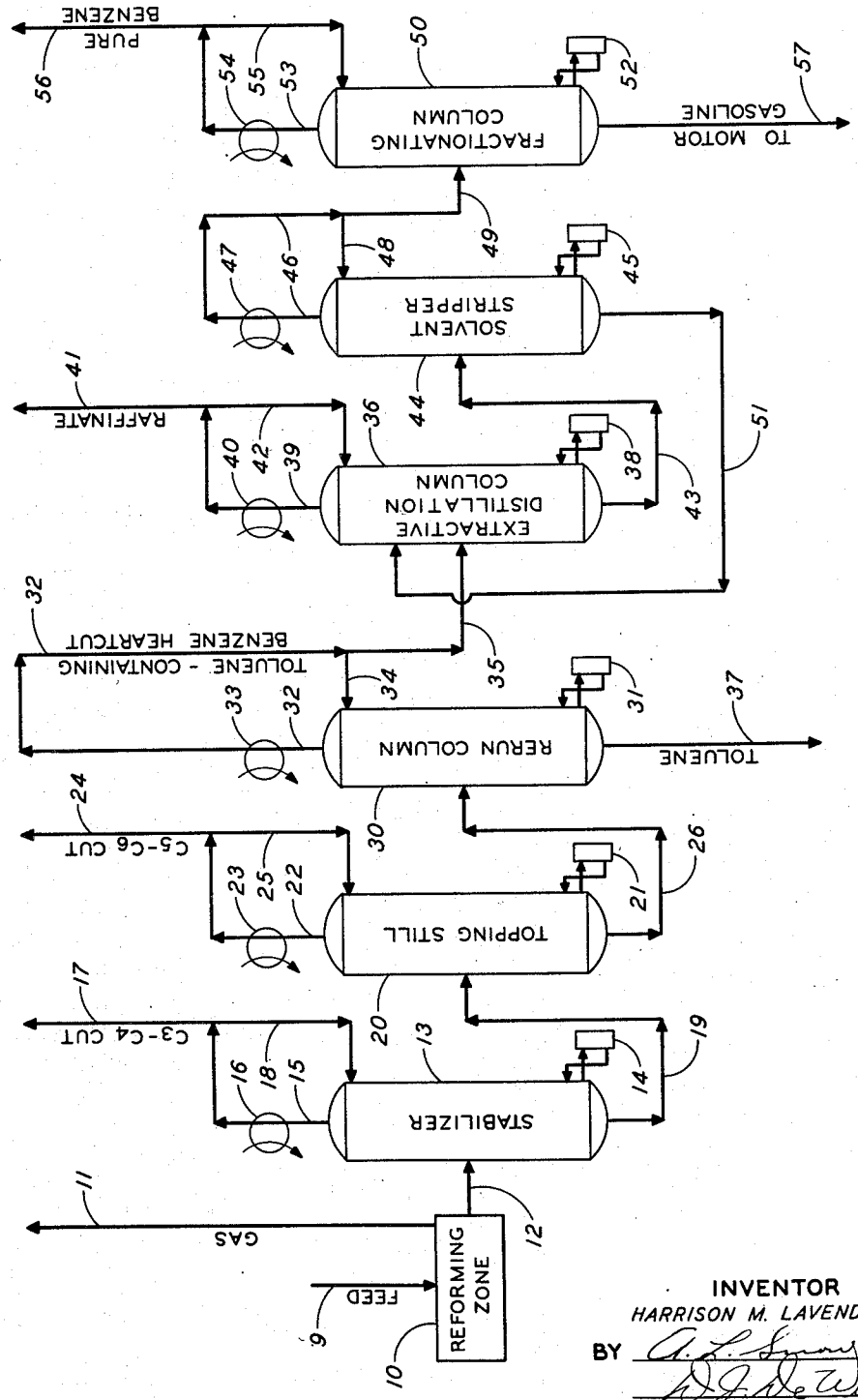
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EXTRACTIVE DISTILLATION PROCESS FOR RECOVERING AROMATICS

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EXTRACTIVE DISTILLATION PROCESS FOR RECOVERING AROMATICS

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This invention relates to an extractive distillation process for recovering substantially pure aromatic compounds from hydrocarbon distillate fractions containing said compounds in admixture with various nonaromatic components. The invention finds primary application, however, in an improved process for the recovery of benzene and toluene from catalytic reformates, and it therefore will be particularly described hereinafter as it relates to said process.

In producing the benzene and toluene-containing reformate streams to which this invention particularly relates, a petroleum naphtha fraction consisting essentially of a mixture of naphthenic, paraffinic and aromatic hydrocarbons having from six to seven carbon atoms in the molecule is contacted in the vapor phase with a platinum-alumina or other platinum-containing reforming catalyst under suitable conversion conditions so as largely to convert the naphthenic hydrocarbons containing six carbon atoms to benzene and the seven carbon atom naphthenic hydrocarbons to toluene, the straight carbon chain paraffinic hydrocarbons in the feed being isomerized in part to branched-chain compounds.

While the gaseous and other components of the reformate product obtained in this fashion which boil below hexane can readily be removed without appreciable loss of the desired aromatic compounds, this is not the case with the remaining nonaromatic contaminants which normally comprise from about 25 to 75% by volume of the product remaining after removal of the lighter components. The problem of recovering benzene from the reformate is particularly acute, since the established specifications for the pure grade of benzene which must be recovered from the unit, if the process is to be operated in an economic fashion, are such as to permit the presence of only trace amounts of other aromatic compounds as well as of nonaromatic contaminants. This is borne out by the fact that as little as 0.1% of toluene is sufficient to bring the boiling range to the limit of the specification, which calls for a distillation range of 1° C., initial to dry.

Since the distillate fractions initially obtained following various petroleum reforming and other operations which are productive of aromatic product streams normally contain substantial amounts of at least one other aromatic compound than the desired product, along with various nonaromatic materials, the practice which is now followed by a large segment of the industry is to redistill such fractions under rigorous conditions whereby a fraction is obtained which contains the desired aromatic compound but is free of other aromatic contaminants. Thus, in the case of the benzene-containing fraction recovered from a catalytic reforming operation, which normally contains a substantial amount of toluene along with associated nonaromatic components, the practice is to subject this fraction to one or more preliminary fractional distillation steps designed to provide a benzene heart cut which is substantially free of any toluene (less than 0.1% by volume, in terms of the benzene content),

and thereafter to subject this concentrate to an extractive distillation treatment whereby contaminating nonaromatic components are removed overhead, while the bottoms (which contain the benzene along with the extractive solvent) are then distilled so as to recover substantially pure benzene. The foregoing method has the disadvantage that a heart cut which contains but a single aromatic compound and is free of contaminating aromatic components can only be obtained by a practice of the most exacting techniques involving the use of high reflux ratios and distillation columns containing as many as 75 to 80 or more trays, thereby greatly adding to the cost of the recovery procedure.

While the marketing requirements for toluene are considerably less stringent than those for the benzene component of the reformate, nevertheless the toluene-containing stream recovered as bottoms from the highly efficient column referred to above, wherein the benzene-containing heart cut is taken overhead, must be redistilled so as to remove overhead a substantial proportion of the nonaromatic contaminants present (largely C_7 paraffins and naphthenes) if a product is to be obtained which contains less than about 10% of said materials.

In view of the foregoing difficulties, it would be desirable if a process were available which, while yielding benzene and toluene of the desired purity, would at once eliminate the need for effecting a substantially complete separation of the toluene from the benzene heart cut feed to the extractive distillation zone, and also eliminate the need for redistilling the toluene-containing bottoms fraction recovered from the benzene heart cut still, and it is a primary object of this invention to provide an improved method of this character.

The present invention is based upon the discovery that the foregoing objects are achieved by a procedure whereby the conversion product obtained by subjecting a suitable hydrocarbon feed stock to a catalytic conversion process productive of a reaction mixture containing benzene and toluene, along with various nonaromatic components, is first freed of gaseous and other relatively light constituents and is thereafter passed into a distillation column maintained under such conditions that the benzene is taken overhead in the form of a concentrate, or heart cut which includes from about 0.2 to 10% toluene (in terms of the volume or benzene present) as well as various nonaromatic contaminants, while the balance of the toluene is recovered as a bottoms stream in such purity as to require no further redistillation in order to meet required standards. The benzene-containing concentrate is then introduced into an extractive distillation column to which a higher boiling extractive solvent (e. g., phenol) is also supplied, the conditions within this extractive distillation column being such that a large proportion of the nonaromatic components are taken overhead, while the aromatic components of the feed, along with any higher boiling nonaromatic components are withdrawn as bottoms. Said bottoms are then passed to a solvent stripping column operated under such conditions that the nonsolvent portions of the feed (containing the desired aromatics) are taken overhead and passed to a final fractionation column, while a stream made up essentially of solvent is withdrawn as bottoms and recycled back to the extractive distillation column. Quite unexpectedly, it has been found that even though the feed to said final distillation column contains appreciable quantities of toluene and nonaromatic contaminants, nevertheless the benzene can be distilled overhead in a high degree of purity (at least 99% benzene, and less than 0.1% of other aromatics, by volume), while recovering as bottoms a stream containing said toluene and nonaromatics. The latter stream can then either be diverted for use as a component of motor gasoline, or it

can be recycled back to the column from which the benzene heart cut is taken overhead and the toluene is withdrawn as bottoms.

While phenol has been given above as an example of an extractive solvent, and is, in fact, the preferred solvent for use in this invention when recovering benzene or toluene, a wide variety of other solvents can be employed. In general, the solvent selected should have a boiling point which is well above the end point of the stock being treated and which can thus be readily separated from the dissolved components. Thus, suitable solvents which can be employed in a practice of this invention are: phenol, aniline, cresylic acids, alkyl phenols, various polyglycols including di-, tri- and tetraethylene glycol, carbitols, diethanolamine, nitrobenzene, quinoline, furfural alcohol, furfural, monoglycerol ethers, resorcinol, xylidine, acetone and acetone-water mixtures.

The mode of practice of the invention with reference to several embodiments and the various features and advantages thereof will be apparent from the following detailed description with reference to the appended drawing wherein the figure represents a flow diagram of a process for recovering pure benzene, as well as a relatively pure toluene stream, from a petroleum naphtha feed stock. In the figure, a feed mixture comprising a petroleum naphtha fraction consisting primarily of a mixture of naphthenic, paraffinic and aromatic hydrocarbons having from six to seven carbon atoms in the molecule is passed at a rate of 1000 volumes per day through line **9** in the vapor phase into contact with a reforming catalyst in reforming zone **10** under elevated conditions of temperature and pressure suitable for effecting the desired conversion of the C_6 naphthenes to benzene and the C_7 naphthenes to toluene, and to largely isomerize the straight chain paraffinic hydrocarbons present to branched chain compounds. From the reforming zone hydrogen along with about 49 volumes of other gases are removed through line **11** while the balance of the reformate passes through line **12** into a stabilizer column **13** provided with a suitable reboiler **14**, from which column the lighter fractions comprising predominantly C_3–C_4 hydrocarbons are taken overhead at a temperature of about 30° F. through line **15** and condenser **16**, with a portion of said lighter hydrocarbons being sent to product recovery through line **17** at a rate of about 35 volumes per day, while the balance is returned as reflux to the column through line **18**.

The bottoms from stabilizer column **13** are withdrawn through line **19** and passed into a topping still **20** provided with a reboiler **21**. From this still a lighter fraction comprising essentially C_5 and C_6 hydrocarbons boiling below hexane is taken overhead at a temperature of about 155° F. through line **22** and condenser **23**, with a portion of the condensate (215 volumes per day) being sent to product recovery through line **24**, while the balance is returned to the column as reflux through line **25** (reflux ratio, 15:1).

The bottoms from the topping still **20** are withdrawn through line **26** and charged into a mid-portion of a rerun column **30** provided with a reboiler **31**. From this column a benzene heart cut fraction is taken overhead at a temperature of about 210° F. through line **32** and condenser **33**, which fraction contains substantially all of the benzene supplied to the column, as well as toluene in an amount equal to from about 0.2 to 10% by volume, based on the benzene content of the fraction, along with a substantial proportion of nonaromatic components. Of the resulting condensate, a portion is returned to the column as reflux through line **34** (reflux ratio, 2:1), while the balance of the stream (485 volumes per day) is passed through line **35** into a mid-point of an extractive distillation column **36** having a reboiler **38**. The balance of the toluene introduced into rerun column **30** through line **26** is removed as bottoms from said column through line **37**, along with a small percentage of hydrocarbons boiling above benzene, at a rate of about 173 volumes per day.

In a representative run, the benzene concentrate in line **35** contains 50.3% benzene and 3.7% toluene, based on benzene, the balance being nonaromatics, while the bottoms stream in line **37** contains 94.8% toluene and 5.2% nonaromatics.

As stated above, the benzene concentrate is introduced into column **36** at the rate of 485 volumes per day, and to this column phenol is added through line **51** at a rate of 1300 volumes per day. In column **36** nonaromatic hydrocarbons are taken overhead through line **39** and condenser **40**, with a portion being returned to the column as reflux through line **42** (reflux ratio 4:1), while a raffinate stream amounting to 330 volumes per day is sent to a suitable recovery system (not shown) through line **41**, said raffinate, at a still head temperature of about 180 F., consisting of 95.2% nonaromatics and but 4.8% benzene.

The bottoms from the column **36**, which contain the desired benzene along with associated higher boiling aromatic (toluene) and nonaromatic contaminants as well as solvent, are supplied through line **43** at a temperature of about 325° F. to a mid-point of a stripping column **44** provided with a reboiler **45**. From the column **44** (when operated, for example, at a still head temperature of 200° F. and at a reflux ratio of about 2:1), an overhead stream consisting of 91.4% benzene, 3.5% toluene and 5.1% nonaromatics is taken over head through line **46** and condenser **47**, with a portion being returned to the column as reflux through line **48**, while the balance is passed through line **49** at a rate of 255 volumes per day to a fractionating column **50**. The bottoms from the stripping column **44**, which contain the extractive solvent along with a small percentage of toluene and of nonaromatics, are withdrawn through line **51** at a temperature of about 395° C. and recycled back to the extractive distillation column **36** at a rate of 1300 volumes per day.

The fractionating column **50**, which is provided with a reboiler **52**, is operated at an overhead temperature of about 190° F. and at a reflux ratio of approximately 2:1. From this column an overhead stream containing 99.2% benzene and approximately 0.8% nonaromatics is taken overhead through line **53** and condenser **54** with a portion of the stream being returned as reflux through line **55**, while the balance is withdrawn from the unit, at a rate of 233 volumes per day, through line **56**. This substantially pure benzene product may, if desired, be passed to a treating zone where the material is subjected to conventional finishing treatments required for the production of a product of nitration grade. A bottoms stream made up 11 volumes of nonaromatics and 9 volumes of toluene is withdrawn from column **50** through line **57** at a temperature of about 240° F., this product being either sent to motor gasoline storage, or recycled back to column **30**.

In the foregoing description, the various percentages given are on a volume basis, and the volumes given refer to the product when in a liquid state. Further, in the flow diagram various of the required pumps, heat exchangers, valves and other items of flow control equipment have been omitted in the interests of simplicity and clarity of expression, the placement of such auxiliary equipment being evident to those skilled in the art.

While the character of this invention has been described in detail and numerous illustrative examples given, this has been done by way of illustration only and with the intention that no limitation should be imposed upon the invention thereby. It will be apparent to those skilled in the art that numerous modifications and variations may be effected in the practice of this invention which is of the scope of the claims appended hereto.

I claim:

1. In a process for recovering substantially pure benzene from a catalytic reformate containing benzene, toluene and nonaromatic components, the steps compris-

ing freeing the reformate of normally gaseous and other lighter nonaromatic constituents; passing the remaining reformate product so obtained to a re-run column from which a benzene concentrate containing substantially all the benzene content of said reformate, along with nonaromatic components and an appreciable amount of toluene, is taken overhead, and from which a fraction comprised in major portion of toluene is withdrawn as bottoms; passing said concentrate to an extractive distillation column, and there contacting the concentrate with a selective solvent at elevated temperatures whereby a substantial portion of the nonaromatic components are separated as an overhead product, while withdrawing a bottoms product containing substantially all of the benzene and toluene present in the concentrate, along with any remaining nonaromatic components and solvent; passing said bottoms product to a solvent stripping column maintained at a temperature adapted to distill overhead the nonsolvent portions of the feed to the column while withdrawing as bottoms, and recycling to the extractive distillation column, a solvent fraction which is low in nonsolvent components; passing the overhead from the solvent stripping column to a fractionating column maintained under such conditions as to distill the benzene overhead as a substantially pure benzene stream, while withdrawing as bottoms a fraction containing toluene and any remaining nonaromatic components, as present in the benzene concentrate.

2. The process of claim 1 wherein the solvent is phenol.

3. The process of claim 1 wherein the bottoms stream from the last-mentioned fractionation column is recycled to the re-run column.

4. In a process for producing and separating substantially pure benzene wherein a petroleum naphtha fraction consisting primarily of a mixture of naphthenic, paraffinic and aromatic hydrocarbons having six to seven carbon atoms in the molecule is passed into contact in the vapor phase with a reforming catalyst under suitable conversion conditions to largely convert the six carbon atom naphthenic hydrocarbons to benzene, the seven carbon atom naphthenic hydrocarbons to toluene and to largely isomerize the straight carbon chain paraffinic hydrocarbons present to branched-chain compounds, with the resulting catalytic conversion product being thereafter freed of normally gaseous and other lighter constituents present,

the improvement which comprises passing the remaining conversion product to a re-run column from which is taken overhead a benzene concentrate including substantially all the benzene present, together with nonaromatic components and a small percentage of toluene, and from which a fraction comprised in major portion of toluene is withdrawn as bottoms; passing said benzene concentrate to an extractive distillation column, and there contacting the concentrate with a selective solvent at elevated temperatures whereby a substantial portion of the nonaromatic components are separated as an overhead product, while withdrawing a bottoms product containing substantially all of the benzene and toluene present in the concentrate, along with any remaining nonaromatic components and solvent; passing said bottoms product to a solvent stripping column maintained at a temperature adapted to distill overhead the nonsolvent portions of the feed to the column while wthdrawing as bottoms, and recycling to the extractive distillation column, a solvent fraction which is low in nonsolvent components; passing the overhead from the solvent stripping column to a fractionating column maintained under such conditions as to distill the benzene overhead as a substantially pure benzene stream, while withdrawing as bottoms a fraction containing toluene and any remaining nonaromatic components, as present in the benzene concentrate.

5. The process of claim 4 wherein the bottoms from the last-mentioned fractionating column are recycled to the re-run column.

6. The process of claim 4 wherein the overhead from the re-run column contains from about 0.2 to 10 volume percent toluene, based on the amount of benzene present, and wherein the bottoms from said column contain at least 90 volume percent toluene.

7. The process of claim 6 wherein the solvent is phenol.

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