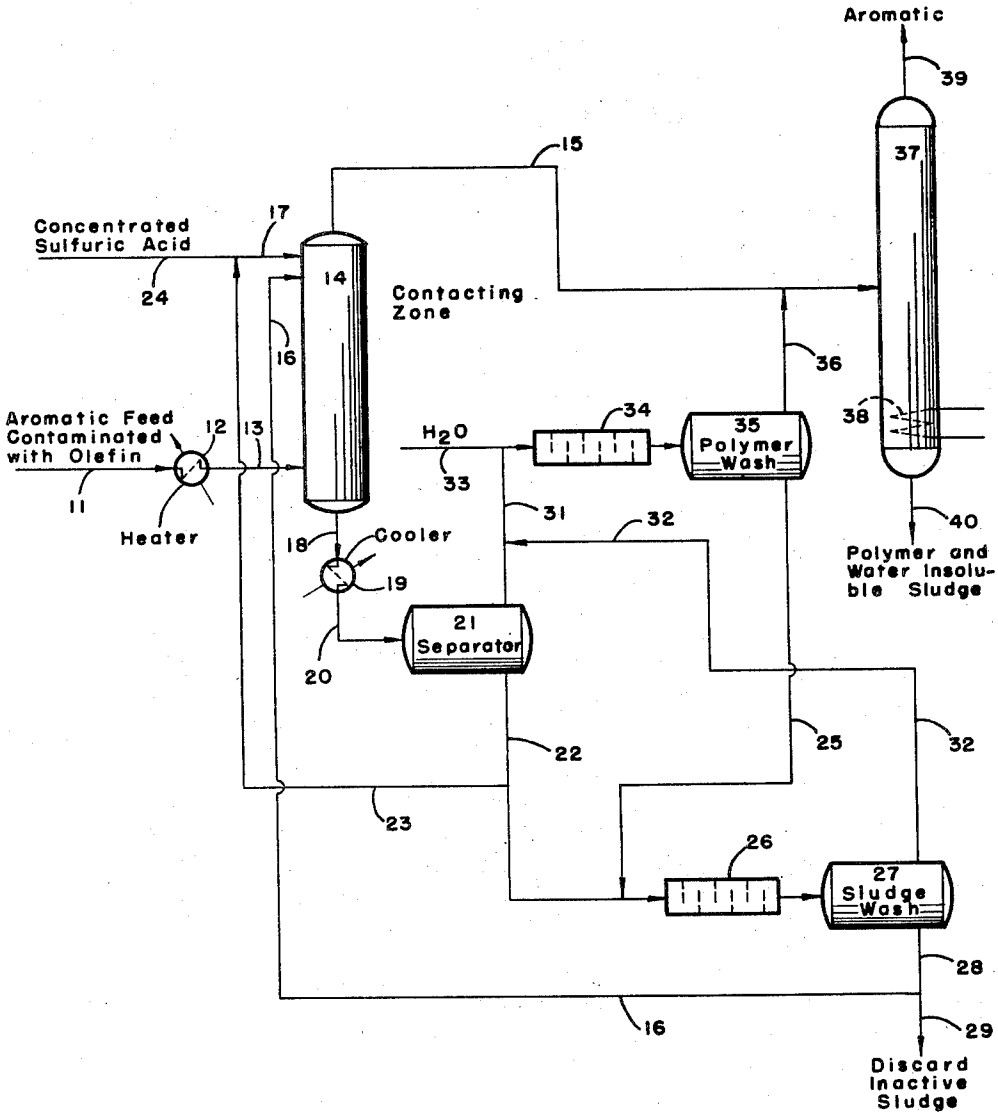
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PROCESS FOR REMOVING OLEFINS FROM AROMATIC HYDROCARBONS

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PROCESS FOR REMOVING OLEFINS FROM AROMATIC HYDROCARBONS

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The present invention is directed to a process for treating a feed stock comprising a major portion of aromatic hydrocarbon and a minor portion of olefin to remove the olefin therefrom and obtain a purified aromatic hydrocarbon fraction.

It is known to the art to treat a hydrocarbon fraction contaminated with a minor portion of olefin in order to remove the olefin and particularly to purify a hydrocarbon fraction by removing olefin therefrom by contacting the fraction with a suitable extracting liquid. The method known to the art commonly requires a number of manipulative steps in addition to the contacting step in order to separate the hydrocarbon phase from the extracting medium. These processes which employ a substantial number of manipulative steps in order to obtain the desired purified hydrocarbon fraction are relatively expensive and complicated in requiring a substantial amount of equipment and a large amount of handling of liquid fractions.

It is an object of the present invention to treat a hydrocarbon feed stock comprising a major portion of an aromatic and a minor portion of contaminating olefin in a simple process having relatively few manipulative steps. More particularly, it is an object of the present invention to treat a feed stock comprising a major portion of aromatic material contaminated with a minor portion of olefin in a relatively simple process with few manipulative steps and involving vaporization of the feed stock and contacting of the resultant vapors with an extracting liquid in a contacting zone to obtain a purified aromatic fraction.

The present invention may be briefly described as a process for obtaining a substantially pure aromatic fraction involving the steps of contacting a vaporized feed stock including a major portion of aromatics and a minor portion of olefins in a contacting zone at a temperature substantially above atmospheric with a liquid comprising aryl sulfonic acid and concentrated sulfuric acid, removing as a vapor phase a substantially pure aromatic fraction from the contacting zone, removing as a liquid fraction a mixture of hydrocarbons and aryl sulfonic acids from the contacting zone, cooling said liquid phase to a temperature of approximately atmospheric and subjecting the cooled liquid fraction to gravity settling to separate it into a hydrocarbon fraction and an aryl sulfonic acid fraction. The process is continuous with at least a portion of the aryl sulfonic acid fraction returned to the contacting zone and forming a portion of the contacting liquid therein.

The invention will now be described in greater

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detail in conjunction with the drawing in which the sole figure is in the form of a diagrammatic flow sheet.

Turning now specifically to the drawing, a feed stock comprising a major portion of aromatic hydrocarbon contaminated with a minor portion of olefins is passed via inlet line 11 to a heating means, such as a heat exchanger 12, which supplies sufficient heat to vaporize the feed stock and the resultant vapors are passed through line 13 into the lower portion of a contacting vessel 14. The vapors pass upwardly through the contacting vessel and are intimately contacted with a mixture of concentrated sulfuric acid and aryl sulfonic acid which is discharged into the upper end of the vessel and flows downwardly therein countercurrently to the upwardly ascending vapors. Vapors from the upper end of vessel 14 may be removed through outlet line 15. Aryl sulfonic acid and a mixture of concentrated sulfuric acid and aryl sulfonic acid are supplied to the upper end of vessel 14 by lines 16 and 17, respectively. As the aromatic portion of the feed stock is intimately contacted with concentrated sulfuric acid in the liquid mixture, the sulfuric acid is converted to aryl sulfonic acid so that the liquid accumulating in the lower portion of contacting vessel 14 is a mixture of aryl sulfonic acid and high boiling hydrocarbon material resulting principally from the polymerization of the contaminating olefins in the feed stock. The liquid mixture is withdrawn from the lower end of contacting vessel 14 through outlet 18 and is passed to a suitable cooling means, such as a heat exchanger 19, where it is cooled to a temperature no greater than approximately atmospheric. The cooled material passes through line 20 into a separator 21 where it is allowed to separate under the influence of gravity into a lighter hydrocarbon layer and a heavier aryl sulfonic acid layer.

The aryl sulfonic acid phase obtained in separator 21 is withdrawn through outlet line 22 and the stream is split with a major portion of the stream passing through line 23, admixed with concentrated sulfuric acid supplied through inlet 24 to form a mixture of aryl sulfonic acid and concentrated sulfuric acid and the resulting mixture discharged through inlet line 17 into the upper portion of contacting zone 14. The minor portion of the aryl sulfonic acid withdrawn from separator 21 passes by line 22 and water is introduced thereto through line 25; the mixture of aryl sulfonic acid and water is thoroughly admixed by passing through mixing device 26 and the resultant admixture is discharged into a separating de-

vice 27 where it is separated under the influence of gravity into a heavy, aqueous solution of aryl sulfonic acid and a lighter fraction composed of aromatics, polymer and water insoluble sludge. The heavy aqueous solution of aryl sulfonic acid is withdrawn from separator 27 via line 28; a portion of this fraction may be discharged from the system through outlet 29 while the remainder passes into line 16 and is discharged into the upper portion of contacting zone 14 where it serves as a portion of the contacting liquid therein.

The hydrocarbon fraction from the separator 21 is withdrawn through outlet line 31 and has added thereto the fraction withdrawn from separator 27 through line 32. To the hydrocarbon is added water via inlet line 33 and these materials are then admixed by passing through mixing device 34. The mixture is discharged into a separating vessel 35 where the constituents thereof are allowed to settle under the influence of gravity into a lighter hydrocarbon fraction and a wash water fraction. The wash water fraction from separator 35 is withdrawn through line 25 and admixed with the aryl sulfonic acid in line 22 as previously described.

The hydrocarbon fraction separated in separator 35 is removed through line 36 and discharges into line 15 where it mixes with the vapors removed from the upper portion of contacting vessel 14; the resultant mixture passes into a distillation unit which is indicated by a single tower 37 provided with heating coil 38. In distillation unit 37 the mixture of hydrocarbons is separated into an overhead fraction comprising substantially pure aromatic hydrocarbon which is removed through outlet 39 and a heavy hydrocarbon fraction comprising principally material polymerized in the contacting zone 14 and which is removed from unit 37 through outlet line 40.

It is desirable to cool the liquid fraction withdrawn from the contacting zone 14 to a temperature within the range of 85 to 100° F. and subsequently separate the material cooled to this temperature by settling under the influence of gravity to obtain a hydrocarbon phase and an aryl sulfonic acid phase. It will be understood that the liquid material withdrawn from the contacting zone 14 may be cooled to a temperature substantially below 85° F. if desired in order to obtain phase separation, but for economic reasons, such as the availability of cooling water at approximately atmospheric temperature, it is preferred to cool this material to approximately atmospheric temperatures in order to obtain phase separation.

The amount of liquid employed to contact the vapors in the contacting zone 14 may be varied over a considerable range and satisfactory results obtained. When the feed stock comprises approximately 3% olefin and 97% aromatic hydrocarbons, good results may be obtained by employing 1.5 pounds of concentrated sulfuric acid in admixture with 12 pounds of aryl sulfonic acid per barrel of vaporized feed stock passed into the contacting zone. Thus, a major portion of the treating mixture is aryl sulfonic acid while a minor portion of the mixture is concentrated sulfuric acid having a strength in the range given. The sulfuric acid employed may conveniently have a concentration within the range of 90 to 100% and under most commercial conditions a 96% concentration of sulfuric acid will be desirable. When treating a feed stock contaminated with no more than 3% olefins, the

aryl sulfonic acid fraction withdrawn from separator 21 may be divided into a major portion including approximately 90% which is returned to the contacting zone 14 and a minor portion comprising approximately 10% which is washed with water in order to remove the sludge therefrom.

A number of aromatic materials may be employed as the feed stock in the present invention. As specific examples, may be mentioned fractions comprising a major portion of toluene. Similarly, the feed stock comprising a major portion of aromatic material may comprise a major portion of p-xylene, o-xylene or m-xylene or mixtures thereof. If desired, the hydrocarbon feed stock may comprise toluene in admixture with any or all of the isomeric xylenes. The aryl sulfonic acid produced in the contacting zone 14 is determined by the composition of the feed stock; if the feed stock comprises a major portion of toluene, the fraction withdrawn from contacting zone 14 will comprise principally toluene sulfonic acid in admixture with polymerized hydrocarbons; similarly, if other aromatic materials are fed to the contacting zone the sulfuric acid will react with these materials to produce the corresponding aryl sulfonic acid which is withdrawn in admixture with polymerized hydrocarbons from the contacting zone 14 through line 18.

It will be understood that the contacting vessel 14 must be operated at a suitable temperature and pressure to maintain at least the aromatic portion of the feed stock in a vaporous state to allow it to pass upwardly through the tower and be withdrawn through outlet line 15. Accordingly, the temperature and pressure conditions within vessel 14 are adjusted to secure this result. It will be found convenient to operate vessel 14 at approximately atmospheric pressure; at such a pressure, if the feed stock comprises a major portion of toluene it may be conveniently maintained at a temperature within the range of 250° to 300° F., while if the feed stock comprises a major portion of xylene it may conveniently be maintained at a temperature within the range of 285° F. to 355° F.

While I have disclosed a preferred method for operating the present invention and given specific operating conditions, it will be understood that these are given only by way of example and not by way of limitation and that various changes will be obvious to a worker skilled in the art without the exercise of invention.

Having fully described and illustrated the practice of the present invention, what I desire to claim and secure by Letters Patent is:

1. A process for treating a predominantly aromatic hydrocarbon feed stock contaminated with a minor portion of hydrocarbons comprising not substantially more than 3% of olefins including the steps of vaporizing said feed stock at a temperature substantially above atmospheric, contacting the vaporized feed stock with a mixture comprising aryl sulfonic acid and concentrated sulfuric acid in a contacting zone, said mixture comprising a major portion of aryl sulfonic acid and a minor portion of sulfuric acid having a strength in the range between 90% and 100% H_2SO_4 separately removing a vapor phase and a liquid phase from the contacting zone, cooling said liquid phase to a temperature no greater than approximately atmospheric to separate it into a hydrocarbon liquid phase and

an aryl sulfonic acid liquid phase and separating said liquid phases under the influence of gravity.

2. A process in accordance with claim 1 in which said feed stock comprises a major portion of toluene.

3. A process in accordance with claim 1 in which said feed stock comprises a major portion of xylene.

4. A process for treating a predominantly aromatic hydrocarbon feed stock contaminated with a minor portion of hydrocarbons comprising not substantially more than 3% of olefins, including the steps of vaporizing said feed stock at a temperature substantially above atmospheric, passing the vaporized feed stock into a contacting zone and there intimately contacting it with a mixture of concentrated sulfuric acid and aryl sulfonic acid, said mixture comprising a major portion of aryl sulfonic acid and a minor portion of sulfuric acid having a strength in the range between 90% and 100% H_2SO_4 separately removing a vapor phase and a liquid phase from said contacting zone, cooling said liquid phase to a temperature no greater than atmospheric to separate it into a hydrocarbon phase and an aryl sulfonic acid phase, separating the hydrocarbon phase from the aryl sulfonic acid phase under the influence of gravity and employing at least a portion of the separated aryl sulfonic acid phase as the aryl sulfonic acid in the contacting zone.

5. A process in accordance with claim 4 in which the aromatic hydrocarbon is toluene and in which the aryl sulfonic acid is toluene sulfonic acid.

6. A process in accordance with claim 4 in which the aromatic hydrocarbon is xylene and in which the aryl sulfonic acid is xylene sulfonic acid.

7. A process for treating a predominantly aromatic hydrocarbon feed stock contaminated with not substantially more than 3% of other hydrocarbons comprising olefins, including the steps of vaporizing said feed stock, passing the vaporized feed stock into a contacting zone and there intimately contacting it with contacting liquid comprising a major portion of aryl sulfonic acid and a minor portion of concentrated sulfuric acid having a concentration within the range of 90% to 100% H_2SO_4, removing a vaporous fraction comprising substantially pure aromatic hydrocarbon

from said contacting zone, removing a liquid fraction from said contacting zone, cooling said liquid fraction to a temperature within the range of approximately 85° to 100° F. and subsequently subjecting it to gravity separation to separate it into a hydrocarbon phase and an aryl sulfonic acid phase, separately removing said phases, dividing the aryl sulfonic acid fraction into a major portion and a minor portion, mixing the major portion with concentrated sulfuric acid and employing the resulting mixture as contacting liquid in the contacting zone, mixing the minor portion of aryl sulfonic acid with water and subsequently separating the resulting mixture under the influence of gravity into a water insoluble fraction and an aqueous aryl sulfonic acid fraction, returning the aqueous aryl sulfonic acid fraction to the contacting zone, mixing the resultant hydrocarbon phase with the vaporous fraction withdrawn from the contacting zone and fractionally distilling the resulting mixture to recover a substantially pure aromatic fraction.

8. A process in accordance with claim 7 in which the aromatic hydrocarbon is toluene and the aryl sulfonic acid is toluene sulfonic acid.

9. A process in accordance with claim 7 in which the aromatic hydrocarbon is xylene and in which the aryl sulfonic acid is xylene sulfonic acid.

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