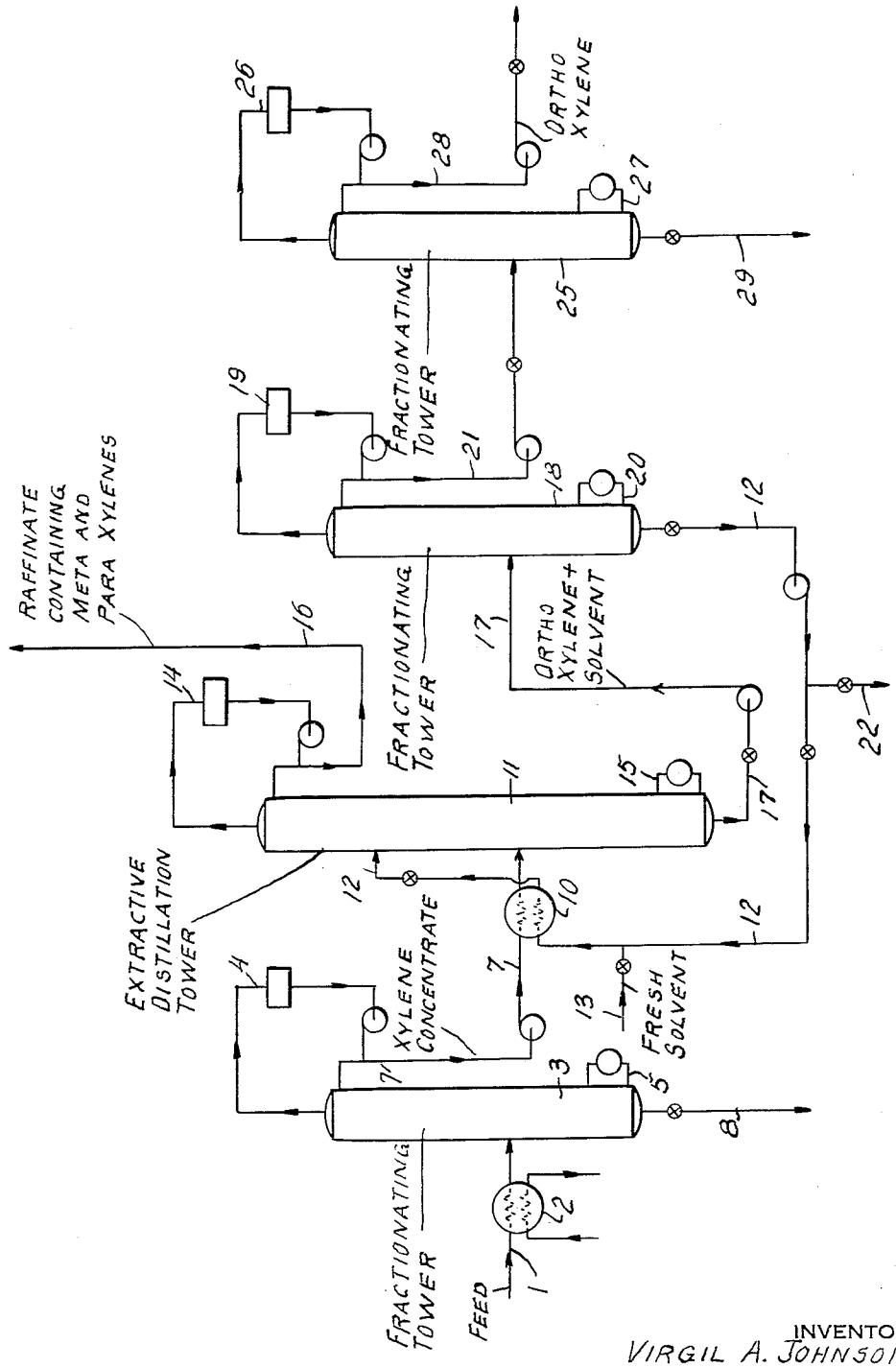
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EXTRACTIVE DISTILLATION OF O-XYLENES FROM A PETROLEUM FRACTION

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EXTRACTIVE DISTILLATION OF O-XYLENES FROM A PETROLEUM FRACTION

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My invention relates to an improved extractive distillation process for separating ortho xylene from petroleum distillate fractions in greater yield and more simply than heretofore possible.

In present commercial practice the isomeric xylenes are separated from petroleum distillates by extractive distillation. A petroleum fraction containing xylenes in small amount is fractionally distilled to prepare a concentrate rich in xylenes. The concentrate, containing at least 5% and advantageously more of xylenes, is then distilled in vapor phase in the presence of a relatively high-boiling selective solvent. In the extraction step, the non-aromatics are taken off overhead while the xylenes are withdrawn as bottoms in admixture with the solvent. The xylenes are stripped from the solvent by distillation and the xylene isomers are separated from each other by an additional distillation step. Ortho xylene, commercially the most valuable xylene isomer, is conventionally recovered in this way.

In conventional practice it is important to initially prepare a concentrate of the xylene isomers by fractional distillation and then to separate the mixture of isomers from the concentrate by extractive distillation. To the best of my knowledge, the xylene isomers have not been separated from each other in the extractive distillation step, apparently because the common selective solvents appeared to show practically no difference in selectivity for the different isomers under normal operating conditions.

I have found that under certain process conditions ortho xylene can be separated directly from the xylene concentrate in the extraction step and then may be recovered from the solvent by simple distillation. My improvement eliminates one fractionation step from conventional operation and results in recovery of ortho xylene in improved yield.

According to my invention, a petroleum distillate fraction containing isomeric xylenes is passed at a temperature in the range approximating 310° to 330° F. into a fractional distillation zone. The overhead composition is regulated so that a lighter fraction whose boiling range includes the larger portion of the xylene isomers is taken off overhead while the constituents boiling higher than ortho xylene are taken off as bottoms. I have found that in order to accomplish this the xylene concentrate taken off should have a dry point of not higher than 282° F. as determined by standard A. S. T. M. distillation. The xylene concentrate is passed in vapor phase at a temperature of about 300° to 320° F. to an extractive distillation zone into contact with a liquid high-boiling selective organic solvent which has been preheated to a temperature of about 340° to 360° F. The bottoms composition is regulated so that a solvent-rich phase consisting essentially of solvent and ortho xylene is recovered as the high boiling product, while a raffinate vapor is taken off overhead. I have found that this can be accomplished by regulating the bottoms temperature, the solvent to fresh feed ratio, and the reflux ratio in the

usual manner so as to give the desired purity and recovery of ortho xylene as a bottoms product while taking off overhead the meta and para isomers. The solvent-rich ortho xylene fraction is then distilled in order to strip it of the solvent, the solvent being advantageously recycled to the extractive distillation step. The ortho xylene recovered ordinarily is further purified by redistillation for removal of gum and other contaminants.

The process according to my invention is particularly applicable to the treatment of petroleum distillates containing xylenes in relatively small amounts. However, it may be employed in treatment of fractions containing xylenes in considerable concentrations. Thus a wide range of petroleum distillates may be used in my process such as straight-run or cracked distillate fractions. However, a cracked light distillate fraction from a naphthenic or mixed base crude, e. g. a 275°–300° F. Houdry naphtha fraction from a catalytic cracking operation is particularly susceptible to this treatment.

As the solvent, I employ relatively high-boiling organic compounds having a selective or preferential solvent power for the ortho xylene under the specific conditions of my process. It is necessary that the solvent have a boiling point sufficiently above the boiling point of ortho xylene so that the two may be separated by fractional distillation. Also, the solvent should be chemically and thermally stable under these same process conditions. An especially suitable selective organic solvent is nitrobenzene. Other solvents which can be employed include phenol, dimethyl phthalate and aniline. The amount of solvent employed may be varied considerably. Generally speaking, however, about one to seven or eight parts by volume of the solvent for each part of xylene concentrate is sufficient.

In a specific embodiment of the process according to my invention, the xylene-containing feed oil is heated to a temperature of about 320° F. and is passed into a fractionating tower. The constituents boiling higher than ortho xylene are taken off as a bottoms cut comprising essentially the heavier fraction. The xylenes and lighter non-aromatics are taken off overhead by carefully controlling the overhead boiling range so that it has a dry point of not higher than 282° F. by the standard A. S. T. M. distillation. I have found that in this way a xylene-rich concentration is obtained containing a relatively large proportion of ortho xylene as well as its isomers, although the precise dry point temperature will vary somewhat with different charge stocks for optimum xylene concentration. Another method that may be used to determine the amount of constituents boiling higher than ortho xylene that can be tolerated in the xylene concentrate I prepare without deleteriously affecting the purity of the final product is to run a Stedman fractionation on several concentrates, removing two per cent cuts up to 300° F. Each cut is analyzed for the xylenes and non-aromatics, and the cut containing a concentration of ortho xylene sufficiently free of heavy non-aromatics for high purity ortho xylene yield upon extractive distillation is determined. The tower top temperature is then controlled at this limiting point while concentrating the charge stock tested. In order to separate ortho xylene in commercially attractive yield, the concentrate should comprise at least 5% isomeric xylenes, advantageously 10% or more and preferably about 30 to 50 per cent.

The xylene-rich fraction or concentrate is passed in vapor phase into an extractive distillation zone and contacted therein with nitrobenzene. The vaporized xylene concentrate is introduced at a temperature of about 310° F., while the liquid solvent is fed into the extractive distillation zone at about 350° F. This distillation zone may be a conventional extractive distillation tower or, to reduce tower size, two towers in a series arrangement. A

solvent-rich fraction containing principally ortho xylene in admixture with the solvent is taken off as a bottoms product. A raffinate phase made up of the meta and para xylene isomers in admixture with practically all of the light and heavy non-aromatics are taken off as overhead. The bottoms temperature is regulated along with the reflux ratio and solvent to fresh feed ratio in the usual manner to give the desired yield and purity of ortho xylene. For instance, a bottoms temperature of about 445° F. may be used. In this way, I have found that a fraction consisting of ortho xylene and solvent is obtained as bottoms, while the para and meta xylene isomers are removed in the overhead in a single stage extractive distillation operation.

The solvent-rich fraction is then subjected to simple distillation to strip out the ortho xylene product, the solvent being obtained as a bottoms product. The bottoms temperature during stripping is advantageously maintained at the boiling point of the pure solvent under the operating pressure of the system. This assures a pure solvent for use again in the system and that all of the ortho-xylene is stripped from the solvent and recovered as overhead. Advantageously, the recovered solvent is recycled to the extractive distillation step. The ortho xylene separated as overhead is ordinarily rerun for additional purity in order to remove gum and other contaminants. Thus my invention provides a process for separating ortho xylene from its isomers in a single stage extractive distillation. In addition, I have found that in the practice of my process ortho xylene is obtained in 85 to 95% yields. In contrast, only 70 to 80% is recovered in conventional practice. Further, my improved process requires less capital and operating expense than the conventional method of manufacturing ortho xylene.

The accompanying drawing illustrates somewhat schematically a flow diagram of the process according to my invention.

According to the process illustrated in the drawing, a suitable petroleum distillate fraction, say a 275°–300° F. naphtha cut from a Houdry unit containing about 45% of xylenes, is charged to the system by line **1**. The fraction is heated to a temperature of about 320° F. in heating zone **2**, which may be for example a conventional steam preheater. The heated fraction is then passed into fractional distillation zone **3** at this temperature to prepare a xylene-rich concentrate. The distillation zone **3** may be a conventional fractionating tower equipped with refluxer **4** and reboiler **5**. The boiling range of the overhead is controlled so it has a dry point of not higher than 282° F. by the standard A. S. T. M. distillation so that only the xylenes and other lighter boiling constituents are taken off overhead by line **7**. The constituents boiling higher than ortho xylene are taken off as bottoms by line **8** and are removed from the system.

The xylene concentrate is then passed by line **7** through heat exchanger **10**, fed by the recirculating solvent, and is introduced into extractive distillation tower **11** in vapor phase at a temperature of about 310° F. Nitrobenzene, heated to a temperature of about 350° F., is introduced into the tower **11** as a liquid by line **12** and contacted therein with the vaporized xylene concentrate. The solvent is advantageously obtained from the stripper by line **12**; however, fresh solvent may be added to the recycle through line **13** whenever necessary. The extraction is carried out in a tall extractive distillation tower which may be equipped with refluxer **14** and reboiler **15**. By careful adjustment in the usual manner of the bottoms temperature, solvent-fresh feed ratio and reflux ratio, a solvent-rich fraction consisting essentially of ortho xylene and nitrobenzene is taken off as bottoms by line **17**. A raffinate phase made up of meta and para xylene and non-aromatic constituents is taken off overhead through line **16**.

The solvent-rich fraction is then passed by line **17** to fractionating tower **18** equipped with refluxer **19** and reboiler **20**. In this zone **18** the ortho xylene is separated from the nitrobenzene by fractional distillation and taken off overhead by line **21**. The solvent is obtained as a bottoms product through line **12** and may be recycled as desired or removed from the system by line **22**. The bottoms temperature is adjusted to the boiling point of the pure solvent at the existing system pressure. This assures a pure solvent for recycling and complete stripping of the ortho xylene from the solvent.

The ortho xylene recovered may be rerun for additional purity, by passing it through line **21** to fractionating tower **25** equipped with refluxer **26** and reboiler **27**. The rerun ortho xylene is taken overhead by line **28** and passed to storage while a bottoms product, comprising gum and other contaminants, but usually small in amount, is taken off by line **29**. Advantageously, fractionating tower **25** is operated at an overhead temperature of 297° F. and at a bottoms temperature of about 350° F.

The following example is intended to more clearly illustrate my invention and is a run through a system similar to that shown in the accompanying drawing.

One thousand six barrels of a 275°–300° F. naphtha cut from a Houdry cracking unit having the following analysis by barrel:

300°–400° F. naphtha	126
Heavy non-aromatics	247
Light non-aromatics	205
Meta and para xylenes	323
Ortho xylene	105

was preheated to a temperature of 320° F. and passed into a fractionating tower to prepare the xylene concentrate. The bottoms temperature was set at 345° F. which gave an overhead xylene concentrate with a boiling range so that the dry point was 282° F. as determined by a standard A. S. T. M. distillation. Essentially all of the 300°–400° F. naphtha was removed as bottoms while the remaining constituents were taken overhead. The overhead or xylene concentrate was heated to 310° F. and passed in vapor phase into an extractive distillation tower, while about 6 parts by volume of liquid nitrobenzene for each part of the concentrate, or 5052 barrels, heated to a temperature of 350° F., were also passed into the same tower. The bottoms temperature of the extractive distillation zone was set at 445° F., resulting in a bottoms solvent-rich fraction consisting essentially of the nitrobenzene solvent and ortho xylene. The bottoms fraction had the following analysis by barrel:

Heavy non-aromatics	9
Meta and para xylenes	7
Ortho xylene	94
Nitrobenzene	5052

The overhead cut containing principally non-aromatics and the meta and para xylene isomers had the following analysis by barrel:

Heavy non-aromatics	238
Light non-aromatics	205
Meta and para xylenes	316
Ortho xylene	11

The solvent-rich fraction containing the ortho xylene was passed to a solvent stripping tower in which the ortho xylene was stripped from the nitrobenzene. In this tower the bottoms temperature was set at a temperature of 430° F., the boiling point of pure nitrobenzene at the existing system pressure. The ortho xylene was rerun to produce an overhead constituting essentially all the purified ortho xylene and had the following analysis by barrel:

Heavy non-aromatics	9
Meta and para xylenes	7
Ortho xylene	94

The bottoms product from this tower was negligible. Thus 90% of the ortho xylene in the charge stock was recovered in this run.

I claim:

1. The method of separating ortho xylene by extractive distillation from petroleum distillate fractions containing isomeric xylenes which comprises passing the fraction at a temperature in the range approximating 310° to 330° F. to a fractional distillation zone, taking off overhead a lighter fraction whose boiling range includes the larger portion of the xylene isomers while removing as bottoms the constituents boiling higher than ortho xylene, passing the xylene concentrate in vapor phase at a temperature of about 300° to 320° F. to an extractive distillation zone into contact with a liquid high-boiling organic solvent having a boiling point above that of ortho xylene and selective to ortho xylene under the process conditions which has been preheated to a temperature of about 340° to 360° F., taking off as bottoms a high-boil- xylene and solvent and as overhead a raffinate vapor phase containing the meta and para isomers and separating ortho xylene from the solvent-rich fraction.

2. The method according to claim 1 wherein the solvent employed is nitrobenzene.

3. The method of separating ortho xylene by extractive distillation from petroleum distillate fractions containing isomeric xylenes which comprises passing the fraction at a temperature in the range approximating 310° to 330° F. to a fractional distillation zone, taking off overhead a lighter fraction having a dry point of not higher than 282° F. as determined by standard A. S. T. M. distillation and whose boiling range includes the larger

portion of the xylene isomers while removing as bottoms the constituents boiling higher than ortho xylene, passing the xylene concentrate in vapor phase at a temperature of about 300° to 320° F. to an extractive distillation zone into contact with a liquid high-boiling organic solvent having a boiling point above that of ortho xylene and selective to ortho xylene under the process conditions which has been preheated to a temperature of about 340° to 360° F., taking off as bottoms a high-boiling solvent-rich fraction consisting essentially of ortho xylene and solvent and as overhead a raffinate vapor phase containing the meta and para isomers, and separating ortho xylene from the solvent-rich fraction.

4. The method according to claim 3 wherein the solvent employed is nitrobenzene.

5. The method according to claim 1 wherein the solvent employed is selected from the group consisting of nitrobenzene, phenol, dimethyl phthalate, and aniline.

6. The method according to claim 3 wherein the solvent employed is selected from the group consisting of nitrobenzene, phenol, dimethyl phthalate, and aniline.

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