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HYDROCARBON SEPARATION BY AZEOTROPIC DISTILLATION WITH TRIOXANE

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1

This invention relates to the preparation of pure hydrocarbons from petroleum, these pure hydrocarbons being contained in a fraction of petroleum hydrocarbons whose components have small differences in boiling points, which renders them inseparable by ordinary fractional distillation. This is a continuation-in-part of my copending application Serial No. 412,814, filed September 29, 1941.

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 or olefinic or aromatic by distilling such fractions of petroleum in the presence of trioxane.

A particular object of my invention is to separate aromatic hydrocarbons from non-aromatic hydrocarbons by distilling the complex hydrocarbon fraction in the presence of trioxane.

The invention comprises adding to such petroleum fractions from which it is desired to segregate a specific hydrocarbon or hydrocarbon fraction, trioxane having a preferential affinity for one or more components contained in the fractions, 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 trioxane will be referred to as azeotrope former.

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 azeotrope former consisting of trioxane 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 aromatic hydrocarbons, the fractional distillation of this mixture to which the azeotrope former has been added results in the formation of an azeotrope consisting of the naphthene

2

hydrocarbons and the azeotrope former which is more volatile than the aromatic hydrocarbons which may or may not contain a portion of the azeotrope former. The fractional distillation of the mixture results in distilling overhead the naphthene hydrocarbons in admixture with the azeotrope former leaving the aromatic hydrocarbons as undistilled bottoms. The same procedure may be employed to segregate paraffin and aromatic hydrocarbons in which case the paraffin hydrocarbons form a lower boiling azeotrope with the azeotrope former. Likewise paraffin hydrocarbons may be separated from naphthene hydrocarbons in which case the naphthene hydrocarbons remain as the undistilled bottoms. While it is preferred to effect the fractional distillation in such manner that one of the components in the hydrocarbon fraction remains as an undistilled bottoms, it is also possible to vaporize the mixture of hydrocarbons completely with the azeotrope former and then by controlled fractionation in a fractionating column effect the condensation of the separate hydrocarbon components at various points in the fractionating column from which the various components may be removed.

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 desired to separate one or more of these components from the other component or components, the separation may be accomplished by stage fractional distillation to remove first one component and then another component. For example, trioxane may be added to a mixture of aromatics, naphthenes and paraffins having a boiling range of 200 to 240° F. and the mixture then distilled to remove as overhead fractions, first an azeotrope of the paraffins with trioxane and then an azeotrope of the naphthenes with more trioxane leaving the aromatics as undistilled bottoms either containing trioxane or not. 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 in order 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 206° F. at which temperature the paraffin hydrocarbons together with trioxane distill from the remaining hydrocarbon components, then when substantially all of the paraffin components have been evaporated from

the mixture, it will be necessary to raise the distillation temperatures so that the overhead temperature will be increased to, for example, 220° F. in order to effect further removal of hydrocarbon components. This increase in temperature indicates that 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.

While the invention is adapted for the separation of hydrocarbons of characteristics different from each other, I have found that this process is particularly useful for producing toluene or xylene having a very 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 toluene and xylene is highly important when these compounds are to be used in the manufacture of explosives by nitration because even small amounts of impurities impair the nitration process and degrade the resulting nitration product.

The above disclosed azeotrope former may be employed in the anhydrous state in which case the resulting azeotropic distillate will comprise azeotrope former and hydrocarbon material or it may be used with water in which case the azeotropic distillate will comprise azeotrope former, hydrocarbon material and water. Thus I may use the anhydrous azeotrope former or I may use the azeotrope former together with water in amounts up to about 0.4 part by weight of water to 1 part of the azeotrope former.

Trioxane is very efficient for separating hydrocarbon fractions having narrow boiling ranges, preferably not more than 50° F., between the limits of 150° F. to 330° F. into hydrocarbon components of different chemical characteristics and is particularly useful for separating paraffin and/or naphthene hydrocarbons having 6 to 10 carbon atoms from aromatic hydrocarbons having 9 or less carbon atoms, as for example, when separating hexanes, heptanes, octanes, nonanes, decanes and/or naphthene hydrocarbons having similar numbers of carbon atoms from benzene, toluene, xylenes and ethyl benzene.

The type of distillation to be used depends somewhat on the quantity of the aforementioned azeotrope former used. I may take any proportion of the petroleum fraction to the added azeotrope former that I desire, depending on 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 readily be adjusted on an ideal point, the definition of this point again depending on whether I desire the portion high in aromaticity to remain as bottoms in the boiler in a practically pure state, i. e., free from nonaromatic hydrocarbons, or whether I wish to distill a portion of the non-aromatic hydrocarbons, leaving a portion of the non-aromatic hydrocarbons as bottoms together with aromatic hydrocarbons. Also, the distillation temperature and amount of azeotrope former may be adjusted to effect the distillation of all of the non-aromatic hydrocarbons together with a portion of the aromatic hydrocarbons. In other words, the efficiency of separation of the aromatic from non-aromatic hydrocarbons is dependent upon the proper adjustment of the

amount of azeotrope former used since a small amount may result in incomplete separation of the non-aromatic hydrocarbons while the use of an excess of the azeotrope former together with a relatively higher distillation temperature may cause distillation of a portion of the aromatic hydrocarbons.

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 distinct 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 saturated heterocyclic organic compounds having different boiling points than the azeotrope former 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 100° F. in order to reject the hydrocarbons from the azeotrope former or to cause the azeotrope former to crystallize and separate from the hydrocarbon mixture. Trioxane is water soluble and is 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. When water is employed to effect the aforesaid separation, the overhead will be water and the bottoms will be the azeotrope former.

Combinations of two or more of the above described processes may be used to separate azeotrope former from the azeotropic distillate. Thus, an azeotrope comprising trioxane and non-aromatic hydrocarbons may be cooled to about 120° F. at which temperature most of the trioxane crystallizes and may be mechanically separated from the hydrocarbons contained in the azeotrope by mechanical means such as filtration. The separated crystalline trioxane may then be reheated and reused as azeotrope former without further purification. The separated hydrocarbons may then be washed with water to remove small amounts of trioxane which did not crystallize and become separated in the above operation.

The preferred method with trioxane is to maintain the azeotropic condensate at 150° F. At this temperature two liquid phases are present, an upper phase of hydrocarbon oil containing very little trioxane and a lower phase of trioxane substantially free of hydrocarbon oil. The upper phase is decanted and washed with water in the usual manner, the lower phase may be recycled directly to the azeotrope column.

The azeotropic distillation may be effected at any desired pressure. In most cases it is preferred to operate at normal atmospheric pressure although I may prefer to operate under a vacuum, particularly in those cases in which the boiling point range of the hydrocarbon fraction undergoing treatment is high, and in some instances I may prefer to operate under super-atmospheric pressures such as at about 100 pounds per square inch gage or even higher.

In carrying out my azeotropic distillation, the

particular fraction to be treated is mixed with a sufficient amount of trioxane to produce the desired separation and the mixture is passed through a heater and into a fractionating column where the mixture is subjected to fractionation. If desired, the azeotrope former may be introduced directly into the fractionating column at a point above the point of entry of the hydrocarbon mixture and preferably at a point near the top of the column and in this case the azeotrope former acts in part as reflux for the fractionation. In the fractionating column the distillation is controlled so as to distill overhead an azeotrope comprising at least one hydrocarbon component originally contained in the hydrocarbon mixture and azeotrope former leaving as undistilled residue at least one hydrocarbon component. By regulating the ratio of azeotrope former to hydrocarbon mixture entering the column, and by controlling the temperature and pressure in the fractionating column the distillation can be controlled so as to distill, for example, substantially all of the non-aromatic hydrocarbons contained in said hydrocarbon mixture together with substantially all of the azeotrope former, thereby leaving the aromatic hydrocarbon originally present in said hydrocarbon mixture as a residue substantially completely separated from non-aromatic hydrocarbons and azeotrope former.

The aromatic hydrocarbon residue may be further purified and/or refined by treatment with clay which may be accomplished at a temperature of about 230° F. employing 1 to 5 pounds of clay per barrel of the residue. In place of clay treatment or in addition to the clay treatment, the aromatic residue may be treated with 1 to 10 pounds of sulfuric acid per barrel of the residue followed by neutralization with caustic alkali or with clay. If desired, the acid and/or clay treated stock may be fractionally distilled to remove undesirable hydrocarbons and/or products of reaction.

The azeotropic distillate may be passed to a washing column provided with packing material where the mixture enters at a point near the bottom and is countercurrently washed with water which is led into the washer at a point near the top of the column. The water dissolves the azeotrope former and the solution of azeotrope former in water is withdrawn from the bottom of the washer and passed through a heater and into a fractionating column maintained at such a temperature that the water vaporizes and distills leaving the azeotrope former as a residue. This residue is recycled to the azeotropic distillation column where it is again used as azeotrope former. The water distilled overhead is condensed and cooled and passed to the washer column. As indicated hereinabove other solvents may be employed in place of water in this extraction process.

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

Example I

A hydrocarbon fraction obtained by fractionating a catalytically reformed gasoline, said

fraction having a boiling range of about 210° F. to about 235° F. and comprising substantially 42 parts by weight of toluene, 9 parts by weight of olefins and 49 parts by weight of paraffin and naphthene hydrocarbons is mixed with trioxane in the ratio of 0.4 part by weight of trioxane to one part by weight of the hydrocarbon fraction. This mixture is passed through a heater and the heated mixture is led into a fractionating column which is provided with a heater or reboiler and a reflux cooling coil where the mixture is subjected to fractionation. The distillation is controlled so as to distill overhead an azeotrope consisting of the paraffin, naphthene and olefin hydrocarbons together with substantially all of the trioxane, leaving toluene as a residue, substantially completely separated from non-aromatic hydrocarbons and trioxane. This is accomplished at a still head temperature of approximately 220° F. and at atmospheric pressure.

The overhead mixture or azeotrope is condensed and passed to a washing column where it is washed countercurrently with water. The water solution of trioxane is withdrawn from the bottom of the washer and is thus separated from the hydrocarbons present in the azeotrope.

The residue from the azeotroping column amounting to about 40% by weight of the original hydrocarbon feed to the column has a gravity of 31.2° A. P. I., a solubility in 99% sulfuric acid of 100% and an olefin content of 0.1%.

Example II

One part by weight of a hydrocarbon fraction of hydroformed gasoline boiling between about 260° F. and 300° F. and comprising 76 parts by weight of xylene and 24 parts by weight of non-aromatic hydrocarbons is mixed with 0.3 part by weight of trioxane and the resulting mixture azeotropically distilled. At a distillation temperature of 230° F. at normal atmospheric pressure, an azeotrope comprising substantially all of the non-aromatic hydrocarbons and all of the trioxane is vaporized and distilled overhead leaving xylene as a residue substantially completely separated from non-aromatic hydrocarbons and trioxane.

The residue comprising xylene amounting to approximately 74% by weight of the original hydrocarbon feed to the azeotroping column has a gravity of 31° A. P. I., and a solubility in 99% sulfuric acid of 100%.

The azeotrope distilled from the column is passed to a cooler where the temperature is reduced to about 100° F. At this temperature most of the trioxane is crystallized and removed by filtration. The crystallized trioxane is then melted and returned to the azeotroping column. The hydrocarbon material from which the crystallized trioxane has been removed is passed into a water washer and contacted countercurrently with water to remove the remaining trioxane which is then separated from the aqueous solution in a conventional manner.

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

I claim:

1. A process for the treatment of a complex hydrocarbon fraction to separate one chemically similar component from the other chemically similar components different from said first

named chemically similar components contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as said first named chemically similar component distills therefrom which comprises azeotropically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of trioxane to vaporize at least one of the chemically similar components contained in said complex hydrocarbon fraction together with said trioxane thereby leaving at least one of the chemically similar components different from the vaporized chemically similar components contained in said complex hydrocarbon fraction in the residue.

2. A process for the treatment of a hydrocarbon fraction containing aromatic and non-aromatic hydrocarbons to separate said aromatic hydrocarbons from said non-aromatic hydrocarbons contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as said aromatic hydrocarbons distill therefrom which comprises distilling said hydrocarbon fraction in the presence of trioxane to vaporize said non-aromatic hydrocarbons together with said trioxane, thereby leaving aromatic hydrocarbons in the residue substantially completely separated from hydrocarbons other than aromatic hydrocarbons.

3. A process for the treatment of a hydrocarbon fraction containing aromatic and non-aromatic hydrocarbons to separate said non-aromatic hydrocarbons from said aromatic hydrocarbons which ordinarily distill from said hydrocarbon fraction in the same temperature range as said non-aromatic hydrocarbons distill therefrom which comprises distilling said hydrocarbon fraction containing aromatic and non-aromatic hydrocarbons in the presence of a sufficient amount of trioxane to vaporize said non-aromatic hydrocarbons together with said trioxane, thereby leaving said aromatic hydrocarbons in the residue substantially completely separated from non-aromatic hydrocarbons, said hydrocarbon fraction containing aromatic and non-aromatic hydrocarbons having a boiling range of not more than 50° F. between the limits of 150° F. to 330° F.

4. A process for the treatment of a hydrocarbon mixture comprising toluene and non-aromatic hydrocarbons boiling in substantially the same temperature range as toluene which comprises distilling said hydrocarbon mixture in the presence of a sufficient amount of trioxane to vaporize said non-aromatic hydrocarbons together with said trioxane, thereby leaving toluene in the residue substantially completely separated from non-aromatic hydrocarbons.

5. A process for the treatment of a hydrocarbon mixture comprising xylene and non-aromatic hydrocarbons boiling in substantially the same temperature range as xylene which comprises distilling said hydrocarbon mixture in the presence of a sufficient amount of trioxane to vaporize said non-aromatic hydrocarbons together with said trioxane, thereby leaving xylene in the residue substantially completely separated from non-aromatic hydrocarbons.

6. A process as in claim 5 wherein said hydrocarbon mixture has a boiling range of approximately 260° F. to 300° F.

7. A process for the treatment of a hydrocarbon fraction containing naphthene and paraffin hydrocarbons to separate the naphthene hydrocarbons from the paraffin hydrocarbons contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as the naphthene hydrocarbons distill therefrom which comprises distilling said hydrocarbon fraction containing naphthene and paraffin hydrocarbons in the presence of a sufficient amount of trioxane to vaporize said paraffin hydrocarbons together with said trioxane thereby leaving naphthene hydrocarbons in the residue substantially completely separated from paraffin hydrocarbons.

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