

March 19, 1946.

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PRODUCTION OF AROMATIC HYDROCARBONS

Filed June 6, 1942

2 Sheets-Sheet 1

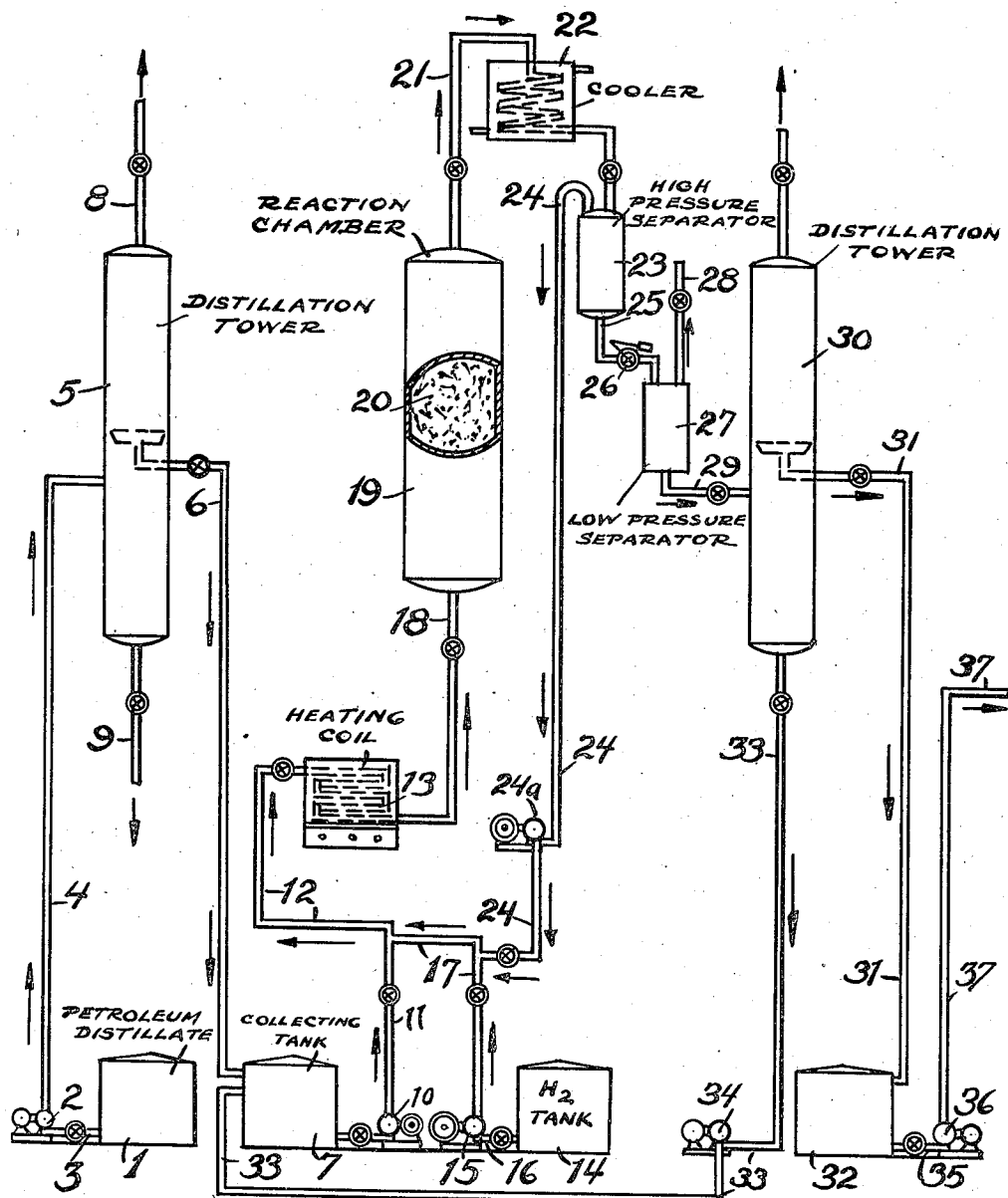


FIG. -1

Joshua H. Tilton Inventor
By *P. H. Young* Attorney

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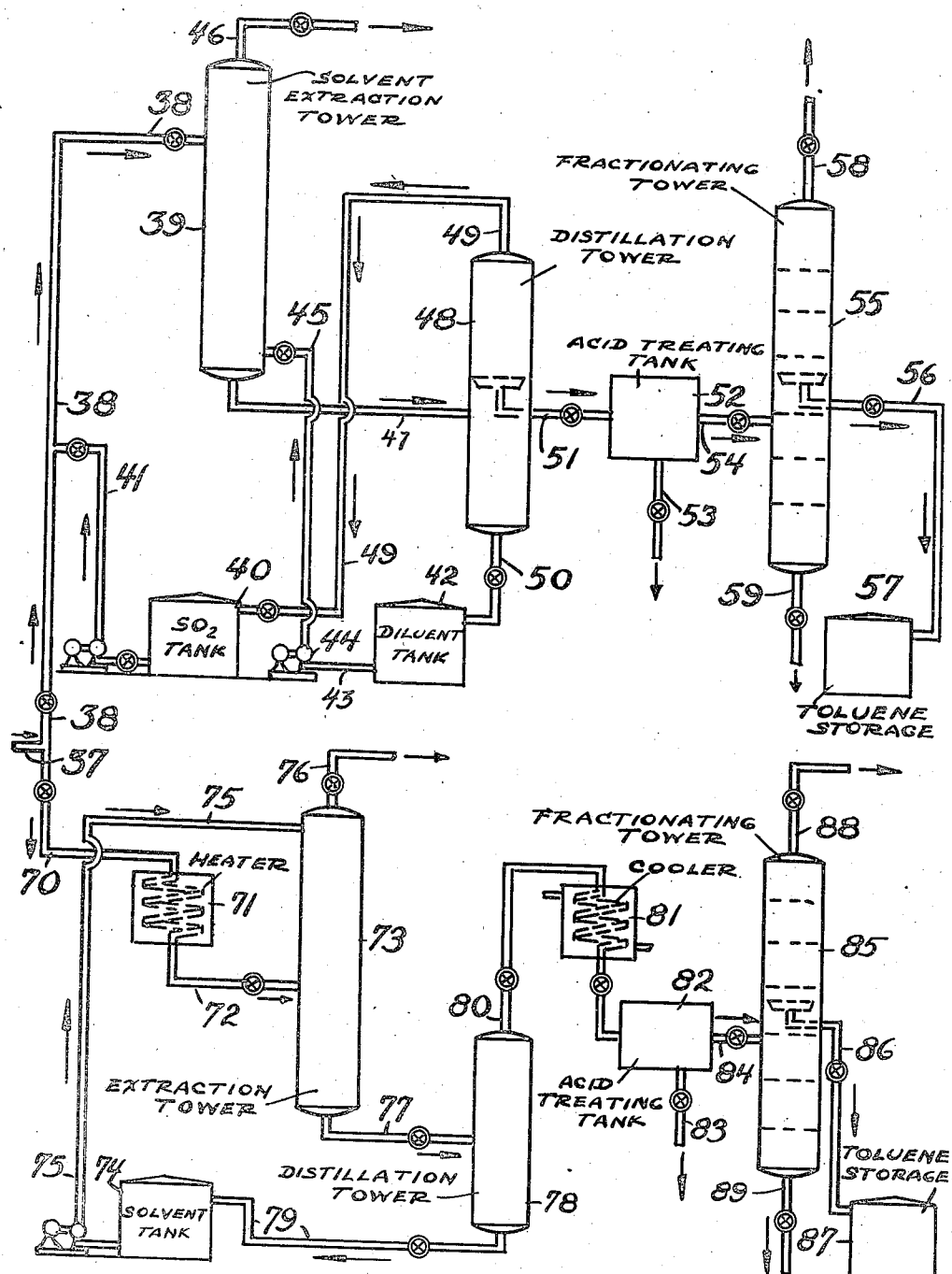


FIG.-1A

Joshua A. Tilton Inventor
By P. P. Young Attorney

UNITED STATES PATENT OFFICE

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PRODUCTION OF AROMATIC HYDRO-CARBONS

Joshua A. Tilton, Baton Rouge, La., assignor to
Standard Oil Development Company, a corporation of Delaware

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6 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 in operation 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 and other aromatics such as xylenes. 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 at temperatures at which they have 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 the aromatics. These are dissolved by the solvent along with the aromatics and it is difficult, if not impossible, 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 aromatic 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 petroleum distillate which may contain in addition to toluenes and xylenes certain naphthenic hydrocarbons which may be

converted to toluene and xylenes. Pump 2 withdraws petroleum distillate from tank 1 through line 3 and forces it through line 4 into a distillation means 5. From distillation means 5 a fraction boiling between about 200 and 350° F. is withdrawn through line 6 and collected in a tank 7. Fractions boiling below 200 and above about 350° F. are removed from distillation means 5 through lines 8 and 9 respectively. The fraction boiling between 200 and 350° F. collected in tank 7 will contain all of the toluene and xylenes present in the original petroleum distillate and in addition will contain any methylcyclohexane and dimethylcyclohexanes which may also have been present. Pump 10 withdraws the hydrocarbon fraction from tank 7 through line 11 and forces it through line 12 into and through a heating means 13. Tank 14 contains a supply of hydrogen. A compressor 15 withdraws hydrogen from tank 14 through line 16 and forces it through line 17 to a junction with line 12. Thereby a mixture of hydrogen and oil is formed which passes through the heating means 13. After being heated in heating means 13 to a suitable reaction temperature, the mixture of oil and hydrogen flows through line 18 into a reaction chamber 19 which contains a catalytic material 20 the nature of which will be described in more detail below.

In reaction chamber 19 the hydrocarbon fraction is subjected to a high temperature and high pressure hydrogenation treatment. It has been found that the conventional destructive hydrogenation operation may be modified to cause substantial dehydrogenation simply by increasing the temperature of operation to substantially above that ordinarily employed. Thus, if any naphthenic hydrocarbons are present, these will be substantially converted in the high temperature hydrogenation operation to the corresponding aromatic hydrocarbons. For example, if methylcyclohexane and dimethylcyclohexanes are present, they will be converted to toluene and xylenes respectively. It is ordinarily found that in this operation more xylenes are produced than toluene. The ratio is usually of the order of one part toluene to one to two parts of xylenes. Cracking of acyclic hydrocarbons which are less refractory than aromatics may occur in the reaction and the cracked products may subsequently be hydrogenated.

Reaction chamber 19 is maintained under conditions which favor dehydrogenation of naphthenes. The temperature may be between 900 and 1150° F. and the pressure should be maintained between about 50 and 200 or more atmos-

phers. The rate at which the hydrocarbon oil is fed through reaction chamber 19 may be between 1.0 and 4.0 volumes of total liquid per volume of catalyst per hour and the quantity of hydrogen which accompanies the oil through the reaction chamber could be between 1500 and 10,000 cubic feet per barrel of oil. The catalyst 20 in reaction chamber 19 may consist of an oxide or sulfide of a metal of the VI group of the periodic system in admixture with smaller amounts of the oxides of zinc, magnesium or aluminum. Especially suitable catalysts comprise mixtures of magnesium oxide, zinc oxide and molybdenum oxide; mixtures of zinc oxide and chromium oxide and mixtures of tungsten sulfide and nickel sulfide.

Products of reaction leave reaction chamber 19 through line 21, pass through a cooling means 22 and then discharge into a separating means 23 wherein gaseous and liquid products are separated under high pressure. The gaseous products which will consist essentially of hydrogen are removed from separating means 23 through line 24 and may be recycled to line 17 by means of booster compressor 24a. The liquid products are removed from separating means 23 through line 25 and after passing through a pressure release valve 26 are collected in a low pressure separating means 27 from which gaseous products are removed through line 28 and may be passed to the refinery fuel line or otherwise disposed of. Liquid products now under low pressure are removed from separating means 27 through line 29 and introduced into a distillation means 30. From distillation means 30 a fraction boiling between 200 and 250° F. is removed through line 31 and collected in tank 32. This fraction will contain substantially all of the toluene which may have been present in the original narrow fraction segregated from the petroleum distillate and which may have been produced in reaction chamber 19. Fractions boiling above about 250° F. are removed from distillation means 30 through line 33 and are recycled to tank 7 by means of pump 34. In the event that these fractions contain substantial quantities of non-aromatic hydrocarbons, it may be desirable to subject them to a solvent extraction treatment and then recycle only the extract to tank 7. In this way an accumulation of non-aromatic material in the system may be prevented. These fractions boiling above 250° F. will contain any xylenes originally present in the petroleum distillate and any which may have been produced in reaction chamber 19 and may also contain some polymers which may be removed by distillation if desired. By recycling these xylenes through the high temperature hydrogenation operation it is found that a considerable proportion thereof may be converted to toluene. Thus it will be seen that a toluene fraction is continuously removed from the products of the high temperature hydrogenation operation while the fractions boiling above toluene are continuously recycled to the high temperature hydrogenation operation wherein they are eventually converted to toluene.

The toluene containing fraction collected in tank 32 is removed therefrom through line 35 by means of pump 36 and forced through line 37. 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 liquid-vapor extraction.

If the liquid-liquid type extraction is to be used, a hydrocarbon fraction flowing through line 37 is passed through line 38 into the upper portion of a conventional solvent extraction tower 39. The hydrocarbon is mixed with several volumes of a suitable selective solvent such as liquid sulfur dioxide which is supplied to line 38 from tank 40 through line 41. In extraction tower 39 the mixture of liquid SO₂ and hydrocarbon is countercurrently washed with a non-aromatic hydrocarbon diluent which is supplied from tank 42 through line 43, pump 44 and line 45 to the bottom portion of tower 39. The extraction tower 39 is preferably maintained at a low temperature, say between about -20 and -60° F. The non-aromatic hydrocarbon diluent is preferably precooled to a temperature between -20 and -60° F. prior to its introduction into the tower but may be supplied at atmospheric temperature if other means are provided for cooling the tower. The non-aromatic hydrocarbon diluent supplied from tank 42 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 isopentane. Examples of a higher boiling diluent are a paraffinic solvent naphtha and a light kerosene.

In the event that the fraction boiling between 200 and 250° F. collected in tank 32 contains a substantial proportion of non-aromatic hydrocarbons, it may be preferable to subject this fraction to a preliminary extraction with liquid SO₂ in order to segregate the aromatics from the bulk of the non-aromatic hydrocarbons. If this procedure is adopted, the solvent extraction phase from the preliminary extraction will be introduced into the top of tower 39 either with or without the addition of further quantities of liquid SO₂.

The primary function of the non-aromatic hydrocarbon diluent with which the mixture of hydrocarbon and liquid SO₂ is countercurrently washed is what may be called "dilution displacement." 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 can not be separated therefrom by distillation or fractionation. By countercurrently washing the mixture of liquid SO₂ 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 39 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-aromatic hydrocarbons having a much different boiling range, it is now possible to separate the non-aromatics from the toluene by ordinary fractionation.

For purposes of description it will be assumed that the non-aromatic hydrocarbon diluent supplied from tank 42 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 SO₂ 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 SO₂ and hydrocarbon fraction. The volume of non-aromatic hydrocarbon diluent should not however be so great as to displace the liquid SO₂ from the hydrocarbon fraction.

A raffinate phase which will consist chiefly of non-aromatic hydrocarbon diluent, non-aromatic hydrocarbons, and possibly some liquid SO₂ is removed from extraction tower 39 through line 46. It will be understood that the liquid SO₂ and non-aromatic hydrocarbon diluent may be recovered from this raffinate phase and reused in the extraction. It will also be understood that any toluene which may be present in the raffinate removed from the top of tower 39 may be recovered by recycling said raffinate to the top of tower 39.

An extract phase is removed from the bottom of extract tower 39 through line 47 and introduced into a distillation means 48. This extract phase will contain most of the sulfur dioxide and aromatic hydrocarbons present in tower 39 and in addition will contain a small quantity of non-aromatic hydrocarbon diluent. In distillation means 48 the sulfur dioxide is distilled off and is removed through line 49 and may be returned to liquid SO₂ supply tank 40. Non-aromatic hydrocarbon diluent is removed from distillation means 48 through line 50 and returned to the diluent supply tank 42. The remainder of the extract phase is withdrawn from distillation means 48 through line 51 and is then subjected in an apparatus designated by numeral 52 to a treatment with sulfuric acid to remove olefinic and unsaturated naphthenic hydrocarbons. Acid sludge may be removed from apparatus 52 through line 53. The acid-treated extract, after neutralization, is removed from apparatus 52 through line 54 and introduced into a fractionating means 55. Substantially pure toluene is removed from fractionating means 55 through line 56 and collected in a tank 57. Fractions boiling below and above toluene are removed from fractionating means 55 through lines 58 and 59 respectively. It will be understood that these fractions may be recycled to the extraction system in order to recover any toluene which they may contain.

In the event that the fraction boiling between 200 and 250° F. which is collected in tank 32 has a high olefin content, it may be preferable to subject this fraction to treatment with sulfuric acid prior to the extraction because olefins react with sulfur dioxide at high temperatures and this would tend to cause fouling of the heaters in the distillation and stripping means.

If the liquid-vapor type of extraction is to be used, the toluene containing fraction flowing through line 37 is passed through line 70 into and through a heating means 71 wherein it is heated to a temperature somewhat above its vaporizing temperature and the vapors are then introduced through line 72 into the middle portion of a conventional extraction tower 73 which is adapted

for countercurrent flow of liquid and vapors. Numeral 74 designates a supply of a selective solvent having a boiling point substantially above the boiling range 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 extent. Examples of suitable solvents of this type are phenol, cresol, cresylic acid, mixtures of phenol and cresylic acid, furfural, aniline and beta-beta dichlorethyl ether. Phenol is a particularly suitable solvent.

Solvent is removed from tank 74 through line 75 and introduced into the upper portion of tower 73 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 1000% of the liquid volume of the hydrocarbons to be extracted. It will be understood that extraction tower 73 is maintained by suitable means at a temperature above the vaporizing temperature of the hydrocarbons but below the vaporizing temperature of the solvent.

Vapors substantially free from aromatic hydrocarbons are removed from extraction tower 73 through line 76. Aromatic hydrocarbons dissolved in the selective solvent are removed from the bottom of extraction tower 73 through line 77 and introduced into a distillation means 78. Solvent is removed from distillation means 78 through line 79 and may be returned to solvent supply tank 74. Vapors of toluene together with those of any other aromatic hydrocarbons which may be present are removed from distillation means 78 through line 80, passed through a cooling means 81 and then, if necessary, subjected to acid treatment in an apparatus designated by the numeral 82 in order to remove olefins and unsaturated naphthenic hydrocarbons. Acid sludge may be removed from apparatus 82 through line 83. The acid treated extract is removed from apparatus 82 through line 84 and introduced into a fractionating means 85 from which substantially pure toluene is removed through line 86 and then collected in a tank 87. Fractions boiling below and above toluene are removed from fractionating means 85 through lines 88 and 89 respectively. As in the case of the liquid-liquid extraction, the fractions boiling below and above toluene may be recycled to extraction tower 73 in order to insure that all the toluene will be recovered therefrom.

While the process has been described with particular reference to the treatment of a fraction boiling between 200 and 350° F. which will contain methylcyclohexane and dimethylcyclohexanes it should be understood that the process is also applicable to the treatment of higher boiling naphthenic hydrocarbons, say, for example, those contained in fractions boiling up to about 450° F.

In carrying out the process many variations in the operating details may be made without departing from the scope of the invention. The usual provisions may be made for heat exchange between hot products and colder material at various points throughout the system and the usual heating or cooling coils may be provided in the solvent extraction towers, and 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 merely for purposes of illustration but is limited only in and by the following claims:

I claim:

1. An improved process for obtaining high yields of substantially pure toluene from a naphthenic base petroleum which comprises segregating from petroleum a fraction boiling between 200 and 350° F., subjecting this fraction to treatment with hydrogen at high temperature and high pressure, under which conditions dehydrogenation of naphthenes occurs, segregating from the products of hydrogenation a fraction boiling between 200 and 250° F. and a fraction rich in xylenes boiling above 250° F., recycling this latter fraction to the high temperature hydrogenation, extracting the fraction boiling between 200 and 250° F. with a solvent which is selective for aromatic hydrocarbons, treating the solvent extract with sulfuric acid to remove olefins and unsaturated naphthenic hydrocarbons, and fractionating the acid-treated extract to obtain substantially pure toluene.

2. Process according to claim 1 in which the hydrogenation is carried out at a temperature between 900 and 1150° F., under a pressure in excess of 50 atmospheres and in the presence of a catalyst comprising a major proportion of an oxide of a metal of the VI group of the periodic system.

3. Process according to claim 1 in which the fraction boiling between 200 and 250° F. segregated from the products of hydrogenation is extracted with liquid sulfur dioxide at a temperature between -20 and -60° F. and the extract phase is countercurrently washed with a non-aromatic hydrocarbon diluent having a boiling range widely different from that of the hydrocarbons in the extract phase.

4. Process according to claim 1 in which the fraction boiling between 200 and 250° F. segregated from the products of hydrogenation is countercurrently extracted in vapor phase with a selective solvent which remains in liquid phase at the temperature of extraction.

5. An improved process for obtaining high yields of toluene of at least 99% purity from a petroleum distillate containing naphthenic hydrocarbons, which comprises segregating from said distillate a fraction boiling between 200 and 350° F., subjecting this fraction to treatment with hydrogen at a temperature between 900 and 1150° F. and under a pressure above 50 atmospheres, segregating from the products of this treatment a fraction boiling between 200 and 250° F., continuously recycling to the hydrogen treatment fractions of the product rich in xylenes boiling above 250° F., subjecting the fraction boiling between 200 and 250° F. to extraction in vapor phase with phenol which remains in liquid phase at the temperature of extraction, removing the phenol from the extract phase, treating the extract with sulfuric acid to remove unsaturated hydrocarbons, and fractionating the acid-treated extract to obtain toluene of at least 99% purity.

6. An improved process for obtaining high yields of toluene of at least 99% purity from petroleum distillate containing naphthenic hydrocarbons which comprises segregating from said distillate a fraction boiling between 200 and 350° F., subjecting this fraction to treatment with hydrogen at a temperature between 900 and 1150° F. under a pressure above 50 atmospheres in the presence of a catalyst comprising a mixture of magnesium oxide, zinc oxide and molybdenum oxide, segregating from the product of this treatment a fraction boiling between 200 and 250° F., continuously recycling to the hydrogen treatment fractions of the product, rich in xylenes, boiling above 250° F., subjecting the fraction between 200 and 250° F. to extraction in vapor phase with phenol which remains in liquid phase at the temperature of extraction, removing the phenol from the extract phase, treating the extract with sulfuric acid to remove unsaturated hydrocarbons and fractionating the acid-treated extract to obtain toluene of at least 99% purity.

JOSHUA A. TILTON.