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SEPARATION OF C_9 AROMATIC HYDROCARBONS

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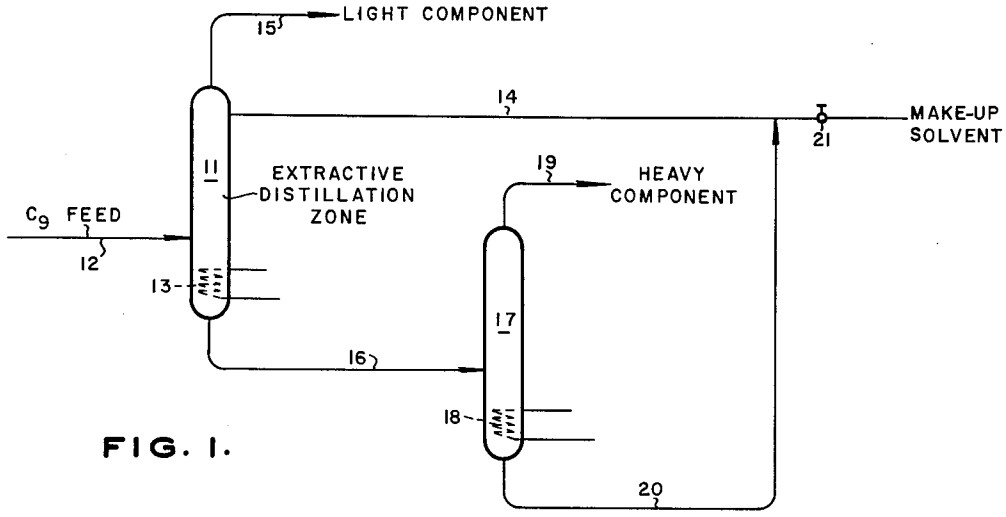

FIG. 1.

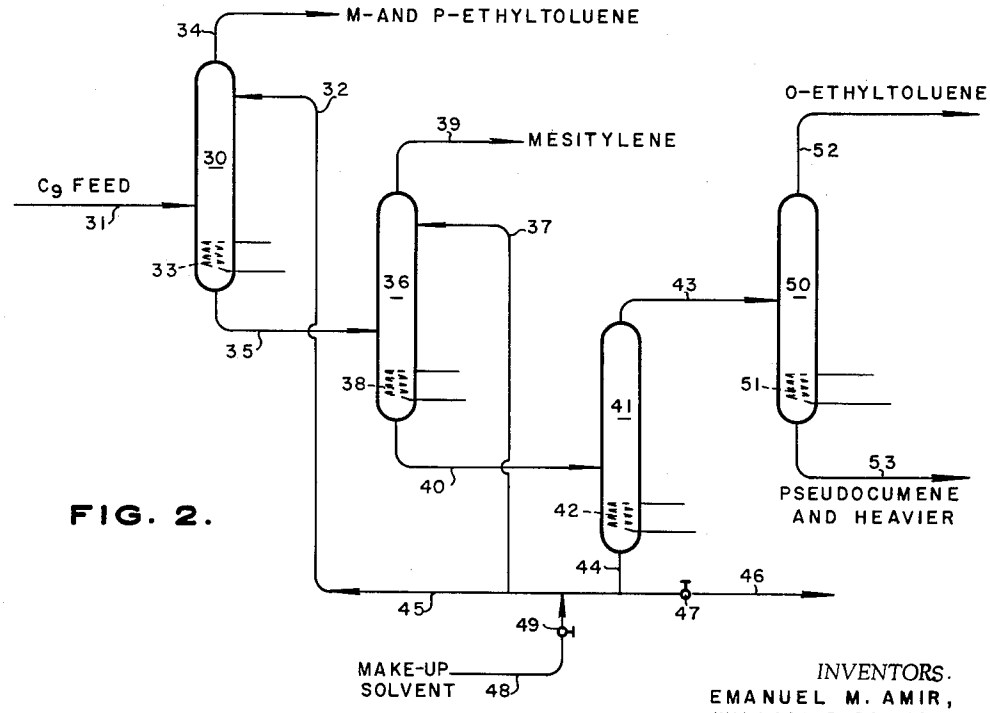

FIG. 2.

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3,220,933

SEPARATION OF C_9 AROMATIC HYDROCARBONS

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6 Claims. (Cl. 202—39.5)

This application is a continuation-in-part of Serial No. 38,067, filed June 22, 1960, entitled, "Separation of C_9 Aromatic Hydrocarbons," for Emanuel M. Amir and William R. Edwards, now abandoned.

The present invention is directed to a method for separating aromatic hydrocarbons. More particularly, the invention is concerned with the extractive distillation of C_9 aromatic hydrocarbons. In its more specific aspects, the invention is concerned with separating C_9 aromatic hydrocarbons under vapor-liquid contacting conditions with the polyalkyl esters of an aromatic polycarboxylic acid having adjacent carboxylic groups.

Some C_9 isomers of aromatic hydrocarbons boil so closely together that it has been extremely difficult, if not impossible, from a practical viewpoint to separate these particular aromatic hydrocarbons. An expensive superfractionation of the isomers can result in separating the isomers into a m- and p-ethyltoluene fraction and a mesitylene, o-ethyltoluene fraction. However, the desired C_9 isomers are mesitylene and o-ethyltoluene as separate fractions. In accordance with the present invention, these C_9 isomers of aromatic hydrocarbons are separated by extractive distillation techniques even though their respective boiling points are very close together as illustrated in Table I below.

Table I

	B.P., °F.
m-Ethyltoluene	322.4
p-Ethyltoluene	323.6
Mesitylene	328.5
o-Ethyltoluene	329.3

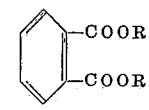
It is noted from Table I that the boiling points of these isomers are within a few degrees Fahrenheit of each other. The boiling point difference between mesitylene and o-ethytoluene is less than one degree Fahrenheit. Using the extractive distillation techniques, which will be more fully described hereinafter, an enrichment of the mesitylene fraction and the o-ethytoluene fraction can be made. Furthermore, according to another aspect of the present invention, separation of the m- and p-ethyltoluene can be made from the mesitylene by an easy and practical extractive distillation. Throughout the description of the present invention, the designation "m- and p-ethyltoluene" is to be considered as a mixture of the isomers recovered as a single, separate fraction.

In accordance with one aspect of the present invention, an extractive distillation solvent has been found which will separate o-ethyltoluene from the lower boiling C_9 aromatic hydrocarbons consisting of a mixture of m- and p-ethyltoluene, mesitylene and o-ethyltoluene. It has been found that if a mixture of the C_9 aromatic hydrocarbons is contacted with a polyalkyl ester of an aromatic polycarboxylic acid having adjacent carboxylic groups under vapor-liquid contacting conditions to form an overhead

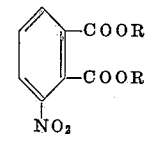
and a bottoms fraction, the bottoms fraction will be enriched in o-ethyltoluene.

In the separation of o-ethyltoluene from the lower boiling C_9 aromatic hydrocarbons, the polyalkyl esters of the aromatic carboxylic acids which may be employed in the practice of this aspect of the present invention are the polyalkyl esters of benzene, toluene, xylene, and naphthalene polycarboxylic acids having adjacent carboxylic groups. As examples, reference may be had to Table II where particularly desirable polyalkyl esters of aromatic polycarboxylic acids are listed which are suitable for the use in the present invention.

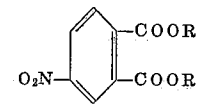
Table II



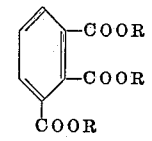
dialkyl-o-phthalate



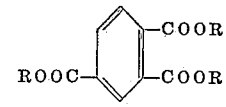
dialkyl-3-nitro-o-phthalate



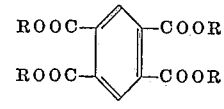
dialkyl-4-nitro-o-phthalate



trialkyl hemimellitate



trialkyl trimellitate



tetraalkyl pyromellitate

where R is a C_1 to C_8 alkyl group and preferably a C_1 to C_3 alkyl group.

In separating o-ethyltoluene in the extractive distillation process, the desirable polyalkyl esters of aromatic acids are dimethyl-o-phthalate, dipropyl-3-nitrophthalate, tripropyl hemimellitate, timethyl trimellitate, and tetra-n-propylpyromellitate and the like. It was further found in separating o-ethyltoluene in the extractive distillation process that those compounds having three adjacent substitutions on the aromatic ring were extractive solvents of a different order of magnitude than those having two adjacent substitutions. Thus, the dialkyl-3-nitro-o-phthalates and trialkyl hemimellitates are superior to dialkyl-4-nitro-o-phthalates and trialkyl trimellitates, respectively. The solvent-to-hydrocarbon ratios used in

the separation of o-ethyltoluene from the lower boiling C_9 aromatic hydrocarbons may suitably range from 1:3 to 10:1 under vapor-liquid extractive distillation conditions.

The present invention is considered to be the finding of suitable solvents to separate the isomers of C_9 aromatic hydrocarbons. The extractive distillation techniques used in the separation of the C_9 isomers are those known to persons skilled in the art of carrying out extractive distillation operations. Thus, as is known in carrying out extractive distillations, the solvent used in an extractive distillation process must have a higher boiling point than the highest boiling product which is to be obtained in a separate fraction. In addition, there must be complete miscibility between the solvent and the materials being separated at the temperatures existing in the extractive distillation tower. It has been found, according to the present invention, that in the extractive distillation of the C_9 isomers the polyalkyl esters of the polycarboxylic acids alter the vapor-pressure characteristics of the C_9 aromatic hydrocarbons so that the relative volatilities are altered. Thus, the relative volatilities are altered to the extent that in the presence of the polyalkyl esters of the polycarboxylic acids having adjacent carboxylic groups the isomers may be separated into enriched fractions by using the techniques used in extractive distillation which are similar to that of a regular distillation. The operating conditions in a regular distillation are such that the temperature is dependent upon variables governed mainly by the pressure and the boiling point of the materials being separated. However, in an extractive distillation, such as in the extractive distillation of C_9 aromatics, the key to the extractive distillation is the specific solvent such as the particular polyalkyl ester of the polycarboxylic acid used since it is the choice of solvent which alters the relative volatilities of the close boiling materials which enables the separation in the first place. The ratio of the particular solvent to hydrocarbon employed, and in a minor extent the engineering factors to be used in a specific separation, has an effect on the conditions; but these effects are known to those skilled in the art. The temperature per se, of course, is not critical to the separation; however, it is obvious that a temperature above the boiling point of the close boiling materials must be used to obtain an overhead fraction and the vapor-liquid conditions. The pressure employed is normally atmospheric, but a superatmospheric or subatmospheric pressure may be used in a particular operation since pressure, as such, is not critical to the separation but merely changes operating conditions.

It was further found in accordance with another aspect of the invention that m- and p-ethyltoluene could be separated from mesitylene by extractive distillation techniques using a C_1 to C_4 dialkyl ester of o-phthalic acid. It is quite unusual that the same material will be an extractive solvent for two separations of an isomer mixture. Thus, the finding that the C_1 to C_4 dialkyl esters of o-phthalic acid can separate m- and p-ethyltoluene from mesitylene as well as separate mesitylene and o-ethyltoluene is quite unexpected. For example, if a tetraalkyl pyromellitate is used, no separation of m- and p-ethyltoluene from mesitylene can be obtained. Since p-ethyltoluene and mesitylene have boiling points which are within almost 5° F. of each other, a commercial regular distillation between these fractions would be extremely difficult. However, according to this aspect of the present invention, the m- and p-ethyltoluene fraction may be separated from mesitylene by extractive distillation techniques very easily and inexpensively. The preferred solvent is dimethyl-o-phthalate, and the solvent-to-hydrocarbon ratios employed may suitably range from 1:3 to 10:1 and preferably 2:1 under the vapor-liquid extractive distillation conditions.

In finding that the C_1 to C_4 dialkyl esters of o-phthalic acid would enable the separation of m- and p-ethyltoluene from mesitylene, as well as enabling the separation of mesitylene and o-ethyltoluene into separate fractions by extractive distillation techniques, another aspect of the present invention is a simplified process whereby these fractions can be separated one from the other by using the same solvent in extractive distillation zones while utilizing a single stripper for separating the solvent from the hydrocarbon, thereby eliminating one solvent stripping tower. According to the simplified process, a mixture of the C_9 isomers consisting of m- and p-ethyltoluene, mesitylene and o-ethyltoluene may be separated in high purities by using two extractive distillations in series without an intermediate solvent stripper using the same solvent followed by a simple distillation to recover the solvent and to separate the heavier C_9 aromatic hydrocarbon as a high purity fraction if this is desired. If isomers heavier than o-ethyltoluene are present, they may be separated by a second simple distillation. The solvents used in this simplified process are the C_1 to C_4 dialkyl esters of o-phthalic acid, the preferred solvent being dimethyl-o-phthalate.

The present invention will be further illustrated by reference to the drawings in which:

FIG. 1 is a schematic flow diagram illustrating a simple extractive distillation unit; and

FIG. 2 is a flow diagram of the simplified process for separating C_9 isomers of aromatic hydrocarbons.

Referring now to the drawings and particularly to FIG. 1, the drawings have reference to a conventional extractive distillation apparatus which may be used according to the present invention to make a separation of o-ethyltoluene from the lower boiling C_9 aromatic isomers. The feed mixture consisting of about 25 mol percent p-ethyltoluene, about 50 mol percent m-ethyltoluene, about 12 mol percent mesitylene, and about 13 mol percent o-ethyltoluene is introduced into extractive zone **11** by feed line **12**. The distillation zone **11** is a distillation tower provided with internal vapor-liquid contacting means such as bell cap trays or other equivalent means. The extractive distillation zone is also provided with means (not shown) for introducing reflux back into the tower and auxiliary condensing and cooling means. Further, the extractive distillation zone **11** is provided with means illustrated by steam coil **13** to control the conditions within the tower. The desired solvent, which may be tetra-n-propylpyromellitate, is introduced by line **14** in countercurrent flow to the distillation zone. An overhead fraction which is enriched in the lower boiling C_9 isomers, namely m- and p-ethyltoluene and mesitylene, is withdrawn by line **15**. The bottoms fraction is recovered by line **16** which is enriched in o-ethyltoluene. The bottoms fraction is discharged by line **16** into a distillation zone **17** which may be a simple distillation column containing internal vapor-liquid contacting means such as bell cap trays and the like. The distillation zone **17** is equipped with the usual means for inducing reflux and provided with auxiliary condensing and cooling means and provided with internal heating means illustrated by steam coil **18**. In the distillation zone **17** a simple distillation of the o-ethyltoluene from the solvent takes place, and the o-ethyltoluene fraction is recovered by line **19** while the solvent, tetra-n-propylpyromellitate, is recovered by line **20**. The solvent is circulated through line **20** into solvent line **14** for reintroduction into the extractive distillation zone **11**. Make-up solvent may be introduced into line **14** by opening valve **21**. The extractive distillation zone **11** may be maintained under a wide range of operating conditions depending on the specific polyalkyl ester of the present invention employed and on the degree of purity desired for the o-ethyltoluene fraction. By way of illustration, however, temperatures at the top of the extractive dis-

tillation zone **11** may be within the range of 325° to 330° F. at atmospheric pressure with a solvent-to-hydrocarbon ratio of 2:1 to obtain a fraction substantially depleted of o-ethyltoluene overhead.

As is known to those skilled in extractive distillations, the extractive distillation process is one wherein the fractions are enriched rather than obtaining ideal separations. Accordingly, while it is not shown in FIG. 1, it will be understood that facilities will be provided for removing any of the solvent carried over in the overhead fraction from the extractive distillation zone **11**. Such facilities may include a stripping zone such as described in the description of distillation zone **17**.

It was further found in accordance with the present invention that the C_1 to C_4 dialkyl esters of o-phthalic acid were unique in separating m- and p-ethyltoluene from mesitylene. Accordingly, a simplified process may be accomplished by utilizing the scheme illustrated in FIG. 2 which illustrates apparatus for separating m- and p-ethyltoluene, mesitylene and o-ethyltoluene as separate fractions. In accordance with this aspect of the present invention, the preferred solvent is dimethyl-o-phthalate although other dialkyl esters having 1 to 4 carbon atoms in the alkyl group may be employed. The C_9 feed may include all the C_9 aromatic isomers, namely m-ethyltoluene, p-ethyltoluene, mesitylene, o-ethyltoluene and pseudocumene, which is introduced into extractive distillation zone **30** by feed line **31**. The extractive distillation zone **30** is suitably a distillation tower provided with the usual internal vapor-liquid contacting means and other auxiliary equipment. The solvent, dimethyl-o-phthalate, is introduced by line **32** near the upper portion of the extractive distillation zone **30**. The conditions within the extractive distillation zone are controlled by means illustrated by steam coil **33**, the conditions within the extractive distillation zone **30** being controlled in a manner known to those skilled in the art. For example, the conditions would be such that the temperatures at the top of this zone **30** would be within the range of about 320° to 325° F. at atmospheric pressure. An overhead fraction enriched in m- and p-ethyltoluene is withdrawn from extractive distillation zone **30** by line **34**. The bottoms fraction is withdrawn from zone **30** by line **35**.

The bottoms fraction which would contain the C_9 isomers heavier than m- and p-ethyltoluene and the solvent is introduced into a second extractive distillation zone **36**. Additional solvent is introduced near the upper portion of the second extractive distillation zone **36** by line **37**. Extractive distillation zone **36** is similar to that of zone **30** and is provided by the usual internal vapor-liquid contacting means as well as means for inducing reflux and auxiliary condensing and cooling means and the like. A suitable means for maintaining the conditions within extractive distillation zone **36** is illustrated by steam coil **38**. The overhead fraction eriched in mesitylene is withdrawn from zone **36** by line **39**. The bottoms fraction is removed by line **40**.

The bottoms fraction from zone **36** is enriched in o-ethyltoluene and the heavier C_9 isomers along with the solvent, dimethyl-o-phthalate. This bottoms fraction is introduced into a stripper column **41** wherein an ordinary distillation is carried out to separate the solvent from the remaining C_9 aromatic isomers. The stripper column **41** may be a tower provided with similar construction as the extractive distillation zones **30** and **36**. Accordingly, besides the other apparatus modifications, the conditions within the stripping tower **41** are maintained by means such as illustrated by steam coil **42**. In the simple distillation carried out in stripping tower **41**, the aromatic hydrocarbons and other materials having a boiling point lower than the solvent are removed overhead by line **43** while the solvent is recovered by line **44**. The solvent may be recycled by line **45** and reintroduced by lines **32** and **37** into extractive distillation zones **30** and **36**, respectively. The solvent may be purged from the system through line **46** by operating valve **47**, and makeup solvent introduced by line **48** which is controlled by valve **49**.

The overhead fraction from the stripper column **41** may be introduced into a second distillation tower **50** to obtain the o-ethyltoluene isomer in high purity. Distillation tower **50** may be provided similarly as stripper tower **41**, and the conditions therein controlled by means illustrated by steam coil **51**. The overhead fraction, namely o-ethyltoluene, is recovered by line **52** while the bottoms fraction is recovered by line **53** which may contain pseudocumene and other heavier components.

To illustrate the present invention, a binary mixture of 1,3,5-trimethylbenzene (mesitylene) and 1-methyl-2-ethylbenzene (o-ethyltoluene) is extractively distilled in the presence of a solvent having the nature described herein with separation of the mixture into its component parts. While these particular aromatic hydrocarbons boil at 328.5° and 329.3° F. in the absence of a solvent at atmospheric pressure, a good separation is possible in utilizing a polyalkyl ester of polycarboxylic acid having adjacent carboxylic groups according to the present invention.

For example, in a 110 plate column the relative volatilities of m- and p-ethyltoluene and mesitylene to o-ethyltoluene were determined. Without a solvent, the relative volatility of m- and p-ethyl-toluene to o-ethyltoluene is 1.06 and for mesitylene to o-ethyltoluene is 1.009; whereas with tetra-n-propylpyromellitate as a solvent, the relative volatility of m- and p-ethyltoluene to o-ethyltoluene is 1.18 and for mesitylene to o-ethyltoluene is 1.12.

In a 50 plate Oldershaw column equipped with means for introducing preheated solvent on the top plate, a mixture of mesitylene and ethyltoluene isomers is charged to the still pot and the hydrocarbons set on total reflux. Hourly samples of overhead and bottoms were taken until the analyses of the samples from hour to hour remained constant. The relative volatilities of the compounds were then determined, and the data indicate that when the solvent is a C_1 to C_4 dialkyl-o-phthalate, not only separation of the mesitylene and the o-ethyltoluene is obtainable, but also separation of m- and p-ethyltoluene and mesitylene is obtainable. For example, the relative volatility of p-ethyltoluene to mesitylene without the solvent is 1.058 and is increased to 1.125 when dimethyl-o-phthalate is present as the solvent in about 50 mol percent concentration.

The present invention is quite important and useful and allows the obtaining of numerous advantages in that separation of the particular C_9 aromatic hydrocarbons in purified condition is important. These particular C_9 aromatic hydrocarbons heretofore have not been separated practically, whereas now it is possible to obtain a good separation under vapor-liquid separating conditions. The particular compounds in purified condition are important and useful as chemicals and in the manufacture of other chemicals.

The nature and objects of the present invention having been completely described and illustrated, what we wish to claim as new and useful and secure by Letters Patent is:

1. A method for separating C_9 aromatic hydrocarbons which comprises extractively distilling a mixture of hydrocarbons containing m- and p-ethyltoluene, mesitylene and o-ethyltoluene by contacting with a C_1 to C_4 dialkyl ester of o-phthalic acid in a first extractive distillation zone whereby an overhead fraction enriched in m- and p-ethyltoluene and a bottoms fraction enriched in mesitylene and o-ethyltoluene are formed, contacting said bottoms fraction with additional amounts of said ester in a second extractive distillation zone under extractive distillation conditions whereby a second overhead fraction enriched in mesitylene and a bottoms fraction enriched in o-ethyltoluene are formed, and recovering said o-ethyltoluene from said second bottoms fraction by simple distillation.

2. A method according to claim 1 wherein said ester is dimethyl-o-phthalate.

3. A method for separating o-ethyltoluene from a mixture containing the lower boiling C_9 aromatic hydrocarbons which comprises contacting said mixture in an extraction zone under extractive distillation conditions with a polyalkyl ester of an aromatic polycarboxylic acid having adjacent carboxylic groups and having 1 to 8 carbon atoms in the alkyl groups to form an overhead fraction and a bottoms fraction, and recovering o-ethyltoluene from said bottoms fraction.

4. A method in accordance with claim 3 wherein said ester is tetra-n-propylpyromellitate.

5. A method for separating m- and p-ethyltoluene from a mixture containing the higher boiling C_9 aromatic hydrocarbons which comprises contacting said mixture under extractive distillation conditions with a C_1 to C_4 dialkyl ester of o-phthalic acid whereby an overhead fraction enriched in m- and p-ethyltoluene is formed.

6. A method in accordance with claim 5 wherein said ester is dimethyl-o-phthalate.

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NORMAN YUDKOFF, *Primary Examiner.*