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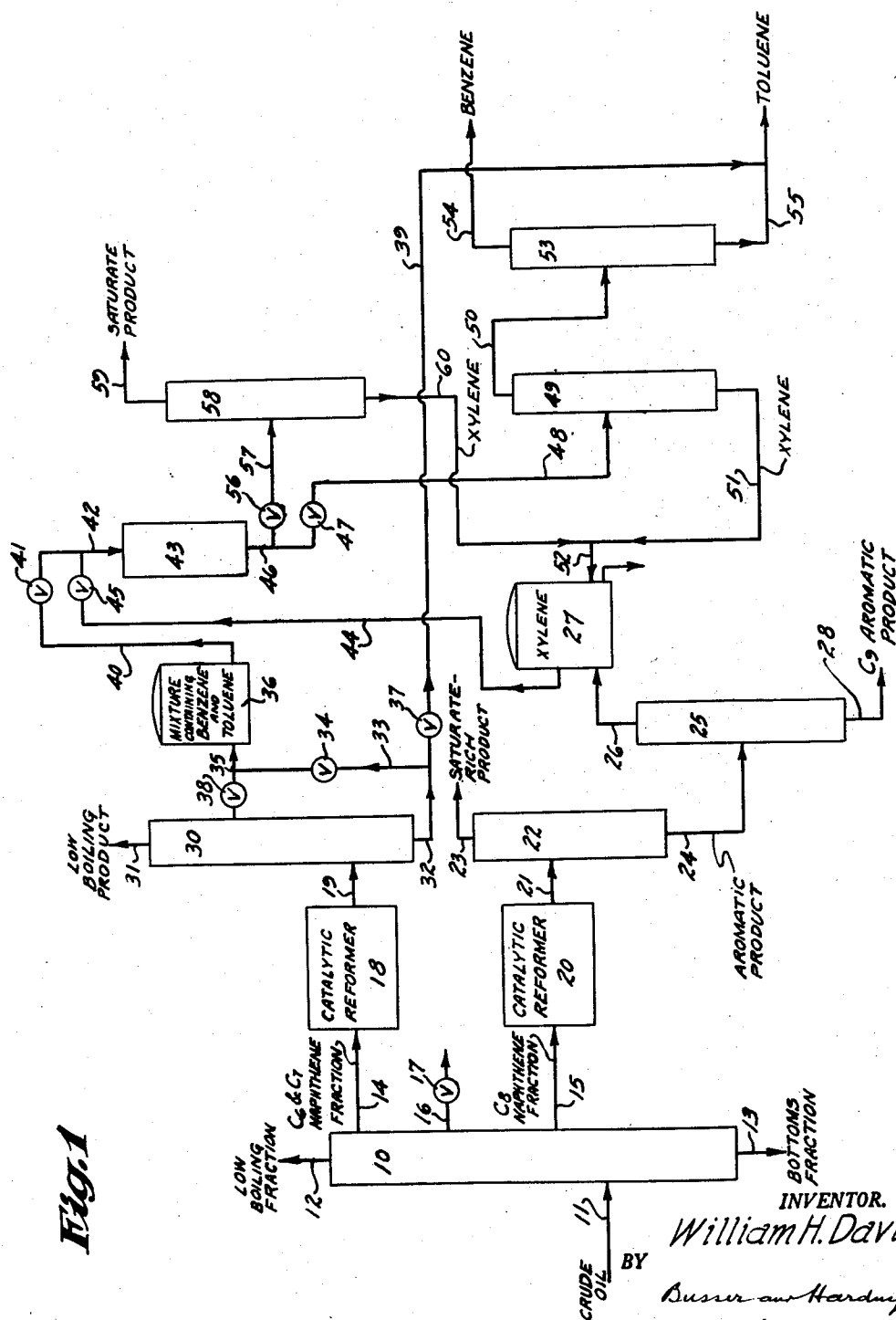
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PREPARATION OF AROMATIC HYDROCARBONS

Filed May 4, 1951

2 Sheets-Sheet 1



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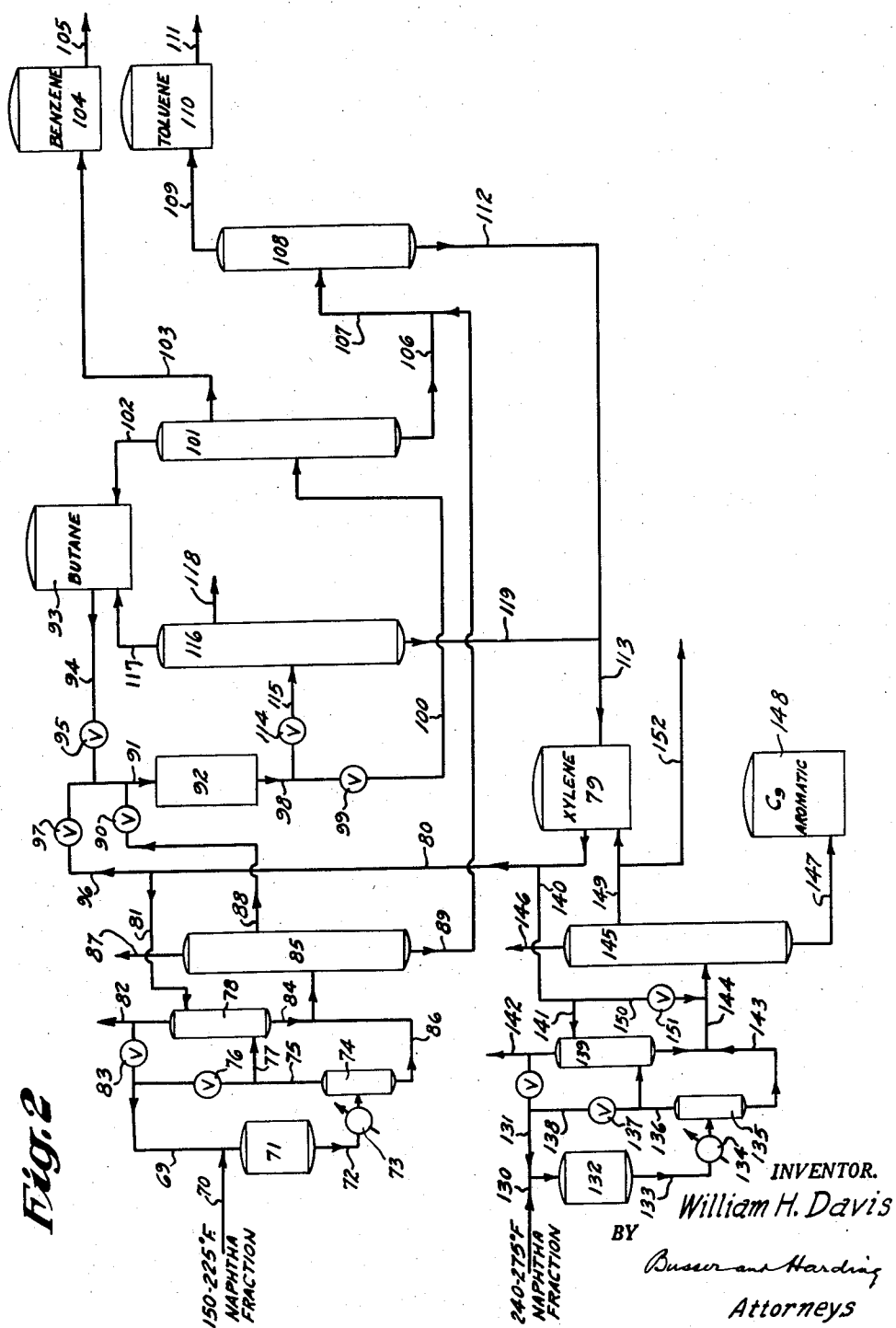
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2 Sheets-Sheet 2



UNITED STATES PATENT OFFICE

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PREPARATION OF AROMATIC
HYDROCARBONS

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This invention relates to the preparation of aromatic hydrocarbons of high purity. More particularly the invention is concerned with a process involving a series of interrelated steps wherein petroleum stocks containing naphthenes are treated under catalytic conditions to convert the naphthenes to aromatics and the resulting aromatics are recovered in purified form.

Aromatic hydrocarbons of high purity have numerous uses in the chemical industry. There is an increasing demand particularly for benzene, toluene and the xylenes as starting materials for synthesizing various compounds of commercial importance. It is known that aromatic hydrocarbons can be formed from the naphthene hydrocarbons occurring in petroleum by treatment of petroleum fractions with a dehydrogenating catalyst under conditions effective to withdraw hydrogen atoms from naphthene rings and thereby convert them to aryl rings. This type of reaction occurs in catalytic conversion operations commonly referred to as reforming. The resulting aromatic hydrocarbons, however, are associated with numerous non-aromatic components from which they must be separated if relatively pure aromatic products are to be obtained.

The present invention provides an improved process for forming aromatic hydrocarbons from petroleum stocks and separating them from associated non-aromatic hydrocarbons to obtain aromatic products of high purity. In one aspect the process of the invention involves distilling crude petroleum to produce two naphtha fractions for use as charge materials for separate dehydrogenating or reforming steps. One of the fractions has a boiling range such as to include the C_6 and C_7 naphthenes of the crude stock. The other is a heavier fraction which includes C_8 naphthenes and boils essentially below the boiling range of xylenes. The lower boiling fraction is sent to a reforming operation wherein the contained naphthenes are catalytically converted to benzene and toluene. The heavier fraction is separately reformed under catalytic conditions to convert the naphthenes to xylenes. The reaction mixture from the second reforming step is distilled to remove the contained non-aromatic hydrocarbons which boil generally lower than xylenes produced and to yield a xylene-rich product. Benzene and toluene of high purity are recovered from reaction product of the first reforming step by treating such reaction product with an aromatic-selective adsorbent and subsequently displacing the adsorbed benzene and tol-

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uene by means of the xylene-rich product obtained from the higher boiling charge fraction. Xylene retained by the adsorbent is thereafter displaced and recovered from it while the adsorbent is being re-used for further treatment of reaction product containing benzene and toluene.

In another modification of the process the lower boiling naphtha fraction which is reformed may contain C_6 naphthenes without substantial amounts of C_7 naphthenes, in which case the main aromatic product of the process will be benzene and xylenes. In still another modification the lower boiling naphtha fraction may contain C_7 naphthenes without substantial amounts of C_8 naphthenes, the main aromatic products then being toluene and xylenes.

It will be understood that the term "xylenes" as used herein refers to the C_8 aromatic hydrocarbons in a generic sense and may include ethylbenzene in addition to ortho, meta and para xylenes.

The reforming steps of the process can be conducted with any suitable dehydrogenating catalyst which is effective to convert the naphthenes contained in the naphtha charge fractions to corresponding aromatic hydrocarbons. Numerous reforming catalysts are known for effecting this type of reaction. Examples are platinum or palladium deposited in minor proportion on a supporting component such as silica, alumina, magnesia or mixtures of such components; and the oxides of molybdenum, vanadium or chromium, alone or in combination, together with a supporting component. Preparation of the catalysts may include various known special treatments for improving their effectiveness for conversion of naphthenes to aromatics while minimizing undesirable reactions such as cracking. It is also desirable that the catalyst selected be one which is effective not only for dehydrogenating but also for isomerizing naphthenes which have rings of five carbon atoms into six carbon ring compounds so that maximum yield of aromatics will be obtained. Such isomerizing ability is particularly desirable when benzene is to be one of the products, since most crude petroleum contain substantial amounts of methylcyclopentane which can, in addition to the contained cyclohexane, be converted into benzene if a suitable isomerizing and dehydrogenating catalyst is used.

Reforming of the naphtha fractions with catalysts of the foregoing types preferably should be done in the presence of free hydrogen in order to minimize cracking and coke formation. Hydrogen can be maintained in desired amount

within the reaction zones by the usual reforming procedure of recycling to the reactors hydrogen separated from the bulk of the reaction product.

In the accompanying drawings Figure 1 is a diagrammatic flowsheet illustrating the process of the invention and Figure 2 is a flowsheet illustrative of a more specific manner of practicing the process.

Referring to Figure 1 the two naphtha fractions for charging to the reforming or dehydrogenating steps may be prepared by fractionation of a crude oil in a distillation column 10 to which it is introduced via line 11. The lowest boiling portions of the crude are distilled overhead through line 12 and heavy portions are removed from the bottom by means of line 13. A light naphtha fraction and a heavier naphtha fraction are obtained as sidestream products through lines 14 and 15 respectively. The process as illustrated in Figure 1 is conducted to produce both benzene and toluene in addition to xylenes; consequently the light naphtha fraction which flows through line 14 has a boiling range to include both the C_6 and C_7 naphthenes present in the crude charge. The heavier naphtha fraction obtained through line 15 has a boiling range such that the fraction includes C_8 naphthenes present in the crude but its boiling range is not so high as to overlap substantially into the xylene boiling range. As examples of suitable boiling ranges for these fractions, it may be considered that the lower boiling naphtha includes the hydrocarbons boiling essentially from 150° F. to 225° F. and that the higher boiling naphtha includes those boiling essentially from 225° F. to 275° F.

Alternatively, if the process is to be operated for the production of benzene and xylene but not toluene, the lower boiling fraction obtained in line 14 may have a boiling range such as to include the C_6 naphthenes and an intermediate fraction containing the C_7 naphthenes may be withdrawn from column 10 through line 16 and valve 17. For example, the lower boiling fraction may have a range of 150° F. to 185° F. and the higher boiling fraction a range of 225° F. or 235° F. to about 275° F. On the other hand, if the process is to be practiced for producing toluene and xylene but not benzene, then the distillation in column 10 may be conducted to remove all hydrocarbons boiling up through the C_6 naphthene range through overhead line 12 so that the naphtha fraction withdrawn through line 14 will contain C_7 naphthenes without substantial amounts of C_6 naphthenes. In such case the lower boiling naphtha may have a range of say 185° F. to 230° F.

In the present description the naphtha fraction obtained from column 11 through line 14 will be considered to include both C_6 and C_7 naphthenes. This fraction is sent to catalytic reformer 18 wherein it is reacted under conditions effective to produce benzene and toluene by dehydrogenation of the naphthenes. Preferably the catalyst is one which is effective also to isomerize naphthenes having rings of five carbon atoms, such as methylcyclopentane and dimethylcyclopentanes, into compounds of six carbon rings so that the maximum yields of benzene and toluene will be obtained.

The reaction mixture from catalytic reformer 18, which includes benzene and toluene in admixture with numerous non-aromatic hydrocarbons boiling generally below and within the range of the charge fraction, is passed through

line 19 to a distillation operation as hereinafter described.

The heavier naphtha fraction, which is withdrawn from column 10 through line 15, is reacted in another catalytic dehydrogenating or reforming step illustrated by catalytic reformer 20. This operation may be conducted in the same reaction zone or zones as the reforming operation above-described in a "blocked-out" type of operation or separate reactors may be provided so that each reforming step may be carried out concurrently and continuously. The conditions maintained in catalytic reformer 20 are such that the C_8 naphthenes are dehydrogenated to produce mainly xylenes. Such xylenes generally will include a relatively small amount of ethylbenzene, and also small amounts of higher boiling aromatic products usually will be produced. Essentially all of the aromatics formed in this reaction will boil above the boiling range of the heavier naphtha charge and therefore can readily be separated from the associated non-aromatic components by distillation.

The reaction product from catalytic reformer 20 is passed through line 21 to distillation zone 22 wherein components boiling below the xylene boiling range are distilled and removed through overhead line 23. These components comprise the saturate hydrocarbons which were present in the charge fraction and also include any toluene that may have been present in the charge naphtha. From the bottom of tower 22 material boiling within the xylene boiling range and higher is removed through line 24 and passes to distillation column 25 for separation of the xylenes from any higher boiling aromatic components. A xylene-rich product is withdrawn overhead through line 26 and flows to xylene storage tank 27. The higher boiling material, comprising mainly C_9 aromatics, are removed from the base of the column by means of line 28.

Referring back to the reaction product from the first reforming step, this material is introduced into distillation column 30 wherein those hydrocarbons which boil below the boiling point of benzene are distilled and removed through overhead line 31. In one manner of practicing the process, the remainder of the reaction product may be withdrawn from the bottom of the column through line 32 and passed through line 33, valve 34 and line 35 into surge tank 36, valves 37 and 38 being closed. When the operation is conducted in this manner, the mixture fed to tank 36 will contain substantially all of the benzene and toluene produced during the reaction in reformer 18. In a preferred manner of practicing the process, however, the distillation in column 30 is conducted to produce a sidestream fraction which contains essentially all of the benzene but only a part of the toluene and a toluene fraction of high purity is obtained from the bottom of column 30 through line 31. This can be done by operating the column to cut between the sidestream and bottom products at a temperature of about 230° F. The sidestream fraction is sent through valve 38 and line 35 to tank 36, valve 34 being closed; while the bottom fraction is passed through valve 37 and line 39 as a toluene product of high purity. Operation in this manner is particularly advantageous in that only a portion of the total toluene produced need be passed through the subsequently described purification steps.

The mixture in surge tank 36 contains benzene and toluene together with associated saturated

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hydrocarbons derived from the naphtha charged to reformer 18. In order to separate these saturate components from the aromatics the mixture is treated by means of a suitable aromatic-selective adsorbent, such as silica gel or activated carbon, to selectively adsorb the benzene and toluene, and these aromatics are subsequently displaced from the adsorbent by means of xylene-rich material obtained from tank 27. This may be done by first introducing some of the mixture from tank 36 through line 40, valve 41 and line 42 into a contact zone 43 which contains the aromatic-selective adsorbent. After a suitable amount of the mixture from tank 36 has been introduced into the adsorbent, valve 41 is closed and xylene-rich material from tank 27 is passed into contact zone 43 through line 44, valve 45 and line 42 in order to displace the benzene and toluene. This adsorption step may be conducted by employing a fixed bed of adsorbent or by continuous countercurrent adsorption. In the present description the adsorption step will be considered as involving a cyclic operation utilizing a stationary adsorbent bed or a plurality of such beds in parallel flow arrangement to permit continuous passage of the charge and desorbent streams to the adsorption operation.

During each cycle of operation a portion of the charge mixture from tank 36 is introduced to the adsorbent, after which a portion of the xylene-rich material from tank 27 is introduced. The saturate components of the charge mixture tend to pass through the adsorbent ahead of the benzene and toluene which are selectively retained and will therefore be removed from these aromatic constituents. Upon addition of the xylene material following the charge mixture displacement of benzene and toluene from the adsorbent occurs. The xylenes in turn are displaced by the benzene and toluene present in the next portion of material introduced to contact zone 43 from tank 36.

During each cycle the efflux stream which passes from contact zone 43 through line 46 is cut into two portions. One portion contains the benzene and toluene displaced from the adsorbent and also some xylene, and this portion is sent through valve 47 and line 48 to distillation column 49. Benzene and toluene are distilled overhead via line 50 while the xylene is obtained as a bottom product which is returned by means of lines 51 and 52 to storage tank 27. The mixture of benzene and toluene from column 49 passes to column 53 for separating these components from each other. Purified benzene is withdrawn through line 54 as one product of the process. Purified toluene is removed by means of line 55 as another product and may be mixed with the toluene obtained from line 39.

In another part of the cycle efflux from contact zone 43 will be composed essentially of xylene and saturate hydrocarbons derived from the mixture introduced from tank 36. At this time valve 47 is kept closed and the efflux is sent through valve 56 and line 57 to distillation column 58. Saturate hydrocarbons are removed overhead through line 59, while the recovered xylene is withdrawn from the bottom of column 58 and passed through lines 60 and 52 back to storage tank 27.

In order that the distillations carried out in columns 49, 53 and 58 will be continuous surge tanks (not shown) may be provided in lines 48, 57 and 50 for holding suitable inventories

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of the materials to be distilled. This will permit a continuous supply of feed materials of substantially constant composition.

Figure 2 illustrates a more specific embodiment of the invention which is generally similar to that described in connection with Figure 1 but which includes several features that are highly advantageous for commercial practice. For purpose of describing the process of Figure 2 the lower boiling naphtha fraction which is reacted in the first reforming step will be considered as having a true boiling point range of about 150–225° F., while the higher boiling naphtha fraction reacted in the second reforming step will be considered as having a true boiling point range of about 240–275° F. The aromatic-selective adsorbent used for purifying the aromatic reaction products will be referred to as silica gel.

The naphtha fraction having a boiling range of 150–225° F., which contains naphthenes having six and seven carbon atoms per molecule, is sent through line 70 to catalytic reformer 71 which contains a dehydrogenating and isomerizing catalyst such as, for example, platinum deposited in minor amount on an acid treated silica-alumina carrier component. Hydrogen produced by the dehydrogenation reaction and separated from the reaction products as hereinafter described is recycled through line 69 for admixture with the charge naphtha sent into the reactor. While in Figure 2 only one reaction zone is illustrated for conducting this reforming step, it will be understood that a plurality of reactors may be provided in series with suitable heating means between reactors to supply heat for the endothermic dehydrogenation reaction and thereby maintain the desired temperature level. Suitable reaction conditions for promoting the desired dehydrogenating and isomerizing reactions generally will include a temperature within the range of 800–1000° F., a pressure of 150–400 lbs./square inch, a space rate of 1–4 liquid volumes of naphtha charge per volume of catalyst per hour and a hydrogen recycle ratio of 2–6 moles per mole of naphtha charge. More preferable reaction conditions include a temperature of 900–950° F., a pressure of 250–300 lbs./square inch, a space rate of 1.5–3 liquid volumes of naphtha charge per volume of catalyst per hour and a hydrogen recycle ratio of 3–4 moles per mole of naphtha charge.

Reaction mixture from reformer 71 is passed through line 72 and cooler 73 into separator 74 wherein gaseous components are removed from liquid product. The gaseous product flows through line 75 and a portion of it may be returned through valve 76 and line 69 to the reactor in order to maintain the desired concentration of hydrogen within the reaction zone. As is well known the presence of hydrogen in the reforming zone is highly advantageous in suppressing cracking reactions and minimizing coke formation. The remainder of the gaseous stream from separator 74 is passed through line 77 into absorber 78 wherein it flows countercurrent to xylene which has been obtained from xylene tank 79 and supplied to the absorber by means of lines 80 and 81. The purpose of having absorber 78 in the system is to provide for removal of hydrogen and low boiling hydrocarbon gases, which are withdrawn through line 82, without inordinate loss of higher boiling hydrocarbons, particularly benzene and toluene. If desired, hydrogen may be recycled from the top of absorber 78 by opening valve 83 and closing valve 76, but

it is preferred to supply the desired hydrogen for the reforming operation in the manner previously described.

The xylene which flows from the bottom of absorber 78 through line 84 contains hydrocarbons recovered from the gas stream and is introduced into distillation column 85 along with the liquid reaction product which flows from separator 74 through line 86. The distillation in column 85 is conducted so as to remove all components boiling below 150° F. through overhead line 87 and to obtain a sidestream fraction through line 88 which is essentially free of xylene. The xylene used as absorption medium is thus recovered through line 89 as a bottom product from tower 85. In practice of the process this material may also contain some toluene which is recovered therefrom by distillation as subsequently described.

The sidestream fraction flowing through line 88, which is composed essentially of benzene, toluene and saturate hydrocarbons, is passed through valve 90 and line 91 into adsorption zone 92 for recovery of the benzene and toluene by selective adsorption on silica gel. In the presently described practice of the process a low boiling saturate hydrocarbon such as butane is introduced into the silica gel immediately following the sidestream fraction from line 88. The purpose of so introducing butane is to achieve a more effective separation of the benzene and toluene from associated saturate hydrocarbons by displacing such saturates from the adsorbed aromatics and toluene. The amount of butane employed in each cycle of operation should be sufficient to effect such displacement of the saturates without substantial desorption of benzene and toluene from the silica gel. The periodical addition of butane is done by withdrawing butane during a portion of each cycle from storage tank 93 and passing it through line 94, valve 95 and line 91 into the silica gel immediately following each addition of sidestream fraction from line 88.

After introduction of the desired amount of butane, xylene which has been obtained from tank 79 by means of line 80 is passed through line 96, valve 97 and line 91 into the adsorbent in amount effective to displace the benzene and toluene. Following the introduction of the xylene desorbent, another portion of sidestream fraction from line 88 is introduced into adsorption zone 92. During this time the xylene remaining in the silica gel is displaced from it by the benzene and toluene contained in the sidestream fraction.

The efflux stream passing from adsorption zone 92 through line 98 is, during each cycle, separated into two portions. During a part of the cycle the efflux is composed mainly of butane, benzene, toluene and xylene, and this portion is sent through valve 99 and line 100 to distillation column 101. Butane is recovered through overhead line 102 and is returned to storage tank 93. Purified benzene is obtained through line 103 and passes to storage tank 104 from which it may be withdrawn through line 105 as a product of the process. Toluene and xylene are removed together from column 101 by means of line 106 and the mixture is sent through line 107 into another distillation column 108. The bottom product from distillation column 85, which is composed mainly of xylene but contains some toluene, is introduced from line 89 into line 107 and also sent into column 108. The mixture is therein distilled to obtain purified toluene through overhead line 109, the toluene then passing to

storage tank 110 from which it may be withdrawn via line 111 as another product of the process. From the base of column 108 xylene is recovered and is sent through lines 112 and 113 back to storage tank 79.

The other portion of effluent from adsorption zone 92 during each cycle is composed essentially of butane and xylene together with the saturate hydrocarbons that were present in the sidestream fraction in line 88. This portion flows through valve 114 and line 115 into distillation column 116. Butane is distilled overhead and is returned by means of line 117 to tank 93. Xylene is recovered as a bottom product and passes through lines 119 and 113 back to storage tank 79. The saturate hydrocarbons present in this efflux portion are removed from column 116 as a sidestream via line 118. In conducting this distillation it is an important feature for commercial practice to adjust the fractionation in column 116 so that a minor proportion of the butane will pass out of the column along with the sidestream fraction in line 118 rather than all overhead. This will insure the removal of hydrocarbons boiling between the boiling points of butane and benzene and will prevent a build-up in concentration of such hydrocarbons within the system during prolonged operation. The inclusion of a minor amount of butane in the saturate material produced through line 118 will not be objectionable for refinery practice, since such material generally will be used for making motor fuel in which the presence of a minor amount of butane is desirable.

The heavier naphtha charge, which illustratively has a boiling range of 240-275° F., is separately reacted in another catalytic reforming step generally similar to that previously described for the lighter naphtha charge. Naphtha charge, containing C₈ naphthenes, enters the system through line 130 and is mixed with a recycled hydrogen stream from line 131, the mixture then passing into catalytic reformer 132 for conversion of the naphthenes to aromatic hydrocarbons. Reaction conditions for this reforming step generally should include a temperature of 800-1000° F., a pressure of 300-650 lbs./square inch, a space rate of 1-4 liquid volumes of catalyst per hour and a hydrogen recycle ratio of 2-7 moles per mole of naphtha charged. More preferable conditions include a temperature of 900-950° F., a pressure of 450-550 lbs./square inch, a space rate of 1.5-3 liquid volumes of naphtha per volume of catalyst per hour and a hydrogen recycle ratio of 3-5 moles per mole of naphtha charged.

The reaction mixture from reformer 132 passes through line 133 and cooler 134 and into separator 135 wherein liquid product is separated from gaseous product. The gaseous stream flows from the top of the separator through line 136 and a portion may be recycled through valve 137 and lines 138 and 131. The remainder is introduced into absorption zone 139 wherein it flows upwardly countercurrent to xylene obtained from tank 79 and supplied to the absorber by means of lines 140 and 141. Excess hydrogen and unabsorbed hydrocarbons are removed from the top of absorber 139 through line 142.

The liquid product from the bottom of separator 135 flows through line 143 and is mixed with the xylene stream from the bottom of absorber 139. The mixture is then introduced through line 144 into distillation column 145. Hydrocarbons boiling below the xylene boiling

range are distilled overhead through line 146, while hydrocarbons boiling above the xylene boiling range are obtained as bottom product which is passed through line 147 to tank 148. The latter product is composed mainly of C_8 aromatics and generally is obtained in relatively small proportion compared to the amount of xylene produced.

As a sidestream from column 145 a xylene-rich product is obtained through line 147 and is sent to storage tank 79. Inasmuch as the xylene in tank 79 is utilized in other parts of the process as previously described, there is a tendency for saturate hydrocarbons which boil above the boiling point of toluene to be present in the xylene returned to tank 79 through line 113. It is particularly important in commercial practice to prevent accumulation of such material in the system; otherwise the material will contaminate the xylene withdrawn as a product and also, in order to escape from the system upon continued operation of the process, will contaminate the toluene product. Accordingly, an important feature of the process of Figure 2 is the circulation of xylene from tank 79 through line 140 for use in absorber 139 and then back to distillation column 145. This insures removal of those hydrocarbons which boil between toluene and xylene through overhead line 146 and prevents their accumulation in the system. A by-pass line around absorber 139, which is shown as line 150 having valve 151, preferably is provided so that xylene from tank 79 may be recycled to distillation column 145 in an amount in excess of that required in absorber 139. By operating in the described manner the sidestream xylene product in line 149 will be substantially purer than the xylene in tank 79. Accordingly xylene is withdrawn as another product of the process preferably from line 149 by means of line 152.

It will be understood that the terms " C_6 naphthenes," " C_7 naphthenes" and " C_8 naphthenes" as used herein refer to naphthenes having a total number of carbon atoms per molecule of six, seven and eight, respectively, regardless of whether the number of carbon atoms in the naphthene ring is five or six.

I claim:

1. Method of producing high purity aromatic hydrocarbons which comprises distilling a petroleum stock to produce a fraction containing C_6 and C_7 naphthenes and another fraction containing C_8 naphthenes and boiling essentially below the boiling range of xylenes, contacting the first-mentioned fraction with a dehydrogenating catalyst under conditions effective to convert contained naphthenes to benzene and toluene, contacting the second-mentioned fraction with a dehydrogenating catalyst under conditions effective to convert contained naphthenes to xylenes, distilling reaction product resulting from the second contacting step to separate a xylene-rich product, passing the xylene-rich product to a source of supply, and recovering benzene and toluene from reaction product of the first contacting step by means of a cyclic operation in each cycle of which such reaction product is contacted with an aromatic-selective adsorbent to adsorb benzene and toluene while displacing xylene remaining in the adsorbent from the preceding cycle, after which the adsorbent is contacted with xylene-rich product from said source of supply to displace the benzene and toluene, collecting effluent from the adsorbent in two portions one of which is composed mainly of non-

aromatic hydrocarbons and xylene and another of which is composed mainly of benzene, toluene and xylene, distilling each portion to recover xylene-rich product therefrom, returning xylene-rich product to said source of supply, and removing from the system xylene-rich product containing xylene used in said cyclic operation to thereby prevent progressive contamination of xylene by saturate hydrocarbons boiling above toluene.

2. Method according to claim 1 wherein the adsorbent during said cyclic operation is contacted with butane, immediately following contact with the reaction product of the first contacting step, in amount to remove associated non-aromatic hydrocarbons from the adsorbed benzene and toluene without substantial displacement of benzene and toluene from the adsorbent.

3. Method of producing high purity aromatic hydrocarbons which comprises distilling a petroleum stock to produce a fraction boiling essentially below 230° F. and containing C_6 and C_7 naphthenes and a heavier fraction boiling essentially below 275° F., contacting the first-mentioned fraction with a dehydrogenating catalyst under conditions effective to convert contained naphthenes to benzene and toluene, distilling the reaction product to separate hydrocarbons boiling essentially below 230° F. from a toluene-rich fraction boiling essentially above 230° F., contacting said heavier fraction with a dehydrogenating catalyst under conditions effective to convert contained naphthenes to aromatics, distilling the resulting reaction mixture to separate a xylene-rich product, passing the xylene-rich product to a source of supply, and recovering benzene and toluene from said separated hydrocarbons boiling essentially below 230° F. by means of cyclic operation in each cycle of which the said separated hydrocarbons are contacted with an aromatic-selective adsorbent to adsorb benzene and toluene while displacing xylene remaining in the adsorbent from the preceding cycle, after which the adsorbent is contacted with xylene-rich product from said source of supply to displace the benzene and toluene, collecting effluent from the adsorbent in two portions one of which is composed mainly of non-aromatic hydrocarbons and xylene and another of which is composed mainly of benzene, toluene and xylene, distilling each portion to recover xylene-rich product therefrom, returning xylene-rich product to said source of supply, and removing from the system xylene-rich product containing xylene used in said cyclic operation to thereby prevent progressive contamination of xylene by saturate hydrocarbons boiling above toluene.

4. Method according to claim 3 wherein the adsorbent during said cyclic operation is contacted with butane, immediately following contact with the said separated hydrocarbons, in amount to remove associated non-aromatic hydrocarbons from the adsorbed benzene and toluene without substantial displacement of benzene and toluene from the adsorbent.

5. Method of producing high purity aromatic hydrocarbons which comprises fractionating a hydrocarbon stock to produce a fraction boiling essentially within the range 150 – 225° F. and a heavier fraction boiling above toluene and essentially below 275° F., contacting the first-mentioned fraction with a dehydrogenating catalyst under conditions effective to convert contained naphthenes to benzene and toluene, distill-

ing the reaction product to separate hydrocarbons boiling essentially below 230° F. from a toluene-rich fraction boiling essentially above 230° F., contacting said heavier fraction with a dehydrogenating catalyst under conditions effective to convert contained naphthenes to aromatics, distilling the resulting reaction mixture to separate hydrocarbons boiling essentially below 275° F. and to yield a xylene-rich product and a heavier product rich in C₉ aromatics, passing the xylene-rich product to a source of supply, and recovering benzene and toluene from said separated hydrocarbons boiling essentially below 230° F. by means of cyclic operation in each cycle of which the said separated hydrocarbons are contacted with an aromatic-selective adsorbent to adsorb benzene and toluene while displacing xylene remaining in the adsorbent from the preceding cycle, after which the adsorbent is contacted with xylene-rich product from said source of supply to displace the benzene and toluene, collecting effluent from the adsorbent in two portions one of which is composed mainly of non-aromatic hydrocarbons and xylene and another of which is composed mainly of benzene, toluene and xylene, distilling each portion to recover xylene-rich product therefrom, returning xylene-rich product to said source of supply, and removing from the system xylene-rich product containing xylene used in said cyclic operation to thereby prevent progressive contamination of xylene by saturate hydrocarbons boiling above toluene.

6. Method according to claim 5 wherein the adsorbent during said cyclic operation is contacted with butane, immediately following contact with the said separated hydrocarbons, in amount to remove associated non-aromatic hydrocarbons from the adsorbed benzene and toluene without substantial displacement of benzene and toluene from the adsorbent.

7. In a process for producing high purity aromatics the steps which comprise contacting a petroleum fraction of relatively low boiling range containing naphthenes within the C₆ and C₇ group with a dehydrogenating catalyst under conditions effective to convert contained naphthenes to aromatic hydrocarbon of 6-7 carbon atoms, contacting a second petroleum fraction of relatively high boiling range such as to include C₈ naphthenes but below the boiling range of xylenes with a dehydrogenating catalyst under conditions effective to convert C₈ naphthenes to xylenes, distilling reaction product resulting from the second contacting step to separate a xylene-rich product, passing the xylene-rich product to a source of supply, and recovering aromatic hydrocarbon of 6-7 carbon atoms from reaction product of the first contacting step by means of a cyclic operation in each cycle of which such reaction product is contacted with an aromatic-selective adsorbent to adsorb aromatic hydrocarbon of 6-7 carbon atoms while displacing xylene remaining in the adsorbent from the preceding cycle, after which the adsorbent is contacted with xylene-rich product from said source of supply to displace the aromatic hydrocarbon of 6-7 carbon atoms, collecting effluent from the adsorbent in two portions one of which is composed mainly of non-aromatic hydrocarbons and xylene and another of which is composed mainly of aromatic hydrocarbon of 6-7 carbon atoms and xylene, distilling each portion to recover xylene-rich product therefrom, returning xylene-rich product to said source of supply, and removing from the system xylene-

rich product containing xylene used in said cyclic operation to thereby prevent progressive contamination of xylene by saturate hydrocarbons boiling above the toluene.

8. In a process for producing high purity aromatics the steps which comprise contacting a petroleum fraction of relatively low boiling range such as to include C₆ naphthenes with a dehydrogenating catalyst under conditions effective to convert C₆ naphthenes to benzene, contacting a second petroleum fraction of relatively high boiling range such as to include C₈ naphthenes but below the boiling range of xylenes with a dehydrogenating catalyst under conditions effective to convert C₈ naphthenes to xylenes, distilling reaction product resulting from the second contacting step to separate a xylene-rich product, passing the xylene-rich product to a source of supply, and recovering benzene from reaction product of the first contacting step by means of a cyclic operation in each cycle of which such reaction product is contacted with an aromatic-selective adsorbent to adsorb benzene from associated non-aromatic hydrocarbons while displacing xylene remaining in the adsorbent from the preceding cycle, after which the adsorbent is contacted with xylene-rich product from said source of supply to displace the benzene, collecting effluent from the adsorbent in two portions one of which is composed mainly of non-aromatic hydrocarbons and xylene and another of which is composed mainly of benzene and xylene, distilling each portion to recover xylene-rich product therefrom, returning xylene-rich product to said source of supply, and removing from the system xylene-rich product containing xylene used in said cyclic operation to thereby prevent progressive contamination of xylene by higher boiling saturate hydrocarbons from reaction product of said contacting steps.

9. In a process for producing high purity aromatics the steps which comprise contacting a petroleum fraction of relatively low boiling range such as to include C₇ naphthenes with a dehydrogenating catalyst under conditions effective to convert C₇ naphthenes to toluene, contacting a second petroleum fraction of relatively high boiling range such as to include C₈ naphthenes but below the boiling range of xylenes with a dehydrogenating catalyst under conditions effective to convert C₈ naphthenes to xylenes, distilling reaction product resulting from the second contacting step to separate a xylene-rich product, passing the xylene-rich product to a source of supply, and recovering toluene from reaction product of the first contacting step by means of a cyclic operation in each cycle of which such reaction product is contacted with an aromatic-selective adsorbent to adsorb toluene from associated non-aromatic hydrocarbons while displacing xylene remaining in the adsorbent from the preceding cycle, after which the adsorbent is contacted with xylene-rich product from said source of supply to displace the toluene, collecting effluent from the adsorbent in two portions one of which is composed mainly of non-aromatic hydrocarbons and xylene and another of which is composed mainly of toluene and xylene, distilling each portion to recover xylene-rich product therefrom, returning xylene-rich product to said source of supply, and removing from the system xylene-rich product containing xylene used in said cyclic operation to thereby prevent progressive contamination of xylene by saturate hydrocarbons boiling above the boiling point of toluene.

10. In a process for producing high purity aromatics the steps which comprise contacting a petroleum fraction of relatively low boiling range such as to include C_6 and C_7 naphthenes with a dehydrogenating catalyst under conditions effective to convert the naphthenes to benzene and toluene, contacting a second petroleum fraction of relatively high boiling range such as to include C_8 naphthenes but below the boiling range of xylenes with a dehydrogenating catalyst under conditions effective to convert C_8 naphthenes to xylenes, distilling reaction product resulting from the second contacting step to separate a xylene-rich product, passing the xylene-rich product to a source of supply, and recovering benzene and toluene from reaction product of the first contacting step by means of a cyclic operation in each cycle of which such reaction product is contacted with an aromatic-selective adsorbent to adsorb benzene and toluene while displacing xylene remaining in the adsorbent from the preceding cycle, after which the adsorbent is contacted with xylene-rich product from said source of supply to displace the benzene and toluene, collecting effluent from the adsorbent in two portions one of which is composed mainly of non-aromatic hydrocarbons and xylene and another of which is composed mainly of benzene, toluene and xylene, distilling each portion to recover xylene-rich product therefrom, returning xylene-rich product to said source of supply, and removing from the system xylene-rich product containing xylene used in said cyclic operation to thereby prevent progressive contamination of xylene by saturate hydrocarbons boiling above the boiling point of toluene.

11. Process according to claim 10 wherein the relatively low boiling petroleum fraction boils essentially within the range of 150–225° F. and the relatively high boiling petroleum fraction boils essentially within the range of 240–275° F.

12. Method of reducing high purity aromatics which comprises: contacting a petroleum fraction of relatively low boiling range such as to include C_6 and C_7 naphthenes but essentially below the boiling point of toluene with a dehydrogenating catalyst in the presence of free hydrogen under conditions effective to convert the naphthenes to benzene and toluene; cooling the reaction mixture and separating a liquid phase from a gaseous phase; passing gaseous phase countercurrent to hereinafter specified xylene-rich product to absorb desired heavier components therefrom; distilling a mixture of said liquid phase and the xylene-rich product carrying absorbed components to obtain a light fraction boiling essentially below benzene, an intermediate fraction containing benzene and part of the toluene produced in the reaction, and a heavier fraction composed mainly of toluene and xylene; separating benzene and toluene from said intermediate fraction by means of a cyclic operation in each cycle of which the intermediate fraction is introduced into a bed of aromatic-selective adsorbent to adsorb benzene and toluene, butane is then introduced into the adsorbent in amount to remove associated non-aromatic hydrocarbons from the adsorbed benzene and toluene without substantial displacement of benzene and toluene from the adsorbent, and another portion of the said specified xylene-rich product is then introduced into the adsorbent to displace the benzene and toluene; collecting the effluent from the adsorbent bed during each cycle in two portions one of which is composed mainly

of butane, xylene and non-aromatic hydrocarbons derived from said intermediate fraction and the other of which is composed mainly of benzene, toluene and xylene; distilling said one portion to recover a butane fraction, an intermediate fraction rich in said non-aromatic hydrocarbons, and a xylene-rich fraction; distilling said other portion to recover a benzene-rich product and a fraction composed mainly of toluene and xylene; distilling the last-mentioned fraction in admixture with the said heavier fraction composed mainly of toluene and xylene to yield a toluene-rich product and to recover xylene-rich product; contacting a second petroleum fraction of relatively high boiling range such as to include C_8 naphthenes but essentially below the boiling range of xylenes with a dehydrogenating catalyst in the presence of free hydrogen under conditions effective to convert C_8 naphthenes to xylenes; cooling the resulting reaction mixture and separating a liquid phase from a gaseous phase; passing gaseous phase counter-current to hereinafter specified xylene-rich product to absorb desired heavier components therefrom; and distilling a mixture of said liquid phase and the resulting xylene-rich product carrying absorbed components to obtain a relatively light fraction boiling essentially below the xylene boiling range and composed mainly of non-aromatic hydrocarbons, an intermediate fraction constituting the said specified xylene-rich product, and a heavier fraction containing aromatics boiling above the xylene boiling range.

13. Method according to claim 12 wherein the distillation of the said one portion of effluent from the adsorbent bed is conducted in a manner so as to include a minor portion of the contained butane in the said intermediate fraction produced therefrom to thereby prevent progressive contamination of the butane by saturate hydrocarbons boiling between butane and benzene.

14. Method of producing high purity aromatics which comprises: contacting a petroleum fraction of relatively low boiling range such as to include C_6 and C_7 naphthenes but essentially below the boiling point of toluene with a dehydrogenating catalyst in the presence of free hydrogen under conditions effective to convert the naphthenes to benzene and toluene; cooling the reaction mixture and separating a liquid phase from a gaseous phase; passing gaseous phase countercurrent to a xylene-rich product obtained from the hereinafter specified source of supply to absorb desired heavier components therefrom; distilling a mixture of said liquid phase and the xylene-rich product carrying absorbed components to obtain a light fraction boiling essentially below benzene, an intermediate fraction containing benzene and part of the toluene produced in the reaction, and a heavier fraction composed mainly of toluene and xylene; separating benzene and toluene from said intermediate fraction by means of a cyclic operation in each cycle of which the intermediate fraction is introduced into a bed of aromatic-selective adsorbent to adsorb benzene and toluene, butane cycled from a butane supply source is then introduced into the adsorbent in amount to remove associated non-aromatic hydrocarbons from the adsorbed benzene and toluene without substantial displacement of benzene and toluene from the adsorbent, and another portion of said xylene-rich product obtained from the said specified source of supply is then introduced

into the adsorbent to displace the benzene and toluene; collecting the effluent from the adsorbent bed during each cycle in two portions one of which is composed mainly of butane, xylene and non-aromatic hydrocarbons derived from said intermediate fraction and the other of which is composed mainly of benzene, toluene and xylene; distilling said one portion to recover a butane fraction, an intermediate fraction rich in said non-aromatic hydrocarbons and containing a minor portion of butane so as to prevent progressive contamination of the recovered butane by saturate hydrocarbons boiling between butane and benzene, and a xylene-rich fraction; returning recovered butane to said butane supply source; distilling said other portion to recover a benzene-rich product and a fraction composed mainly of toluene and xylene; distilling the last-mentioned fraction in admixture with the said heavier fraction composed mainly of toluene and xylene to yield a toluene-rich product and to recover xylene-rich product; returning xylene-rich product recovered from the two effluent portions to said specified source of supply; contacting a second petroleum fraction of relatively high boiling range such as to include C_8 naphthenes but essentially below the boiling range of xylenes with a dehydrogenating catalyst in the presence of free hydrogen under conditions effective to convert C_8 naphthenes to xylenes; cooling the resulting reaction mixture and separating a liquid phase from a gaseous phase; passing gaseous phase countercur-

rent to xylene-rich product obtained from said specified source of supply to absorb desired heavier components therefrom; distilling a mixture of said liquid phase and the resulting xylene-rich product carrying absorbed components to obtain a relatively light fraction boiling essentially below the xylene boiling range and composed mainly of non-aromatic hydrocarbons, an intermediate fraction constituting the xylene-rich product, and a heavier fraction containing aromatics boiling above the xylene boiling range; and feeding a portion of such intermediate fraction to said specified source of supply while withdrawing the remainder as xylene-rich product of the process, whereby progressive contamination, by saturate hydrocarbons boiling above toluene, of the xylene circulated to the adsorbent bed is prevented and the withdrawn xylene-rich product is of a purity higher than the average purity of the xylene-rich product in said source of supply.

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