

Sept. 28, 1965

P. D. MEEK ET AL

3,209,044

C₈ AROMATICS PROCESSING

Filed April 21, 1961

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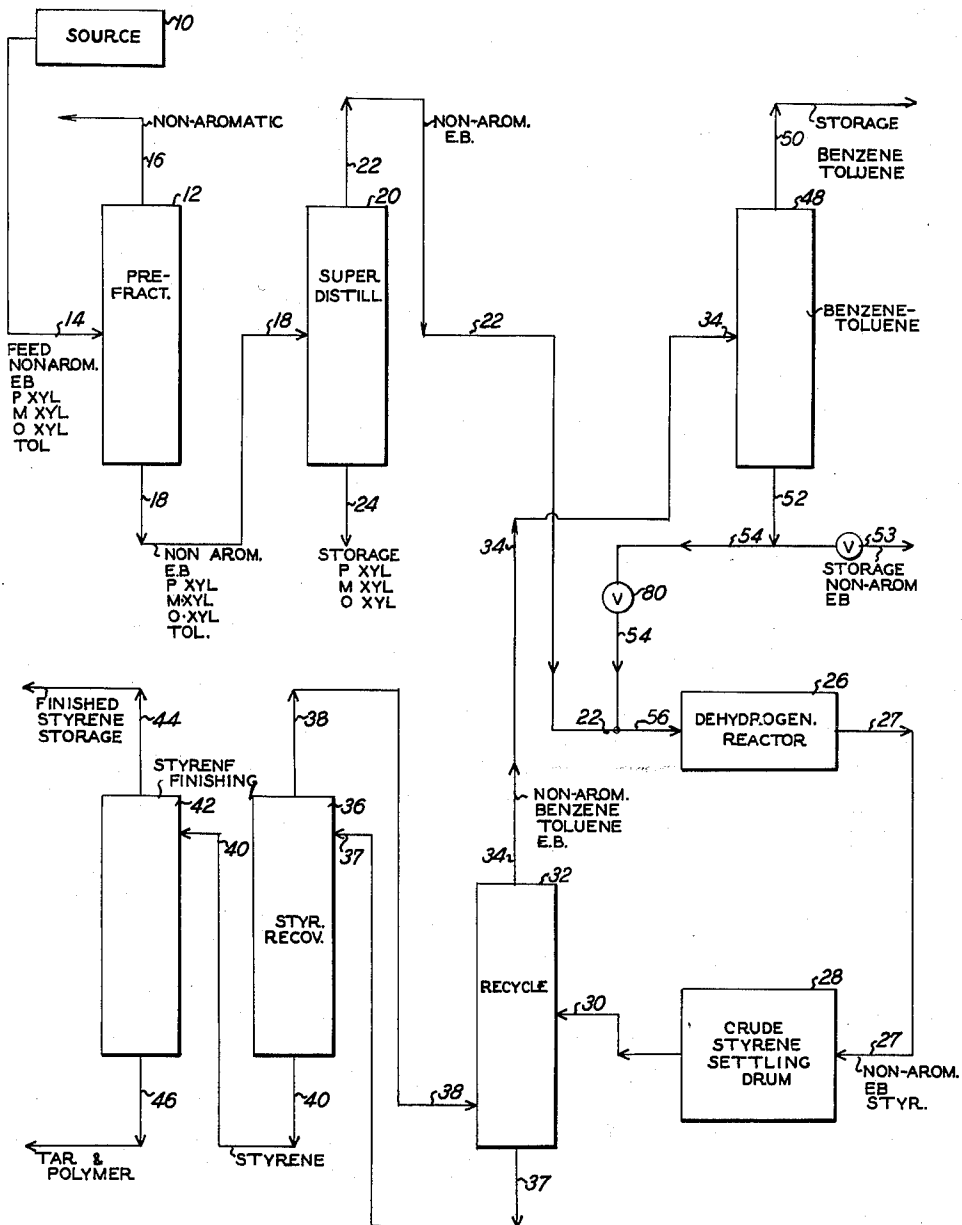


Fig. 1

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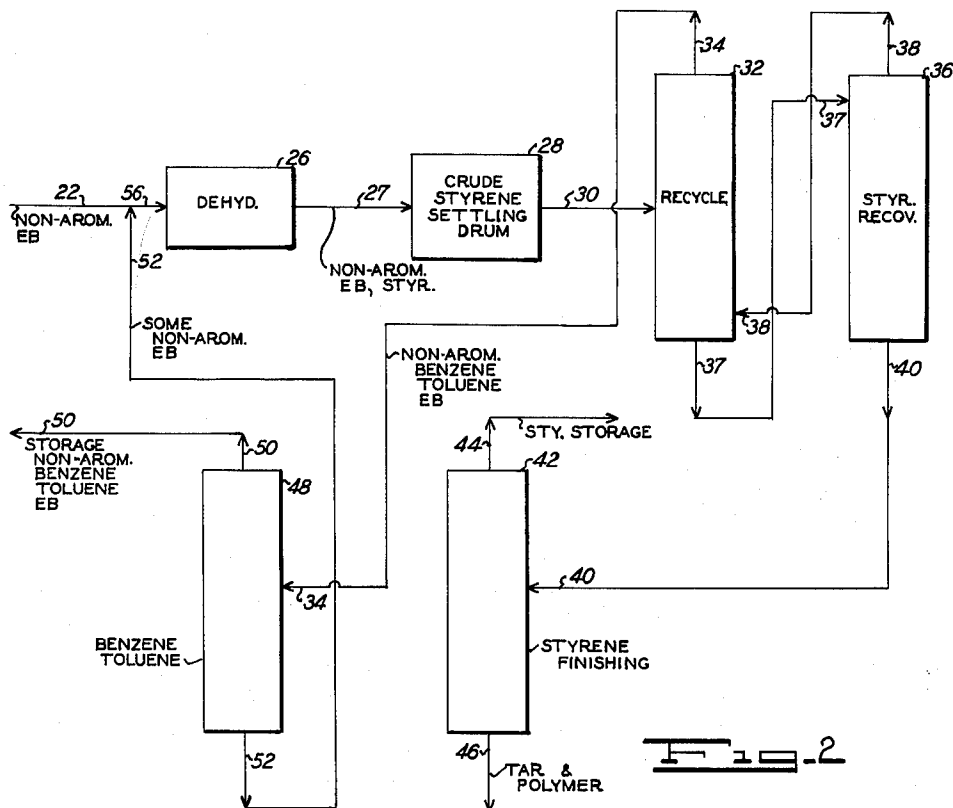
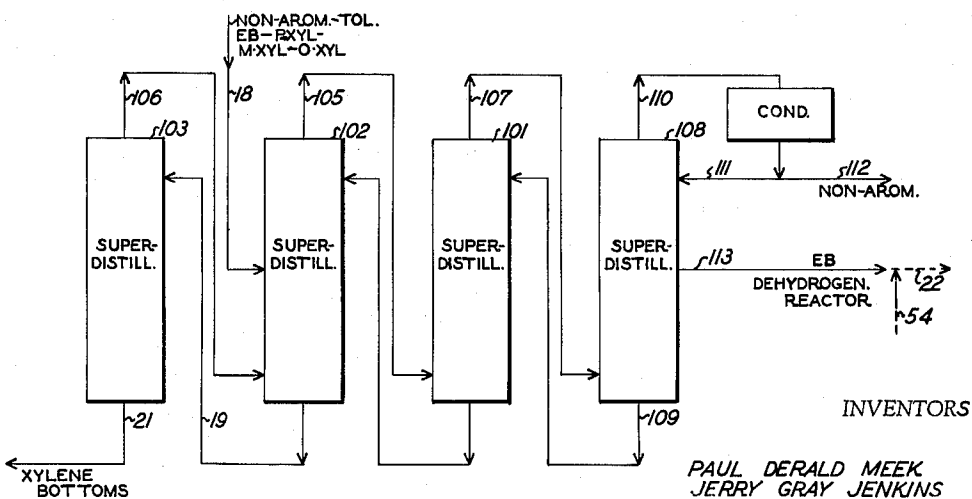


Fig-7

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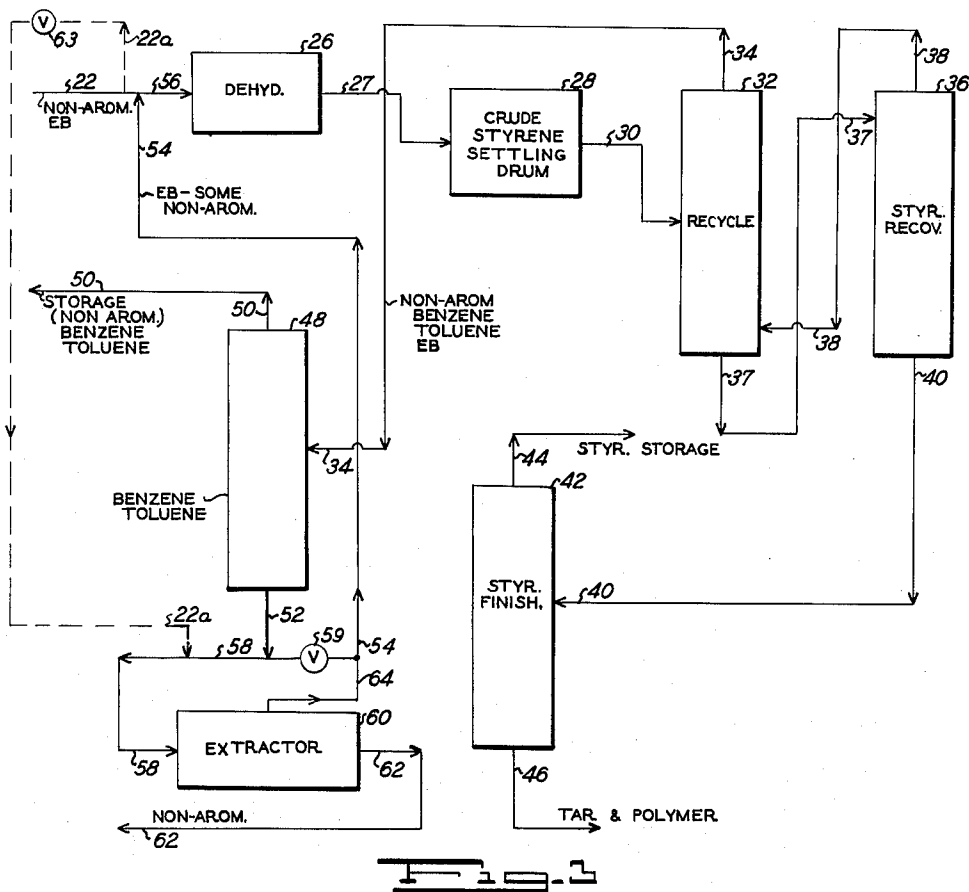
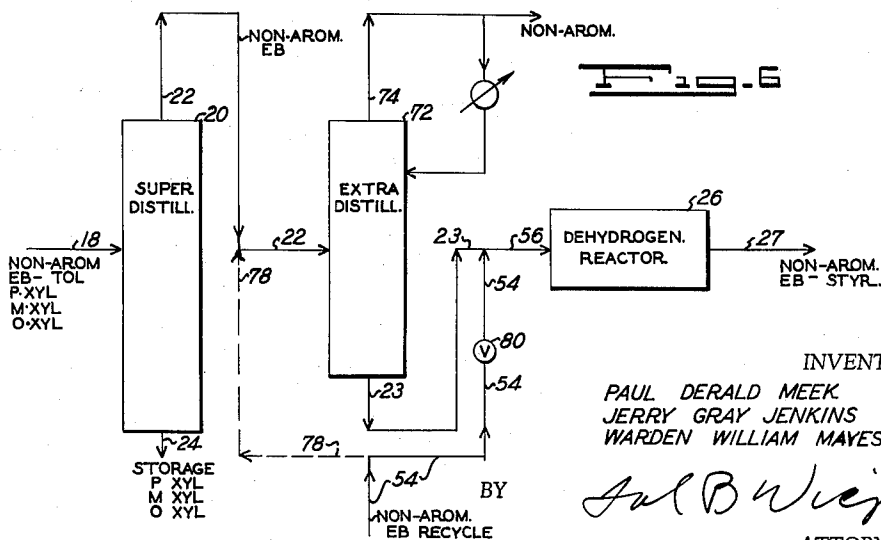
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3,209,044

G₈ AROMATICS PROCESSING

Filed April 21, 1961

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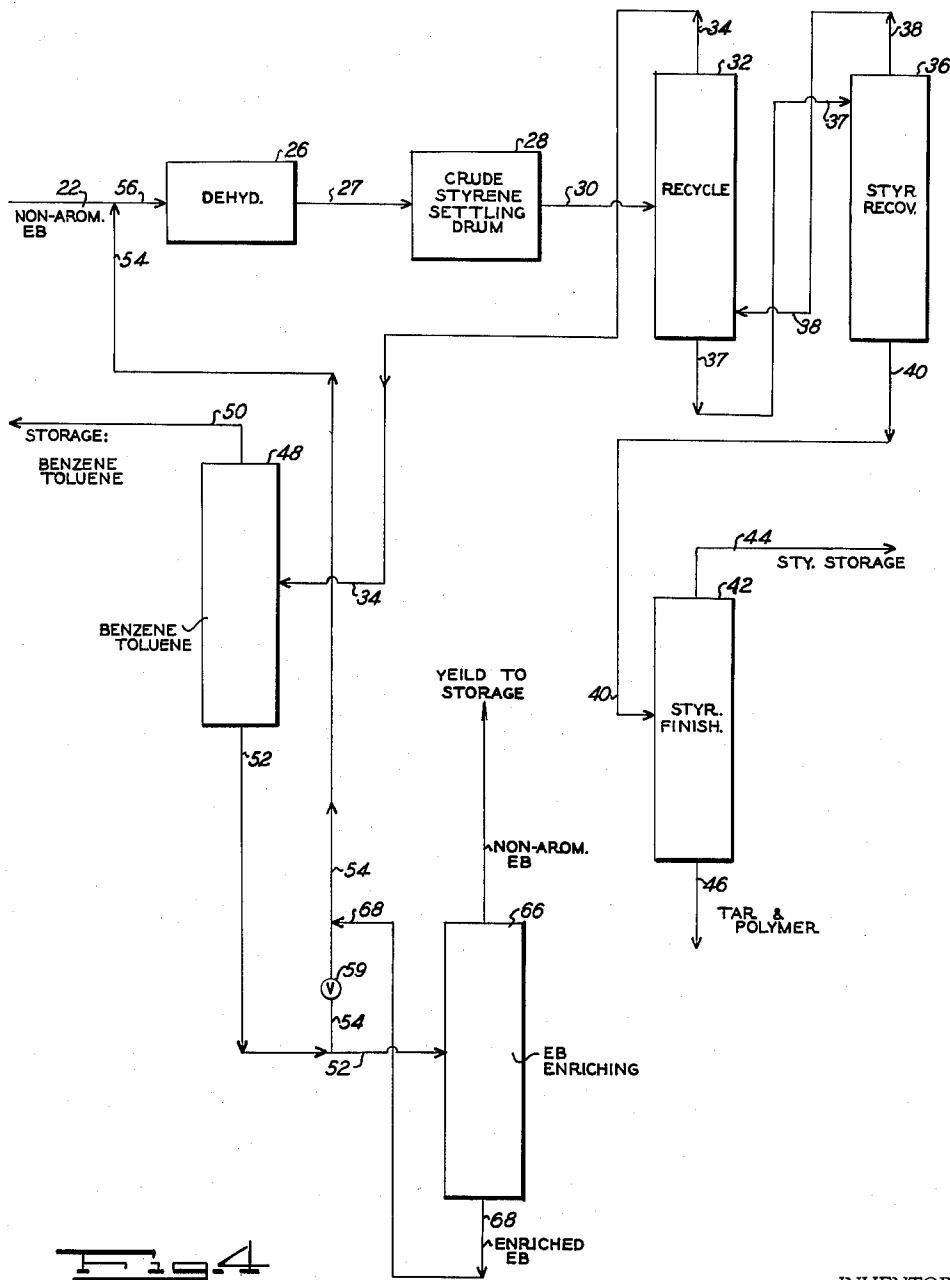
Sept. 28, 1965

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C₈ AROMATICS PROCESSING

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Filed April 21, 1961

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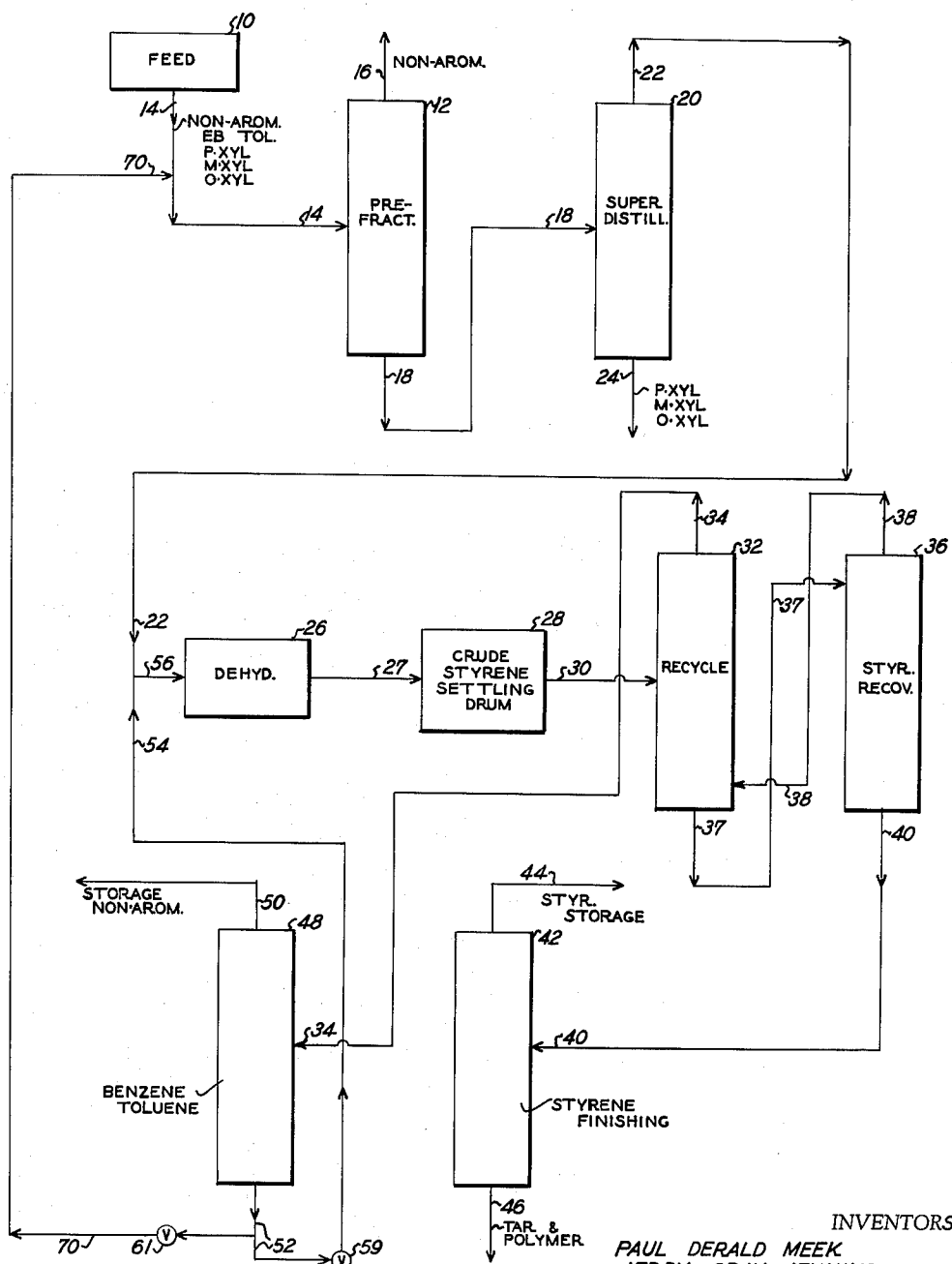
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3,209,044

C₈ AROMATICS PROCESSING

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Filed Apr. 21, 1961, Ser. No. 104,654
9 Claims. (Cl. 260-669)

This invention relates to improved processing of C₈ aromatics refinery cut comprising recoverable quantities of ethyl benzene in admixture with isomeric xylenes including some non-aromatic hydrocarbon boiling in about the same range to form pure styrene.

In prior U.S. Patent 2,959,626, assigned to the present applicants' assignee, it was found that ethyl benzene could be successfully removed in a super distillation column from other C₈ aromatics, namely the isomeric xylenes under critical distillation conditions comprising distilling in a still of at least 150 stages at a reflux ratio exceeding 40:1. However, in order to effect that separation by even super distillation, it was considered that substantially all non-aromatic hydrocarbons boiling in the critical boiling range, about 130 to 140° C., needed first to be removed. It was considered that such non-aromatic impurities in the critical boiling range would prevent a sharp separation of the mixed aromatics even under super distillation conditions, and further, that any non-aromatics carried by the separated ethyl benzene would impair the catalytic dehydrogenation reaction either to destroy the catalyst or be unremovable from the styrene produced thereby. It is now found that despite the presence of substantial quantities of non-aromatics in the system, better than 99.0%, and usually better than 99.7% pure styrene can be produced.

According to this invention, we have found that in a mixture of aromatics containing a recoverable quantity of ethyl benzene, o, m, p-xylenes and a non-critical large quantity such as up to about 5% of non-aromatics, the non-aromatics do not interfere with the separation of ethyl benzene from the other C₈ aromatics under super distillation conditions as described in the said patent. The non-aromatics remain with the ethyl benzene which, nevertheless, is substantially completely separated from other C₈ aromatics. The effect, surprisingly, is that the non-aromatics go overhead with the ethyl benzene even though they boil higher than ethyl benzene and other xylenes. This is due to the formation of an azeotrope (ethyl benzene-non aromatics). Consequently, the recovery of ethyl benzene is greatly simplified from the procedure described in said patent because it is not first necessary to extract the entire aromatic raw feed fraction to remove all but trace quantities of non-aromatics boiling in the critical C₈ boiling range before super distillation. A further immediate consequence is that the ethyl benzene mixture with the non-aromatics passing overhead and substantially freed of other aromatics, is in comparatively small volume so that it is more economic to process the small quantity to remove the non-aromatics.

We have further discovered, that the ethyl benzene with comparatively large quantity of non-aromatics can be further processed by extraction or by distillation thereby removing large quantities of non-aromatics from the ethyl benzene.

We have further discovered that the non-aromatic impurities passing overhead with the ethyl benzene in the super distillation do not adversely affect the production of substantially pure styrene. Although a portion of the non-aromatic impurities are cracked in the dehydrogenation reactor, coking of the dehydrogenation catalyst conventionally used is not a problem. Cyclic operation of the reactor to provide for a decoking step is not required

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as it is in many applications of the same general type of catalyst in dehydrogenation of non-aromatic materials. In the recovery and purification of styrene from the dehydrogenation reaction mixture the excess of non-aromatic impurities remains with the ethyl benzene and builds up in the recycle to the reactor. A substantial quantity of the non-aromatic materials boil in the same range with styrene, but their behavior is vastly different from that occurring in the prior distillation step where about 20% of the non-aromatic materials came out the bottom of the super fractionator. In the ethyl benzene-styrene separation none of the aromatics come out the bottom of the fractionation system; consequently, substantially pure styrene may be produced from the dehydrogenation reaction mixture of super distilled ethyl benzene despite the presence of substantial quantities of non-aromatics. Several treatment processes are available to remove the excess of non-aromatics from the system. Such removal of non-aromatics may vary through several procedures but is usually applied upon the ethyl benzene recycle overhead separated from the crude styrene reaction mixture.

First, it will be appreciated that where the non-aromatics are allowed to build up to about from 5 to 20% of the total ethyl benzene recycle, a comparatively high concentration with respect to the initial super distillation mixture feed to the styrene reactor, this build-up of non-aromatics in the recycle will eventually become readily controlled. A portion of the recycle concentrate sufficient to prevent the build-up of non-aromatics in the ethyl benzene recycle may be withdrawn from the system. However, there are other more economical procedures for removing non-aromatics sufficient to prevent this build-up of the non-aromatics in the ethyl benzene recycle.

In an ordinary distillation of a C₈ aromatic fraction the non-aromatics can be removed down to about a 1 to 2% content of the final product. Accordingly, while the feed stock to the super fractionator can contain up to 5% of non-aromatics, without critical effect on the system, it is often useful to apply a preliminary distillation to the C₈ aromatic feed to remove non-aromatics down to about 1 to 2% before super distillation. Accordingly, by one embodiment of the procedure the ethyl benzene recycle from the reactor can be passed to the prefractionator for removing excess non-aromatics, the ethyl benzene being again distilled in admixture with the total C₈ fraction in the super distillation. By this procedure it will be recognized that the ethyl benzene then becomes completely recycled to the prefractionator, passing thence to the super fractionator, before passing to the dehydrogenation reactor. Nevertheless, that procedure suffices to prevent continuous build-up of non-aromatics in the reactor system.

According to a second procedure to remove or reduce the non-aromatic content of the ethyl benzene recycle overhead, the total recycle overhead fraction is passed through a benzene-toluene still. The non-aromatics pass overhead with the benzene and toluene to leave ethyl benzene recycle bottoms from which much, if not all, of the non-aromatics have been removed. Therefore, the ethyl benzene recycle bottoms to the reactor has controlled non-aromatic build-up within it and as a result, with the system.

In a third procedure the ethyl benzene and non-aromatics recycled, after separation of benzene and toluene, can have a small side stream withdrawn and passed to a small extraction unit in which the non-aromatics are separated, but usually only in quantity sufficient to prevent their build-up in the total feed to the dehydrogenation reactor.

As a fourth alternate procedure, a second still following the benzene-toluene column can take a small side stream portion of the recycle, distill enough of the non-aromatics therefrom and return a more concentrated ethyl benzene side stream back to the ethyl benzene recycle. The quantity of non-aromatics removed is adjusted only to be sufficient to prevent the non-aromatic build-up in the reactor feed. This alternate is particularly applicable to a system in which the benzene-toluene is removed prior to separation of the ethyl benzene recycle from the dehydrogenation reaction mixture.

The several alternate procedures useful herein to prevent build-up of non-aromatics in the recycle are illustrated diagrammatically in the drawings herewith in which:

FIG. 1 is a flow diagram illustrating prefractionation, ethyl benzene super distillation, and controlled discharge of recycle from the system to prevent non-aromatic build-up in the ethyl benzene recycle to the dehydrogenation reactor.

FIG. 2 is a flow diagram illustrating removal of a sufficient quantity of non-aromatics with the benzene and toluene distillate to prevent build-up in the ethyl benzene recycle.

FIG. 3 illustrates a similar flow diagram in which a slip stream taken from the ethyl benzene recycle is extracted to withdraw enough non-aromatics to prevent the build-up of non aromatics.

FIG. 4 is a flow diagram similar to FIG. 3 except that the non-aromatics are removed from the slip stream by distillation.

FIG. 5 is a flow diagram illustrating recycle of ethyl benzene to the pre-fractionator to remove excess non-aromatics through redistilling the ethyl benzene in the super distillation column.

FIG. 6 is a detail illustrating the use of an extra column to distill from the pure mixture of ethyl benzene and non-aromatics a concentrate rich in non-aromatics which is withdrawn discarded from the system, to prevent substantial build-up in the ethyl benzene recycle.

FIG. 7 illustrates a similar detail flow diagram in which an extra column is connected in series with the super distillation column to remove non-aromatics from the overhead fraction and thereby prevent excess non-aromatic build-up.

Referring to the drawings:

FIGURE 1 shows a procedure for processing a mixed aromatic feed 10 which may contain a substantial quantity of non-aromatics boiling in the C_8 aromatics range. For instance, a 2 to 10% non-aromatic content is passed through a prefractionator column 12 by way of line 14, the conditions so adjusted to take off a fraction substantially high in non-aromatic overhead through line 16 and a bottoms feed through line 18 which usually contains from 1 to 3% of non-aromatics. The prefractionated feed is passed to a super distillation column 20 which actually comprises several columns which together exceed 150 distillation stages and is described in greater detail in FIG. 5 of U.S. Patent 2,959,626, that figure being herein incorporated by reference. The column 20 can separate the C_8 aromatics so that the overhead through line 22 is a pure mixture of non-aromatics and ethyl benzene and the bottoms withdrawn through line 24 is substantially pure xylene. If, for example, the original feed to the super distillation still 20 contained 20% ethyl benzene and 78.8% xylenes with 1.2% non-aromatics, the overhead at line 22 would comprise about 95.3% ethyl benzene, the non-aromatic passing over therewith azeotropically being correspondingly increased to about 4.5% while carrying with it only trace quantities such as 0.2% of m and p xylenes. Such ethyl benzene non-aromatic mixture then passes to the standard dehydrogenation reactor 26 which is a catalyst bed of alkali promoted iron oxide which is well known in the art; for instance, Shell catalyst 105 and further described in U.S. Patent 2,414,585 and 2,460,811

wherein the hydrocarbon and steam at raised temperatures, about 500 to 800° C., and in ratio of about 15-30:1 steam to hydrocarbon are passed over the catalyst. In consequence, a mixture of styrene, ethyl benzene, other aromatics and the residual non-aromatics which did not crack in the catalytic reactor are passed to a settling drum 28 by way of line 27.

The crude reaction mixture after settling out condensed steam in drum 28 passes by way of line 30 to a recycle column 32 in which unreacted ethyl benzene and non-aromatics together with small quantities of benzene and toluene produced in the reactor are passed overhead as recycle by way of line 34. The bottoms from the recycle column 32 comprises styrene and a substantial quantity of ethyl benzene which are distilled in a second still 36 and are passed thereto by line 37. The ethyl benzene from still 36 is removed by line 38 and returned to the recycle column 32. The partially distilled styrene leaves still 36 by way of line 40 where it passes to a styrene finishing column 42 to separate pure styrene overhead through line 44 from the residue through line 46. All of columns 32, 36 and 42 are operated under sub-atmospheric pressure and at a temperature below the polymerization temperature of styrene to minimize polymer losses. Newly formed polymers pass out of the system as bottoms through line 46 from the styrene finishing column 42. The ethyl benzene recycle in line 34 passes to a still 48 which is on the down side of the styrene separation and operating upon the stable hydrocarbon recycle from which the styrene has been removed. The unit may be operated at atmospheric pressures or even higher and corresponding distillation temperature as desired. The more volatile benzene and toluene contained in the recycle pass overhead and are removed from the system through line 50 and the ethyl benzene recycle comprising bottoms are withdrawn through line 52 and are largely returned through line 54 to the dehydrogenation reactor 26 entering therein through line 56. The nonaromatics tend in this system to accumulate, for instance, if there was a 1% non-aromatic content entering with the feed through line 18, and about a 20% ethyl benzene content which was separated in the super distillation still 20, the non-aromatic ethyl benzene mixture may become about 95% ethyl benzene and 5% non-aromatics, first entering the dehydrogenation reactor 26 as raw feed from line 22. Since the single pass conversion of ethyl benzene across the dehydrogenation catalyst is substantially greater than that of the non-aromatics, the ratio of non-aromatics to the ethyl benzene in the recycle stream line 34 is greater than that in the raw feed from line 22. It is apparent accordingly that non-aromatics continuously build up in the system. In as much as the non-aromatics are more highly concentrated in this recycle line, the build-up of non-aromatics in the system may be prevented by the withdrawal of recycle material. For this purpose the bottoms leaving the benzene-toluene column 48 in line 52 is divided, a portion thereof being withdrawn from the system through line 53. The remainder of the stream in line 54 is combined in line 56 with raw feed as recycle and passed to the dehydrogenation reactor 26. In this manner, non-aromatics are prevented from building up excessively in the system.

In an alternate procedure shown in FIG. 2, the non-aromatics can be prevented from building up in the system by removal with the overhead fraction in the benzene-toluene column 48. This is practical because the non-aromatics, although they are higher boiling components, tend to form an azeotrope with the aromatics. The non-aromatics will azeotrope to some extent with the more volatile aromatics, benzene and toluene, as with the ethyl benzene. Therefore, rather than withdraw a portion of the ethyl benzene recycle through line 53 of FIG. 1 this alternate procedure based on the azeotrope principle may be used. It is feasible economically merely to take a deeper cut in the still 48, thereby removing some of the

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non-aromatics with the benzene and toluene together with some ethyl benzene for purposes of controlling the build-up quantity of non-aromatics in the system. Accordingly, the ethyl benzene loss from the system is less than the loss of ethyl benzene by the procedure of FIG. 1.

It is possible, however, and often most feasible in an alternate procedure to separate in very high yield practically all of the ethyl benzene from the non-aromatics, as shown in the flow diagram FIG. 3. According to this procedure the ethyl-benzene non-aromatic recycle in line 52 leaving the benzene-toluene column 48 as bottoms can be separated in the extractor 60. If all of the bottoms from column 48 through line 52 were extracted, the recycle would be diverted from line 54 through line 58 to an extractor 60 in which the non-aromatics and aromatics are separated in a solvent extraction column. The non-aromatics are withdrawn from line 62 and the ethyl benzene returned to line 54 by way of line 64. However, there is no need to remove all of the non-aromatics in the extractor 60. It is necessary only to remove enough to prevent build-up in the system. The extraction process may, by alternate procedure, be operated with control valve 59. Valve 59 limits the volume of flow in line 54 thereby diverting a sufficient quantity through line 58 which passes into the extraction unit 60. The remainder of the bottoms from the benzene-toluene column 48 passes through to line 54 and admixes with pure ethyl benzene from line 64 which now has no more non-aromatics or usually somewhat less than passing through line 22 for recycle to the dehydrogenation reactor 26 by way of line 56.

The extraction unit 60 may also be fed from the super-distillation overhead fraction in line 22. The non-aromatic, ethyl benzene mixture may be taken from line 22 by line 22a and cycled to the extraction unit 60 by way of line 58. The amount of the overhead cycled to the extraction unit 60 may be any fractional amount of the overhead. Furthermore, it is also possible that the total volume of overheads from line 22 be sent through line 22a to the extraction unit 60. In this manner, the non-aromatics will be extracted before being sent through the dehydrogenator 26, either in total or in part depending upon whether the valve 59 is open or closed.

The diverted quantity in line 58 may be a minimum presupposing that highly efficient solvent extraction is obtained in extraction unit 60 to remove substantially all of the non-aromatic from the ethyl benzene. An advantage of this embodiment, of course, is that a relatively small volume from line 52 needs to be treated. Consequently, the extraction unit may be relatively small, certainly very small in comparison to the preliminary extraction unit of the entire aromatics feed described in the Patent 2,959,626 referred to above. Alternately, a larger or even all of the flow may be constricted to pass through line 58 by manipulation of valve 59 so that all or a relatively large part of the recycle may be treated in the extraction unit 60. A larger unit 60 may be used and operated relatively inefficiently since only a lower relative portion of non-aromatics need to be separated from the ethyl benzene, non-aromatic feed from line 52. The limiting condition, of course, is to remove enough of the non-aromatics by recycle extraction to prevent the non-aromatic content of the system from building up in line 56 when it combines with the raw feed overhead in line 22.

In a fourth alternate procedure, the non-aromatic ethyl benzene recycle appearing as bottoms of the benzene-toluene column 48 in line 52 is returned as a recycle stream to line 22 entering the dehydrogenation reactor 26 through line 56 as shown in the flow diagram FIG. 4. A fractional portion, however, by constriction of the ethyl benzene stream with valve 59, is distilled in column 66, thereby removing enough of the non-aromatics to prevent build-up in the system. The bottoms of still 66 leaving through line 68 is returned to line 54 downstream

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of the valve 59 so that the recycle continues through line 54 to join the raw feed in line 22. The distillation column 66 may be operated economically without direct concern on the efficiency of the unit. The basic requirement of the distillation process is the removal of enough of the non-aromatics to reduce the concentration in line 54 to less than an amount which when combined with that from line 22 will remain constant with continuous operation of the dehydrogenation system.

In a fifth alternate procedure, the ethyl benzene-non-aromatic recycle leaving column 48 through line 52 can be divided by constriction of flows through valves 59 and 61 such that a portion high in non-aromatics is recycled through line 54 to line 22 and entering dehydrogenation reactor 26 through line 56 according to the flow diagram FIG. 5. Another portion continues on through line 70 returning to the raw feed inlet of line 14 for recycling through the prefractionator 12. By this means the content is removed in the prefractionator 12 and passes out of the unit as overhead via line 16. The non-aromatic content in line 22 is increased by tie relatively higher non-aromatic content of the recycle through line 54 such that the feed to the dehydrogenation reactor 26 entering through line 56 has a somewhat higher non-aromatics content than that in line 22. The ratio of flows through lines 54 and 70, may be such that the selected higher content of non-aromatics in the system at line 56 will remain about constant and will not continue to build up.

In a sixth alternate embodiment of this invention, feed stock is supplied to the super distillation column 20 as shown diagrammatically in FIG. 6. The column 20 separates the feed into an overhead fraction in line 22 and a bottoms fraction through line 24. The bottoms fraction comprises principally the xylene isomers. The overhead fraction in line 22 comprises substantial quantities of ethyl benzene and non-aromatics. By way of line 22, the overhead stock is passed to an ordinary column still 72 which is regulated to remove much of the non-aromatics together with some of the ethyl benzene overhead through line 74. A portion of the overhead stock is recycled back to the column as a reflux. The bottoms from the column 72 are taken by line 23 and connected to line 56 where it combines with the recycled stock which is fed directly to the dehydrogenator 26. Valve 80 is used to constrict the flow in line 54 such that a portion of the stock may be cycled by line 78 and fed to column 72. Furthermore, if the valve 80 is completely closed, the total recycled stock is fed to line 22 for distilling and then fed from line 23 to the dehydrogenator 26. The amount of recycle in line 54 is based primarily on the percent of non-aromatics in line 23 and the amount of non-aromatics which is detrimental to economic operation of the dehydrogenator 26. Normally, the bottoms from the column 72 contain up to about 5% of non-aromatics which are sent through line 23 to the recycle addition from line 54 and entering the dehydrogenation reactor 26 via line 56. With this modification, the prefractionator 12 may not be essential to the operation of the process. Crude aromatic C₈ fractions containing up to about 5% non-aromatics is initially fed by line 18 to the superdistillation column 20 to separate the ethyl benzene from the other C₈ aromatic components. The ethyl benzene-non-aromatic mixture is only subsequently fractionated to reduce the non-aromatic content immediately before dehydrogenation. The build-up in the system of non-aromatic can, therefore, be prevented by any of these procedures previously described.

In a seventh alternate procedure of the illustrated diagram in FIG. 1, the several distillation columns comprising the super still 20, described in detail in FIG. 5 of U.S. Patent 2,959,626 herein incorporated by reference has an extra column 108 included therewith to aid in controlling non-aromatic build-up as shown in FIG. 7. Thus, the crude feed entering through line 18 passes first to the middle column 102 and the bottoms thereof passes as reflux through line 19 to the preceding column 103 so that

the bottoms therefrom are substantially pure xylenes. The xylenes are then removed through line 21. The overhead of columns 102 and 103 passes to the succeeding columns through lines 105 and 106. The final super distillation still 101 passes the relatively refined ethyl benzene non-aromatic overhead stock through line 107 to a final column 108. A relatively pure ethyl benzene reflux is returned to the preceding column 101 by way of line 109. The overhead of column 108 in line 110 is a mixture of most of the non-aromatics along with some ethyl benzene, some of the overhead being condensed and returned in line 111 while the rest is removed through line 112. The relatively refined ethyl benzene product is very low in non-aromatics and is withdrawn through an intermediate level in line 113. The stock in line 113 is combined with the recycle stock in line 54 and passed to the reactor 26. The non-aromatics in the recycle stock of line 54 may also be controlled to prevent a detrimental build-up which affects the dehydrogenation 26. Accordingly, therefore, any of the previously described processes which are designed to control the non-aromatic build-up in the system may readily be applied to the recycle stock of line 54 operating with the extra column 108. The extra column 108 used to remove non-aromatics may also be used to remove some of the non-aromatics from the recycle stock of line 54.

The following examples illustrate the operation of these several procedures:

Example 1

Following the procedure illustrated in FIG. 1 a crude feed composed of 3.0% non-aromatics, 1.5% toluene, 20.0% ethyl benzene, 10.5% p-xylene, 56.0% m-xylene, and 9.0% o-xylene by weight, is fed to a prefractionating column. The prefractionation column consists of a column still having 60 stages and operated at a reflux ratio of 15:1. The continuously drawn overhead fraction is composed of 55.6% non-aromatics, 41.6% toluene, and 2.8% ethyl benzene. The bottoms fraction from the prefractionator was analyzed and found to contain 58.0% m-xylene, 9.4% o-xylene, 10.9% p-xylene, 20.7% ethyl benzene, and 1.0% non-aromatics.

The bottoms from the prefractionator are passed to a three column still having a total of 390 stages for super distillation. The C₈ fraction sent to the three column still for super distillation was first heated in a heat exchanger wherein the temperature is raised sufficient to volatilize some of the C₈ aromatics. Upon leaving the heat exchanger the feed enters the first column of a three column series, each having 130 plates and distilled at a reflux ratio of 75 to 1. The overhead vapors from the first column are introduced at the bottom of the intermediate column and the vapor overhead from the column passes to the bottom of the third column. Simultaneously, liquid collected as bottoms is returned to the preceding column near the top for reprocessing. The sum effect is a column having 390 stages with a reflux ratio of 75:1. The top overhead from the third column, consisting of 95.3% ethyl benzene, 4.5% non-aromatics, and 0.2% xylenes is passed to a dehydrogenation reactor. The xylene bottoms from the first column are sent to the storage vessels. The compositions of the bottoms consist of 85.1% m- and p-xylene, 3.1% ethyl benzene, 11.5% o-xylene, and 0.3% non-aromatics.

The concentrated ethyl benzene stock is mixed with recycle ethyl benzene and passed to a catalytic dehydrogenation reactor. The reactor is operated at a temperature of 1125° F. and a pressure of 10 p.s.i.g. and at a steam to hydrocarbon ratio of 17.1. The liquid portion of the dehydrogenated product produced consists of 0.6% benzene, 2.5% toluene, 6.6% non-aromatics, 56.8% unreacted ethyl benzene, and 32.8% styrene. Gases produced leave the system through a vent (not shown). The mixture is passed to a crude styrene separating still to form an ethyl benzene rich recycle overhead. The

bottoms are substantially styrene and minor decomposition products. The crude styrene still is operated under sub-atmospheric pressure and at a temperature below the polymerizing temperature to minimize the polymerization. The overhead ethyl benzene recycle has a composition comprising 84.4% ethyl benzene, 9.9% non-aromatics, 0.9% benzene, 3.8% toluene, and 1.0% xylenes. The overhead recycle is passed to a benzene-toluene still where the benzene and toluene are roughly removed to produce a product which now comprises 10% non-aromatics, 86% ethyl benzene, 3% toluene and 1% xylenes. The dehydrogenator operates at about 40% conversion of ethyl benzene per pass while the non-aromatic conversion across the catalyst is only about 15%. In this continuous process all unconverted ethyl benzene is returned as recycle to the reactor. Since the non-aromatic conversion is only in the order of 1/3 of the conversion of ethyl benzene, this total recycle condition will cause the ratio of non-aromatics to ethyl benzene to increase in the system. This increase can be controlled in accordance with the procedure as outlined in FIGURE 1 by withdrawing a portion of the reactor recycle through line 53. By this means the system is brought to steady state conditions and the concentration of non-aromatics in the recycle feed to the reactor can be controlled at 10% by weight.

It will be seen as illustrated in this example that the non-aromatics content of the recycle stream, containing on first pass 6% non-aromatics, will continuously increase until ultimately 10% non-aromatics by weight are contained in the recycle. When the non-aromatic content reaches 10% in the recycle feed, the recycle stream is bled by 14% continuously. Since substantially no non-aromatics pass with the styrene, but instead with the recycle stock, the amount bled from the recycle stream is basically dependent upon the allowable non-aromatic concentration to be fed to the dehydrogenator. When the permissible non-aromatic concentration is reduced to 8% by weight of the recycle feed to the dehydrogenator, the amount of recycle stock bled is 32%. Consequently, the build-up of non-aromatics in the system is inversely dependent on the amount of recycle stock discarded from the system. However, the greater the amount of recycle stock discarded, the less the styrene production from the super-distilled ethyl benzene.

Example 2

The procedure of Example 1 is repeated except that the benzene-toluene column is operated to take a deeper cut of the recycle stock, removing enough of the non-aromatics together with some ethyl benzene to reduce the non-aromatic content of the recycle stream which admixes with the super distillation column overhead prior to processing in the dehydrogenator. Consequently, the benzene-toluene still is operated to produce an overhead composition in the still of approximately 14% toluene, 9.5% benzene, 12% non-aromatics, 64.5% ethyl benzene. The bottoms from the benzene-toluene column are recycled to the dehydrogenation reactor and comprise primarily ethyl benzene containing 10% non-aromatics including therein trace quantities of benzene and toluene. Ethyl benzene losses are cut almost in half over the losses by the procedure of Example 1 while the non-aromatics buildup is still adequately controlled.

Example 3

The procedure is again followed as in Example 1, but instead of withdrawing the recycle, it is necessary only to treat a portion of the recycle to remove the non-aromatics or a substantial portion thereof. Consequently a portion of the stream as shown in FIG. 3, for instance 7% of the recycle stream is bled through an extraction unit 60, wherein substantially all of the non-aromatics are removed by extraction according to any standard procedure; for instance, an extraction unit designed for operation at raised temperature of 290° F.

and at a pressure of 128 p.s.i.g. Di-ethylene glycol with 6% water is used as the solvent in the extraction unit. The feed enters the extraction system and is pumped, first through a heat exchanger to preheat the feed to almost 290° and thence to an intermediate level of the extractor. Hot solvent at 290° F. and 128 p.s.i.g. enters the top of the extractor in a ratio of about 10 parts of solvent to 1 part of recycle feed. Simultaneously, a light hydrocarbon reflux of solvent stripper overhead is supplied to the bottom of the extractor. The paraffinic recycle is supplied at about 15% of the solvent rate.

The non-aromatics contained in the recycle feed to the extraction unit pass overhead from the extractor thereby being removed from the system. Hot aromatics rich extract solution in the solvent is withdrawn from the bottom of the extractor and is cooled to 230° F. in a heat exchanger. The solvent is then sent to a solvent stripper. The solvent stripper, by reduction of pressures to below 15 p.s.i.g. causes the volatile non-aromatic hydrocarbon components to flash overhead as vapors while the unvolatilized solvent solution of aromatics in the bottom of the flashing section are transferred by float controlled valve to a point near the top of the solvent stripper section. Since the non-aromatics in the solvent solution are the most volatile they are efficiently removed from the top of the column together with some of the most volatile aromatics. This material is condensed in a heat exchanger and returned as reflux to the bottom of the extractor. The substantially 100% pure aromatic ethyl benzene stream is taken off of the stripper as a side stream together with steam. This vapor mixture is cooled in a heat exchanger to condense the ethyl benzene to liquid and passed to an accumulator wherefrom the ethyl benzene is withdrawn and cycled to the recycle feed to the dehydrogenator reactor.

Example 4

A similar effect is produced as according to the above Example 3 by substituting a separate distillation column 66 in the recycle stream following the benzene-toluene distillation column in place of the extraction unit. The separate distillation column is used to distill off a quantity of non-aromatics rather than to extract the non-aromatics as previously exemplified.

The bottoms from the benzene-toluene column are passed to the dehydrogenator. However, 50% of this stream is bled from the line and by-passed to the separate distillation column where it is processed. The stock enters the still at an intermediate point as feed stock. The unit operates at a reflux ratio of 10:1 and produces an overhead fraction composed of 15% non-aromatics and 85% ethyl benzene having included therein trace quantities of residuals. The relatively more pure ethyl benzene fraction is withdrawn from the column as bottoms and is returned to the recycle stream. The still is operated inefficiently and returns 9.5% non-aromatics with the ethyl benzene fraction back to the recycle stream. The recycle stream is admixed with the overhead from the super distillation still, as in Example 1 and processed through the dehydrogenation unit. The combination of the recycle stock with the super-distilled ethyl benzene containing 4.5% by weight non-aromatics will ultimately produce a feed to the dehydrogenator containing a maximum 8% non-aromatics.

Example 5

In an alternate procedure, the overhead fraction in line 22 containing 4.5% non-aromatics from the super distillation column 20 is passed by line 22a to an extraction unit 60 as shown in FIG. 3. This extraction unit is operated as disclosed in Example 3. The enriched ethyl benzene stream, containing 1.8% non-aromatics, is then passed as feedstock through line 54 to the dehydrogenator 26. The dehydrogenation product is processed as previously described in Example 1 except that no recycle stock

is bled from the system. Enough of the non-aromatics can be removed by processing only 50% of the overhead fraction from the super distillation column through the extraction unit to control buildup in the system.

Example 6

It is somewhat more economical to use the prefractionator still 12 as illustrated in FIG. 5 for fractionating a portion of the recycle in line 54. For this purpose the recycle in line 54, controlled by valves 59 and 61 is divided to pass 15% through line 70 entering prefractionator 12, the remaining fraction joining line 22 and combined as feed to the dehydrogenator by way of line 56. The bottoms from the prefractionator have approximately the same amount of aromatics but are substantially richer in ethyl benzene. The composition passing overhead of the super distillation column to the dehydrogenator remains unchanged and the system operated the same as described in the preceding example with the slight economy of making greater use of the prefractionator, thereby eliminating the necessity of the enrichment column 66. The result of this method is a somewhat heavier load on the super distillation column to again require separation therein of ethyl benzene from xylenes.

Example 7

In an alternate procedure to avoid the need to again superdistill ethyl benzene, and with extra economy, the prefractionator 12 can be omitted, a construction as shown in FIG. 6 can be used. According to the present example, a still 72 having about 60 trays is interposed in line 22. The overhead super distillate mixture of non-aromatics and ethyl benzene is passed to the center of the column 72, operated with a reflux ratio of 10:1. The overhead in line 22 comprises, by omission of the prefractionator 12, about 12.9% by weight non-aromatics, 0.7% toluene, and the balance, ethyl benzene. The bottoms withdrawn through line 23 contain 3.0% non-aromatics and the balance is ethyl benzene. The bottoms are then passed to the dehydrogenator 26. As in the previous example, a portion of the recycle in line 54 can be bled off through line 78 and passed to the inlet feed line 22 of the still 72. In this manner the complete function of the prefractionator is provided by the still 72, removing excess non-aromatics so that the prefractionator is unnecessary. In addition, a small portion of the recycle is distilled to prevent excessive build-up of non-aromatics in the system. For example, by constricting the valve 80, 15% of the recycle from line 54 is passed to the still 72, the remaining recycle in line 54, having the composition of Example 1, joins line 23 and the combined feed passes through by line 56 to the dehydrogenation reactor 26.

Example 8

It is possible to operate the super still shown in U.S. Patent 2,959,626, FIG. 5, thereof, to effect a separation of non-aromatics in an additional leg 108, which is somewhat analogous to the still 72. The advantage is that the non-aromatics can be more efficiently separated and the ethyl benzene fed into line 22 can be removed as a side stream from an intermediate portion of the still. Hence, the actual feed to the dehydrogenator is about as good in quality as in previous examples. The build-up of excess non-aromatics is restrained by proceeding, as in any of the previous examples.

As thus described in the prior patent, considerable economies are available in the handling of a crude C₈ aromatics feed stock to produce substantially pure styrene, made available in each instance in as high a degree of purity as available in the art, 99.7% and better. Prior expensive pre-extraction procedures considered to be necessary to remove all non-aromatics, as in the prior patent referred to, can now be dispensed with, and a fraction relatively high in non-aromatics is found to be easily processed. Preferably, the processing is with prefraction-

ation merely to reduce the non-aromatics to a reasonable amount up to 5%, and the distillate is then super distilled according to that patent. It is found that these non-aromatics do not interfere with the close separation by super distillation of ethyl benzene from xylene isomers in the C₈ fraction. The non-aromatics boiling in the critical C₈ range are generally composed of nonanes whose actual boiling point, surprisingly, is higher than that of ethyl benzene. These are found to volatilize, probably as an azeotrope with the ethyl benzene, appearing overhead therewith during the super distillation. It is further found that these non-aromatics are not completely destroyed during the dehydrogenation of the ethyl benzene, but tend to build up in the reaction system. No coke build-up on the catalyst is experienced due to cracking of these non-aromatics. The presence of the non-aromatics in the styrene-ethyl benzene separation system does not adversely affect styrene purity.

Several available procedures are described above to prevent excessive build-up of non-aromatics in the system. In summary, the relatively high concentration in the recycle makes it feasible to treat the recycle entirely by distillation or extraction, including combined treatments as desired.

It is also feasible merely to bleed off enough of the recycle to prevent build-up, or to treat only a bleed off portion by distillation or extraction to separate some or all of the non-aromatics from the ethyl benzene. The amount bled from the system needs be only sufficient to prevent excessive build-up in the dehydrogenation reactor system.

Other methods known in the art to separate non-aromatics from aromatic hydrocarbons such as use of molecular sieves, clathration, extractive distillation and the like, may be included.

Accordingly, it is intended that the examples and drawings herein above be regarded as intended for purposes of illustration and not limitation except as defined in the claims appended hereto.

We claim:

1. In the preparation of styrene from a mixture of ethylbenzene, xylene isomers and non-aromatic hydrocarbon components, the steps of prefractionating the mixture to form C₈ aromatics containing a large quantity from about 1% to about 5% of non-aromatic components boiling in about the C₈ aromatic hydrocarbon boiling range, superdistilling the said hydrocarbon mixture in a distillation column of at least 150 distillation stages and at a reflux ratio exceeding 40:1 to separate the xylenes and passing the mixture of pure ethyl benzene and non-aromatic hydrocarbon mixture to a dehydrogenation reactor to convert the ethyl benzene to styrene in the presence of said non-aromatic hydrocarbon, separating substantially pure styrene from the crude dehydrogenation reaction mixture by distillation and recycling at least a portion of said unreacted mixture of ethyl benzene and non-aromatic hydrocarbon to said prefractionator in quantity sufficient to prevent large non-aromatic accumulation in the system.

2. The method of dehydrogenating ethyl benzene mixed with non-aromatic hydrocarbons formed as overhead by superdistilling a C₈ aromatic mixture containing a large quantity in the range of about 1% to about 5% of non-aromatic hydrocarbons in a distillation column of at least 150 distillation stages and at a reflux ratio exceeding 40:1 to separate the xylenes comprising, passing the said ethyl benzene non-aromatic to a dehydrogenating reactor under dehydrogenating conditions to form styrene, separating the reaction mixture into a first stream of substantially pure styrene by distillation, and a second stream of unreacted non-aromatics and ethyl benzene, dividing said second stream into processing and recycle portions, returning the recycle portion to the dehydrogenation reactor, treating the processing portion to remove therefrom a substantial quantity of the non-aromatics forming

a concentrate rich in ethyl benzene and returning the enriched ethyl benzene to the recycle, said processing being controlled in quantity to remove sufficient non-aromatics to prevent excessive non-aromatics build up in the system.

3. The method as defined in claim 2 wherein the processing portion is processed by extraction to remove a substantial portion of said non-aromatic, the raffinate ethyl benzene being returned to the recycle portion.

4. The method as defined in claim 2 wherein the processing portion is processed by distillation to separate an overhead fraction rich in non-aromatics and ethyl benzene, withdrawing from said system the overhead fraction, returning the bottoms, poorer in non-aromatics, to the recycle portion, the quantity of non-aromatics removed in said distillation treatment being sufficient to prevent excessive non-aromatic build up in the reaction system.

5. In the preparation of styrene from a C₈ aromatic hydrocarbon mixture containing a large quantity from about 1% up to about 5% non-aromatic hydrocarbons boiling in about the same boiling point range, the steps of superdistilling the said hydrocarbon mixture in a distillation column of at least 150 distillation stages and at a reflux ratio exceeding 40:1 to separate a mixture of ethylbenzene and the said non-aromatic hydrocarbon substantially free of other C₈ aromatic hydrocarbons, passing said mixture of ethylbenzene and other non-aromatic hydrocarbon to a dehydrogenation reactor, dehydrogenating said mixture to convert a quantity thereof to styrene and separating a substantially pure styrene product from said ethylbenzene and non-aromatic mixture by distillation.

6. In the preparation of styrene from a mixture of ethylbenzene, xylene isomers and non-aromatic hydrocarbon components, the step of prefractionating said mixture to reduce the non-aromatic components boiling in about the C₈ aromatic hydrocarbon boiling range to a large quantity in the range of about 1% to about 5%, superdistilling the same hydrocarbon mixture in a distillation column of at least 150 distillation stages and at a reflux ratio exceeding 40:1 to separate an overhead fraction of substantially pure ethylbenzene and non-aromatic hydrocarbons substantially free of other C₈ aromatic hydrocarbons, passing said mixture of ethylbenzene and non-aromatic hydrocarbons to a dehydrogenation reactor, dehydrogenating the mixture to convert the ethylbenzene to styrene in the presence of said non-aromatic hydrocarbon, separating a substantially pure styrene by distillation and recycling a substantial portion of the remainder of said mixture in quantity sufficient to prevent large non-aromatic accumulation in the system.

7. The method of dehydrogenating ethylbenzene mixed with non-aromatic hydrocarbons formed as overhead by superdistilling a C₈ aromatic mixture containing a large quantity in the range of about 1% up to about 5% of non-aromatic hydrocarbons in a distillation column of at least 150 distillation stages and at a reflux ratio exceeding 40:1 to separate the xylenes, comprising passing the said mixture of ethylbenzene and non-aromatic hydrocarbons to a dehydrogenation reactor and under ethylbenzene dehydrogenation conditions to form a reaction mixture containing styrene, unreacted ethylbenzene and non-aromatic hydrocarbon, and then separating substantially pure styrene from the said reaction mixture by distillation.

8. The method of dehydrogenating ethylbenzene mixed with non-aromatic hydrocarbons formed as overhead by superdistilling a C₈ aromatic mixture containing a large quantity in the range of about 1% up to about 5% of non-aromatic hydrocarbons in a distillation column of at least 150 distillation stages and at a reflux ratio exceeding 40:1 to separate the xylenes, comprising passing the said mixture of ethylbenzene and non-aromatic hydrocarbons to a dehydrogenation reactor and under ethylbenzene dehydrogenation conditions to form a reaction mixture containing styrene, unreacted ethylbenzene and non-aromatic hydrocarbon, separating the reaction mixture into a first stream of substantially pure styrene by

distillation and a second stream of unreacted ethylbenzene and non-aromatic hydrocarbon, withdrawing a portion of the non-aromatic hydrocarbon from the second stream in quantity sufficient to prevent substantial non-aromatic build up in the system, and recycling the remaining portion containing ethylbenzene to said dehydrogenation reactor.

9. The method as defined in claim 8 wherein the non-aromatic build up in the system is prevented by fractionally distilling a stable portion of the reaction mixture from which the unstable styrene components have been removed to separate sufficient non-aromatics overhead with benzene and toluene, recycling bottoms to said reactor said bottoms comprising ethyl benzene from which sufficient non-aromatics have been removed by said distillation to prevent build up in the reaction system.

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