DISTILLATION OF BENZENE FRACTIONS WITH BUTYRALDEHYDE

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INVENTOR
Richard B. Greenburg

BY
Charleew Brown
ATTORNEY
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 difficulty 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 similarly difficulty 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 difficulty 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, distills 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 butyraldehyde, either normal- or iso-butyraldehyde. The non-aromatic hydrocarbons which in the absence of the butyraldehyde 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 butyraldehyde. 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 butyraldehyde with a benzene fraction, the material first to distill over is a mixture of low-boiling azeotrope consisting chiefly of butyraldehyde 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 butyraldehyde and the non-aromatic hydrocarbons distilled from the benzene fraction. It may contain benzene, the amount depending on the effectiveness of fractionation.

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, butyraldehyde and nonaromatic hydrocarbons. Water appears to aid in the production of a pure benzene product. By washing the distillate with an aqueous solution of sodium sulfite, the butyraldehyde 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 the butyraldehyde therefrom for return to the distillation and reuse in the azeotropic distillation of additional benzene fraction. Butyraldehyde 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 any sulfur dioxide present 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 butyraldehyde 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 76° and 80° C. and from which the benzene is not readily separable by conventional distillation.

The azeotropic distillation in the presence of the butyraldehyde should be carried out with effective rectification of the vapors. Sufficient butyraldehyde 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 butyraldehyde 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 butyraldehyde 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 butyraldehyde 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 the non-aromatic 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 benzene 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 distils therefrom. In practicing my invention the rectification 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, a small amount of 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 effectuated, 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 are azeotropes with the agent used which have boiling points close to the temperature 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 within 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 nitrobenzene grade may be conveniently 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-bolling, non-romatic 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-bolling, non-romatic hydrocarbons for every 90 parts by weight of benzene.

My invention will be more particularly described and illustrated by the following examples of processes for the azeotropic distillation of a benzene fraction in the presence of butyraldehyde.

The apparatus used for carrying out the process of these examples, diagrammatically illustrated in the accompanying drawing, comprised a still 1 with heater 2 and rectification column 3 of conventional design, the rectification column containing a sufficient contact element 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 draining 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.

Example 1.—The above-described apparatus was employed for the distillation of a benzene fraction having a bolling range of about 75°C to about 80°C and containing 90% by volume of benzene, the remainder principally consisting of like-bolling paraffins. 100 volumes of this benzene fraction, 100 volumes of N-butyraldehyde, 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 through 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 vapor at the top of the fractionation column at about 57°C and, as the distillation proceeded, the temperature rose to 67.4°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 67.4°C, a residue of 76 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 solution was analyzed for benzene. This oil was found to contain 93% benzene by the specific dispersion method and 100% benzene by the Kattwinkel method. The procedure of this Example 2 may likewise be modified to carry out the distillation of the benzene fraction under substantially anhydrous conditions. Thus, a charge of 100 volumes of the benzene fraction and 100 volumes of isobutyraldehyde introduced into still 1 was distilled. Distillation started with the temperature of the vapor at the top of the fractionation column at about 50°C and, as the distillation proceeded, the temperature rose until, when 125 volumes distillate had been taken off through pipe 6, the temperature at the top of the column were at 78.9°C. The residue in the still, amounting to 63 volumes, was washed with sodium acid sulfite and caustic soda solutions to give an oil which analyzed at least 93% benzene.

While both of the examples described above employ a batch operation for the distillation of the benzene fraction, this distillation may be carried out continuously. For example, butyraldehyde 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 butyraldehyde and non-romatic hydrocarbons are continuously vaporized and withdrawn as distillate from the top of the distillation column. Sufficient butyraldehyde 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 butyraldehyde is present. Whenever these vapor temperatures tend to exceed 75°C for normal-butyraldehyde and 64°C for isobutyraldehyde under anhydrous conditions, or 67.4°C for normal-butyraldehyde and 60°C for isobutyraldehyde when water is present before the benzene has been separated to the desired degree from the like-bolling, non-romatic hydrocarbons, by supplying additional butyraldehyde (with or without water) to the still or rectification column the desired separation of the benzene was achieved.
zene and like-boiling, non-aromatic hydrocarbons may be accomplished. This point of temperature observation in the apparatus in which the above examples of the process were 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 examples 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. 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 azeotropic distillation as being carried out under substantially atmospheric pressure. The temperatures as given herein are corrected temperatures for 1 atmosphere absolute (760 mm). 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 butyraldehyde 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 from a benzene fraction containing the same and containing a mixture of like-boiling, non-aromatic hydrocarbons which comprises distilling said benzene fraction in the presence of butyraldehyde and water, said butyraldehyde 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.

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 normal-butyraldehyde and water, said butyraldehyde 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 normal-butyraldehyde 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.

5. 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 normal-butyraldehyde and water, said butyraldehyde 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.

6. 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 normal-butyraldehyde, said butyraldehyde being present in amount such that at a point in the fractionation of the vapors evolved in distilling the benzene fraction the temperature does not exceed 76° C. for anhydrous conditions and does not exceed 67½° C. when water is present 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.

7. 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 isobutyraldehyde 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.

8. 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 isobutyraldehyde and water, said butyraldehyde 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.

9. 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 isobutyraldehyde, said butyraldehyde being present in amount such that at a point in the fractionation of the vapors evolved in distilling the benzene fraction the temperature does not exceed 64° C. for anhydrous conditions and does not exceed 60° C. when water is present 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.

RICHARD B. GREENBURG.
CERTIFICATE OF CORRECTION.


RICHARD B. GREENBURG.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 37, claim 1, for "form" read --from--; line 51, claim 2, after the word "of" insert --a quantity of--; line 60, claim 3, after the word "fraction" insert --and rectifying the distilled vapors--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of May, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.