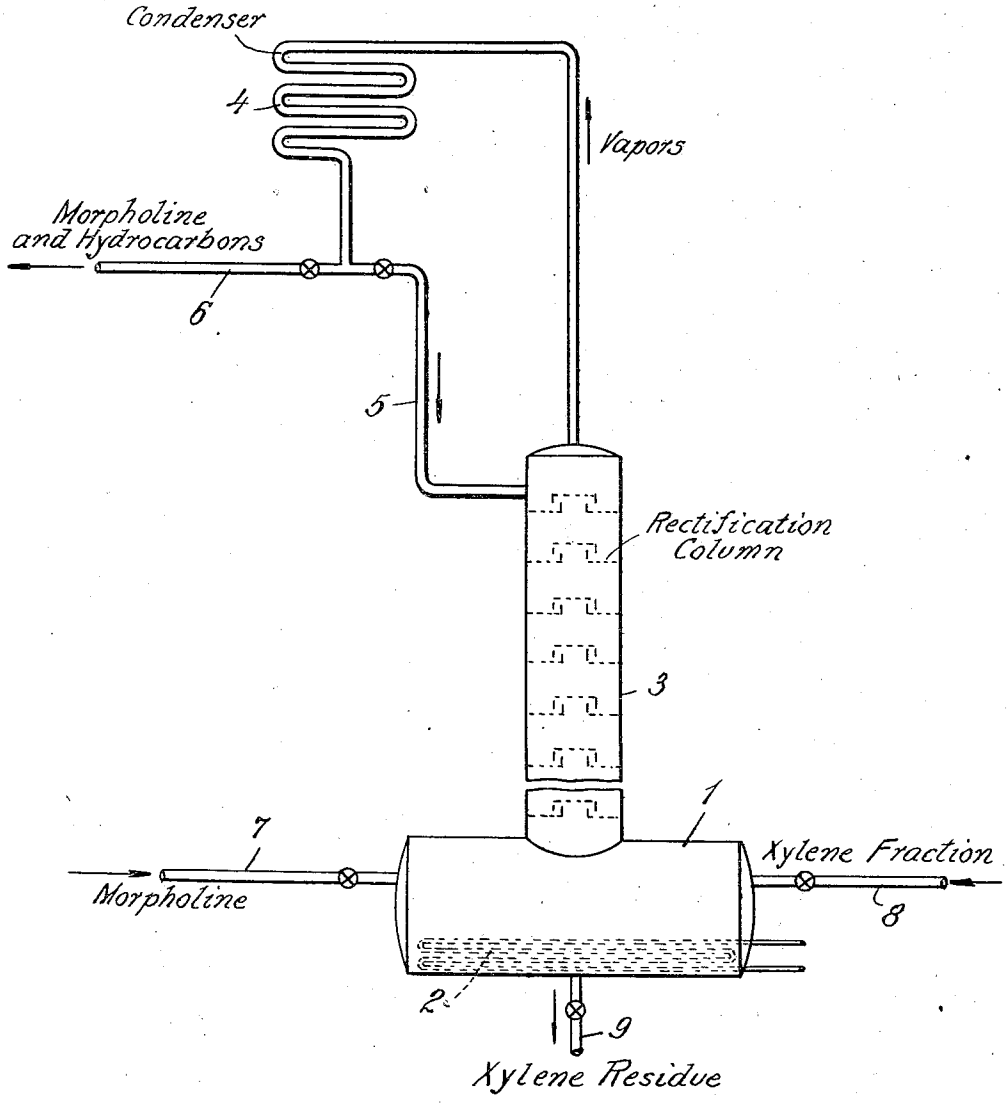
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RECOVERY OF XYLENE FROM OILS CONTAINING THE SAME

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RECOVERY OF XYLENE FROM OILS CONTAINING THE SAME

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This invention relates to a process for producing concentrated xylene products from mixtures containing xylene and other hydrocarbons.

Xylene oils as produced and marketed contain as their characteristic ingredients the aromatic hydrocarbons of the benzene series having boiling points similar to the boiling points of the three xylene hydrocarbons boiling at 138° C., 138.8° C. and 144° C. For example, the specifications for "10° xylene" as given in The Barrett Company's "Specifications for Coke Oven Light Oil Distillates" call for a material having a specific gravity at 15.5° C. between .860 and .870; distilling from start to dry within 10° C., initial or first drop starting at not below 135° C.; and all distilling (dry point) at not above 145° C. The specifications for "nitration xylene" call for a material having a specific gravity at 15.5° C. between .865 and .870; distilling from start to dry within 3° C.; initial (or first drop) starting at not below 137.2° C.; all distilling (dry point) at not above 140.5° C.; and the paraffin content not exceeding 4.0%, preferably not more than 0.5%. In this specification and the appended claims the term "xylene" is used to refer to the several aromatic hydrocarbons of the benzene series having boiling points above that of toluene and below that of cumene, which are the characteristic aromatic constituents of the foregoing and other commercial xylene oils.

The term "xylene fraction" is used broadly to designate any oil fraction containing both xylene and a mixture of non-aromatic hydrocarbons which, under the conditions maintained in direct distillation processes as commonly used for distilling oils, distill from the fraction within the same temperature range as does the xylene.

Numerous hydrocarbon oils are known which contain xylenes in varying proportions. For example, gasoline fractions obtained by the distillation of certain types of petroleum or from the products of aromatizing processes such as the catalytic reformation processes, frequently contain substantial proportions of xylene, although mainly consisting of other hydrocarbons. Oils of petroleum origin having a considerable content of aromatics, including xylene, may be treated by well known selective solvent processes to produce fractions rich in aromatics; for example, extraction of suitable fractions of such petroleum oils with sulfur dioxide may yield fractions of increased xylene content. In such cases xylene is accompanied by a mixture of non-aromatic hydrocarbons which may be largely paraffinic, naphthenic or olefinic in character. A considerable portion of these hydrocarbons cannot be completely separated from the xylene by direct fractional distillation because of the closeness of their boiling points to that of xylene or because they form constant boiling mixtures with xylene. Furthermore, while ordinarily xylene may be separated by direct fractional distillation from light oils produced by the gasification of coal, in some cases the xylene is accompanied by difficultly separable non-aromatic hydrocarbons of the same general character as described, owing to carbonization conditions, type of coal used or other special circumstances. Also synthetic hydrocarbon gas mixtures produced by various catalytic processes may contain xylene which, when recovered, is accompanied by similar difficultly separable constituents.

By fractional distillation of the above-described oils containing xylene, fractions of increased xylene content may be obtained. The xylene fractions, however, will still contain large amounts of other constituents of the oil having boiling points in the neighborhood of the boiling point of xylene or forming mixtures of constant boiling points in the range of temperatures at which xylene distills from the oil. Hereafter, in this specification and in the appended claims, these other constituents of the oil are denoted by the term "like-boiling, non-aromatic hydrocarbons." The fact that oils containing xylene have generally a relatively low content of xylene makes it particularly difficult to recover by fractional distillation or selective solvent extraction or a combination of both of these procedures a xylene product of a high degree of purity. Accordingly, recovery of xylene of a relatively high purity from these sources presents a difficult industrial problem.

For many purposes to which xylene is put, it is desirable to use as pure a material as may be economically available. Direct fractional distillation, because of the difficulties pointed out above, will not effect a recovery of pure xylene from oils such as enumerated and in many cases will not give fractions of suitably high xylene content or free from materials which even in small concentrations adversely affect chemical treatment of the xylene or the products produced therefrom.

It is an object of my invention to provide a process whereby xylene products of any desired degree of purity may be recovered from oils containing xylene and a mixture of like-boiling non-aromatic hydrocarbons which distill out over the

same temperature range as the xylene, by azeotropic distillation with morpholine.

In using my invention for the treatment of an oil fraction containing xylene and like-boiling, non-aromatic hydrocarbons, such as paraffins, naphthenes or olefines which distill from the oil fraction in the same temperature range as the xylene, I prefer that the xylene oil fraction be one from which hydrocarbons boiling at temperatures materially below 136° C. and materially above 144° C. have been excluded. For example, I prefer to treat a fraction boiling within the range 125° C. to 150° C. However, xylene fractions having even a wider boiling range may be treated by the process of my invention.

I have discovered that when a xylene fraction of the type described above is subjected to azeotropic distillation in the presence of morpholine the like-boiling, non-aromatic hydrocarbons, which in the absence of the morpholine distill from the xylene fraction in the same temperature range as the xylene and hence it is not practicable to separate them from the xylene by fractional distillation, in the presence of morpholine may be distilled from the xylene fraction to leave a residue containing xylene of any desired purity with respect to its content of these non-aromatic hydrocarbons. On fractionally distilling a mixture of the morpholine with a xylene fraction, the material first to distill over is a mixture of low-boiling azeotropes consisting chiefly of morpholine and non-aromatic hydrocarbons. On continued distillation, the non-aromatic hydrocarbons are selectively removed and a residue enriched in xylene is obtained. The distillate will contain morpholine and the non-aromatic hydrocarbons distilled from the xylene fraction. It may contain xylene, the amount depending on the effectiveness of the fractionation of the vapors evolved in the distillation.

The azeotropic distillation should be carried out under substantially anhydrous conditions. By washing the distillate with water the morpholine in the distillate may be separated in an aqueous phase from an oil phase containing the hydrocarbons carried over into the distillate. The aqueous phase may be treated to recover substantially anhydrous morpholine therefrom for return to the distillation and reuse in the azeotropic distillation of additional xylene fraction. Morpholine which may be left in the residue similarly may be removed by washing the residue with water. The oil phase thus obtained, containing xylene which has been separated from non-aromatic hydrocarbons in the original xylene fraction, may then be given a conventional acid wash and caustic soda wash and redistillation to further purify the xylene. In washing the distillate or residue with water to remove morpholine, an acid may be added to the water to increase the effectiveness with which the morpholine is removed from the oil.

The azeotropic distillation in the presence of the morpholine should be carried out with effective rectification of the vapors. Sufficient morpholine should be present to carry over as azeotropes the non-aromatic hydrocarbons so that the residue containing xylene is freed to the desired degree of these non-aromatic hydrocarbons. The quantity of morpholine thus required will, of course, depend upon the amount of xylene fraction distilled, the quantity of non-aromatic hydrocarbons contained therein, etc. Any excess of morpholine present will not materially interfere with the separation of the non-aromatic hydrocarbons from the xylene, although it is obvious that a large excess is undesirable in that it requires removal and recovery of the morpholine from the xylene product of the process.

As pointed out above, it is highly desirable to recover from xylene fractions a relatively pure xylene product and the process of my invention permits of obtaining an enriched xylene residue of any desired purity with respect to hydrocarbons which, in the absence of an azeotropic agent, distill from the xylene fraction in the same temperature range as the xylene. My invention contemplates, therefore, continuing the azeotropic distillation of the xylene fraction under the conditions described above until the distillation residue is enriched to a desired extent in xylene with respect to other like-boiling hydrocarbons; i. e., hydrocarbons which will distill from the xylene fraction, in the absence of an azeotropic agent, in the same temperature range as the xylene distills therefrom. In practicing my invention the rectification preferably is controlled to obtain a xylene residue which contains at least 90 parts by weight of xylene to 10 parts of like-boiling, non-xylene hydrocarbons.

The xylene fraction treated in accordance with my invention preferably will contain little, if any, hydrocarbons distilling from the hydrocarbon-xylene fraction at temperatures materially above those at which xylene distills therefrom. On the other hand, high boiling materials may be left with the xylene residue at the conclusion of the azeotropic distillation of the xylene fraction under the conditions set forth above to separate the xylene from the hydrocarbons of similar boiling range. Once this separation has been effected, the xylene may be separated from the high boiling hydrocarbons by fractional distillation in the absence of an azeotropic agent. Whether or not high boiling constituents should be left in the xylene fraction to be azeotropically distilled or whether, if left in the xylene fraction, they will remain in the residue after azeotropic distillation, depends upon a number of factors, among which their boiling range and chemical characteristics are important. If the high boiling constituents form azeotropes with the agent used which have boiling points close to the temperature at which the azeotrope of xylene distills over, it is preferable to separate such high boiling constituents from the xylene fraction by a direct fractional distillation before azeotropically distilling the xylene fraction.

When pure xylene is to be recovered it is preferred the xylene fraction subjected to azeotropic distillation in accordance with my invention be a fraction boiling in the range of 125° C. to 150° C. Such a fraction may be azeotropically distilled by my process and pure xylene obtained with a relatively small quantity of azeotropic agent present during the distillation. Pure xylene may be obtained by distilling with an azeotropic agent a wider boiling xylene fraction but the quantity of azeotropic agent present in the distillation of the xylene fraction of wider boiling range must be substantially increased as compared with the quantity which suffices for distilling the fraction of the narrower boiling range.

Xylene of high purity is desired for nitration and other purposes and the process of my invention provides a method whereby a pure xylene of nitration grade may be economically recovered from xylene oils. The invention, however, is not

limited thereto. Xylene products of lower purity than nitration grade xylene are industrially used for various purposes, e. g., as solvents. The process of my invention may be used advantageously for recovering such products from hydrocarbon oils of lower xylene content. My process is particularly advantageous when the xylene is to be separated from most of the like-boiling, non-aromatic hydrocarbons present in an oil fraction together with xylene, e. g., when a product is to be obtained containing xylene and no more than 10 parts by weight of like-boiling, non-aromatic hydrocarbons for every 90 parts by weight of xylene.

My invention will be more particularly described and illustrated by the following example of a process for the azeotropic distillation of a xylene fraction in the presence of morpholine.

The apparatus used for carrying out the process of this example, diagrammatically illustrated in the accompanying drawing, comprised a still 1 with heater 2 and rectification column 3 of conventional design, the rectification column containing sufficient liquid-vapor contact elements for it to effectively fractionate the vapors evolved in the still and passed therefrom through the rectification column. A condenser 4 was provided to which the vapors from the top of the column were led and in which they were cooled and condensed. A pipe 5 was provided for returning condensate from the condenser to the top of the rectification column to serve as reflux for the column. A second pipe 6 was also provided for drawing off from the condenser a portion of the condensate formed therein. Pipes 7 and 8 are provided for the introduction of liquids into still 1. A pipe 9 serves for withdrawal of residue from this still.

The above-described apparatus was employed for the distillation of a xylene fraction having a boiling range of about 127° C. to about 150° C. and containing 59% by volume of xylene.

100 volumes of this xylene fraction and 100 volumes of morpholine were charged into the still of the apparatus described above. This charge was boiled in the still and the vapors passing therefrom to the fractionating column were rectified in this column. The vapors leaving the top of the column were condensed, a part of the condensate was withdrawn as distillate through pipe 6, and the remainder of the condensate returned as reflux through pipe 5 to the top of the fractionation column. Distillation started with the temperature of the vapors at the top of the fractionation column at about 107° C. and, as the distillation preceeded, the temperature rose to 127.8° C. After taking off through pipe 6 a total of 125 volumes of distillate and with the temperature at the top of the column at 127.8° C., a residue of 74 volumes was left in still 1. This residue was washed with water. The oil which separated from the aqueous solution of morpholine thus extracted from the residue, amounting to 51 volumes, was analyzed by xylene. This oil was found to contain 93% xylene by the specific dispersion method for its analysis described in Industrial & Engineering Chemistry, Analytical Edition, vol. 11, page 614, November 15, 1939.

While the example described above employs a batch operation for the distillation of the xylene fraction, this distillation may be carried out continuously. For example, morpholine and xylene fraction may be continuously supplied to a column still in which the xylene is concentrated, and, flowing to the bottom of the still, is continuously withdrawn therefrom. The azeotropes of morpholine and non-aromatic hydrocarbons are continuously vaporized and withdrawn as distillate from the top of the distillation column. Sufficient morpholine should be supplied to carry over as distillate all of the hydrocarbons to be distilled from the xylene fraction and separated from the xylene. By observation of the vapor temperatures at a suitable point in the vapor rectification column, one may ascertain whether adequate morpholine is present. Whenever these vapor temperatures tend to exceed about 128° C. before the xylene has been separated to the desired degree from the like-boiling, non-aromatic hydrocarbons, by supplying additional morpholine to the still or rectification column the desired separation of the xylene and like-boiling, non-aromatic hydrocarbons may be accomplished. This point of temperature observation in the apparatus in which the above example of the process was carried out, is preferably the top of the rectification column. One skilled in the art of fractional distillation will recognize for any particular type of apparatus suitable points for this temperature control.

While in the example given the xylene has been recovered as distillation residue, the distillation may be continued after the removal of non-xylene constituents so that an enriched xylene product is recovered as overhead. The distillate may be treated to recover the xylene product separate from any morpholine taken over in distilling off the enriched xylene product. Furthermore, the distillation may be carried out as a continuous procedure instead of the batch procedure described above. In a continuously operating process enriched xylene products may be taken off from the bottom of the still or as one or more side streams from the fractionation column below the point of feeding the xylene fraction thereto. These modifications are within the scope of my invention.

In this specification I have described the azeotropic distillation as being carried out under substantially atmospheric pressure. The temperatures as given herein are corrected temperatures for 1 atmosphere absolute (760 mm. of Hg). When carried out under pressures other than atmospheric, the temperature conditions will differ from those given. In any given case, however, the temperatures will correspond to the change in boiling points of the materials due to the difference in pressure.

I claim:

1. The process for the recovery of xylene from a xylene fraction containing the same and containing a mixture of like-boiling, non-aromatic hydrocarbons which comprises distilling said xylene fraction and rectifying the distilled vapors in the presence of substantially anhydrous morpholine in an amount which selectively carries over as distillate said like-boiling, non-aromatic hydrocarbons and leaves a hydrocarbon residue of the distillation enriched in xylene.

2. The process for the recovery of xylene which comprises distilling a xylene oil fraction boiling within the range 125° C. to 150° C. and containing xylene and a mixture of like-boiling non-aromatic hydrocarbons and rectifying the distilled vapors in the presence of a quantity of substantially anhydrous morpholine which selectively carries over as distillate said like-boiling, non-aromatic hydrocarbons and leaves a

hydrocarbon residue of the distillation enriched in xylene.

3. The process for the recovery of xylene from a xylene fraction containing the same and containing a mixture of like-boiling, non-aromatic hydrocarbons which comprises distilling said xylene fraction and rectifying the distilled vapors in the presence of substantially anhydrous morpholine, said morpholine being present in amount such that at a point in the fractionation of the vapors evolved in distilling the xylene fraction the temperature does not exceed about 128° C. until said like-boiling, non-aromatic hydrocarbons have been vaporized leaving a hydrocarbon residue of the distillation containing xylene and no more than 10 parts by weight of like-boiling, non-aromatic hydrocarbons for every 90 parts by weight of xylene.

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