

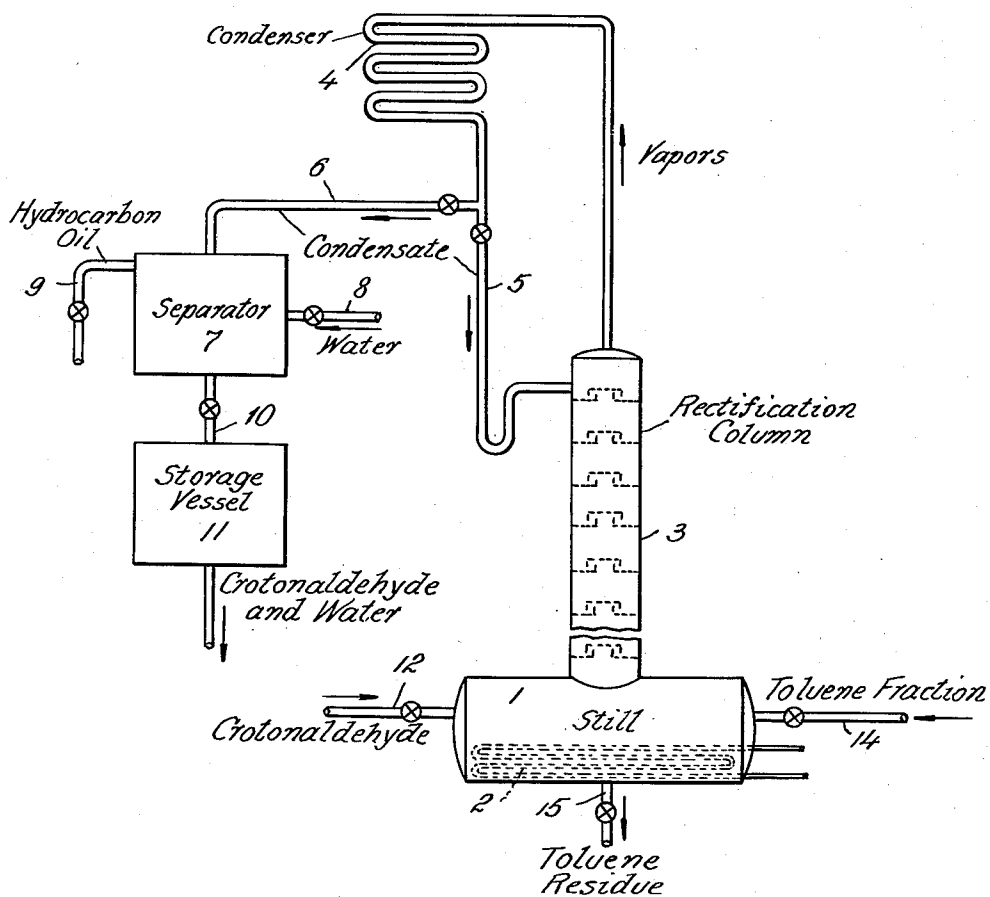
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F. W. SULLIVAN, JR

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PROCESS FOR RECOVERING TOLUENE

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INVENTOR
Frederick W. Sullivan, Jr.
BY
Charles W. Brown
ATTORNEY

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PROCESS FOR RECOVERING TOLUENE

Frederick W. Sullivan, Jr., Westfield, N. J., assignor to The Barrett Company, New York, N. Y., a corporation of New Jersey

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This invention relates to a process for recovering toluene from hydrocarbon mixtures containing toluene and like-boiling, non-aromatic hydrocarbons.

Numerous hydrocarbon oils are known which contain toluene and like-boiling, non-aromatic hydrocarbons. For example, catalytic treatment of a suitable petroleum fraction in the presence of hydrogen gives an oil consisting chiefly of hydrocarbons of both aromatic and non-aromatic character, and containing about 20% toluene. Gasoline fractions obtained by the distillation of certain types of petroleum frequently contain substantial proportions of toluene, although mainly consisting of other hydrocarbons. Oils of petroleum origin having a considerable content of aromatics, including toluene, 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 toluene content. In such cases toluene is accompanied by non-aromatic oils which may be largely paraffinic, naphthenic or olefinic in character. A considerable portion of these oils cannot be completely separated from the toluene by direct fractional distillation because of the closeness of their boiling points to that of toluene or because they form constant boiling mixtures with toluene. Furthermore, while ordinarily toluene is readily separable by direct fractional distillation from light oils produced by the gasification of coal, in some cases the toluene is accompanied by difficultly separable non-aromatic oils 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 toluene which, when recovered, is accompanied by similar difficultly separable constituents.

By fractional distillation of these oils containing toluene, fractions relatively high in toluene content may be obtained. These toluene fractions, however, will still contain substantial amounts of the other constituents of the oil having boiling points in the neighborhood of the boiling point of toluene or forming mixtures of constant boiling points in the range of temperatures at which toluene distills from the oil. The separation of the toluene from materials distilling from the toluene oil fraction at temperatures substantially higher or lower than the toluene does not present any great technical difficulties. The difficulty in recovering pure tolu-

ene from an oil fraction containing it, such as those referred to above, is presented by the problem of separating the toluene from the like-boiling, non-aromatic hydrocarbons; i. e., from those

5 hydrocarbons which by direct fractional distillation processes as commonly operated for the fractional distillation of oils, distill from the toluene fraction within the same temperature range as the toluene distills therefrom.

10 A process has been developed whereby toluene of any desired purity up to substantially 100% toluene may be successfully recovered from oils separate from the like-boiling, non-aromatic hydrocarbons. That process involves the azeotropic
15 distillation of the toluene fraction with fractionation of the vapors of toluene and other hydrocarbons in the presence of a material forming low-boiling azeotropes with the toluene and with the accompanying like-boiling, non-aromatic hydrocarbons. Although the toluene and like-boiling, non-aromatic hydrocarbons distill from mix-
20 tures containing the same in the same temperature ranges, their azeotropes with materials such as methanol, ethanol, the propanols, acetic acid, pyridine, and the numerous other materials which
25 form low-boiling azeotropes with toluene, have sufficiently different boiling temperatures for these azeotropes to be separated by fractionation. Accordingly, by azeotropic distillation of toluene
30 fractions in the presence of azeotropic agents such as those mentioned, the toluene may be separated from like-boiling, non-aromatic hydrocarbons, the latter being distilled off as azeotropes. Since materials contained in toluene
35 fractions distilling therefrom below or above the toluene distillation range may be readily separated from the toluene by ordinary fractional distillation, this process employing azeotropic distillation provides a method whereby the diffi-
40 cultly separable like-boiling, non-aromatic hydrocarbons may be separated from the toluene and a toluene of desired purity obtained.

45 An important factor in the successful azeotropic distillation of toluene fractions is the provision of an azeotropic agent which sharply separates the toluene and the like-boiling, non-aromatic hydrocarbons so that a high yield of toluene of a desired purity may be obtained in distilling the toluene fraction. It is also highly desirable that the azeotropic agent have a high capacity for carrying over as distillate the non-aromatic hydrocarbons; i. e., that the agents form with those hydrocarbons azeotropes having a high ratio of hydrocarbons to azeotropic agent. Accordingly, it is an object of this invention to pro-

vide a process for azeotropically distilling a toluene oil in the presence of an azeotropic agent which is particularly effective for separating the toluene from like-boiling, non-aromatic hydrocarbons contained in the toluene oil.

I have discovered that crotonaldehyde is particularly effective when used for the azeotropic distillation of toluene fractions to separate the toluene from the like-boiling, non-aromatic hydrocarbons. Accordingly, my invention comprises fractionally distilling a toluene oil containing like-boiling, non-aromatic hydrocarbons in the presence of crotonaldehyde. It appears crotonaldehyde forms a low-boiling azeotrope with the toluene. However, I have discovered crotonaldehyde forms with the non-aromatic hydrocarbons low-boiling azeotropes which may be separated by fractional distillation from the toluene or any azeotrope containing toluene and crotonaldehyde which may be formed. There is a relatively wide spread between the boiling points of the azeotropes of the like-boiling, non-aromatic hydrocarbons and of toluene or any azeotropes of toluene and crotonaldehyde which facilitates the separation of these materials by fractional distillation. In addition, the ratio of hydrocarbons to crotonaldehyde in the azeotropes formed with these non-aromatic hydrocarbons is relatively high. These characteristics of the crotonaldehyde contribute materially to its effectiveness as an azeotropic agent in the distillation of toluene oil fractions.

The toluene fraction treated in accordance with my invention preferably will contain little, if any, hydrocarbons distilling from the hydrocarbon-toluene fraction at temperatures materially above those at which toluene distills therefrom. On the other hand, high boiling materials may be left with the toluene residue at the conclusion of the azeotropic distillation of the toluene fraction under the conditions set forth above to separate the toluene from the hydrocarbons of similar boiling range. Once this separation has been effected, the toluene 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 toluene fraction to be azeotropically distilled or whether, if left in the toluene 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 constituents form azeotropes with the agent used which have boiling points close to 102° to 103° C., it is preferable to separate them by a direct fractional distillation before azeotropically distilling the toluene fraction. If they do not form azeotropes having boiling points close to 102° to 103° C., or if their amount is small, this procedure is not so important.

When pure toluene is to be recovered it is preferred the toluene fraction subjected to azeotropic distillation in accordance with my invention be a fraction boiling in the range of 100° C. to 111° C. Such a fraction may be azeotropically distilled by my process and pure toluene obtained with a relatively small quantity of azeotropic agent present during the distillation. Pure toluene may be obtained by distilling with an azeotropic agent a toluene fraction boiling, for example, from 95° C. to 118° C. but the quantity of azeotropic agent present in the distillation of the toluene 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.

Toluene of high purity is desired for nitration purposes and the process of my invention provides a method whereby such pure nitration grade toluene may be economically recovered from toluene oils. The invention, however, is not limited thereto. Toluene products of lower purity than nitration grade toluene are industrially used for various purposes, e. g., products containing 85% to 90% toluene are used as solvents. The process of my invention may be used advantageously for recovering such products from hydrocarbon oils of lower toluene content. My process is particularly advantageous when the toluene is to be separated from most of the like-boiling, non-aromatic hydrocarbons present in an oil fraction together with toluene, e. g., when a product is to be obtained containing toluene and no more than 5 parts by weight of like-boiling, non-aromatic hydrocarbons for every 95 parts by weight of toluene.

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

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 and introducing it into a separator 7. Separator 7 is provided with a pipe 8 through which water may be introduced to the separator. The separator is also provided with a pipe 9 for withdrawal of an upper liquid layer and a pipe 10 for withdrawal of a lower liquid layer which may be formed from the material treated in the separator. Suitable baffles may be provided in separator 7 to facilitate continuous separation therein. Pipe 10 leads to a storage vessel 11. Pipes 12 and 14 are provided for the introduction of liquids into still 1. A pipe 15 serves for withdrawal of residue from this still.

The above-described apparatus was employed for the treatment of a toluene fraction recovered from the product obtained by the catalytic reforming in the presence of hydrogen of a petroleum oil. This toluene fraction had the following characteristics:

Toluene content----- per cent----	74.5
Boiling range----- degrees C----	109.5-110.8

The toluene content of this oil was determined by the specific dispersion method for analyzing hydrocarbon oils described in Industrial and Engineering Chemistry, Analytical Edition, vol. 11, page 614, November 15, 1939.

100 volumes of the above toluene fraction and 60 volumes of a crude crotonaldehyde product available in the market were charged into the still of the apparatus described above. This

crude crotonaldehyde was a material boiling over the range 82.5° C. to 112° C. It contained substantially 90% or more crotonaldehyde and upwardly to 10% water with small amounts of other impurities. The charge of crotonaldehyde and toluene fraction 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 withdrawn as distillate, and the remainder of the condensate returned as reflux to the top of the fractionation column. Distillation started with the temperature of the vapors at the top of the fractionation column at about 96° C. This vapor temperature rose as the distillation proceeded to about 102.5° C. During the initial stage of the distillation the oil recovered from the distillate by washing it with water in separator 7 and separating the oil layer thus obtained from the aqueous layer containing the crotonaldehyde consisted of non-aromatic hydrocarbons and was free from toluene. As the distillation proceeded, however, with the temperature at the top of the rectification column rising to 102.4° and 102.8° C., the amount of toluene in the oil distillate increased. At the latter temperature, the distillate substantially consisted of toluene and crotonaldehyde.

When the hydrocarbons in the distillate consisted of toluene, the residue left in the still and rectification column was withdrawn and washed with water to separate any trace of remaining crotonaldehyde it contained. The oil layer recovered from the aqueous layer formed in thus washing the residue of the distillation was 100% toluene. Of the toluene initially present in the toluene fraction subjected to the distillation, 90% was recovered as residue of the distillation in the form of the pure toluene product. This high yield of toluene is attributable to the very small amounts of toluene carried over in the distillate during the first stage of the azeotropic distillation due to the sharpness with which the crotonaldehyde separated the toluene from the like-boiling, non-aromatic hydrocarbons. In the initial stage of the distillation the oil contained in the distillate, comprising 90% of the non-aromatic hydrocarbons of the toluene fraction, contained only 4% of toluene. This oil represented a little more than 23 volumes out of the total of 33 volumes of oil distillate which it was found necessary to take over in order to leave a toluene residue substantially free from non-toluene hydrocarbons.

A further saving of the toluene may be effected by collecting separately all intermediate distillates, relatively rich in toluene, boiling over a range of about 102.0° to 103.0° C. and returning these distillates to a fresh batch of crude toluene fraction. Toluene contained in the intermediate distillates may then be recovered by a subsequent azeotropic distillation. Incidentally, the crotonaldehyde contained in such distillates will function directly, without any intervening recovery being necessary, as azeotropic distillation component.

The crotonaldehyde in the lower-boiling distillates containing very little toluene, may be recovered separate from the hydrocarbons in the distillate for reuse in the distillation of additional toluene fraction. As pointed out above, by treating the distillate with water the hydrocarbon oils may be taken off from separator 7 through pipe 9 separate from an aqueous liquid phase containing crotonaldehyde drawn through pipe 10 to

storage vessel 11. Anhydrous crotonaldehyde may be recovered from this aqueous phase.

Water may be present in the distillation of the toluene fraction in the presence of the crotonaldehyde, although it is preferred to carry out this distillation under substantially anhydrous conditions. Water forms ternary azeotropes with crotonaldehyde, toluene and non-toluene hydrocarbons which have closer boiling points than the binary azeotropes of the crotonaldehyde with the non-toluene hydrocarbons and the toluene. Accordingly, the presence of water in the distillation reduces the effectiveness with which the toluene is separated from the like-boiling, non-aromatic hydrocarbons. Nevertheless, the presence of water in the azeotropic distillation is within the scope of my invention. For example, in carrying out the process of the above example modified to charge into the still a mixture containing 100 volumes of toluene fraction containing 75.5% toluene, 30 volumes of crotonaldehyde and 15 volumes of water, this mixture was fractionally distilled to leave as residue a product in which the hydrocarbons were 100% toluene and which contained 82% of the toluene present in the original toluene fraction. The distillation of this mixture containing water started with a temperature at the top of the rectification column of about 80° C. This temperature rose to 85.3° C. when the non-aromatic hydrocarbons had been carried over as distillate, leaving a residue the hydrocarbon content of which was 100% toluene.

One advantage which may be taken of the fact that crotonaldehyde is effective in the presence of water for the azeotropic separation of toluene from like-boiling, non-aromatic hydrocarbons is that the azeotropes with water, when cooled, separate into two phases, an oil layer and an aqueous layer, both containing crotonaldehyde. The aqueous layer may be returned from storage vessel 11 or directly from separator 7 to the azeotropic distillation to reuse therein the crotonaldehyde without necessitating a separation of the crotonaldehyde from the water.

While both of the examples described above employ a batch operation for the distillation of the toluene fraction, this distillation may be carried out continuously. For example, crotonaldehyde and toluene fraction may be continuously supplied to a column still in which the toluene is concentrated and, flowing to the bottom of the still, is continuously withdrawn therefrom. The azeotropes of crotonaldehyde and non-aromatic hydrocarbons are continuously vaporized and withdrawn as distillate from the top of the distillation column. Sufficient crotonaldehyde should be supplied to carry over as distillate all of the hydrocarbons to be distilled from the toluene fraction and separated from the toluene. By observation of the vapor temperatures at a suitable point in the vapor rectification column, one may ascertain whether adequate crotonaldehyde is present. Whenever these vapor temperatures tend to exceed 102° C. to 103° C. under anhydrous conditions or 85° to 86° C. when water is present before the toluene has been separated to the desired degree from the like-boiling, non-aromatic hydrocarbons, by supplying additional crotonaldehyde (with or without water) to the still or rectification column will assure the presence of sufficient crotonaldehyde to obtain the desired separation of the toluene and like-boiling, non-aromatic hydrocarbons; e. g., until a residue of the distillation is obtained which contains toluene and no more than 5 parts by weight of

like-boiling, non-aromatic hydrocarbons for every 95 parts by weight of toluene. This point of temperature observation in the apparatus in which the above examples of the process were carried out, was 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 major part of the toluene has been recovered as distillation residue, the distillation may be combined after the removal of non-toluene constituents so that an enriched toluene product is recovered as overhead. Alternatively, enriched toluene products may be taken off as one or more side streams. Both of 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 toluene from a toluene fraction containing the same and containing like-boiling, non-aromatic hydrocarbons which comprises fractionally distilling said toluene fraction in the presence of crotonaldehyde, thereby vaporizing and removing as distillate said like-boiling, non-aromatic hydrocarbons and leaving a hydrocarbon residue of the distillation enriched in toluene.

2. The process for the recovery of toluene which comprises azeotropically distilling in the presence of crotonaldehyde a toluene oil fraction boiling in the absence of said crotonaldehyde in the range 95° C. to 118° C., thereby vaporizing and removing as distillate said like-boiling, non-aromatic hydrocarbons and leaving a hydrocarbon residue of the distillation enriched in toluene.

3. The process for the recovery of toluene from a toluene fraction containing the same and containing like-boiling, non-aromatic hydrocarbons which comprises fractionally distilling said toluene fraction in the presence of substantially anhydrous crotonaldehyde, thereby vaporizing and removing as distillate said like-boiling, non-aromatic hydrocarbons and leaving a hydrocar-

bon residue of the distillation enriched in toluene.

4. The process for the recovery of toluene from a toluene fraction containing the same and containing like-boiling, non-aromatic hydrocarbons which comprises fractionally distilling said toluene fraction in the presence of crotonaldehyde, said crotonaldehyde being present in amount such that at a point in the fractionation of the vapors evolved in distilling the toluene fraction the temperature does not exceed 102° C. to 103° C. for anhydrous conditions and does not exceed 85° C. to 86° C. when water is present until said like-boiling, non-aromatic hydrocarbons have been vaporized leaving a hydrocarbon residue of the distillation containing toluene and no more than 5 parts by weight of like-boiling, non-aromatic hydrocarbons for every 95 parts by weight of toluene.

5. The process for the recovery of toluene from a toluene fraction containing the same and containing like-boiling, non-aromatic hydrocarbons which comprises fractionally distilling said toluene fraction in the presence of water and crotonaldehyde, thereby vaporizing and removing as distillate said like-boiling, non-aromatic hydrocarbons and leaving a hydrocarbon residue of the distillation enriched in toluene.

6. The process for the recovery of toluene which comprises azeotropically distilling in the presence of water and crotonaldehyde a toluene oil fraction boiling in the absence of said crotonaldehyde and water in the range 95° C. to 118° C., thereby vaporizing and removing as distillate said like-boiling, non-aromatic hydrocarbons and leaving a hydrocarbon residue of the distillation enriched in toluene.

7. The process for the recovery of toluene from a toluene fraction containing the same and like-boiling, non-aromatic hydrocarbons which comprises distilling said toluene fraction in the presence of water and of crotonaldehyde, thereby vaporizing and removing as distillate azeotropes of said like-boiling, non-aromatic hydrocarbons with said water and crotonaldehyde and leaving a hydrocarbon residue of the distillation enriched in toluene, cooling and condensing the aforesaid distillate, thereby obtaining a condensate which separates into two liquid phases, one a hydrocarbon-oil-crotonaldehyde phase and the other an aqueous crotonaldehyde phase, and employing said aqueous phase in the azeotropic distillation of said toluene fraction containing toluene and like-boiling, non-aromatic hydrocarbons.

FREDERICK W. SULLIVAN, JR.