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2,404,104

METHOD OF PRODUCING ETHYL BENZENE

Filed Dec. 11, 1942

2 Sheets-Sheet 1

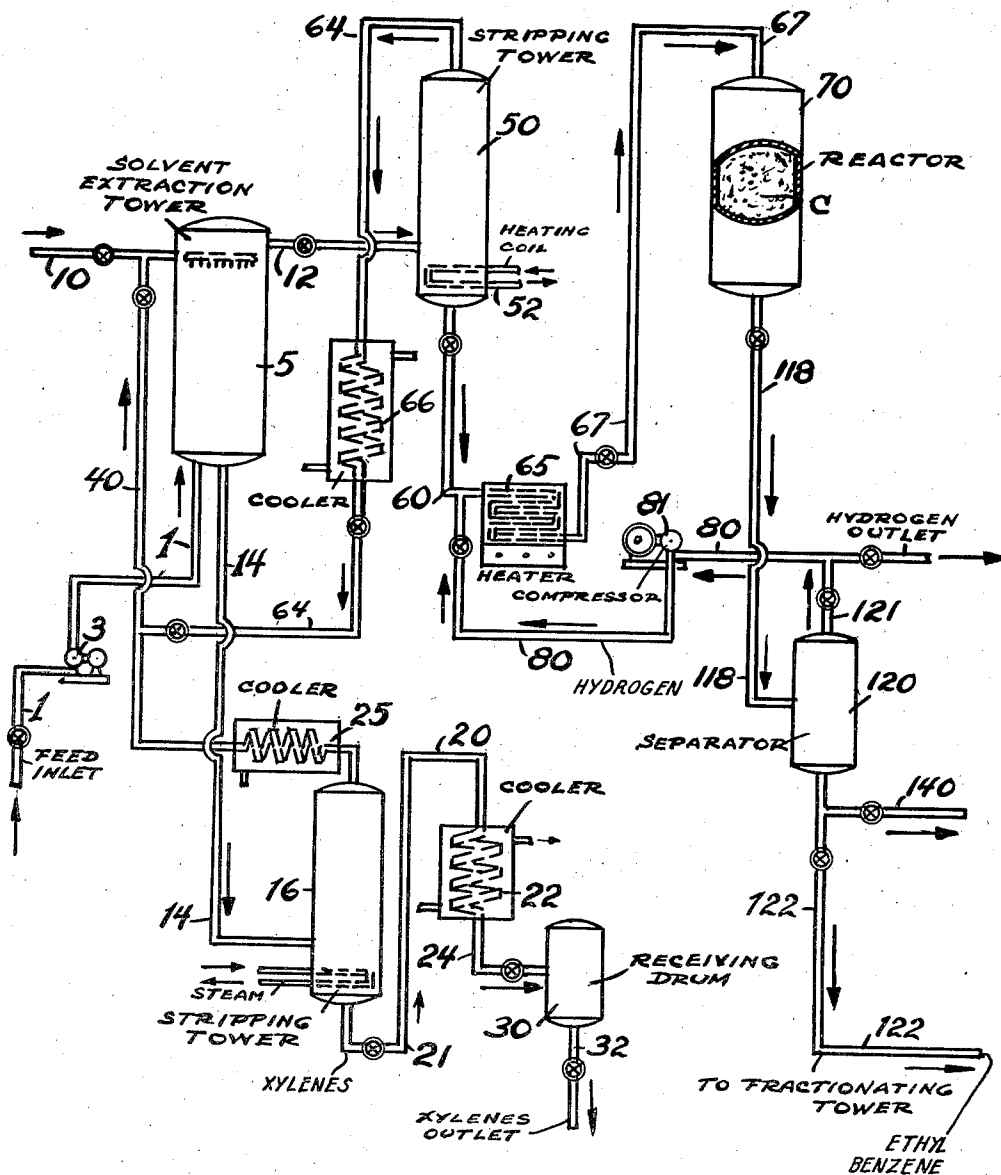


FIG.-1

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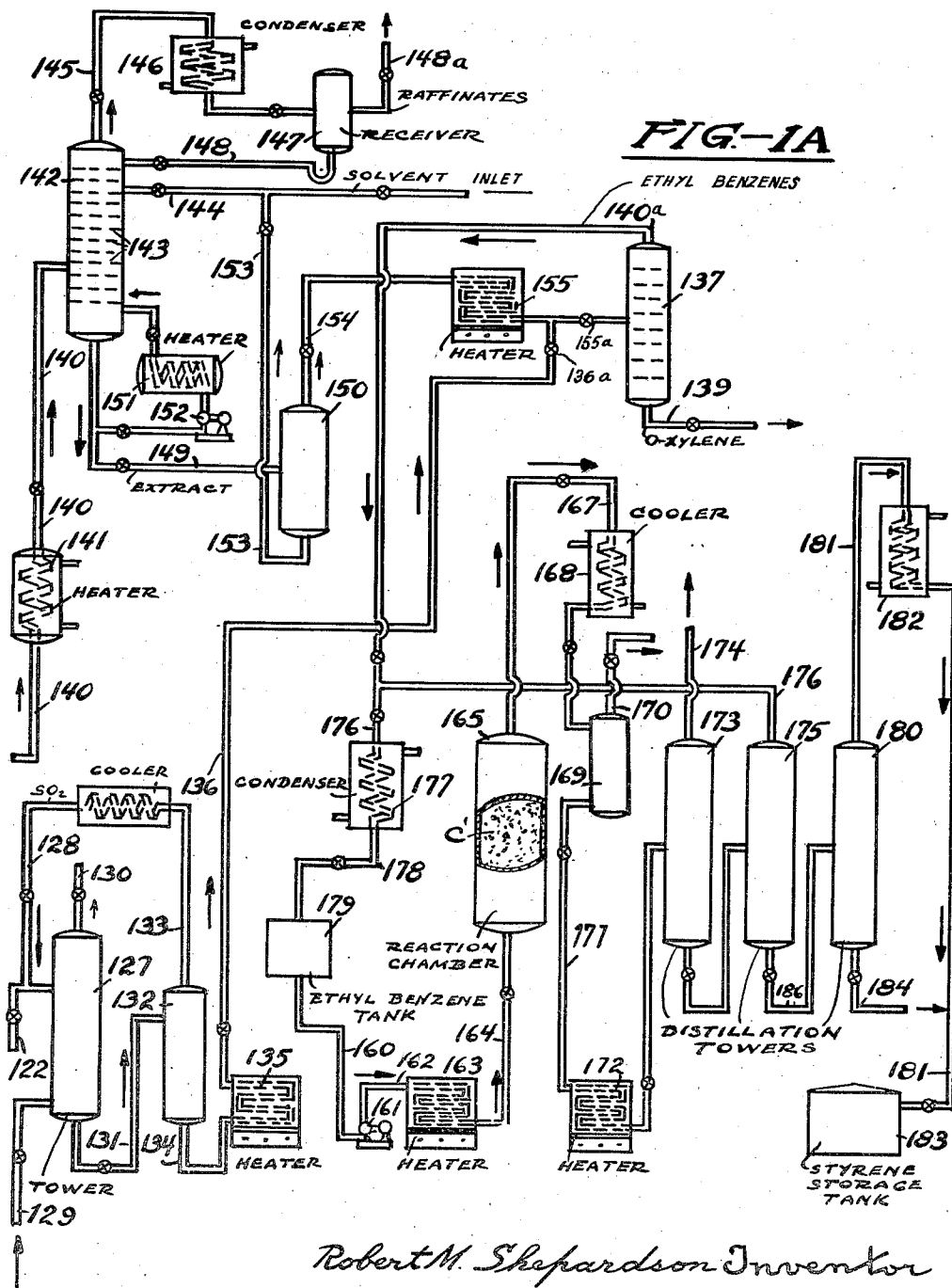
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METHOD OF PRODUCING ETHYL BENZENE

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2 Sheets-Sheet 2



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## UNITED STATES PATENT OFFICE

2,404,104

## METHOD OF PRODUCING ETHYL BENZENE

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to Standard Oil Development Company, a cor-  
poration of Delaware

Application December 11, 1942, Serial No. 468,612

2 Claims. (Cl. 260-668)

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The present invention relates to improvements in the art of processing hydrocarbon oils and, more particularly, it relates to the production of substituted aromatics, such as ethyl benzene and styrene, by dehydrogenation of cyclo paraffins.

In the prior application of the present inventor and another, Serial No. 429,012, filed January 31, 1942, entitled "Production of aromatics," there is described and claimed a process for producing styrene from a petroleum distillate derived from a naphthenic crude, the said distillate boiling within the range of about 260-275° F., by subjecting the latter fraction to catalytic dehydrogenation, extracting the products of catalytic dehydrogenation with a selective solvent, fractionating the extract to obtain substantially pure ethyl benzene, subjecting the ethyl benzene to a dehydrogenation treatment and then recovering substantially pure styrene from the products of this last dehydrogenation by controlled distillation. The styrene thus obtained finds uses, among others, in the production of products such as synthetic resins, but is particularly suitable as one of the raw materials used in the production of synthetic rubber or rubber substitutes.

According to my present invention, which constitutes an improvement over the invention described in the aforesaid application, I first subject an ethyl cyclohexane fraction to solvent extraction to remove xylenes and thereafter dehydrogenate the ethylcyclohexane to form ethylbenzene which can then be dehydrogenated to form styrene.

In the production of styrene by dehydrogenation of ethylbenzene, it is important that the ethylbenzene be quite pure. The presence of xylenes greatly reduces the amount of ethylbenzene converted to styrene, for which reason I wish to keep the quantity of xylenes present in the ethylbenzene below 10%. Although the "ethylcyclohexane" fraction or cut, which boils within the range of 260-275° F., boils below the xylenes, boiling points of the latter in the pure state being in the range of 281-291° F., it has been found that the xylenes boil below their true boiling point in admixture with paraffins and naphthenes, as a result of which appreciable quantities of xylenes are found in the narrow "ethylcyclohexane" cut of 260-275° F. boiling range. Although the xylenes do not interfere in the dehydrogenation of ethylcyclohexane to ethylbenzene, it is not practical to separate meta- and para-xylenes from ethylbenzene after the latter has been produced, and I have found that it improves the process to remove the xylenes from the "ethylcyclohexane" but by solvent extraction before the latter is dehydrogenated to ethylbenzene.

The main object of the present invention, therefore, is to prepare a charging stock for the pro-

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duction of ethylbenzene from cycloparaffins which is substantially free of aromatics, such as xylene.

A more specific object of my present invention is to remove by solvent extraction from an ethylcyclohexane fraction the isomeric xylenes prior to the dehydrogenation of the ethylcyclohexane to form ethylbenzene, so that following the dehydrogenation it will not be necessary to separate the ethylbenzene from meta- and para-xylenes, this separation being extremely difficult.

Other and further objects of my invention will appear from the following more detailed description and claims.

In the accompanying drawings, Figs. 1 and I—A, I have shown a flow plan which illustrates a preferred method of carrying my invention into practical effect.

Referring in detail to the drawings, a charging oil comprising a highly naphthenic petroleum fraction boiling within the range of from about 260-275° F. is introduced into the system thru line 1, and thence pumped by pump 3 into a solvent extraction zone 5 where it is contacted with a solvent which has a selective solvent power for aromatics, the said solvent being discharged into the top of extraction tower 5 thru line 10. Within the tower an extract phase and a raffinate phase are formed. In the specific example I am illustrating, the solvent extraction is a liquid-liquid phase, that is to say, both the solvent which may be, for example, SO<sub>2</sub>, and the oil are in liquid phase. Better results may be obtained by heating the oil to vaporize the same and contacting the vapors with a high boiling solvent, such as phenol, furfural and resorcinol. However, these details of solvent extracting a naphthene and/or paraffinic mixture containing naphthenes, paraffins, and aromatics are well known to the industry and numerous solvents suitable for this purpose are disclosed in the prior art. Later on in the present description I have given a full description of methods of solvent extracting aromatics from non-benzenoid hydrocarbons, and the methods later described in detail or similar methods may be used in the operation taking place.

A raffinate phase containing the naphthenes and paraffins of the charging oil is withdrawn through line 12, while an extract phase is withdrawn through line 14. The extract phase, as stated, will contain the various isomers of xylene, and to recover and separate these and other aromatics from the solvent they are discharged into a stripping tower 16 where they are stripped with indirect steam or by other means. The xylenes are withdrawn from the stripper thru line 21, are cooled in 22, thence discharged thru line 24 into a receiving drum 30. The disposition of the xylenes does not form per se the real gist of this present invention, but in passing, it may

be said that these xylenes may be reacted with benzene in the presence of aluminum chloride to cause a formation of toluene by interaction between benzene molecules and the xylene molecules resulting in the transfer of a methyl group from the xylene molecule to the benzene molecule. The solvent freed of its aromatics and other hydrocarbon content may be withdrawn through line 25, passed through a cooler and recycled to line 10 for further use in the process, extracting further quantities of aromatics from the charging oil. The separated xylenes are withdrawn through line 32.

Referring back to the solvent extraction zone, the raffinate phase withdrawn through line 12 is discharged into a stripping zone 50 where it is treated with indirect steam discharged into said zone through line 52 in order to strip and remove solvent from the hydrocarbons. The solvent is withdrawn through line 64 and recycled via cooler 66 and line 40 to line 10 leading to the solvent extraction zone 5. The hydrocarbons are recovered from stripping tower 50 through line 60 and thence discharged into a fired coil 65 where they are heated to a temperature of 600–1100° F., depending upon the catalyst employed, thence withdrawn through line 67 and discharged into a reactor 70 containing catalyst C. The catalyst may be a IV, V, VI, or VIII group metal, metal sulfide or oxide, or mixtures of two or more, such as nickel sulfide and tungsten sulfide, and the catalyst itself may have the physical form of pills, pellets, extruded shapes, granules, lumps, and the like. The catalyst may be deposited on a suitable support such as activated alumina, magnesia, carbon, or even silica, or may be of the unsupported type. Catalysts which have been found satisfactory are chromium sesquioxide supported on activated alumina, the amount of the chromium oxide being 5–40% by weight, the balance being the alumina, molybdenum oxide, say 5–12% by weight supported on activated alumina, platinum, say 5% by weight, on activated carbon or a mixture of nickel sulfide and tungsten sulfide without a support.

It is preferable in my process to discharge hydrogen into line 60 from line 80 where it mixes with the hydrocarbons and passes with them through furnace 65 and then into the reaction zone, the amount of hydrogen being from 2000–8000 cu. ft. per barrel of cold oil fed. With hydrogen recirculation, the reactor will be maintained under superatmospheric pressure of 100–1000#, whereas without hydrogen recirculation, substantially atmospheric operation is preferable. The feed rate of the hydrocarbon to the reaction zone is from 0.1–10 volumes of hydrocarbon per volume of catalyst per hour on a cold oil basis. The temperature prevailing within the reaction zone will vary from 600 to 1000° F., depending upon the catalyst employed. With the platinum catalyst or a mixture of nickel sulfide and tungsten sulfide, low temperatures of 600–900° F. are preferred whereas temperatures of 900–1000° F. are generally needed with chromium oxide or molybdenum oxide on alumina. Also, in the case of the former two catalysts, it is preferable to add heat to the reactor while dehydrogenation is in progress to maintain a constant temperature, this being accomplished by firing small diameter, say 1 to 6 inch, tubes or maintaining these tubes in a high temperature salt bath, these small tubes containing the cat-

alyst. With the latter two catalysts, however, a constant temperature is not required through the reaction zone, and the heat of reaction can be supplied as sensible heat in the charge stock, temperature decreasing through the reaction zone in this case. In the low temperature operation with catalysts consisting of platinum on charcoal or nickel sulfide plus tungsten sulfide, regeneration of the catalyst by burning with air is not required, but this will be required frequently, say after 2–24 hours of operation, when the higher temperatures above 900° F. are employed. Under the conditions stated, the ethylcyclohexane undergoes dehydrogenation to form ethylbenzene.

The reaction products are withdrawn from reactor 70 through line 118 and are discharged into a separation drum 120 where gaseous and liquid products may be separated. The gaseous products which will contain substantial quantities of free hydrogen and small quantities of low molecular weight hydrocarbons, such as methane, ethane and propane, are removed from separating means 123 through line 121 and recycled by means of booster compressor 81 in line 80 to line 60 to provide the hydrogen-containing gas required in the reaction chamber. Part of the hydrogen-containing gas is withdrawn through the hydrogen outlet indicated on the drawing. The reaction is preferably conducted under conditions such that there is no overall net consumption of free hydrogen.

The liquid product is removed from separating means 120 through line 122. This liquid product will contain substantial amounts of ethylbenzene together with non-aromatic hydrocarbons and possibly smaller amounts of other aromatics. All of the dimethylcyclohexanes except cis 1,2 dimethylcyclohexane which would dehydrogenate to orthoxylene have been excluded from the ethylcyclohexane fraction charged to dehydrogenation by choosing a fraction with a boiling range of 260–275° F. The boiling points of the various dimethylcyclohexanes, ethylcyclohexane and the corresponding aromatics are tabulated below:

| Naphthenes                           | ° C. |     | ° F. |  | Aromatics         | ° C. |     | ° F. |  |
|--------------------------------------|------|-----|------|--|-------------------|------|-----|------|--|
|                                      |      |     |      |  |                   |      |     |      |  |
| 1,4 dimethylcyclohexane (trans)..... | 119  | 246 |      |  | P-xylene.....     | 138  | 280 |      |  |
| 1,3 dimethylcyclohexane (trans)..... | 119  | 246 |      |  | M-xylene.....     | 139  | 282 |      |  |
| 1,3 dimethylcyclohexane (cis).....   | 121  | 250 |      |  | O-xylene.....     | 144  | 291 |      |  |
| 1,4 dimethylcyclohexane (cis).....   | 121  | 250 |      |  |                   |      |     |      |  |
| 1,1 dimethylcyclohexane.....         | 123  | 253 |      |  |                   |      |     |      |  |
| 1,2 dimethylcyclohexane (trans)..... | 124  | 255 |      |  |                   |      |     |      |  |
| 1,2 dimethylcyclohexane (cis).....   | 127  | 261 |      |  |                   |      |     |      |  |
| Ethylcyclohexane.....                | 130  | 266 |      |  | Ethylbenzene..... | 136  | 276 |      |  |

Analyses obtained on the ethylcyclohexane fractions of 260–275° F. boiling range from naphthenic crudes generally do not show the presence of appreciable quantities of cis 1,2 dimethylcyclohexane in which case the dehydrogenated product would not contain appreciable ortho-xylene. However, in some cases the cis 1,2 dimethylcyclohexane has been found in which case ortho-xylene would be found in the dehydrogenated product. In addition, if the dehydrogenation reaction is carried out at temperatures above 900° F., some thermal decomposition and polymerization generally occurs with the result that benzene, toluene, and a very small quantity of aromatics boiling above xylenes are produced.

If the liquid-liquid extraction method is to be employed, the liquid products removed from separating means 120 thru line 122 are first introduced into the upper portion of a conventional

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solvent extraction tower 127, as shown in Fig. 1—A, adapted for countercurrent flow of liquids. A modification of my invention involves fractionating the product from line 122 to recover a 250° to 300° F. fraction and sending this only to the solvent treater 127.

Prior to being introduced into extraction tower 127, the liquid products are mixed with several volumes of a solvent supplied thru line 123 which is capable of making a separation between aromatics and non-aromatics. Many different solvents of this type are known. Thus, liquid sulfur dioxide used at low temperatures, say below 0° F., during the extraction is chosen as illustrative herein. The mixture of liquid sulfur dioxide and the liquid products of dehydrogenation are caused to flow in tower 127 countercurrent to a non-aromatic hydrocarbon diluent which is introduced into the bottom of tower 127 thru a line 129. This non-aromatic hydrocarbon diluent should have a boiling range substantially different from that of liquid sulfur dioxide and the hydrocarbons in the liquid products. Examples of a lower boiling diluent are pentane and isopentane. Examples of a higher boiling diluent are a paraffinic heavy naphtha and a light kerosene.

The primary function of the non-aromatic hydrocarbon diluent is what may be called "dilution displacement." This may be explained as follows:

Although paraffins and naphthenes are practically insoluble in liquid SO<sub>2</sub> at temperatures below 0° F., a mixture of liquid SO<sub>2</sub> and aromatics will dissolve an appreciable quantity of non-aromatic hydrocarbons, the total hydrocarbon present in the extract being composed of possibly 20% of non-aromatic and 80% of aromatic hydrocarbons. Some of these non-aromatic hydrocarbons will boil in the same range as the ethylbenzene and therefore cannot be separated therefrom by fractionation. By countercurrently washing the mixture of liquid sulfur dioxide and hydrocarbons with a relatively large amount of a non-aromatic hydrocarbon having a boiling range widely different from the ethylbenzene, the non-aromatic hydrocarbons originally associated with the ethylbenzene are displaced by the non-aromatic washing agent of widely different boiling range. Having essentially replaced the non-aromatic hydrocarbons originally associated with the mixture which boils in the same range as the ethylbenzene with non-aromatics having a much different boiling range, it is then possible to separate the non-aromatics from the ethylbenzene by fractionation.

The volume of non-aromatic hydrocarbon diluent with which the mixture of liquid sulfur dioxide and dehydrogenated hydrocarbons is washed should be at least sufficient to effect a substantial dilution displacement and may be from 50 to 150% or more of the volume of said mixture. The volume of non-aromatic diluent should not, however, be so great as to displace the liquid sulfur dioxide from the mixture.

A raffinate phase which will consist chiefly of non-aromatic hydrocarbon diluent, non-aromatic hydrocarbons from the original feed and some liquid sulfur dioxide is removed from tower 127 thru line 130. This mixture may be distilled to recover the SO<sub>2</sub> and the diluent (in apparatus not shown) for further use in the process. An extract phase which will consist chiefly of aromatic hydrocarbons, liquid sulfur dioxide and some non-aromatic hydrocarbon diluent is removed from tower 127 thru line 131 and introduced into stripping means 132 in which the sulfur dioxide is stripped out and removed thru

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line 133. The sulfur dioxide is recycled after cooling to line 128 and reused.

The raw ethylbenzene is substantially freed of other aromatics such as the various isomers of xylene as follows: It is withdrawn from stripper 132 thru pipe 134, thence passed thru a heater 135, then passed via line 136 into a fractionating tower 137 from the bottom of which orthoxylene is withdrawn thru line 139 while purified ethylbenzene is withdrawn thru line 140a, thence condensed in cooling coil 177 and thence conducted thru pipe 178 to ethylbenzene storage drum 179.

If the vapor-liquid extraction method is to be used, and this method is generally preferred, the liquid products removed from separating means 120 thru line 122 are passed directly thru valved line 140 and a heating means 141 into a tower 142 adapted for countercurrent flow of liquid and vapor and provided with a plurality of plates 143. When this method is used, valve 136a is closed and valve 155a is open. Prior to their introduction into tower 142, the liquid products are heated in heating means 141 to a temperature at which they are substantially completely vaporized. A high boiling selective solvent which remains in liquid phase at the temperature at which the liquid products are vaporized, is introduced into the upper portion of the tower thru a line 144. Suitable examples of this type of selective solvent are phenol, resorcinol and furfural. A raffinate substantially free from selective solvent is removed in vapor phase from the top of tower 142 thru line 145, is passed thru a cooling and condensing means 146 and is then collected in a tank 147. A portion of the condensed raffinate may be recycled to the top of the tower thru line 148 to act as reflux. The remainder of the raffinate is removed from tank 147 thru line 148—a.

A liquid extract phase, which consists essentially of selective solvent and aromatics, is removed from the bottom of tower 142 thru line 149 and introduced into a stripping means 150 provided with a heating coil which vaporizes the ethylbenzene. A portion of the extract phase may be continuously circulated thru the bottom of tower 142 and a heating means 151 by means of pump 152. Unvaporized selective solvent is removed from the bottom of stripping means 150 thru line 153 and may be recycled thru line 144 to the upper portion of tower 142. Ethylbenzene of substantially pure form or at least substantially pure and free of xylenes, except some ortho-xylene, is recovered thru line 154 and discharged into heater 155 and thence into fractionator 137 where it is fractionated to recover pure ethylbenzene as previously explained.

The ethylbenzene fraction collected in tank 179 which may have been obtained by either one of the two methods of solvent extraction described above is removed from tank 179 thru line 160 by means of pump 161 and forced thru line 162 into a heating means 163. The heated ethylbenzene fraction passes thence thru line 164 into a reaction chamber 165 wherein it is subjected to dehydrogenation to convert the ethylbenzene to styrene. The dehydrogenation of the ethylbenzene may be effected either by a thermal, non-catalytic reaction or by a catalytic reaction. If the dehydrogenation of the ethylbenzene is to be a thermal reaction, chamber 165 is maintained at a temperature between 1200 and 1500° F. and under atmospheric or subatmospheric pres-

sure. The partial pressure of the ethylbenzene should be maintained between about 50 and 400 mm. of mercury and this partial pressure may be obtained by diluting the ethylbenzene with steam or other inert gases such as nitrogen, methane, flue gas and the like, by maintaining the reaction zone under vacuum, or by a combination of both methods. The ethylbenzene should be passed thru reaction chamber 165 at a rapid rate, for example, between 0.1 and 10.0 volumes of liquid ethylbenzene per volume of reaction space per hour in order to obtain a very short time of contact.

If the dehydrogenation of the ethylbenzene is to be catalytic, a suitable catalyst C' is placed in reaction chamber 165 and the temperature is somewhat lower, say between 1000° and 1300° F. The feed rate may be of the order of 0.1 to 10 volumes of liquid ethylbenzene per volume of catalyst per hour depending upon the nature of the catalyst used. The pressure may be atmospheric or below atmospheric and diluents such as steam or inert gas may be used. The other conditions may be essentially the same as in the thermal type of dehydrogenation. A good catalyst for use in reaction chamber 165 is that described in the application of Kenneth K. Kearby, Serial No. 430,873, filed February 14, 1942, which consists of:

|                                      | Parts by weight |
|--------------------------------------|-----------------|
| MgO .....                            | 50 to 95        |
| Fe <sub>2</sub> O <sub>3</sub> ..... | 3 to 49         |
| K <sub>2</sub> O .....               | 0.5 to 10       |
| CuO .....                            | 0.5 to 20       |

with the preferred composition being:

|                                      | Parts by weight |
|--------------------------------------|-----------------|
| MgO .....                            | 72.4            |
| Fe <sub>2</sub> O <sub>3</sub> ..... | 18.4            |
| K <sub>2</sub> O .....               | 4.6             |
| CuO .....                            | 4.6             |

Whichever type of dehydrogenation is carried out in reaction chamber 165, the products of reaction are removed therefrom thru line 167, passed thru a cooling means 168 and thence into a separating means 169. Gaseous products, including hydrogen, which may be recycled to reactor 70 of the dehydrogenation are removed from separating means 169 thru line 170. Liquid products of the dehydrogenation are removed from separating means 169 thru line 171, thence passed thru heating means 172 and introduced into tower 173 which is the first of a series of distillation towers for the separation of styrene from ethylbenzene and other products which may be associated with it. From the first tower 173 benzene and toluene are taken overhead thru line 174. The bottoms are passed into a second tower 175 from which ethylbenzene is taken overhead thru line 176 and after passing thru a cooling means 177, may be returned to tank 179. The bottoms from tower 175 are passed thru line 186 into a third tower 180 from which the desired styrene is taken overhead thru line 181 and after being cooled in cooling means 182, is collected in tank 183. The bottoms from tower 180, which will consist essentially of polymerized fractions, are removed thru line 184. The distillation in towers 173, 175 and 179 is preferably conducted under vacuum or in the presence of steam in order to permit reduced temperatures. It is also desirable to introduce a small quantity of an inhibitor

into the upper portion of each tower to inhibit the polymerization of the styrene.

In the operation of the process, it will be understood that many variations may be made in the operating details without departing from the spirit and scope of the invention. For example, the reactions in reaction chambers 70 and 165 may be conducted in the presence of finely divided catalysts suspended in the vapors to be treated instead of in the presence of rigidly arranged stationary catalysts as illustrated in the drawings. From time to time when the catalysts C and C' require regeneration to restore their activity, this may be accomplished in any suitable manner, for example, by shutting off the flow of hydrocarbon vapors and passing hot, inert gases containing regulated quantities of air or oxygen thru the catalyst mass to remove the carbonaceous contaminants by combustion. It will be understood that if the catalyst is used in finely divided, suspended form, regeneration cannot be in situ as would be the case when the catalyst is used in stationary form but must be effected outside the reaction chambers. The method of regeneration, however, will be essentially the same in both cases.

I claim:

1. A process of producing ethyl benzene which comprises solvent treating, with a liquid solvent having preferential solvent power for aromatics, a petroleum oil fraction boiling in the range from 260° F. to 275° F. and containing ethyl cyclohexane with xylenes but substantially free from dimethyl cyclohexanes that boil below 260° F. to remove the xylenes, thereafter converting into ethyl benzene the ethyl cyclohexane in the solvent-treated fraction, freed of the xylenes, by dehydrogenation under superatmospheric pressure at a temperature of from about 600° to 1100° F. with added hydrogen in the presence of a catalyst containing a component selected from the class consisting of metals, oxides, and sulfides of metallic elements in groups IV, V, VI, and VIII of the periodic system, and recovering the ethyl benzene product.

2. A process of producing ethyl benzene which comprises solvent treating, with a liquid solvent having a preferential solvent power for aromatics, a petroleum oil fraction boiling in the range from 260° F. to 275° F., and containing ethyl cyclohexane with xylenes but substantially free from dimethyl cyclohexanes that boil below 260° F. to remove the xylenes, thereafter converting into ethyl benzene the ethyl cyclohexane in the solvent-treated fraction, freed of the xylenes, by dehydrogenating the ethyl cyclohexane in said solvent-treated fraction under superatmospheric pressure of 100 to 1000 pounds per square inch at a temperature of from about 600° F. to 1100° F. with added hydrogen in an amount of 2000 to 8000 cubic feet per barrel of the solvent-treated fraction on a cold feed basis in the presence of a catalyst containing a component selected from the class consisting of metals, oxides, and sulfides of metallic elements in groups IV, V, VI, and VIII of the periodic system, the feed rate of the solvent-treated fraction into contact with the catalyst being 0.1 to 10 volumes of oil per volume of catalyst per hour on a cold oil basis, and recovering the ethyl benzene product formed in the dehydrogenation.

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