effect of forming a minimum boiling mixture with the lower boiling of said naphthenic hydrocarbons whereby said lower boiling naphthenic hydrocarbon is obtained in the azeotropic distillate and the higher boiling naphthenic hydrocarbon remains in the azeotropic bottoms.

4. A process for the treatment of a complex hydrocarbon fraction to separate one naphthenic hydrocarbon from another naphthenic hydrocarbon contained therein which comprises azeotropically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an inorganic halogenide which boils at least 10° C. below the boiling point of the higher boiling naphthenic hydrocarbon in said fraction and not more than 15° C. below the boiling point of the lower boiling naphthenic hydrocarbon in said fraction which halogenide has the effect of forming a minimum boiling mixture with the lower boiling of said naphthenic hydrocarbons whereby said lower boiling naphthenic hydrocarbons is obtained in the azeotropic distillate and the higher boiling naphthenic hydrocarbon remains in the azeotropic bottoms.

5. A process for the separation of cyclohexane and methylcyclopentane which comprises azeotropically distilling the cyclohexane-methylcyclopentane containing fraction in the presence of a

8

sufficient amount of methyl borate whereby an azeotrope of methyl borate and methylcyclopentane is obtained as the azeotropic distillate and the cyclohexane remains as the azeotropic bottoms.

6. A process for the separation of cyclohexane and methylcyclopentane which comprises azeotropically distilling the cyclohexane-methylcyclopentane containing fraction in the presence of a sufficient amount of chloroform whereby an azeotrope of chloroform and methylcyclopentane is obtained as the azeotropic distillate and the cyclohexane remains as the azeotropic bottoms.

7. A process for the separation of cyclohexane and methylcyclopentane which comprises azeotropically distilling the cyclohexane-methylcyclopentane containing fraction in the presence of a sufficient amount of isobutyl nitrite whereby an azeotrope of isobutyl nitrite and methylcyclopentane is obtained as the azeotropic distillate and the cyclohexane remains as the azeotropic bottoms.

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