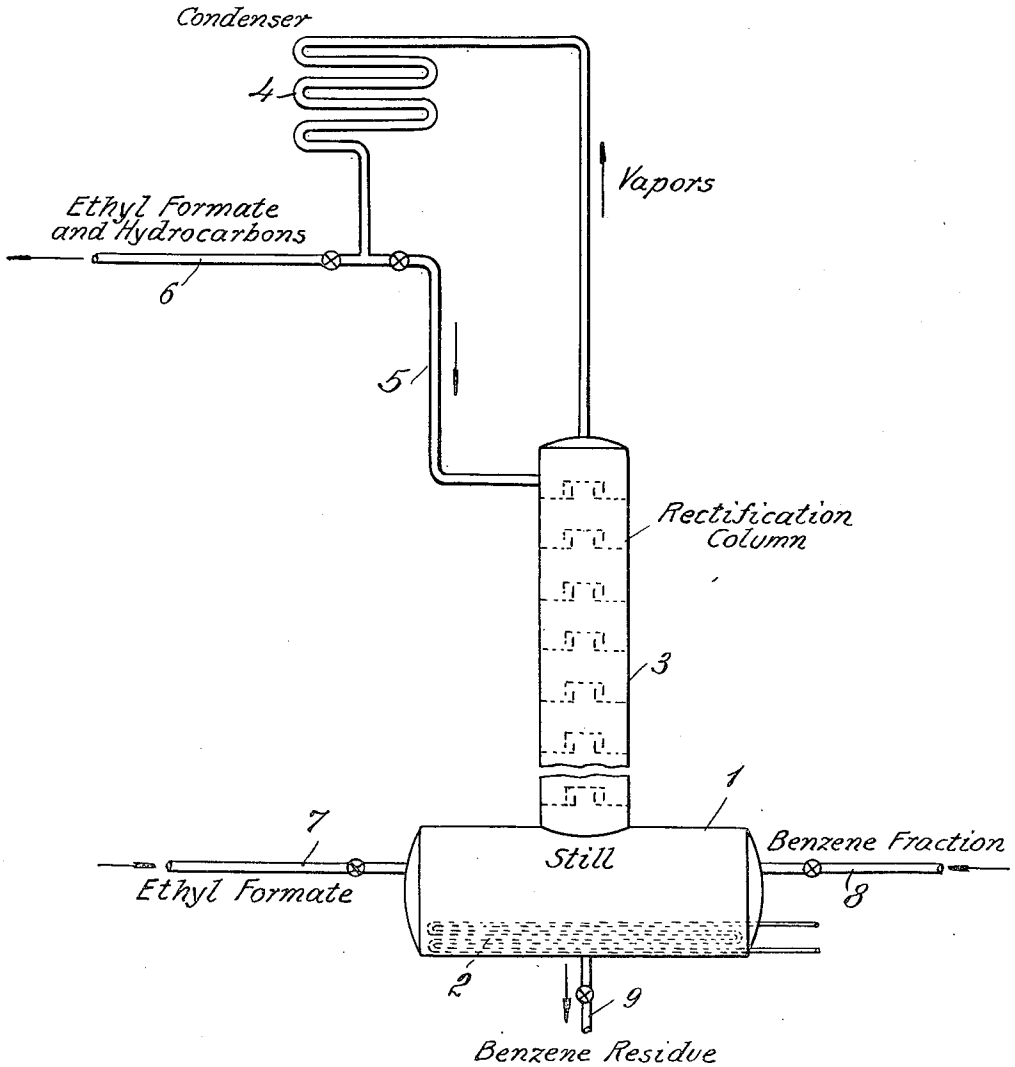
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DISTILLATION OF BENZENE FRACTIONS

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DISTILLATION OF BENZENE FRACTIONS

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This invention relates to a process for recovering benzene from mixtures containing it and other hydrocarbons.

Numerous hydrocarbon oils are known which contain benzene in varying proportions. Gasoline fractions obtained by the distillation of certain types of petroleum or recovered from the products of catalytic reformation processes, frequently contain substantial proportions of benzene, although mainly consisting of other hydrocarbons. Oils of petroleum origin having a considerable content of aromatics, including benzene, 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 high benzene content. In such cases benzene is accompanied by non-aromatic hydrocarbons which may be largely olefinic, paraffinic, or naphthenic in character. A considerable proportion of these hydrocarbons cannot be completely separated from the benzene by direct fractional distillation because of the closeness of their boiling points to that of benzene or because they form constant boiling mixtures with benzene. Furthermore, while ordinarily benzene is readily separable by direct fractional distillation from light oils produced by the gasification of coal, in some cases the benzene 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 oil mixtures produced by various catalytic processes may contain benzene which, when recovered, is accompanied by similar difficultly separable constituents.

By fractional distillation of these oils containing benzene, fractions relatively high in benzene content may be obtained. These benzene fractions, however, will still contain large amounts of the other constituents of the oil having boiling points in the neighborhood of the boiling point of benzene or forming mixtures of constant boiling points in the range of temperatures at which benzene distills from the oil. (In this specification and claims, I refer to such difficultly separable constituents, which distill out over the same temperature range as the benzene and from which the benzene is not separable by a conventional distillation, as "like-boiling, non-aromatic hydrocarbons.") Accordingly, recovery of benzene of a relatively high purity from these sources presents a difficult problem of great industrial importance.

For many purposes to which benzene is put, it is desirable to use as pure a material as may be economically available. For example, benzene is used for the production of pharmaceutical chemicals, dyes and synthetic phenol. For these purposes a pure benzene is preferred. Direct fractional distillation, because of the difficulties pointed out above, will not effect a recovery of pure benzene separate from like-boiling, non-aromatic hydrocarbons such as enumerated, and in many cases will not give fractions of suitably high benzene content or free from materials which even in small concentrations adversely affect the processes by which the benzene is treated or the products produced therefrom.

It is an object of my invention to provide a process whereby benzene of any desired degree of purity may be recovered from hydrocarbon oil mixtures comprising non-aromatic hydrocarbons from which the benzene is not separable by a conventional distillation.

In using my invention for the treatment of an oil in which the benzene concentration is low or when the oil is one containing materials of wide boiling range, I prefer first to fractionally distill the oil to recover therefrom an enriched benzene fraction. Although benzene fractions having an end boiling point substantially above the boiling point of benzene (e. g., a boiling point up to about 85° C.) may be azeotropically distilled in the manner hereinafter described, I prefer the benzene fraction treated by my process to be one having an end boiling point substantially corresponding to the boiling point of pure benzene, e. g., an end boiling point of about 80° C. Further, for the reasons which will be more specifically pointed out below, I prefer that a benzene fraction recovered by a preliminary distillation of a crude benzene oil be so cut as to exclude therefrom the forerunnings which do not contain substantial proportions of benzene; for example, to exclude substantial proportions of oils distilling below 65° C.

In this specification and claims, the term "benzene fraction" is used broadly to designate any oil fraction containing both benzene and other 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 benzene.

I have discovered that benzene may be separated from a benzene fraction such as described

above by subjecting it to azeotropic distillation in the presence of ethyl formate. The non-aromatic hydrocarbons, which in the absence of the ethyl formate distill from the benzene fraction in the same temperature range as the benzene and hence are not separable therefrom by direct fractional distillation, may be distilled from the benzene fraction in the presence of the ethyl formate to leave a residue containing benzene of any desired purity with respect to its content of these like-boiling, non-aromatic hydrocarbons. On fractionally distilling a mixture of the ethyl formate with a benzene fraction, the material first to distill over is a mixture of low-boiling azeotropes consisting chiefly of ethyl formate and non-aromatic hydrocarbons (together with water if present). On continued distillation, the non-aromatic hydrocarbons are selectively removed and a residue enriched in benzene is obtained. The distillate will contain ethyl formate and the non-aromatic hydrocarbons distilled from the benzene fraction. It may also contain some benzene carried over in the distillation.

The azeotropic distillation may be carried out either under anhydrous conditions or in the presence of substantial quantities of water. When water is present a part or all of the water, depending upon the quantity present, is carried over in the distillate as an azeotrope of the water, ethyl formate and non-aromatic hydrocarbons. Water appears to aid in the production of a pure benzene product. By washing the distillate with an aqueous solution of sodium acid sulfite the ethyl formate 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 ethyl formate therefrom for return to the distillation and reuse in the azeotropic distillation of additional benzene fraction. Ethyl formate which may be left in the residue may be removed by washing the residue with sodium acid sulfite solution. The oil phase thus obtained, containing benzene which has been separated from non-aromatic hydrocarbons in the original benzene fraction, may then be washed with caustic soda solution to remove sulfur dioxide and, if desired, may be given a conventional acid wash and redistillation to further purify the benzene.

My invention comprises, therefore, azeotropically distilling in the presence of ethyl formate a benzene fraction containing non-aromatic hydrocarbons which distill from said fraction in the absence of an azeotropic agent, in the same temperature range as the benzene, e. g., hydrocarbons which normally boil from mixtures thereof with benzene between 70° and 80° C. and from which the benzene is not readily separable by conventional distillation.

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

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

The benzene fraction treated in accordance with my invention preferably will contain little, if any, hydrocarbons distilling from the hydrocarbon-benzene fraction at temperatures materially above those at which benzene distills therefrom. On the other hand, high boiling materials may be left with the benzene residue at the conclusion of the azeotropic distillation of the benzene fraction under the conditions set forth above to separate the benzene from the hydrocarbons of similar boiling range. Once this separation has been effected, the benzene 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 benzene fraction to be azeotropically distilled or whether, if left in the benzene 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 temperatures at which benzene distills over, it is preferable to separate such high boiling constituents from the benzene fraction by a direct fractional distillation before azeotropically distilling the benzene fraction.

When pure benzene is to be recovered it is preferred the benzene fraction subjected to azeotropic distillation in accordance with my invention be a fraction boiling in the range of 65° C. to 80° C. Such a fraction may be azeotropically distilled by my process and pure benzene obtained with a relatively small quantity of azeotropic agent present during the distillation. Pure benzene may be obtained by distilling with an azeotropic agent a wider boiling benzene fraction but the quantity of azeotropic agent present in the distillation of the benzene 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.

Benzene of high purity is desired for nitration and other purposes and the process of my invention provides a method whereby a pure benzene of nitration grade may be economically recovered from benzene oils. The invention, however, is

not limited thereto. Benzene products of lower purity than nitration grade benzene 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 benzene content. My process is particularly advantageous when the benzene is to be separated from most of the like-boiling, non-aromatic hydrocarbons present in an oil fraction together with benzene, e. g., when a product is to be obtained containing benzene and no more than 10 parts by weight of like-boiling, non-aromatic hydrocarbons for every 90 parts by weight of benzene.

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

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. 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 benzene fraction having a boiling range of about 75° C. to about 80° C. and containing 69% by volume of benzene, the remainder principally consisting of like-boiling paraffins.

100 volumes of this benzene fraction, 100 volumes of ethyl formate, and 10 volumes of water 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 46° C. As the distillation proceeded, the temperature rose quickly to 50° C. and then gradually rose to about 52.5° C. At this stage of the process the non-aromatic hydrocarbons were largely distilled over as azeotropes with the ethyl formate. As the distillation proceeded, the non-aromatic hydrocarbons became exhausted and the temperature then rapidly rose to 63.0° C., at which point the distillation was discontinued. A total of 125 volumes of distillate was taken off through pipe 6. A residue of 68 volumes was left in still 1. This residue was washed with a solution of sodium acid sulfite, followed by washing with caustic soda solution and the oil separated from the aqueous solutions, amounting to 54 volumes, was analyzed for benzene. This oil was found to contain 98% benzene by the specific dispersion method for its analysis described in Industrial & Engineering Chemistry, analytical edition, vol. 11, page 614, November 15, 1939. By the Kattwinkel method of analysis, Brennstoff-Chem., vol. 8, page 353 (1927), it was shown as 100% benzene.

The process of this example may be modified to carry out the distillation of the benzene fraction and ethyl formate under substantially anhydrous conditions; i. e., without adding to the still charge in the above example the 10 volumes of water. Under these conditions distillation started at about 47° C. The temperature rose quickly to about 52.8° C. and then gradually rose to about 53.9° C. At this stage the non-aromatic hydrocarbons were largely distilled over as azeotropes with the ethyl formate. The temperature then quickly rose to 79.8° C., at which point the distillation was discontinued. A total of 125 volumes of distillate was thus taken off through pipe 6. The residue in the still amounted to 68 volumes. After washing this residue with sodium acid sulfite and caustic soda solutions, analysis of the oil thus recovered showed it contained at least 93% benzene.

While the example described above employs a batch operation for the distillation of the benzene fraction, this distillation may be carried out continuously. For example, ethyl formate and benzene fraction may be continuously supplied to a column still in which the benzene is concentrated and, flowing to the bottom of the still, is continuously withdrawn therefrom. The azeotropes of ethyl formate and non-aromatic hydrocarbons are continuously vaporized and withdrawn as distillate from the top of the distillation column. Sufficient ethyl formate should be supplied to carry over as distillate all of the hydrocarbons to be distilled from the benzene fraction and separated from the benzene. By observation of the vapor temperatures at a suitable point in the vapor rectification column, one may ascertain whether adequate ethyl formate is present. Whenever these vapor temperatures tend to exceed about 54° C., either under anhydrous conditions or when water is present, before the benzene has been separated to the desired degree from the like-boiling, non-aromatic hydrocarbons, by supplying additional ethyl formate (with or without water) to the still or rectification column the desired separation of the benzene 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 benzene has been recovered as distillation residue, the distillation may be continued after the removal of non-benzene constituents so that an enriched benzene product is recovered as overhead. The distillate may be treated to recover the benzene product separate from any ethyl formate taken over in distilling off the enriched benzene 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 benzene 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 benzene fraction thereto. These modifications are within the scope of my invention.

In this specification I have described the azeo-

tropic 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 benzene from a benzene fraction containing the same and containing a mixture of like-boiling, non-aromatic hydrocarbons which comprises distilling said benzene fraction and rectifying the distilled vapors in the presence of ethyl formate 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 benzene.

2. The process for the recovery of benzene which comprises distilling a benzene oil fraction boiling within the range 65° C. to 80° C. and containing benzene and a mixture of like-boiling, non-aromatic hydrocarbons and rectifying the distilled vapors in the presence of a quantity of ethyl formate which selectively carries over as distillate said like-boiling, non-aromatic hydrocarbons and leaves a hydrocarbon residue of the distillation enriched in benzene.

3. The process for the recovery of benzene from a benzene fraction containing the same and containing a mixture of like-boiling, non-aromatic hydrocarbons which comprises distilling said benzene fraction and rectifying the distilled vapors in the presence of ethyl formate and water, said ethyl formate being present 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 benzene.

4. The process for the recovery of benzene from a benzene fraction containing the same and containing a mixture of like-boiling, non-aromatic hydrocarbons which comprises distilling said benzene fraction and rectifying the distilled vapors in the presence of ethyl formate, said ethyl formate being present in amount such that at a point in the fractionation of the vapors evolved in distilling the benzene fraction the temperatures does not exceed about 54° C. until said like-boiling, non-aromatic hydrocarbons have been vaporized leaving a hydrocarbon residue of the distillation containing benzene and no more than 10 parts by weight of like-boiling, non-aromatic hydrocarbons for every 90 parts by weight of benzene.

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