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AZEOTROPIC DISTILLATION OF
HYDROCARBONS

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1

This invention relates to the preparation of pure hydrocarbons from petroleum, and particularly the separation of naphthenic hydrocarbons from paraffinic hydrocarbons. These hydrocarbons when contained in a hydrocarbon mixture of relatively narrow boiling range are virtually impossible to separate by ordinary fractional distillation and the present invention contemplates their separation by means of azeotropic distillation in the manner as hereinafter set forth. This invention is a continuation-in-part of my co-pending application Serial No. 412,814, now abandoned.

An object of the present invention is to further the progress in preparing pure compounds from a heterogeneous petroleum mixture, using in this particular case a method which involves fewer steps than a chemical method and which yields a purer product than that produced by careful fractional distillation and/or extraction with selective solvents.

Another object of the invention is to prepare from a given fraction of petroleum, such as gasoline, kerosene, or a narrow boiling range hydrocarbon fraction prepared from such materials, these fractions consisting of a mixture of paraffinic, isoparaffinic, naphthenic, olefinic and aromatic hydrocarbons, a fraction that is essentially paraffinic or isoparaffinic or naphthenic in character.

A particular object of my invention is to separate naphthenic hydrocarbons from paraffinic hydrocarbons by distilling the complex hydrocarbon fraction in the presence of a saturated heterocyclic organic compound having four or more atoms, particularly one in which at least one of the atoms in the ring is oxygen, sulfur or nitrogen.

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

The invention comprises adding to a petroleum fraction from which it is desired to segregate a specific hydrocarbon or hydrocarbon fraction, a substance or a mixture of substances hereinafter disclosed having a preferential affinity for one or more components contained in the fraction, thus causing a disturbance of the vapor pressure equilibrium that formerly existed in the fraction, in such manner that the partial vapor pressure or fugacity of at least one component in the fraction is changed sufficiently to permit its separation by controlled fractional distillation. This type of fractional distillation will be referred to hereinafter as azeotropic distillation and the substance or substances which are added to the

2

fraction which effect the aforementioned change will be referred to as azeotrope formers.

According to my invention, the separation of a specific hydrocarbon or hydrocarbon fraction from a mixture of hydrocarbons is accomplished by azeotropic distillation wherein a saturated heterocyclic organic compound having four or more atoms is added to the petroleum fraction and the mixture is subjected to controlled fractional distillation. The addition of the azeotrope former to the petroleum fraction results in forming a more volatile azeotrope with certain of the hydrocarbon components which may then be distilled from the remaining hydrocarbon components. Thus when it is desired to segregate naphthene hydrocarbons from paraffin hydrocarbons, the fractional distillation of this mixture to which an azeotrope former has been added results in the formation of an azeotrope consisting of the paraffin hydrocarbons and the azeotrope former which is more volatile than the naphthene hydrocarbons either in themselves or in azeotropic mixture with the azeotrope former employed. The fractional distillation of the mixture results in distilling overhead the paraffin hydrocarbons in admixture with the azeotrope former leaving the naphthene hydrocarbons as undistilled bottoms. While it is preferred to perform the azeotropic distillation on a fraction containing predominantly naphthenic and paraffinic hydrocarbons and thus effect the distillation in such a manner that one of the components in the fraction, i. e., the naphthenic hydrocarbons remain in the substantially pure form as distillation bottoms, the process of the present invention may be employed on a hydrocarbon fraction containing as well as paraffinic and naphthenic hydrocarbons, aromatic hydrocarbons and olefinic hydrocarbons. If such be the nature of the hydrocarbon fraction, a separation between the naphthenic and the paraffinic hydrocarbons, according to the present invention, may still be performed in which case the naphthenic residue from the distillation will be contaminated with aromatic and olefinic hydrocarbons. The naphthenic hydrocarbons, however, may be separated therefrom by continuing the azeotropic distillation with the azeotrope formers herein employed or by subjecting the naphthenic rich residue to a second azeotropic distillation with the present azeotrope former or with other suitable azeotrope formers.

In such cases where the hydrocarbon fraction contains more than two components of different chemical characteristics, as for example, aromatics, naphthenes and paraffins, and it is de-

sired to separate one or more of these components from the other component or components, the separation may be accomplished by stage azeotropic distillation to remove first one component and then another component. For example, an azeotrope former, such as dioxolane, may be added to a mixture of aromatics, naphthenes and paraffins having a boiling range of approximately 200° F. to 240° F. and the mixture then distilled to remove as overhead fractions, first an azeotrope of the paraffins with dioxolane and then an azeotrope of the naphthenes with more dioxolane leaving the aromatics as undistilled bottoms which may or may not contain dioxolane. The point at which one component, the paraffins, for example, is substantially completely distilled from the remaining components may be observed by a rise in distillation temperature necessary to effect further distillation of the material in the still. Thus, in the above example, the distillation is initially carried out at an overhead temperature of approximately 162° F. at which temperature the paraffin hydrocarbons together with azeotrope former distill from the remaining hydrocarbon components. When substantially all of the paraffin components have been evaporated from the mixture, it will be necessary to raise the distillation temperature so that the overhead temperature will be increased to, for example, approximately 164° F. in order to effect further removal of hydrocarbon components. This increase in temperature indicates that substantially all of the paraffins were previously distilled from the mixture and that the next hydrocarbon components, for example the naphthenes, are being distilled at the increased temperature. By thus observing and controlling the distillation temperature, it is possible to remove the various components present in the original feed stock as separate fractions.

A phenomena which often enters into the azeotropic distillation picture and which has been previously reported in the literature is the fact that in a great many cases in the separation of components A and B from each other by azeotropic distillation in the presence of azeotrope former C there is an azeotrope formed between A and C and also between B and C, which azeotropic mixtures may have no greater boiling point spread than existed between the original components A and B. However, it has been shown many times over that in the majority of cases azeotropes formed with components A and B by the azeotrope former C are more readily separated by distillation than are components A and B in the absence of azeotrope former despite the same or even smaller differences in boiling points existing between the azeotropes. I have found this to be true in many instances of azeotropic distillation of naphthenes and paraffins with the azeotrope formers of the present invention. It should be emphasized therefore that I do not wish to limit my invention to the usage of azeotrope formers which form an azeotrope with only one component in the hydrocarbon mixture, nor to the usage of azeotrope formers which form azeotropes with more than one component in the hydrocarbon mixture which azeotropes boil no further apart than the components themselves.

While the invention is adapted to the separation of hydrocarbons of characteristics different from each other I have found that this process is particularly useful for producing naphthenic hydrocarbons such as methylcyclohexane, dimethylcyclohexane, dimethylcyclopentane, and

the like, having a high degree of purity from gasoline fractions produced from straight run or synthetic gasoline, such as those produced by cracking, polymerization or reforming. The production of substantially pure naphthenic hydrocarbons is becoming increasingly important as a result of the expanding usage of naphthenic hydrocarbons as intermediates in the synthesis of organic chemicals such as adipic acid, succinic acid, and the like.

Besides dioxolane mentioned above, other saturated heterocyclic organic compounds may be employed as azeotrope formers. These include the six membered compounds in which at least one of the atoms in the ring is oxygen, nitrogen or sulfur, such as oxane, trioxane, piperidine, thiane, dimethyl dioxane, morpholine, thioxane, piperazine, dithiane, thioformaldehyde, etc., the derivatives of such six membered compounds, such as dibutanol, n-ethyl piperidine, n-methyl morpholine, n-morpholine ethanol, n-phenyl morpholine, pentamethylene sulfone, etc., the five membered compounds in which at least one of the atoms in the ring is oxygen, nitrogen or sulfur, such as oxolane, pyrrolidine, thiolane, dioxolane, methyl dioxolane, etc., and the derivatives of such five membered compounds such as n-ethyl pyrrolidine, tetramethylene sulfide, tetrahydrofurfuryl alcohol, etc., the four membered compounds, such as trimethylene sulfide, trimethylene oxide, trimethylenimine, etc., and the derivatives of such four membered compounds, such as trimethylene sulfone, n-ethyl trimethylenimine, etc.

Of the above-mentioned azeotrope formers, I have found the heterocyclic oxygen containing compounds and particularly dioxane, dioxolane, and trioxane are very efficient azeotrope formers for separating a naphthene-paraffin hydrocarbon fraction having a narrow boiling range preferably not more than 50° F. into a naphthenic and paraffinic rich fraction. The azeotrope former should be chosen with respect to the boiling point of the hydrocarbon fraction, the higher the boiling point of this fraction the higher will be the boiling point of the azeotrope former capable of effecting the azeotropic distillation. The boiling point of the azeotrope former should be not more than about 35° C. above or 35° C. below the average boiling point of the hydrocarbon fraction to be separated. In other words the hydrocarbon fraction to be separated should have an average boiling point not more than 35° C. above or more than 35° C. below the boiling point of the specific azeotrope former to be employed for its separation. Thus, hydrocarbon fractions to be separated with dioxolane, for example, as the azeotrope former should have an average boiling point between 39° C. and 109° C., dioxolane having a boiling point of 74° C. In this regard, I have found that in most cases it is preferable to employ an azeotrope former boiling below the hydrocarbon mixture for it is found that in this manner a greater azeotropic spread is obtained. However, this is not always true for example dioxane boiling at 214° F. is an effective azeotrope former for separating n-heptane boiling at 208° F. from methylcyclohexane boiling at 213.5° F. Further, in this respect I have found that the greatest azeotropic spread is obtained when employing an azeotrope former boiling in the lower limits of this lower temperature range. However, there must also be considered in employing such an azeotrope former the fact that the greater boiling point differential between the

azeotrope former and the hydrocarbon fraction, the greater will be the amount of azeotrope former necessary to accomplish a given separation. It is further necessary to balance these two opposing factors in determining which azeotrope former is to be employed, and in this regard consideration of the composition of the hydrocarbon fraction, the availability of the azeotrope formers and the like must be taken into consideration. Thus, in a fraction comprised predominantly of naphthenic hydrocarbons containing only a minor amount of paraffinic hydrocarbons as impurities it may be economically practical to employ an azeotrope former boiling some 25° to 35° C. below the average boiling point of the hydrocarbon fraction; whereas, in a fraction comprised of approximately equal proportions of naphthenic and paraffinic hydrocarbons it may be deemed advisable to employ an azeotrope former boiling in the range of 10° C. to 25° C. below the average boiling point of the hydrocarbon fraction. These generalizations concerning the selection of the azeotrope former to be employed are intended only to be helpful in the utilization of my invention but should not be considered as limiting its application in any way whatsoever inasmuch as I may use as azeotrope formers compounds of the above identified type boiling not more than about 35° C. below the hydrocarbon fraction, and not more than about 35° C. above the hydrocarbon fraction.

The type of distillation to be used depends somewhat on the quantity of the aforementioned azeotrope former employed. I may take any portion of azeotrope former to the petroleum fraction that I desire, depending upon the efficiency of the operation or the purity of the product desired, and the technique to be used in the distillation. The proportion of the azeotrope former may be readily adjusted to an ideal point, again depending on whether I desire the portion high in naphthenic hydrocarbon content to remain as bottoms in the distillation in practically pure state, i. e., free from paraffinic hydrocarbon, or whether I wish to distill a portion of the paraffinic hydrocarbons leaving a portion thereof as bottoms together with the naphthenic hydrocarbon. Also the distillation temperature and amount of azeotrope former may be adjusted to effect the distillation of all of the paraffinic hydrocarbons together with a portion of the naphthenic hydrocarbons. In other words, the desired efficiency of separation of the naphthenic and paraffinic hydrocarbons is dependent upon the proportion of azeotrope former selected, the efficiency of the distillation column and similar factors.

Further, I have found that in conducting the distillation in a batchwise manner it is preferable to introduce the azeotrope former in increments during the course of the distillation for in this manner there is avoided the loss of any uncombined azeotrope former in the distillate, which normally occurs if the entire quantity thereof is initially employed. By permitting the attainment of an equilibrium in the composition of the residue in a continuous distillation the azeotrope former may be added incrementally in such a distillation whereby the same beneficial effect is obtained as in the batchwise operation.

In order to separate the azeotrope former from the azeotropic distillate, it is merely necessary to extract the condensate mixture with a solvent adapted to extract or dissolve the azeotrope former and substantially none of the hydrocarbons. By allowing this mixture to settle, two dis-

ting layers are formed, an upper layer consisting of the hydrocarbon and a lower layer of azeotrope former dissolved in the solvent. Solvents useful for the purpose include the nitroparaffins, such as nitromethane, nitroethane, nitropropane, propylene glycol and diethylene glycol, and even the saturated heterocyclic organic compounds having different boiling points than the hydrocarbons to be separated from the azeotropic distillate. In some cases, the separation of the azeotrope former from the hydrocarbons may be accomplished by cooling the azeotropic distillate sufficiently, as for example, below 70° F. in order to reject the hydrocarbons from the azeotrope former. Most of the azeotrope formers disclosed herein are water soluble and these are preferably extracted from the azeotropic distillate with water at an appropriate temperature to effect the desired result. The azeotrope former may be recovered from the non-aqueous solvent or water by simple distillation, the overhead being either the azeotrope former or the solvent depending upon the relative boiling points of these two materials.

Other objects, features and advantages of my invention will become apparent to those skilled in the art from the following examples thereof. However, it will be observed that these examples are not to be taken as limiting my invention since the process is applicable to separate other complex hydrocarbon fractions employing the other azeotrope formers disclosed herein for effecting the desired separation.

EXAMPLE I

A blend of equal parts of methylcyclohexane and n-heptane was prepared and a portion of this blend was subjected to simple fractional distillation while another portion was subjected to an azeotropic distillation in the presence of dioxolane as the azeotrope former. Both of these distillations were made on a 64 plate still at an internal reflux ratio of 64 to 1. The results of the simple distillation are summarized briefly in Table 1 below:

TABLE 1

Distillation of 50-50 mixture of n-heptane and methylcyclohexane

Fraction	Volume Per Cent of Charge	M. C. H., Vol. Per Cent	N-heptane, Vol. Per Cent	Temp., ° F.
Initial.....	34.4	15.4	84.6	209-210
Intermediate.....	16.6	33.0	67	210-213
Bottoms.....	49.0	81.3	18.7	-----

The other portion of the methylcyclohexane-n-heptane fraction was distilled in the presence of two parts dioxolane, the results of the distillation being shown in Table 2 below:

TABLE 2

Distillation of 50-50 mixture of n-heptane and methylcyclohexane in the presence of two volumes dioxolane

Fraction	Volume Per Cent of Charge ¹	M. C. H., Vol. Per Cent ¹	N-heptane, Vol. Per Cent ¹	Temp., ° F.
Initial.....	36.0	4.4	95.6	162
Intermediate.....	18.5	32.6	67.4	162-164
Bottoms.....	45.5	96.0	4.0	-----

¹ Calculated on a dioxolane free basis.

It is immediately apparent that heptane and methylcyclohexane cannot be efficiently separated

7

by simple fractional distillation in a column of this character; whereas, a high degree of separation is obtainable by an azeotropic distillation in the presence of dioxolane.

EXAMPLE II

In another example, a closely fractionated cut of straight run gasoline having a boiling range of 209 to 214° F. and consisting principally of paraffin and naphthene hydrocarbons and substantially no aromatic hydrocarbons was fractionally distilled in the presence of one-half its volume of dioxane at an overhead temperature of approximately 198° F. and atmospheric pressure until approximately 28% of the hydrocarbons had been distilled over together with dioxane. The distillation temperature was then increased to 202° F. and the distillation was continued at this temperature until 42% of the hydrocarbons had been distilled together with dioxane, leaving about 30% of the stock in the still. After separating the dioxane from these fractions thus produced, by washing with water, the hydrocarbons recovered in the first distillation had a gravity of 72° A. P. I. indicating about 90% by volume of paraffin hydrocarbons, the hydrocarbons recovered from the second distillation had a gravity of 63° A. P. I. indicating about equal volumes of paraffin and naphthene hydrocarbons and the distillation bottoms had a gravity of 52° A. P. I. indicating about 95% by volume of naphthene hydrocarbons.

8

The foregoing description and examples of my invention are not intended to be taken as limiting my invention but only as illustrative thereof since many variations may be made by those skilled in the art without departing from the spirit or scope of the following claim:

I claim:

A process for the separation of heptane and methcyclohexane which comprises azeotropically distilling said methylcyclohexane and heptane mixture in the presence of a sufficient amount of dioxolane to vaporize the heptane contained in said mixture together with said dioxolane thereby leaving said methylcyclohexane in the residue.

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