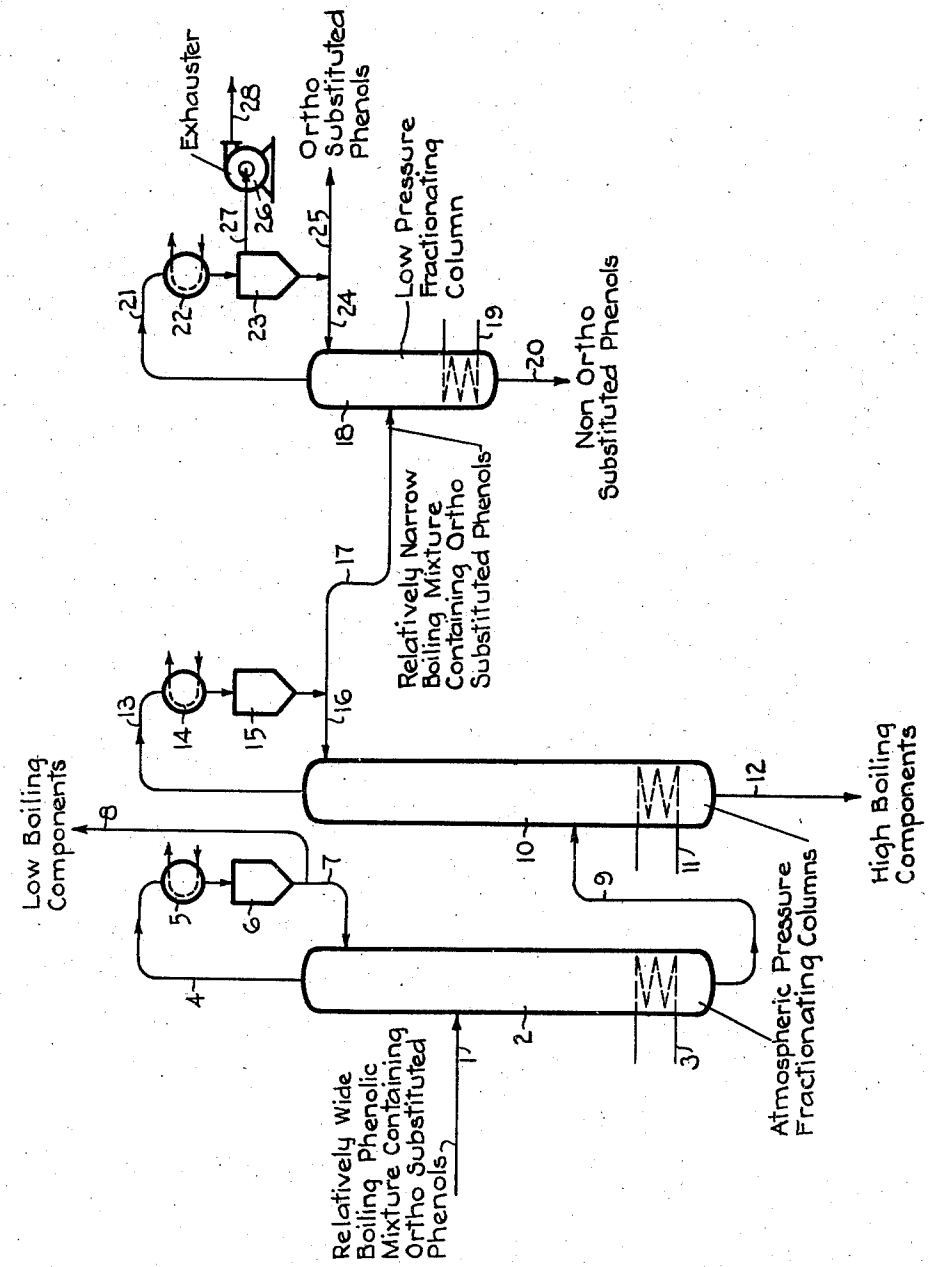
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TWO-STAGE DISTILLATION OF ORTHO-SUBSTITUTED RING COMPOUNDS

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TWO-STAGE DISTILLATION OF ORTHO-SUBSTITUTED RING COMPOUNDS

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The present invention relates to a process for separating polar organic compounds. More particularly, it relates to a process wherein mixtures of poly-substituted conjugated ring compounds with themselves or other organic compounds are separated by distillation under controlled pressures.

It is the object of our invention to separate certain organic compounds by distillation, whose separation by this method heretofore has been considered impossible due to their similar vapor pressures under normal circumstances.

Our invention comprises distilling mixtures of associated polar compounds differing in extent to which the polar radicals are flanked by non-polar radicals such as mixtures of poly-substituted conjugated ring compounds of the type described below at a given pressure to produce a fraction having narrow boiling range and then further distilling the narrow fraction under substantially different pressures to produce at least two fractions rich in different components of the mixture.

Our process is applicable to the separation of other organic compounds from compounds of the following type: derivatives of benzene, pyridine, naphthalene, quinoline and isoquinoline, which contain not more than one polar grouping selected from $—NH_2$, $=N—$, —COOH and —OH, and which further contain in ortho position to the polar group at least one non-polar hydrocarbon radical such as methyl, ethyl, propyl, isopropyl, primary, secondary and tertiary butyl, amyl, hexyl, cyclohexyl, methyl cyclohexyl, phenyl, tolyl, xylyl, phenyl methyl, phenyl ethyl, naphthyl, tetryl, etc.

We have discovered that when mixtures of one or several of these ortho conjugated ring compounds with other organic compounds (the latter including compounds which differ from the former only in that the hydrocarbon radical is in a position other than ortho to the polar group) are distilled under a given pressure to produce a narrow boiling fraction, e. g. of less than 10° C. boiling range and containing at least one ortho and some other compound, it is necessary only to redistill the fraction so produced under substantially different pressure to get a clean separation between the ortho-substituted compounds and the other compounds present in this fraction. Our process is based upon our discovery that certain ortho-substituted derivatives of benzene, naphthalene, pyridine, quinoline and isoquinoline, tend to have significantly lower heats of vaporization than the corresponding meta or

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para derivatives or other derivatives of approximately the same molecular weight. Thus, due to the lower heat of vaporization, ortho compounds have a lower rate of change of vapor pressure with temperature than non-ortho compounds, and it follows that there will be a higher rate of change of boiling point for ortho compounds with pressure than with non-ortho compounds. This abnormal decrease in vapor pressure exhibited by mono-ortho compounds under reduced pressure is even more pronounced when two hydrocarbon radicals are ortho to the polar group, and thus separations can be obtained between di-ortho and mono-ortho compounds using the same principle. For example, by our process we can readily separate 2-ethyl, 5-methyl phenol (mono-ortho) from 2,4,6-trimethyl phenol (di-ortho) both of which boil under normal conditions at about 220° C. by distilling at substantially atmospheric pressures a mixture of acid oils containing them to produce a fraction having a boiling range from below to above 220° C., for example, about 218–222° C., and subsequently redistilling this fraction at a reduced pressure of about 5 mm. Under these conditions the 2,4,6-trimethyl phenol is concentrated in the top product while the 2-ethyl, 5-methyl phenol is concentrated in the bottom product. In the same manner meta cresol can be separated from 2,6-dimethyl phenol, etc.

Examples of other separations according to our process follow: 2,4,6-trimethyl phenol may be separated from mixtures with other phenols; 2,6-dimethyl phenol can be separated from cresols; 3,5- and 3,4-dimethyl phenol can be separated from their mixtures; 3-methyl, 5-ethyl phenol from mixtures of phenols; beta-gamma picoline can be separated from 2,6-lutidine; meta- and para-ethyl phenols from their mixtures, etc.

The separation may be carried out either batchwise or continuously. In the former process an initial material generally having a wide boiling range, e. g. more than 10° C. and containing ortho-substituted compounds and other compounds, is distilled to produce a fraction having a narrow boiling range, usually not greater than about 10° C., and subsequently this narrow fraction is redistilled at a substantially different pressure to separate the ortho compounds from the non-ortho compounds.

In the continuous process the initial material is continuously fed to a fractionating column, from which is withdrawn continuously a fraction of narrow boiling point containing ortho and non-ortho compounds, which fraction is fed to a second column operated under a different pres-

sure from which is continuously withdrawn the ortho compounds concentrated in one fraction while the non-ortho compounds are concentrated in the other. The continuous process is advantageous when it is desired to process large quantities of material.

Still another way to carry out our process may be termed batch-continuous. In this process a broad fraction is charged to a batch still from which is obtained an overhead product of narrow but continuously changing boiling range. This stream is introduced, as rapidly as it is obtained, into a continuous column operating at a different pressure. The top and bottom products from the continuous column are predominantly di-ortho and non-ortho substituted compounds, respectively, if the pressure is diminished for the second distillation, and non-ortho and di-ortho substituted compounds, respectively, if the pressure is increased for the second distillation. The mono-ortho compounds may be obtained in either the top or bottom product by adjusting the reflux and reboiling ratios in the continuous column.

Although we may carry out our initial distillation at any suitable pressure below or above atmospheric and our subsequent distillation at another pressure either above or below atmospheric, it is generally most convenient to make the initial distillation at pressures at or near atmospheric, and carry out the subsequent distillation at reduced pressure, although sometimes we may prefer to carry out the initial distillation at reduced pressure and the subsequent distillation at increased pressures.

The maximum pressure which we apply depends upon the thermal stability of the mixture being separated. In general, we prefer to use pressures below those associated with temperatures at which decomposition occurs. The minimum pressure is limited solely by the apparatus at hand, but in general we prefer to carry out the low pressure distillation at pressures less than 10 mm. Since the ease of separation depends upon the difference between the pressure used in the different distillations, it is therefore generally desirable that this difference be made as large as is convenient and economical, always considering the pressure at the decomposition temperature as the upper limit.

Whether the ortho or non-ortho compound accumulates in the top or the bottom fraction depends upon the pressure relationship. In general, the lower the pressure, the more enhanced is the relative volatility according to the following series:

Di-ortho compounds>mono-ortho compounds>other compounds. Thus, when the initial distillation is made at higher pressures and the subsequent distillation at lower pressure, the di-ortho or ortho compounds appear in the top fraction while the other compounds appear in the bottom product.

This relationship is reversed when the initial distillation is made at lower pressure and the subsequent distillation at higher pressure. In this case the non-ortho compounds are concentrated in the top fraction while the ortho or di-ortho compounds are concentrated in the bottom fraction.

The present invention may be better understood from a consideration of the figure, which is a flow diagram representing one embodiment thereof, wherein a relatively wide boiling phenolic mixture containing ortho-substituted phenols and non-ortho-substituted phenols is continuously fed via line 1 to fractionating column 2 equipped with reboiler 3. The heat input to column 2 is so regulated that a portion of the lower boiling components of the mixture passes overhead via line 4, condenses in condenser 5 and collects in accumulator 6, whence a portion is returned as reflux to column 2 via line 7, while the remaining low boiling components are withdrawn via line 8, passing to storage not shown. The bottom product containing a major portion of the ortho-substituted phenols along with other non-ortho-substituted phenols and heavier boiling constituents, passes via line 9 to column 10 equipped with reboiler 11. The heat input to column 10 is so regulated that the bulk of ortho-substituted phenols passes overhead while the bulk of the remaining higher boiling components is withdrawn via line 12, passing to storage not shown. The relatively narrow boiling ortho-substituted phenols, along with other quantities of non-ortho-substituted phenols, pass overhead via line 13, condense in condenser 14 and collect in accumulator 15, whence a portion is returned to column 10 as reflux via line 16. The remainder is treated as subsequently described. Both column 2 and column 10 are operated at substantially atmospheric pressure and thus exemplify higher pressure distillation for the primary purpose of producing a relatively narrow fraction, which latter passes via line 17 to low pressure fractionation column 18 equipped with reboiler 19. In this distillation, the non-ortho-substituent phenols are withdrawn as bottom product via line 20, while the ortho-substituted phenols pass overhead via line 21 to condenser 22 and collect in accumulator 23, whence a portion is returned as reflux via line 24 to column 18. The remaining ortho-substituted phenols are withdrawn via line 25, passing to storage not shown. Column 18 is maintained under vacuum by exhauster 26 connected to accumulator 23 via line 27. Exhaust gases pass from exhauster 26 via line 28 and may be disposed of as desired.

For purposes of simplicity, by passes, heat exchanges, auxiliary pumps and control means, the proper placement of which is evident to those skilled in the art, have been omitted.

Example I

A fraction of petroleum alkyl phenols containing about 30% o-cresol, 12% 2,6-dimethyl phenol, 27% meta- and para-cresol and 31% higher boiling xylenols was divided into two portions. The first portion was fractionally distilled at atmospheric pressure to give three fractions, the second of which amounted to about 40% of the charge and contained about 25% 2,6-dimethyl phenol and about 50% of meta- and para-cresol together with small amounts of o-cresol and the higher boiling xylenols. Refractionation of this cut at atmospheric pressure resulted only in some further removal of the o-cresol and higher xylenols. Upon fractionation at 10 mm. pressure, however, the first fraction, amounting to about 35% of the charge, contained 60% 2,6-dimethyl phenol together with 30% o-cresol and small amounts of the other phenols. This concentration of 2,6-dimethyl phenol was sufficiently high so that a large part of the substance crystallized out of solution and could readily be isolated.

The second portion of the original mixture was first fractionated at 10 mm. pressure to give a

fraction amounting to 40% of the charge and containing about 65% o-cresol and 25–30% 2,6-dimethyl phenol together with smaller amounts of meta- and para-cresol. Refractionation of this cut at the same pressure resulted in a considerable separation of the o-cresol and 2,6-dimethyl phenol, a middle fraction consisting of 25% of the low boiling fraction obtained in the first stage and containing 35–40% of 2,6-dimethyl phenol being obtainable. However, refractionation at atmospheric pressure gave a cut, consisting of the last 35% of the charge, which contains about 55% 2,6-dimethyl phenol.

Example II

A fraction of petroleum alkyl phenols boiling from about 210° C. to about 230° C. and consisting mostly of methyl ethyl phenols containing one ortho substituent and various polymethyl phenols, including mesitol (2,4,6-trimethyl phenol, boiling point 220° C.) and symmetrical xylenol (3,5-dimethyl phenol, boiling point 219.5° C.), was fractionally distilled through a column equivalent to about ten theoretical plates and operating at about 20 mm. pressure and a reflux ratio of 10:1, the distillate being recovered in ten approximately equal fractions. One of the 10% fractions obtained in the earlier part of the distillation had a boiling point of 216° C. while another fraction obtained in a later stage had a boiling point of 224° C. Each of these was refractionated again into 10% portions at atmospheric pressure in a column equivalent to about 12–15 theoretical plates and operated at 10:1 reflux ratio. While this treatment was not sufficient to result in the separation of any pure phenols, the highest boiling fractions of the 216° C. cut contained sufficient mesitol so that its concentration exceeded its solubility in liquid alkyl phenols (about 25% at 20° C.) and it crystallized out of solution in part. On the other hand the lowest boiling fractions obtained from the 224° C. fraction contained symmetrical xylenol in sufficient concentration (its solubility in liquid alkyl phenols is about 35% at 20° C.) so that it also crystallized out of solution in part.

Thus, in the vacuum fractionation mesitol, a di-ortho substituted phenol, was segregated with material normally boiling at 216° C. while symmetrical xylenol, a non-ortho substituted phenol, was segregated with material normally boiling at 224° C.; upon refractionation at atmospheric pressure the mesitol was separated from the 216° C. material as a higher boiling substance while the symmetrical xylenol was separated from the 224° C. fraction as a lower boiling substance.

We claim as our invention:

1. In a process for separating an ortho substituted conjugated ring compound from other substituted conjugated ring compounds in an associated mixture thereof having a relatively wide boiling range, said ortho compound and at least some of said other compounds having substantially identical boiling points at a given pressure and having a nucleus selected from the group consisting of benzene, pyridine, naphthalene, and quinoline and containing a single polar group selected from the class consisting of —NH_2, —COOH, —OH, and =N—, the ortho positions to said polar group in said ortho compound being occupied by at least one non-polar hydrocarbon radical, while said other compounds are differently substituted, the steps comprising: fractionally distilling said mixture under said given pressure to produce a fraction having a relatively narrow boiling range at said given pressure, said fraction containing at least a portion of said ortho and said some of said other compounds of substantially identical boiling points at said given pressure; and further fractionally distilling said fraction under a pressure substantially increased above said given pressure to produce an overhead and a bottom product, one of which is rich in said ortho-substituted compound and the other is rich in said some of said other compounds.

2. In a process for separating an ortho phenol from other phenols in a mixture thereof having a relatively wide boiling range, said ortho phenol and at least some of said other phenols having substantially identical boiling points at a given pressure, the ortho position to the hydroxyl group in said ortho phenol being occupied by at least one non-polar hydrocarbon radical, while the ortho positions in said other phenols are differently substituted, the steps comprising: fractionally distilling said mixture under said given pressure to produce a fraction having a relatively narrow boiling range, said fraction containing at least a portion of said ortho and said some of said other phenols having substantially identical boiling points at said given pressure; and further fractionally distilling said fraction under a pressure substantially increased above said given pressure to produce an overhead and a bottom product, one of which is rich in said ortho phenol and the other of which is rich in said some of said other phenols.

3. In a process for separating an ortho phenol from other phenols in a mixture thereof having a relatively wide boiling range, said ortho phenol and at least some of said other phenols having substantially identical boiling points under atmospheric pressure, the ortho positions to the hydroxy group in said ortho phenol being occupied by at least one non-polar hydrocarbon radical, while the ortho positions in said other phenols are differently substituted, the steps comprising: fractionally distilling said mixture under substantially atmospheric pressure to produce a fraction having a relatively narrow boiling range under atmospheric pressure, said fraction containing at least a portion of said ortho phenols and said some of said other phenols; and further fractionally distilling said fraction under a pressure substantially above atmospheric pressure to produce a bottom product rich in said ortho phenol and an overhead fraction rich in said some of said other phenols.

4. In a process for separating 2,4,6-trimethyl phenol from a mixture of phenols having a relatively wide boiling range, at least a portion of the other phenols in said mixture having a boiling point substantially identical with that of 2,4,6-trimethyl phenol at a given pressure, the steps comprising: fractionally distilling said mixture under said given pressure to produce a fraction having a relatively narrow boiling range, said fraction containing at least a portion of said 2,4,6-trimethyl phenol and of said portion of the other phenols having the substantially identical boiling temperature at said given pressure; and further fractionally distilling said fraction under a pressure substantially different from said given pressure to produce an overhead and a bottom product, one of which is rich in 2,4,6-trimethyl phenol, and the other of which is rich in the phenols of said portion of said phenols.

5. In a process for separating 2,6-dimethyl phenol from other alkyl phenols in a mixture thereof having a relatively wide boiling range, at

least a portion of said alkyl phenols having a boiling point substantially identical with that of 2,6-dimethyl phenol under a given pressure, the steps comprising: fractionally distilling said mixture under said given pressure to produce a fraction having a relatively narrow boiling range, said fraction containing at least a portion of said 2,6-dimethyl phenol and of said other alkyl phenols having the substantially identical boiling point at said given pressure; and further fractionally distilling said fraction under a pressure substantially different from said given pressure to produce an overhead and a bottom product, one of which is rich in 2,6-dimethyl phenol and the other of which is rich in other alkyl phenols.

6. In a process for separating an ortho substituted conjugated ring compound from other substituted conjugated ring compounds in an associated mixture thereof having a relatively wide boiling range, said ortho compound and at least some of said other compounds having substantially identical boiling points at a given subatmospheric pressure and having a nucleus selected from the group consisting of benzene, pyridine, naphthalene, and quinoline and containing a single polar group selected from the class consisting of —NH_2, —COOH, —OH, and =N—, the ortho positions to said polar group in said ortho compound being occupied by at least one non-polar hydrocarbon radical, while said other compounds are differently substituted, the steps comprising: fractionally distilling said mixture under said given subatmospheric pressure to produce a fraction having a relatively narrow boiling range at said subatmospheric pressure, said fraction containing at least a portion of said ortho and said some of said other compounds of substantially identical boiling points at said given subatmospheric pressure; and further fractionally distilling said fraction under substantially atmospheric pressure to produce an overhead and a bottom product, one of which is rich in said ortho-substituted compound and the other is rich in said some of said other compounds.

7. In a process for separating an ortho substituted conjugated ring compound from other substituted conjugated ring compounds in an associated mixture thereof having a relatively wide boiling range, said compounds having a nucleus selected from the group consisting of benzene, pyridine, naphthalene and quinoline and containing a single polar group selected from the class consisting of —NH_2, —COOH, —OH, and =N—, said ortho compound containing at least one hydrocarbon radical in ortho position to said polar

group while said other compounds are differently substituted, said ortho compound and one of said other compounds having substantially identical boiling points at some given pressure, the steps comprising: batch distilling said mixture under said given pressure to produce an overhead stream having a relatively narrow but continuously changing boiling range, which, over a period of time, includes the boiling temperature at said given pressure of said ortho compound, thereby producing a fraction containing at least a portion of said ortho compound and of said other compound of substantially identical boiling point at said given pressure; and continuously feeding said fraction in the form of said stream to a continuous distillation column wherein it is refractionated at a pressure substantially increased above said given pressure to produce an overhead and a bottom product, one of which is rich in said ortho compound and the other is rich in said one of said other compounds.

8. In a process for separating an ortho substituted conjugated ring compound from other substituted conjugated ring compounds in an associated mixture thereof having a relatively wide boiling range, said compounds having a nucleus selected from the group consisting of benzene, pyridine, naphthalene and quinoline and containing a single polar group selected from the class consisting of —NH_2, —COOH, —OH, and =N—, said ortho compound containing at least one hydrocarbon radical in ortho position to said polar group while said other compounds are differently substituted, said ortho compound and one of said other compounds having substantially identical boiling points at some given pressure, the steps comprising: batch distilling said mixture under said given pressure to produce an overhead stream having a relatively narrow but continuously changing boiling range, which, over a period of time, includes the boiling temperature at said given pressure of said ortho compound, thereby producing a fraction containing at least a portion of said ortho compound and of said other compound of substantially identical boiling point at said given pressure; and continuously feeding said fraction in the form of said stream to a continuous distillation column wherein it is refractionated at a pressure substantially different from said given pressure to produce an overhead and a bottom product, one of which is rich in said ortho compound and the other is rich in said one of said other compounds.

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