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A. B. WELTY, JR

2,380,279

PRODUCTION OF AROMATICS

Filed May 20, 1942

2 Sheets-Sheet 1

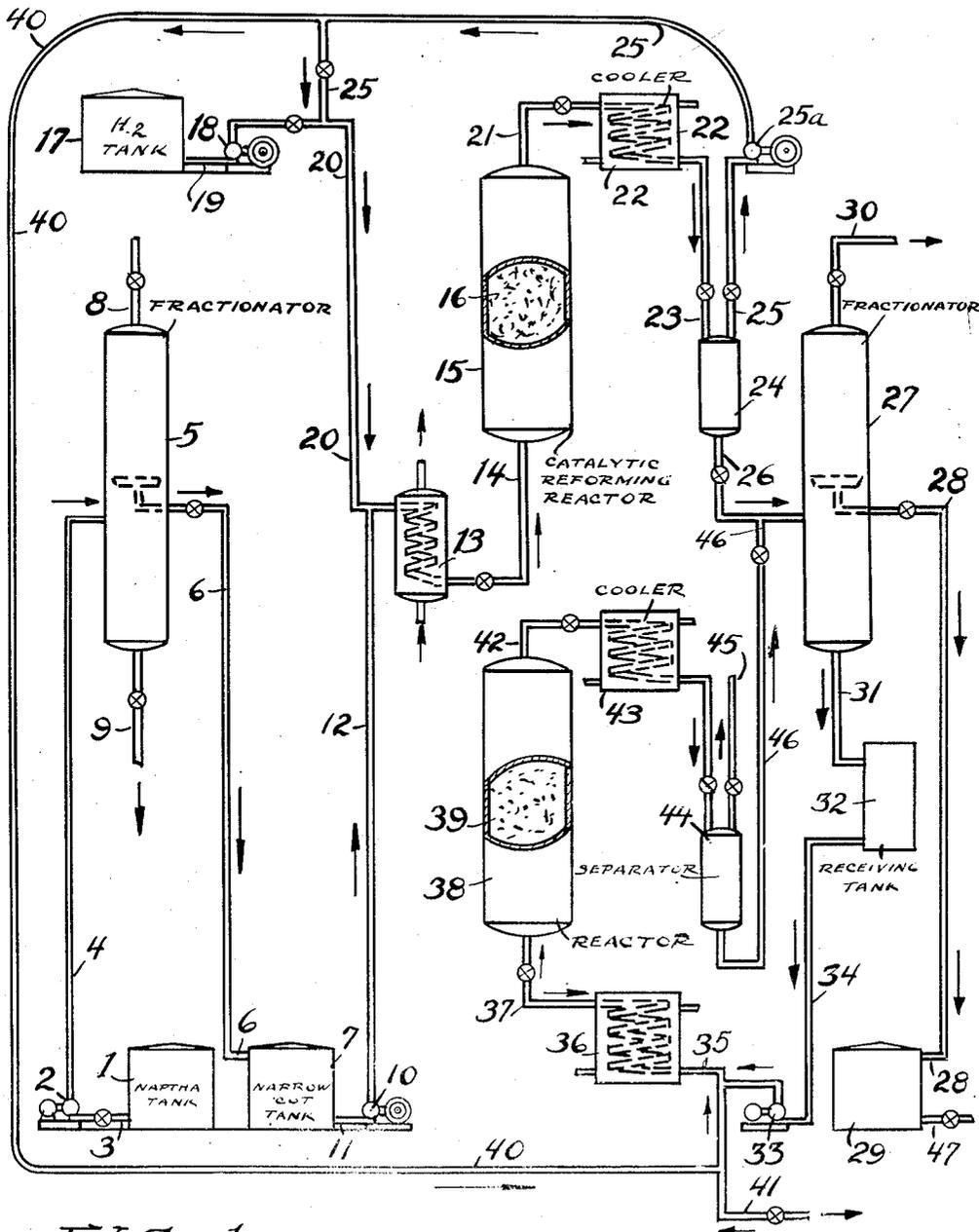


FIG.-1

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2 Sheets-Sheet 2

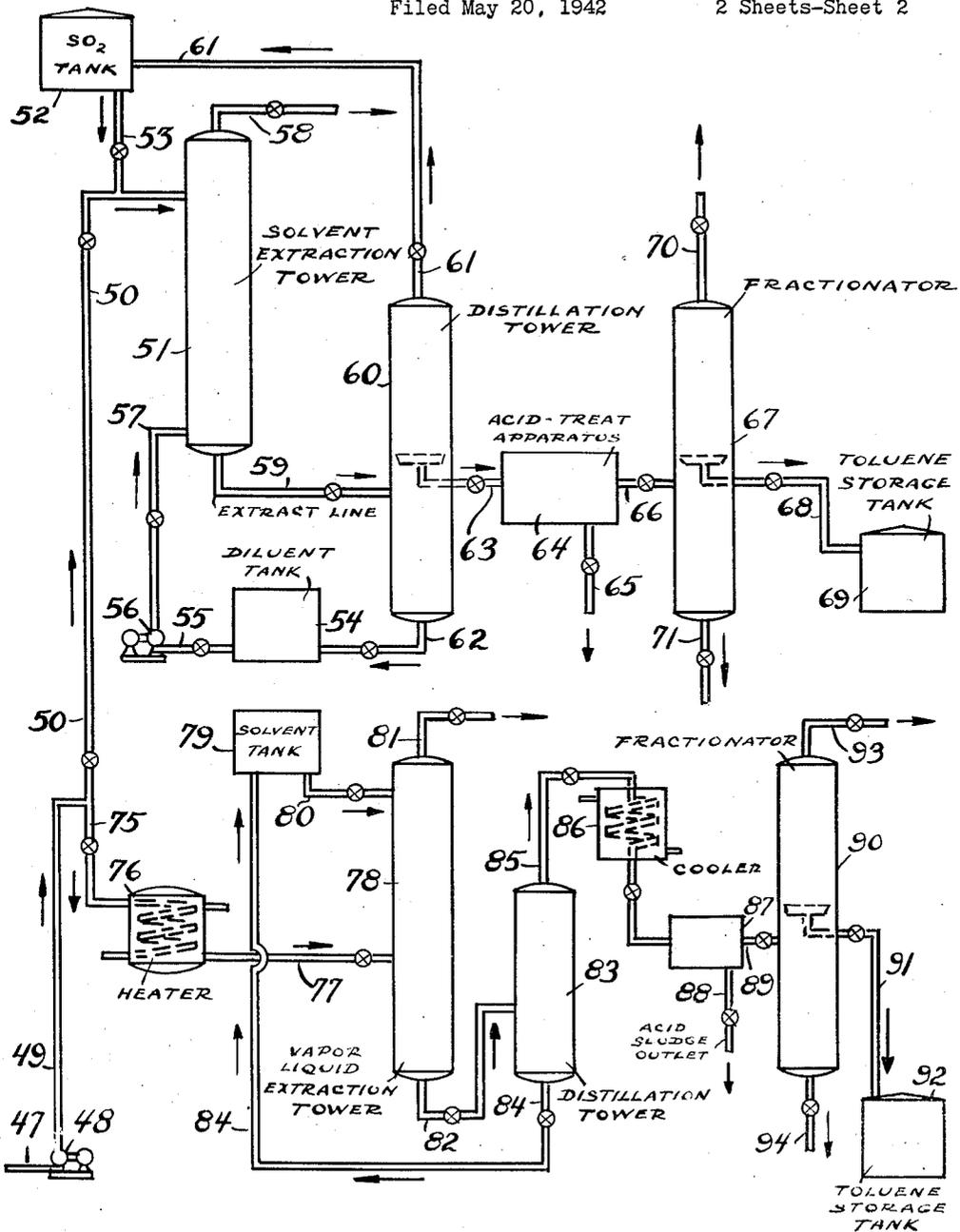


FIG.-1A

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## UNITED STATES PATENT OFFICE

2,380,279

## PRODUCTION OF AROMATICS

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Application May 20, 1942, Serial No. 443,711

2 Claims. (Cl. 260-668)

This invention relates to the production of substantially pure toluene from petroleum distillates and is more particularly concerned with certain improvements by means of which the yield of toluene obtained from said petroleum distillates may be materially increased.

It is known that petroleum distillates derived from certain crudes contain appreciable amounts of toluene. It is also known that fractions rich in aromatic hydrocarbons of various types can be obtained from such distillates by extraction with solvents such as liquid sulfur dioxide, phenol, furfural, nitrobenzene and the like which have preferential solvent power for aromatic hydrocarbons and relatively much less solvent power for paraffinic hydrocarbons. Aromatic hydrocarbon fractions obtained from petroleum distillates by solvent extraction methods, however, usually contain other hydrocarbons besides aromatics. These are dissolved by the solvent along with the aromatics and it is difficult to segregate them by distillation because they have boiling points very close to those of the aromatics.

For many purposes for which a highly aromatic hydrocarbon oil is needed, for example, in solvents, lacquers and high octane number motor fuels, aromatic extracts obtained by the solvent extraction of petroleum distillates are quite satisfactory and it is not particularly important whether the extract consists of a single aromatic hydrocarbon or a mixture of different hydrocarbons. For certain other purposes, however, for example, the nitration of toluene to produce TNT, it is essential to start with toluene of extremely high purity. Thus, the U. S. Army specifications for nitration grade toluene require a purity of at least 99%.

It is a principal object of the present invention to provide a process by means of which it is possible to obtain greater yields of nitration grade toluene from petroleum distillates than have heretofore been obtainable.

The nature of the process and the manner in which it is carried out will be fully understood from the following description when read with reference to the accompanying drawings which are semi-diagrammatic views in sectional elevation of one type of apparatus which is suitable for the purpose.

Referring to the drawings, numeral 1 designates a supply of a petroleum distillate which consists of hydrocarbons boiling essentially in the gasoline range. This petroleum distillate is preferably one which is rich in naphthenic hydro-

carbons, particularly methylcyclohexane and dimethylcyclohexanes. Pump 2 withdraws petroleum distillate from tank 1 through line 3 and forces it through line 4 into a fractionating means 5. A fraction boiling between about 200 and 300° F. is withdrawn from fractionating means 5 through line 6 and collected in a tank 7. Fractions boiling below about 200° F. and above about 300° F. are removed from fractionating means 5 through lines 8 and 9 respectively and are of no further interest insofar as the present process is concerned. Pump 10 withdraws the fraction of narrow boiling range from tank 7 through line 11 and forces it through line 12 into and through a heating means 13 and thence through line 14 into a reaction chamber 15 which contains a catalytic material 16, the nature of which will be described in more detail below.

In reaction chamber 15 the fraction of narrow boiling range is subjected to catalytic reforming. The term "catalytic reforming," wherever used in the specification and claims, shall be understood to mean a process in which a hydrocarbon oil, consisting essentially of naphthenic hydrocarbons boiling within the gasoline range which, upon dehydrogenation, produce aromatic hydrocarbons, is subjected to heat treatment at a temperature in excess of 500° F. and in the presence of a catalyst to produce a dehydrogenated or otherwise chemically reconstructed product of substantially higher aromaticity than the starting material, with or without an accompanying change in molecular weight. The term "catalytic reforming" shall be understood to include chiefly dehydrogenation but some aromatization and isomerization may also occur. The term "catalytic reforming in the presence of hydrogen," wherever used in the specification and claims, shall be understood to mean a process of catalytic reforming carried out in the presence of substantial quantities of added or recycled hydrogen or gases rich in free hydrogen under conditions such that there is either no overall net consumption of free hydrogen or there is an overall net production of free hydrogen.

For purposes of description it will be assumed that the reaction in reaction zone 15 is catalytic reforming in the presence of hydrogen.

Hydrogen or a gas rich in free hydrogen is supplied from a tank 17. Compressor 18 withdraws hydrogen from tank 17 through line 19 and forces it through line 20 which meets line 12 carrying the hydrocarbon fraction of narrow boiling range. A mixture of hydrocarbon oil and

hydrogen is formed at the junction of lines 20 and 12 and this mixture passes through heating means 13 and line 14 into reaction zone 15. Reaction zone 15 is maintained under conditions which favor catalytic reforming in the presence of hydrogen. The temperature is maintained between 850 and 1050° F. and the pressure is maintained between slightly above atmospheric and about 500 pounds per square inch, preferably between 30 and 400 pounds per square inch. The rate at which the hydrocarbon oil is passed through the reaction zone should be relatively low, say between 0.1 and 3.0, preferably between 0.5 and 1.5, volumes of liquid oil per volume of catalyst per hour. The quantity of gas which is passed through the reaction zone along with the hydrocarbon oil should be between 500 and 5000 cubic feet per barrel of oil and this gas should contain between about 30 and 90 mol percent of free hydrogen. The catalyst 16 in reaction zone 15 should be one which promotes catalytic reforming. Suitable materials for this purpose comprise aluminum oxide in any of its various forms, such as bauxite, acid-treated bauxite, aluminum hydrate, alumina gel, activated alumina, partially or completely peptized alumina or alumina gels, silica-alumina gels, and hydrofluoric acid-treated alumina together with from 1 to 50% by weight of an oxide or a sulfide of a metal of the IV, V, VI or VIII groups of the periodic system. Especially suitable catalysts comprise activated alumina or peptized alumina gels mixed or impregnated with from 1 to 20% by weight of the oxides or sulfides of molybdenum, chromium, tungsten, vanadium, cobalt or nickel.

Products of the catalytic reforming in the presence of hydrogen leave reaction zone 15 through line 21, pass through a cooling means 22 and thence flow through line 23 into a separating means 24 wherein the normally gaseous and the normally liquid products of reaction may be separated. The normally gaseous products of reaction which will consist principally of hydrogen and will contain small amounts of low molecular weight hydrocarbons such as methane, ethane and propane, are removed from separating means 24, through line 25 and recycled by means of booster compressor 25a to line 20. In some cases it may be desirable to subject these gases, before recycling, to a treatment to remove at least a portion of the hydrocarbon constituents therefrom in order to increase the concentration of free hydrogen therein. Such a treatment may, for example, consist of scrubbing the gases with a light hydrocarbon oil.

The normally liquid products of reaction are removed from separating means 24 through line 26 and introduced into a fractionating means 27. A fraction boiling between about 200 and 250° F. is removed from fractionating means 27 through line 28 and collected in a tank 29. This fraction will contain substantially all of the toluene which was initially present in the hydrocarbon oil and which was formed in the catalytic reforming reaction. Fractions boiling below 200° F. are removed from fractionating means 27 through line 30. Fractions boiling above 250° F. are removed from fractionating means 27 through line 31 and collected in a tank 32. These fractions will contain appreciable amounts of xylenes which have boiling points between about 280 and 290° F., and which were formed during the catalytic reforming reaction by the dehydrogenation of dimethylcyclohexanes.

Pump 33 withdraws hydrocarbon oil collected in tank 32 through line 34 and forces it through line 35 into and through a heating means 36 and thence discharges it through line 37 into a reaction zone 38 which contains a catalytic material 39, the nature of which will be described in more detail below. In reaction zone 38 the hydrocarbon fractions collected in tank 32 which contain appreciable quantities of xylenes are subjected to a catalytic cracking operation by means of which a substantial proportion of the xylenes is converted to toluene. The catalytic cracking reaction in reaction zone 38, like the catalytic reforming reaction in reaction zone 15, may be conducted in the presence of hydrogen or gases rich in free hydrogen. It will be recalled that when the catalytic reforming reaction is conducted in the presence of hydrogen, the conditions are such that there may be an overall net production of free hydrogen in the catalytic reforming reaction. Hence at least a portion of the net hydrogen produced in the catalytic reforming reaction may be utilized in the catalytic cracking reaction. This hydrogen may therefore be supplied to line 35 through lines 25 and 40. It will be understood that hydrogen may also be supplied to line 35 from an extraneous source through a line 41.

Two different types of catalytic cracking may be carried out in reaction zone 38. One type is a high temperature operation and the other is a low temperature operation.

In the high temperature operation, reaction zone 38 is maintained at a temperature between 850 and 1250° F., preferably between 930 and 1100° F., and under a pressure between slightly above atmospheric and about 300 pounds per square inch. The rate at which the hydrocarbon oil is passed through the reaction zone 38 may be between 0.1 and 4.0, preferably between 0.5 and 2.5, volumes of liquid oil per volume of catalyst per hour. The catalyst used in this high temperature operation may consist of natural or synthetic mixtures of alumina and silica. If this operation is to be conducted in the presence of hydrogen, the quantity of gas which accompanies the oil through the reaction zone may be between 500 and 5000 cubic feet per barrel of oil and the gas should preferably contain between 30 and 90 mol percent of free hydrogen.

In the low temperature type of operation, reaction zone 38 is maintained at a temperature between 250 and 400° F., under a pressure between slightly above atmospheric and about 100 pounds per square inch and the time of contact of the hydrocarbon oil in the reaction zone should be between about 10 seconds and 2 or 3 minutes. The catalyst used in this low temperature operation is aluminum chloride preferably accompanied by hydrogen chloride or other volatile chlorine compound. If this operation is conducted in the presence of hydrogen, the quantity of gas containing hydrogen which accompanies the oil through the reaction zone may be substantially the same as that described above in connection with the high temperature operation.

Whichever method of catalytic cracking is employed in reaction zone 38, products of the catalytic cracking reaction are removed from reaction zone 38 through line 42, passed through a cooling means 43 and then discharged into a separating means 44 wherein normally gaseous and normally liquid products may be separated. The normally gaseous products are removed from separating means 44 through line 45. The normally liquid

products are removed from separating means 44 through line 46 and introduced through line 26 into fractionating means 27 together with the normally liquid products removed from separating means 24. In this way those fractions of the catalytically cracked product which boil between 200 and 250° F. are recovered along with those fractions of the catalytically reformed product which boil between 200 and 250° F. and collected in tank 29. A portion of the catalytically cracked product which boils above 250° F. may then be recycled to the catalytic cracking operation in the manner described above.

It will be seen that the fraction boiling between 200 and 250° F. collected in tank 29 now contains all the toluene produced in both the catalytic reforming and the catalytic cracking operations, in addition to that which may have been present in the original petroleum distillate.

This fraction is withdrawn from tank 29 through line 47 by means of pump 48 and forced through line 49. It is then subjected to either one of two types of solvent extraction for the recovery therefrom of substantially pure toluene. One type of solvent extraction may be designated liquid-liquid extraction and the other type may be designated vapor-liquid extraction.

If the liquid-liquid type extraction is to be used, the hydrocarbon fraction flowing through line 49 is passed through line 50 into the upper portion of a conventional solvent extraction tower 51. Prior to its introduction into the extraction tower, the hydrocarbon is mixed with several volumes of a suitable selective solvent such as liquid sulfur dioxide which is supplied from tank 52 through line 53. In extraction tower 51 the mixture of liquid SO<sub>2</sub> and hydrocarbon is countercurrently washed with a non-aromatic hydrocarbon diluent which is supplied from tank 54 through line 55, pump 56 and line 57 to the bottom portion of tower 51. It will be understood that in certain cases, particularly when the hydrocarbon fraction contains a substantial proportion of non-aromatic hydrocarbons, it may be subjected to a preliminary extraction with liquid SO<sub>2</sub> to concentrate the aromatics and then the extract phase from this extraction will be subjected to the countercurrent washing with non-aromatic hydrocarbon diluent. Solvent extraction tower 51 is preferably maintained at a low temperature, say between about 0 and -60° F. The selectivity of liquid SO<sub>2</sub> increases noticeably as the temperature is lowered so that operation at the lowest temperatures may avoid the necessity of using the countercurrent washing step. The non-aromatic hydrocarbon diluent is preferably pre-cooled to a temperature between 0 and -60° F. but may be supplied at atmospheric temperature if other means are supplied for cooling the tower. The non-aromatic hydrocarbon diluent supplied from tank 54 should be a highly paraffinic hydrocarbon oil having a boiling range substantially different from those of the liquid sulfur dioxide and the toluene and other hydrocarbons present in the hydrocarbon fraction. The diluent may have a boiling range either higher or lower than the hydrocarbons in the hydrocarbon fraction. Examples of a suitable lower boiling diluent are pentane or iso-pentane. Examples of a higher boiling diluent are a paraffinic heavy naphtha and a light kerosene.

The primary function of the non-aromatic hydrocarbon diluent with which the mixture of hydrocarbon and liquid SO<sub>2</sub> is countercurrently washed is what may be called "dilution displace-

ment." This may be explained as follows: The hydrocarbon fraction will contain in addition to toluene and possibly other aromatics a smaller amount of non-aromatic hydrocarbons which boil in the same range as toluene and said other aromatics and which therefore cannot be separated therefrom by distillation or fractionation. By countercurrently washing the mixture of liquid SO<sub>2</sub> and hydrocarbon fraction with a relatively large volume of a non-aromatic hydrocarbon oil having a boiling range widely different from that of any of the constituents in the hydrocarbon fraction, the concentration of the non-aromatic hydrocarbons originally associated with the hydrocarbon fraction is greatly diluted and these non-aromatic hydrocarbons are replaced by non-aromatic hydrocarbons of widely different boiling range. Hence the extract obtained from extraction tower 51 after the countercurrent washing treatment will contain toluene, possibly other aromatics, liquid sulfur dioxide and a small amount of non-aromatic hydrocarbons of widely different boiling range than any other constituents of said extract phase. Having essentially replaced the non-aromatic hydrocarbons originally associated with the hydrocarbon fraction which boil in the same range as toluene with non-aromatics having a much different boiling range, it is now possible to separate the non-aromatics from the toluene by fractionation.

For purposes of description it will be assumed that the non-aromatic hydrocarbon diluent supplied from tank 54 is a paraffinic hydrocarbon oil boiling between about 350 and 400° F. or higher. The volume of non-aromatic hydrocarbon diluent with which the mixture of liquid SO<sub>2</sub> and hydrocarbon fraction is countercurrently washed should be at least sufficient to effect a substantial dilution displacement and may be from about 50 to about 150% or more of the volume of the mixture of liquid SO<sub>2</sub> and hydrocarbon fraction. The volume of non-aromatic hydrocarbon diluent should not however be so great as to displace the liquid SO<sub>2</sub> from the hydrocarbon fraction.

A raffinate phase which will consist chiefly of non-aromatic hydrocarbon diluent, non-aromatic hydrocarbons and some liquid sulfur dioxide is removed from extraction tower 51 through line 58. It will be understood that the liquid SO<sub>2</sub> and non-aromatic hydrocarbon diluent may be recovered from this raffinate phase and re-used in the extraction.

An extract phase is removed from the bottom of extraction tower 51 through line 59 and introduced into a distillation means 60. Sulfur dioxide is removed from distillation means 60 through line 61 and is returned to liquid sulfur dioxide supply tank 52. Non-aromatic hydrocarbon diluent is removed from distillation means 60 through line 62 and is returned to the diluent supply tank 54. The remainder of the extract phase is withdrawn from distillation means 60 through line 63 and subjected in apparatus designated by numeral 64 to a treatment with sulfuric acid to remove olefinic and unsaturated hydrocarbons. Acid sludge is removed from apparatus 64 through line 65. The acid-treated hydrocarbon is removed from apparatus 64 through line 66, and after the usual neutralization treatment of caustic and water washing, is introduced into a fractionating means 67 wherein substantially pure toluene may be separated from the other hydrocarbons. Substantially pure toluene is removed from distillation means 67 through line

68 and collected in tank 69. The fractions boiling below and above toluene are removed from distillation means 67 through lines 70 and 71 respectively. It will be understood that these fractions may be recycled through the extraction system in order to recover any toluene which they may contain.

In the event that the hydrocarbon fractions boiling between 200 and 250° F. which are collected in tank 29 have a high olefin content, it may be preferable to subject these fractions to acid treatment prior to the countercurrent washing because some of the olefins may react with sulfur dioxide at high temperatures and this would tend to foul the heaters in the distillation and stripping means.

If the liquid-vapor type of extraction is to be used, the hydrocarbon fractions boiling between 200 and 250° F. flowing through line 49 are passed through line 75 into and through a heating means 76 wherein they are heated to a temperature somewhat above their vaporizing temperature and the vapors are then introduced through line 77 into the middle portion of a conventional type extraction tower 78 which is adapted for countercurrent flow of liquid and vapors.

Numeral 79 designates a supply of a selective solvent having a boiling point substantially above the boiling point of the hydrocarbons to be extracted, i. e. in the present case, above about 250° F. This solvent should be one which is characterized by its ability to reduce the vapor pressure of aromatic hydrocarbons to a substantial extent while at the same time reducing the vapor pressure of other types of hydrocarbons to a much smaller degree. Examples of suitable solvents of this type are phenol, cresol, cresylic acid, mixtures of phenol and cresylic acid, alpha naphthylamine, diethylene glycol, furfural, dimethylphthalate, aniline and beta beta dichloroethyl ether. Phenol is a particularly suitable solvent.

Solvent is removed from tank 79 through line 80 and after being heated to the temperature at which the hydrocarbon vapors are to be extracted, is introduced into the upper portion of extraction tower 78 wherein it remains in liquid phase and flows downwardly countercurrent to the upwardly rising hydrocarbon vapors. The quantity of solvent used may be between 50 and 500% of the liquid volume of the hydrocarbons to be extracted. It will be understood that extraction tower 78 is maintained at a temperature above the vaporizing temperature of the hydrocarbons. The solvent, however, remains in liquid phase.

Vapors substantially free from aromatic hydrocarbons are removed from the upper portion of tower 78 through line 81. It will be understood that these vapors may be condensed and the condensate added to the feed in tank 7 for resubjection to the catalytic reforming and catalytic cracking reactions.

A solvent extract is removed from extraction tower 78 through line 82 and after being heated in means, not shown, to a temperature sufficiently high to insure that all the toluene will be vaporized, is introduced into a distillation means 83. The solvent is removed from distillation means 83 through line 84 and returned to solvent supply tank 79. Vapors of toluene together with those of any other hydrocarbons which may be present are removed from distillation means 83 through line 85, passed through a cooling means 86 and then, if necessary, subjected to acid treatment in an apparatus designated by the numeral 75

87 in order to remove olefins and other unsaturated hydrocarbons. Acid sludge is removed from apparatus 87 through line 88 and the acid-treated oil is then passed through line 89 into a fractionating means 90 from which substantially pure toluene is removed through line 91 and collected in tank 92. Fractions boiling below and above toluene are removed from fractionating means 90 through lines 93 and 94 respectively. As in the case of fractionating means 67, described above, the fractions boiling below and above toluene may be recycled to the extraction tower 78 in order to insure that all the toluene will be recovered therefrom.

From the above description it will be seen that the process of the invention consists essentially of the following steps: (1) segregating from a petroleum distillate a fraction boiling between about 200 and 300° F.; (2) subjecting this fraction to catalytic reforming or catalytic reforming in the presence of hydrogen; (3) segregating from the products of catalytic reforming a fraction boiling between about 200 and 250° F.; (4) subjecting the products of catalytic reforming which boil above about 250° F. to catalytic cracking or catalytic cracking in the presence of hydrogen; (5) segregating from the products of catalytic cracking a fraction boiling between 200 and 250° F.; (6) combining this last fraction boiling between 200 and 250° F. with the fraction boiling between 200 and 250° F. obtained from the products of catalytic reforming; (7) subjecting the combined fractions boiling between 200 and 250° F. to either liquid-liquid solvent extraction or liquid-vapor solvent extraction; (8) acid-treating the solvent extract to remove olefins; and (9) fractionating the acid-treated extract to obtain substantially pure toluene.

In carrying out this process, it will be understood that many variations may be made in the details of operation without departing from the scope of the invention. For example, the catalytic reforming and catalytic cracking reactions conducted in reaction zones 15 and 38 respectively may be carried out in the presence of finely divided catalyst rather than in the presence of a fixed or stationary catalyst as illustrated in the drawings. One particular type of operation carried out in the presence of finely divided catalyst is what may be called "fluid catalyst operation." In this type of operation the finely divided catalyst is suspended in oil vapors or other gases and the relative proportions of catalyst and gas and the linear velocity of the gas are adjusted so that the mixture behaves in much the same way as a fluid and may be pumped and circulated through the apparatus in the same manner as a fluid. Also, in view of the fact that the catalysts 16 and 39 in reaction zones 15 and 38 respectively are of the type which gradually lose their activity because of the deposition thereon of carbonaceous contaminants such as coke during the reaction and hence require periodic regeneration treatments, it is desirable, when fixed or stationary catalysts are used, to provide two or more reaction zones 15 and 38 so that while the catalyst in one zone is on regeneration, the reaction may be continued in another zone. It will also be understood that provision may be made for heat exchange between hot products and cold feed material at various points throughout the system; that the usual heating and cooling coils will be provided in the solvent extraction towers and that such other variations in the method of

operating different parts of the apparatus may be made as are customary in the art.

This invention is not limited by any theories of the mechanism of the reactions nor by any details which have been given for purposes of illustration but is limited only in and by the following claims.

I claim:

1. An improved process for producing substantially pure toluene from petroleum distillates which comprises segregating from a petroleum distillate a fraction boiling between 200-300° F., subjecting this fraction to catalytic reforming in the presence of hydrogen in an operation resulting in a net production of hydrogen, segregating from the products of catalytic reforming a fraction boiling from 200 to 250° F. and a fraction boiling above 250° F., subjecting the fraction boiling above 250° F. to catalytic cracking in the presence of at least a portion of the net hydrogen produced in the catalytic reforming in the presence of hydrogen, segregating from the products of catalytic cracking a fraction boiling between 200 and 250° F. and a fraction boiling above 250° F., recycling the last-named fraction to the catalytic cracking, combining the fractions boiling between 200 and 250° F. found in the products of catalytic reforming and catalytic cracking,

respectively, subjecting these combined fractions to extraction with a solvent having a preferential solvent power for aromatic hydrocarbons, subjecting the solvent-free extract to treatment with sulfuric acid to remove unsaturated hydrocarbons therefrom, and fractionating the thus acid-treated material to obtain substantially pure toluene.

2. The method set forth in claim 1 in which the initial fraction boiling between 200 and 300° F. is subjected to catalytic reforming in the presence of hydrogen at a temperature between 850 and 1050° F., under a pressure between slightly above atmospheric and about 500 lbs./sq. in., and in the presence of between 500 and 5000 cubic feet per barrel of oil of a gas containing between 30 and 90 mol per cent of free hydrogen and in which the fractions boiling above 250° F. segregated from the products of catalytic reforming and catalytic cracking, respectively, are subjected to catalytic cracking at a temperature between 850 and 1250° F., under a pressure between slightly above atmospheric and about 300 lbs./sq. in., in the presence of a catalyst comprising silica and alumina and in the presence of at least a portion of the net hydrogen produced in the catalytic reforming in the presence of hydrogen.

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