This invention relates to the preparation of pure aromatic hydrocarbons from petroleum, coal tar and the like, these pure aromatic hydrocarbons being contained in a fraction of hydrocarbons whose components have small differences in boiling points, which renders them inseparable by ordinary fractional distillation.

An 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 paraflinic, isoparaflinic, naphthenic, olefinic and aromatic hydrocarbons, one or more fractions that are composed essentially of one or more specific aromatic hydrocarbons.

A further object of our invention is to separate one or more specific aromatic hydrocarbons from complex hydrocarbon fractions consisting of mixtures of aromatic hydrocarbons or from mixtures containing aromatic and non-aromatic hydrocarbons regardless of the source of the fractions by distilling the said hydrocarbon fractions in the presence of a mono-glycol.

A specific object of our invention is to separate ortho-xylene and meta- and/or para-xylene from a mixture of the xylenes containing ortho-xylene and meta- and/or para-xylene or from a xylene fraction containing non-aromatic hydrocarbons boiling in the same temperature range as the xylenes by distilling the xylene containing fractions in the presence of a mono-glycol.

The invention comprises adding to such hydrocarbon fractions from which it is desired to segregate one or more specific aromatic hydrocarbons, a substance or a mixture of substances hereinafter disclosed having a preferential affinity for one or more components contained in the fractions, this causing a disturbance of the vapor pressure equilibrium that formerly existed in the fraction, in such a 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 fraction and which effect the aforementioned change will be referred to as azeotrope formers.

According to our invention, the separation of one or more specific aromatic hydrocarbons from a mixture of aromatic hydrocarbons or from a mixture of aromatic and non-aromatic hydrocarbons is accomplished by azeotropic distillation wherein a mono-glycol is added to the hydrocarbon fraction and the mixture is subjected to controlled distillation. The addition of the mono-glycol to the hydrocarbon fraction results in forming a more volatile azeotrope with certain hydrocarbons or hydrocarbon components which may then be distilled from the remaining hydrocarbon or hydrocarbon components. For example, an azeotrope former, such as the methyl ether of ethylene glycol may be added to a mixture of aromatic hydrocarbons which may then be distilled to remove as an overhead fraction an azeotrope of one or more of the aromatic hydrocarbons with methyl ether of ethylene glycol leaving as a residue one or more aromatic hydrocarbons either containing methyl ether of ethylene glycol or not depending upon the amount of azeotrope former used. The point at which one aromatic hydrocarbon or one aromatic hydrocarbon component is substantially completely distilled from the remaining aromatic hydrocarbon or aromatic hydrocarbon components may be observed by a rise in the distillation temperature required to effect further distillation of the material in the still. Thus by observing and controlling the distillation temperature it is possible to remove as separate fractions one or more of the various aromatic hydrocarbons present in the original feed stock.

In such cases where the hydrocarbon fraction contains aromatics and non-aromatics and it is desired to separate one or more specific aromatic hydrocarbons from the complex mixture of hydrocarbons the separation may be accomplished by stage fractional distillation to remove first the non-aromatic hydrocarbons and then one or more specific aromatic hydrocarbons leaving as a residue one or more specific aromatic hydrocarbons. For example, to an aromatic fraction containing ortho-xylene and meta- and/or para-xylene and also non-aromatic hydrocarbons such as paraffins, naphthenes, olefins or mixtures thereof, and having a boiling range of about 280-295°F, is added an azeotrope former such as the methyl ether of ethylene glycol and the mix-
ture then distilled to remove as overhead fractions first the azeotrope or azeotropes of the non-aromatic hydrocarbons with the methyl ether of ethylene glycol and then an azeotrope of meta- and/or para-xylene with more of the methyl ethyl or ethylene glycol leaving ortho-xylene as undistilled bottoms either containing methyl ether of ethylene glycol or not. In this example the azeotropes containing non-aromatics and azeotrope forming petrol distill at overhead temperatures of approximately 235° F. to 245° F. depending upon the character of these non-aromatic components, and when substantially all of the non-aromatic components have been distilled from the mixture it will be necessary to raise the distillation temperature so that the overhead temperature will be increased to about 248° F. in order to effect the distillation of the meta- and/or para-xylene, with more of the methyl ether of ethylene glycol leaving ortho-xylene as a distillation residue. While it is preferred to effect the fractional distillation in such a manner that one or more of the aromatic hydrocarbons in the original hydrocarbon fraction remains as an undistilled bottom, as indicated in the foregoing example, it is also possible to distill the mixture of hydrocarbons completely with the azeotrope former and then by controlled fractionation in a fractionating column effect the condensation of the various hydrocarbons or hydrocarbon components at various levels in the fractionating column from which the separated hydrocarbons or hydrocarbon components may be removed.

As a variation of the method described above for separating one or more specific aromatic hydrocarbons or aromatic hydrocarbon components from a hydrocarbon fraction containing aromatic and non-aromatic hydrocarbons the separation may be accomplished by azeotropically distilling and removing as an overhead fraction the non-aromatic hydrocarbons together with one or more of the aromatic hydrocarbons or aromatic hydrocarbon components and leaving as a residue one or more aromatic hydrocarbons or aromatic hydrocarbon components. The overhead from this distillation may then be azeotropically distilled to produce as overhead the non-aromatic hydrocarbons and leaving as a residual the aromatic hydrocarbons or aromatic hydrocarbon components. For example, to the complex hydrocarbon fraction referred to above, containing aromatic and non-aromatic hydrocarbons and boiling in the range of about 280-285° F. is added an azeotrope former such as the methyl ether of ethylene glycol and the mixture distilled to remove as overhead the azeotropes of the non-aromatic hydrocarbons together with the azeotropes of one or more of the lower boiling aromatic hydrocarbons, i.e., meta- and/or para-xylene together with the methyl ether of ethylene glycol leaving ortho-xylene as an undistilled bottoms either containing methyl ether of ethylene glycol or not. The overhead from this distillation may then be fractionally distilled without further treatment to produce as overhead the azeotrope comprising the non-aromatic hydrocarbons and methyl ether of ethylene glycol leaving as bottoms the aromatic hydrocarbons, i.e., meta- and/or para-xylene together with some methyl ether of ethylene glycol. Alternatively the said overhead distillate containing the non-aromatic hydrocarbons and the meta- and/or para-xylene from the first azeotropic distillation may be distilled in the presence of another azeotrope former which forms an azeotrope with the non-aromatic hydrocarbons but which preferably does not form an azeotrope with the aromatic hydrocarbons producing as an overhead distillate the azeotrope comprising the non-aromatic hydrocarbons and azeotrope former and leaving as an undistilled bottoms the aromatic hydrocarbon components which were, in the first stage of this process, separated from the higher boiling aromatic hydrocarbons present in the original complex hydrocarbon fraction. Examples of such azeotrope formers which may be employed in the second azeotropic fractionation stage include methyl alcohol, ethyl alcohol, isopropyl alcohol, pyridine, di-ethyl ketone and ethyl acetate.

While the invention is adapted for the separation of specific aromatic hydrocarbons from mixtures of aromatic hydrocarbons or mixtures of aromatic hydrocarbons containing non-aromatic hydrocarbons, we have found that this process is particularly useful for separating ortho-xylene from mixtures of ortho-xylene with meta-xylene and/or para-xylene or for removing as separate fractions the ortho-xylene and the meta- and para-xylene from a complex relatively narrow boiling range hydrocarbon fraction boiling in the same temperature range as the xylenes. The separation of ortho-xylene from the meta- and para-xylene is highly important when the xylenes are to be used as one of the components in the manufacture of high grade gasolines, particularly the high knock rating aviation fuels. For these uses the ortho-xylene is far less desirable than either the meta- or para-xylene or mixtures of the meta- and para-xylene, however, the ortho-xylene is a particularly valuable chemical raw material from which may be produced important chemicals, such as phthalic acid and/or anhydride and derivatives of these compounds.

Mono-glycols which may be employed as azeotrope formers include ethylene glycol, the ethers of ethylene glycol, such as monomethyl, mono-ethyl and monobutyl ethers, and the esters of the ethers of ethylene glycol, such as for example, the acetate of the monomethyl ether of ethylene glycol. Also, compounds which may be used as azeotrope formers are propylene glycol and butylene glycol, the ethers of propylene glycol and butylene glycol and the esters of the ethers of each of these glycols. Examples of these include propylene glycol and isobutylene glycol. In addition to the dihydroxy alcohols mentioned above, other polyhydroxy alcohols which may be used include the trihydroxy, tetrahydroxy, etc. Examples of the latter include glycerine and erythritol. The mono-glycol should be chosen with respect to the boiling point of the hydrocarbon fraction, the higher the boiling point of the hydrocarbon fraction, the higher the boiling point of the mono-glycol will be to effect the azeotropic distillation. The boiling point of the mono-glycol should be not more than 15° F., preferably not more than 30° F. lower and not more than 40° F. preferably not more than 10 to 15° F. higher than the average boiling point of the hydrocarbon fraction. The mono-glycol should preferably be employed in the anhydrous state, although small quantities of water may be tolerated, particularly in the case of the lower boiling mono-glycols.

The type of distillation to be used depends somewhat on the quantity of azeotrope former used. We may employ any proportion of the hy-
drocarbon fraction to the added azeotrope former that we desire, depending on the efficiency of the operation or the purity of the product desired, and the technique of distillation. The proportion of the mono-glycol may readily be adjusted on an ideal point, the definition of this point again depending on whether we desire one or more aromatic hydrocarbons to remain as bottoms in a relatively pure state, i.e., free from non-aromatic hydrocarbons to the extent of 1 to 5 pounds of clay per barrel of the ortho-xylene. In place of clay treatment the Ortho-xylene may be cooled and then treated with 1 to 10 pounds of sulfuric acid per barrel of ortho-xylene followed by neutralization with clay or caustic alkali. If desired the acid and/or clay treated stock may be fractionated to remove undesirable hydrocarbons and/or products of reaction.

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 the azeotrope former dissolved in the solvent. Solvents for this purpose include the nitro-compounds, such as nitro methane, nitro ethane, and nitro propane, phenolic compounds, ketones, monohydrate alcohols and even polyhydroxy alcohols having considerably different boiling points, i.e., lower or higher than the hydrocarbon to be separated from the azeotropic distillate. Most of the mono-glycols, such as methyl ether of ethylene glycol, are water soluble and these are preferably extracted from the azeotropic distillate with water at an approximate temperature to effect the desired result. The mono-glycol may be recovered from the non-aqueous solvent or from the water by simple distillation, the overhead being either the mono-glycol or the solvent depending upon the relative boiling points of these materials.

The azeotropic distillate comprising meta-xylene and methyl ether of ethylene glycol produced in the above mentioned azeotropic distillation may be separated into a substantially pure meta-xylene and substantially pure azeotropic former in the following manner: The meta-xylene azeotrope is pumped from the aforementioned condenser into a washing unit, entering at a point near the bottom. The washer is provided with a packing material, such as broken tile, and in this unit the mixture is washed countercurrently with water. The water, which is pumped into the washer at a point near the top, flows downward and dissolves the methyl ether of ethylene glycol leaving the meta-xylene. The meta-xylene is withdrawn from the top of the washer and pumped to storage. The solution of water and azeotrope former is withdrawn from the bottom of the washer and pumped through a heater and then into a fractionating column, which will be referred to hereinafter as an azeotrope former recovery column, where the distillation is controlled to separate substantially all of the water as overhead vapor. The fractionation is aided by a heater at the base of the column and a reflux cooling unit at the top of the column. The water vapor from the top of this column is condensed and passed to storage from which it may be withdrawn to wash further quantities of azeotrope.

The unvaporized methyl ether of ethylene glycol is withdrawn from the bottom of the azeotrope former recovery column and pumped to storage from which it may be withdrawn and reused for treating further and residues of the mixture of ortho- and meta-xylene.

Other objects, features and advantages of our 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 our invention since the process is applicable to the separation of other aromatic hydrocarbons or hydrocarbon compo-
ments from other mixtures of aromatic hydrocarbons or from complex mixtures of hydrocarbons employing these or the other azeotrope formers disclosed in the foregoing description for effecting the desired separation.

Example 1

A mixture composed of equal parts by volume of ortho-xylene and meta-xylene was mixed with two-thirds of its volume of methyl ether of ethylene glycol and the mixture was distilled and fractionated in an azeotroping column. The overhead from the column, consisting of an azeotrope containing meta-xylene and substantially all of the added methyl ether of ethylene glycol, was obtained at a distillation temperature of 248° F. at atmospheric pressure. The azeotrope was washed with water to extract the methyl ether of ethylene glycol leaving substantially pure meta-xylene having a gravity of 31.8° API and an index of refraction of 1.4974. The thus distilled and washed meta-xylene amounted to approximately 50% by volume of the hydrocarbon feed to the azeotroping column.

The bottoms from the azeotroping column which also amounted to approximately 50% by volume of the hydrocarbon feed to the column consisted essentially of ortho-xylene substantially completely separated from meta-xylene. This ortho-xylene after washing with water to remove small amounts of the azeotrope former had a gravity of 28.5° API, an index of refraction of 1.5055 and a melting point of −26° F.

Example 2

To 100 parts by volume of a mixture composed of equal parts by volume of ortho-, meta- and para-xylene was added approximately 40 parts by volume of methyl ether of ethylene glycol acetate and the resulting mixture was fractionated in an azeotroping column. The distillation was controlled so as to produce an overhead containing meta- and para-xylene together with substantially all of the added azeotrope former. This overhead mixture which was produced at a distillation temperature of approximately 282° F. at atmospheric pressure was condensed and extracted with water to remove methyl ether of ethylene glycol acetate leaving a mixture of meta- and para-xylene substantially completely separated from ortho-xylene. This product amounted to approximately 67% by volume of the hydrocarbon feed to the azeotroping column, had a gravity of 32.0° API and an index of refraction of 1.4677.

The bottoms from the azeotroping column, after washing with water to remove small amounts of methyl ether of ethylene glycol acetate, amounted to approximately 33% by volume of the hydrocarbon feed to the azeotroping column. This was substantially pure ortho-xylene having a gravity of 28.6° API, an index of refraction of 1.5055 and a melting point of −26° F.

Example 3

To 100 parts by volume of a complex hydrocarbon fraction having a boiling range of 280° F. to 295° F. and containing 50 parts by volume of non-aromatic hydrocarbons, 20 parts by volume of ortho-xylene, 15 parts by volume of meta-xylene and 15 parts by volume of para-xylene was added about 22 parts by volume of methyl ether of ethylene glycol acetate and the mixture fractionated in an azeotroping column. The distillation was controlled so as to distill an azeotrope containing the non-aromatic hydrocarbons together with substantially all of the added methyl ether of ethylene glycol acetate. The distillation was accomplished at a temperature in the order of 275° F. at atmospheric pressure. The azeotrope was washed with water to extract the azeotrope former leaving the non-aromatic hydrocarbon component which amounted to about 50% by volume of the hydrocarbon feed to the azeotroping column and was substantially free from aromatic hydrocarbons as was indicated by the facture was substantially completely insoluble in 98° sulfuric acid.

The bottoms from the azeotroping column amounting to approximately 50% by volume of the hydrocarbon feed to the column and consisting of mixed xylanes substantially completely separated from non-aromatic hydrocarbons was mixed with about 35% of its volume of methyl ether of ethylene glycol acetate and fractionated in a second azeotroping column. At a distillation temperature of approximately 282° F. and at atmospheric pressure an azeotrope containing meta- and para-xylene together with substantially all of the added azeotrope former was produced as an overhead. This distillate was condensed, washed with water to separate the methyl ether of ethylene glycol acetate and thereby obtained a mixture of substantially pure meta- and para-xylene amounting to approximately 30% by volume of the hydrocarbon feed to the first azeotropic distillation stage. This mixture of xylanes had a gravity of 32.0° API and an index of refraction of 1.4677.

The bottoms from the second azeotroping column, after washing with water to remove azeotrope former, amounting to approximately 20% by volume of the hydrocarbon feed to the first azeotroping column and consisting of ortho-xylene substantially completely separated from meta- and para-xylene, had a gravity of 28.6° API, an index of refraction of 1.5055 and a melting point of −26° F.

The foregoing description of our invention is not to be taken as limiting since many variations may be made by those skilled in the art without departing from the scope of the following claims or the spirit thereof.

We claim:

1. A process for the treatment of a xylene fraction containing non-aromatic hydrocarbons boiling in the same temperature range as said xylene fraction to separate therefrom the non-aromatic hydrocarbons, a fraction consisting of meta- and para-xylene and a fraction consisting of ortho-xylene which comprises distilling said xylene fraction in the presence of a sufficient amount of a compound having a boiling point within about 10° F. to 15° F. above to about 30° F. to 40° F. below the average boiling point of said xylene fraction and selected from the class of compounds consisting of mono-glycols, ethers of mono-glycols and esters of ethers of mono-glycols to vaporize the non-aromatic hydrocarbons together with said compound thereby leaving the xylanes substantially completely separated from the non-aromatic hydrocarbons in the residue and subsequently distilling said separated xylanes in the presence of a sufficient amount of said compound to vaporize the meta- and para-xylene together with said compound leaving ortho-xylene substantially completely separated from meta- and para-xylene in the residue.

2. A process for the treatment of a xylene fraction containing non-aromatic hydrocarbons boiling in the same temperature range as said xylene
fraction to separate therefrom the non-aromatic hydrocarbons, a fraction consisting of meta- and para-xylene and a fraction consisting of ortho-xylene which comprises distilling said xylene fraction in the presence of a sufficient amount of the mono-methyl ether of ethylene glycol to vaporize the non-aromatic hydrocarbons together with said compound thereby leaving the xylene substantially completely separated from the non-aromatic hydrocarbons boiling in the same temperature range as said xylene fraction to separate therefrom the non-aromatic hydrocarbons, a fraction consisting of meta- and para-xylene and a fraction consisting of ortho-xylene which comprises distilling said xylene fraction in the presence of a sufficient amount of methyl ether of ethylene glycol acetate to vaporize the meta- and para-xylene together with methyl ether of ethylene glycol acetate thereby leaving at least one isomer in the residue.

3. A process for the treatment of a xylene fraction containing non-aromatic hydrocarbons boiling in the same temperature range as said xylene fraction to separate therefrom the non-aromatic hydrocarbons, a fraction consisting of meta- and para-xylene and a fraction consisting of ortho-xylene which comprises distilling said xylene fraction in the presence of a sufficient amount of methyl ether of ethylene glycol acetate to vaporize the meta- and para-xylene together with methyl ether of ethylene glycol acetate thereby leaving ortho-xylene substantially completely separated from meta- and para-xylene in the residue.

4. A process for the treatment of a xylene fraction containing non-aromatic hydrocarbons boiling in the same temperature range as said xylene fraction to separate therefrom the non-aromatic hydrocarbons, a fraction consisting of meta- and para-xylene and a fraction consisting of ortho-xylene which comprises distilling said xylene fraction in the presence of a sufficient amount of a compound having a boiling point to about 10° F. to 15° F. below the average boiling point of said xylene fraction and selected from the class of compounds consisting of mono-glycols, ethers of mono-glycols and esters of ethers of mono-glycols to vaporize the non-aromatic hydrocarbons and the meta- and para-xylene together with said compound thereby leaving ortho-xylene substantially completely separated from non-aromatic hydrocarbons and from meta- and para-xylene in the residue and subsequently distilling said vaporized non-aromatic hydrocarbons and meta- and para-xylene together with the mono-methyl ether of ethylene glycol to vaporize said non-aromatic hydrocarbons together with the mono-methyl ether of ethylene glycol leaving meta- and para-xylene substantially completely separated from non-aromatic hydrocarbons in the residue.

5. A process for the treatment of a xylene fraction containing non-aromatic hydrocarbons boiling in the same temperature range as said xylene fraction to separate therefrom the non-aromatic hydrocarbons, a fraction consisting of meta- and para-xylene and a fraction consisting of ortho-xylene which comprises distilling said xylene fraction in the presence of a sufficient amount of the mono-methyl ether of ethylene glycol to vaporize the non-aromatic hydrocarbons and the meta- and para-xylene together with the mono-methyl ether of ethylene glycol leaving ortho-xylene substantially completely separated from non-aromatic hydrocarbons and from meta- and para-xylene in the residue.

6. A process for the treatment of an aromatic hydrocarbon fraction composed of the isomeric xylenes ortho-meta- and para-xylene to separate at least one isomer from other isomers which comprises distilling said aromatic hydrocarbon fraction in the presence of a sufficient amount of methyl ether of ethylene glycol acetate to vaporize at least one isomer together with methyl ether of ethylene glycol acetate thereby leaving at least one isomer in the residue.

7. A process for the treatment of an aromatic hydrocarbon fraction composed of the isomeric xylenes ortho-meta- and para-xylene and non-aromatic hydrocarbons boiling in the same temperature range as said isomeric xylenes comprising distilling said aromatic hydrocarbon fraction in the presence of a sufficient amount of methyl ether of ethylene glycol acetate to vaporize the non-aromatic hydrocarbons together with methyl ether of ethylene glycol acetate thereby leaving the isomeric xylenes in the residue substantially completely separated from non-aromatic hydrocarbons and subsequently distilling said residue comprising isomeric xylenes in the presence of a sufficient amount of methyl ether of ethylene glycol acetate to vaporize at least one of the xylene isomers together with methyl ether of ethylene glycol acetate thereby leaving at least one xylene isomer in the residue.

8. A process for the treatment of an aromatic hydrocarbon fraction composed of the xylene isomers, ortho-, meta-, and para-xylenes, to separate at least one isomer from other isomers which comprises distilling said aromatic hydrocarbon fraction in the presence of a sufficient amount of a compound selected from the class of compounds consisting of mono-glycols, ethers of mono-glycols and esters of ethers of mono-glycols to vaporize at least one isomer together with said compound thereby leaving at least one isomer in the residue, said compound having a boiling point within about 10° F. to 15° F. above to about 30° F. to 40° F. below the average boiling point of said aromatic hydrocarbon fraction.

9. A process for the treatment of an aromatic hydrocarbon fraction composed of ortho- and para-xylene to separate the ortho-xylene from meta-xylene which comprises distilling said aromatic hydrocarbon fraction in the presence of a sufficient amount of a compound selected from the class of compounds consisting of mono-glycols, ethers of mono-glycols and esters of ethers of mono-glycols to vaporize the meta-xylene together with said compound thereby leaving ortho-xylene in the residue, said compound having a boiling point within about 10° F. to 15° F. above to about 30° F. to 40° F. below the average boiling point of said aromatic hydrocarbon fraction.

GEORGE R. LAKE.
JOSEPHINE M. MCDOWELL.

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