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METHOD AND DEVICE FOR PURIFICATION OF P-DICHLOROBENZENE

BACKGROUND OF THE INVENTION

The present invention relates to a method and a device for separating p-dichlorobenzene from a mixture composed of at least chlorobenzene and dichlorobenzene isomers by a combination of distillation and crystallization. More specifically, a virtually pure p-dichlorobenzene is economically prepared from said mixture using a divided wall column followed by at least one melt crystallization.

Pure dichlorobenzenes are particularly useful as important intermediates for the production of disinfectant, pesticide and deodorant. Dichlorobenzenes are customarily prepared by chlorination of benzene or chlorobenzene. The composition of the isomeric mixture of dichlorobenzenes depends largely on the catalyst used and the reaction conditions of chlorination, which mixtures can contain, for example, 45 to 80% by weight of p-dichlorobenzene, 0.1 to 5% by weight of m-dichlorobenzene, 15 to 35% by weight of o-dichlorobenzene, 5 to 15% by weight of benzene, 5 to 20% by weight of chlorobenzene and 2 to 8% by weight of trichlorobenzene.

However, during the preparation of nitrochlorobenzene which is typically synthesized by nitration of chlorobenzene, chlorination of benzene to obtain chlorobenzene instead of dichlorobenzene is mostly desired. Therefore, the product from chlorination of benzene if excluding the residual benzene, in ordinary cases, consists essentially of from 80 to 90% by weight of chlorobenzene, from 6 to 10% by weight of p-dichlorobenzene, from 2 to 5% by weight of o-dichlorobenzene, from 0.05 to 1% by weight of m-dichlorobenzene and from 1 to 4% by weight of trichlorobenzene.

Various processes have been proposed for separation of an isomeric mixture of dichlorobenzenes into individual dichlorobenzene isomers. In a first step, a starting mixture essentially composed of benzene, chlorobenzene, dichlorobenzene and more highly chlorinated benzene such as trichlorobenzene is fed to a distillation column to fractionate into a lights enriched stream comprising the lower-boiling components including benzene and chlorobenzene and into a dichlorobenzene enriched stream comprising a major portion of dichlorobenzene isomers and a minor portion of higher-boiling components such as trichlorobenzene and tars. In a second step, a p-dichlorobenzene enriched stream is obtained as the overhead product in a second distillation column, and most of the o-dichlorobenzene and the higher-boiling components remain as the bottoms product. The said stream enriched in p-dichlorobenzene is fed to a subsequent purification system such as e.g. crystallization to obtain virtually pure p-dichlorobenzene. Further steps involve the separation of the o-dichlorobenzene from the higher-boiling

components by a simple distillation and separation of the m-dichlorobenzene from the p-dichlorobenzene by the methods known in the art, see e.g. U.S. Pat. No. 3,170,961; U.S. Pat. No. 2,958,708; JP 53044528; and JP 11158093.

While such an above-mentioned two-column distillation method allows to obtain a stream enriched in p-dichlorobenzene, one disadvantage of the method is its elevated energy requirement. In conventional distillation columns, the feed stream is conventionally fractionated into two product streams, i.e. an overhead product and a bottoms product. Any further separations which are required may, for example be performed by subjecting either the bottoms product stream or the overhead product stream to another distillation column similar to the first. The operating costs of such a two-column distillation method are correspondingly high. In the case of two-column distillation method for the purpose of concentrating p-dichlorobenzene from the said mixture, each of the two columns has to be supplied with the thermal energy required to perform the evaporation and separation of the said mixture based on volatility differences between components.

On the other hand, the investment costs for the two-column distillation system are high. This is not only due to the fact that investment has to be made for two distillation columns, but expenses are also necessary for the equipment associated therewith, for example condensers, drums, reboilers and pumps.

In addition, it has been recognized that the extent of forming tars is increasing with the progress of the exposure of dichlorobenzene to elevated temperatures at the presence of in-leakage air over multi-distillation stages. The formation of tars results in a loss of dichlorobenzene product.

SUMMARY OF THE INVENTION

The object underlying the present invention is to provide a method and a device for separating p-dichlorobenzene from a mixture composed of at least chlorobenzene and dichlorobenzene isomers by a divided wall column followed by at least one melt crystallization. The chlorobenzene is separated off from the said mixture as the overhead product and the p-dichlorobenzene is concentrated as the side-draw product of the said divided wall column, which side-draw is further purified in the melt crystallization to obtain virtually pure p-dichlorobenzene product. The intention of the method by using a divided wall column is to save equipment and energy costs and lessen the formation of tars in compared with the above-mentioned two-column distillation method.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a diagram in accordance with the present invention utilizing a divided wall column for carrying out the separation of mixtures composed of at least chlorobenzene and dichlorobenzene isomers.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

With regard to the conventional two-column distillation sequence, the lights stream enriched in chlorobenzene and benzene is drawn off from the overhead of the first distillation column and then the bottoms product of the first distillation column is fed to the second distillation column and distilled to obtain the p-dichlorobenzene enriched stream as the overhead product of the second distillation column. In order to minimize the amount of tars formed in distillation stages, it is therefore proposed to use only one distillation stage instead of two to reduce the dichlorobenzenes' exposure to the elevated temperatures and in-leakage air. Thus, the residence time of the dichlorobenzenes is greatly reduced and the yield of dichlorobenzenes is increased.

In accordance with the present invention, the two conventional distillation columns are replaced by a single distillation column, i.e. a divided wall column. The expenditure on plant and equipment and the space required for the installation of the distillation column are significantly decreased.

Moreover it is observed that utilizing of the divided wall column in replace of the two conventional distillation columns has advantages that not only the energy consumption is reduced in comparison to the methods known in the prior art, but that the p-dichlorobenzene enriched stream with at least the same purity is obtained, meaning the separation efficiency of the proposed method is comparable with the above-mentioned two-column distillation method.

In accordance with the usual definition of the term "divided wall column", the divided wall column preferably comprises:

a divided wall provided vertically inside the column shell, defining a divided wall section between an upper undivided section as a rectifying zone for concentrating lower-boiling components of having a lower-boiling point than m-dichlorobenzene and a lower undivided section as a stripping zone for concentrating o-dichlorobenzene and higher-boiling components of having a higher boiling point than p-dichlorobenzene;

a divided wall section located between the rectifying zone and the stripping zone having a vertical dividing wall dividing the inner space of the divided wall section into a pre-fractionation zone at one side of the divided wall and a main fractionation zone at the other side of the divided wall;

an inlet for the feed of the mixture containing at least chlorobenzene and dichlorobenzene isomers in the pre-fractionation zone, a side-draw outlet for the concentrated p-dichlorobenzene

product stream in the main fractionation zone, an overhead product stream drawn off from the rectification zone, and a bottoms product stream removed from the stripping zone.

The distillation in the divided wall column is preferably carried out under reduced pressure. The pressure and temperature at the top of the divided wall column are preferably in the ranges of 150 to 700 mbar and of 75 to 120° C, and more preferably of 350 to 500 mbar and of 90 to 100° C. The pressure and temperature at the bottom of the divided wall column are preferably in the ranges of 210 to 760 mbar and of 132 to 180° C, more preferably of 410 to 560 mbar and of 150 to 165° C.

The present invention is not particularly limited with regard to the type of mass transfer elements installed in the divided wall column. Good results are obtained by using suitable mass transfer elements selected from the group consisting of random packings, structured packings and any combinations thereof. It is however, structured packings are particularly suitable as mass transfer elements with the advantages of reducing the liquid hold-up in the column and the overall column pressure drop. It is preferred that the structured packings have a specific surface area in the range of 125 to 750 m²/m³, and more preferably of in the range of 250 to 500 m²/m³.

The length of the divided wall in the divided wall section depends on the process conditions and on the mass transfer elements used. In the column of the present invention, the length of the divided wall is approximately 1/2 of the total length of the mass transfer elements portion installed in the divided wall column. It is preferred that the total mass transfer elements portion of the divided wall column has a length between 10,000 and 55,000 mm, and more preferably between 15,000 and 45,000 mm. Under the same process conditions to achieve a p-dichlorobenzene concentrated stream with a similar purity of p-dichlorobenzene, the optimum length of the mass transfer elements portion depends particularly on the type of mass transfer elements selected, for example when a structured packing having a specific surface area of 500 m²/m³ is used, the total length of mass transfer elements portion of the divided wall column is approximately in the range of 27,000 to 34,000 mm.

In the column of the present invention, the divided wall section is partitioned by the divided wall into a pre-fractionation zone and a main fractionation zone, which each has a different volume, i.e. a different cross-sectional area for each zone. Different processes may be optimized by appropriate selection of the partial cross-sections of the two zones.

Vapor flow from the stripping zone is divided in the pre-fractionation zone and the main fractionation zone in accordance with the cross-sectional area of each zone. The partial cross-sectional areas are set in such a manner that the pressures at the inlet and outlet regions of the pre-fractionation zone are respectively identical with those at the inlet and outlet regions of the main fractionation zone, which means the pressure drop of the packings within the pre-fractionation zone is the same as that for the packings within the main fractionation zone.

In accordance with the present invention, the divided wall column is equipped with at least one reboiler and at least one condenser. The reboiler can be of any of the types commonly found in the chemical industry, including, but not limited to, falling-film evaporators, forced circulation evaporators, thermosiphon evaporators and etc. However, due to its particular reduced liquid

hold-up, a falling film evaporator is preferred to minimize the residence time of dichlorobenzenes in the system and therefore reduce any unfavorable side-reactions. The condenser can be of any of the types commonly used in the chemical industry including co-current and counter-current condensers.

With the divided wall column of the present invention, the p-dichlorobenzene enriched stream as the side-draw product having a purity of at least 90% by weight is obtained. Owing to the very small boiling point differences between the individual dichlorobenzene isomers (o-dichlorobenzene: 180° C; m-dichlorobenzene: 173° C; p-dichlorobenzene: 174.1° C), justifiable efforts are used in the divided wall column to obtain a concentrated p-dichlorobenzene stream with a purity of in the range of 90-95% by weight to save energy consumption.

In certain specific cases, such as for the use of pure p-dichlorobenzene product in the production of polyphenylene sulfide, a purity of p-dichlorobenzene as high as 99.95% by weight is required. It is suggested to subject the concentrated p-dichlorobenzene stream withdrawn from the side-draw outlet of the divided wall column subsequently to a further purification step, which comprises at least one melt crystallization. In order to obtain a particular good purification, the melt crystallization is preferably performed by a suspension melt crystallization, a static crystallization, a falling film crystallization or a combination thereof.

FIG. 1 schematically shows the distillation stage of a divided wall column according to an embodiment of the present invention, which comprises a column shell 2, a condenser 4, a condensate drum 7, a circulation pump 12, a falling film reboiler 14, a substantially fluid tight divided wall 17 extending vertically through the middle part of the column shell 2. The inner space of the column shell 2 is divided by the divided wall 17 into four distinct zones, i.e. a pre-fractionation zone 18 at one side of the divided wall 17, a rectifying zone 19 above the divided wall 17, a main fractionation zone 20 at the other side of the divided wall 17, and a stripping zone 21 below the divided wall 17, in which column the pre-fractionation zone 18 and the main fractionation zone 20 form the divided wall section. The vapors generated at the bottom of the divided wall column flow upwards through the stripping zone 21 and divide into the pre-fractionation zone 18 and the main fractionation zone 20, counter-currently contacting the liquids flowing downwards from rectifying zone 19, effective for a mass transfer. A multi-component feed stream 1 is then separated by the mass transfer within the four operating zones into three product streams, i.e. an overhead product stream 9, a bottoms product stream 16 and a side-draw product stream 10.

A mixture composed of at least chlorobenzene and dichlorobenzene isomers is continuously fed through stream 1 into the pre-fractionation zone 18. The lower-boiling components of having a lower boiling point than m-dichlorobenzene concentrate during the distillation in the rectifying zone 19, and are drawn off through stream 3, which is subsequently condensed in the condenser 4. The condensates flow to the condensate drum 7 through stream 6 and then divide into an overhead product stream 9 distilled out from the top and into a reflux stream 8, which is fed back to the rectifying zone 19. The uncondensed vapors are removed through stream 5. The o-dichlorobenzene and the higher-boiling components of having a higher boiling point than o-dichlorobenzene, are concentrated in the stripping zone 21 and drawn off as a bottom stream 11.

The bottom stream 11 is subsequently divided into a bottoms product stream 16 withdrawn from the bottom of the column, and a recirculation stream 13 reboiled in the falling film evaporator 14 and then fed back to the stripping zone 21 through stream 15. A side-draw product of the concentrated p-dichlorobenzene is withdrawn through stream 10 from the main fractionation zone 20 and fed to melt crystallization system 22 for further purification. The virtually pure p-dichlorobenzene is obtained as stream 24 from the melt crystallization system 22. The purge from the melt crystallization system 22 is discharged through stream 25 and fed to a subsequent m-dichlorobenzene purification system.

In accordance with the present invention, the use of a divided-wall column to obtain the concentrated p-dichlorobenzene stream makes it possible to save one distillation column in comparison with the above-mentioned two-column distillation system. It has advantages that not only the energy consumption and equipment expenditure are reduced, but also the residence time of dichlorobenzenes is less, resulting in less tars formed due to its decreased exposure to the elevated temperatures and in-leakage air.

Subsequently, the present invention is illustrated in more details below with reference to the drawing and the examples.

EXAMPLES

Example 1

A distillation stage of a divided wall column according to an embodiment of the invention as shown in FIG. 1 was performed. Structured packings with a specific surface area of $495 \text{ m}^2/\text{m}^3$ were used as mass exchange elements in the divided wall column. 44% by weight of the liquid was introduced to the pre-fractionating zone 18 and 56 % by weight of the liquid to the main fractionating zone 20. The rectifying zone 19 had 9 theoretical stages and the stripping zone 21 had 64 theoretical stages. The pre-fractionation zone 18 had 45 theoretical stages above and 15 theoretical stages below the feeding point for the feed stream 1 into the pre-fractionation zone. The main fractionation zone 20 had 9 theoretical stages above and 51 theoretical stages below the withdrawal point of the side-draw product stream 10 in the main fractionating zone. The overhead pressure was 360 mbar. The reflux ratio at the withdrawal point of the overhead product stream was 14.4:1. The pressure and temperature at the bottom of the divided wall column were 420 mbar and 153°C , respectively.

8022 kg/h of a feed stream 1 composed of 52.95% by weight of p-dichlorobenzene, 4.25% by weight of m-dichlorobenzene, 17.68% by weight of o-dichlorobenzene, 4.64% by weight of benzene, 15.42% by weight of chlorobenzene, 3.89% by weight of trichlorobenzene, 0.04% by weight of water, 1.12% by weight of tars and 0.01% by weight of hydrogen chloride was fed to the divided wall column, at the 56th stage from the top in the pre-fractionation zone 18. Three product streams were withdrawn from the divided wall column: 1607 kg/h of an overhead product stream 9 composed of 0.06% by weight of p-dichlorobenzene, 0.01% by weight of m-dichlorobenzene, 22.89% by weight of benzene, 76.84% by weight of chlorobenzene, 0.19% by weight of water and 0.01% by weight of hydrogen chloride; 1708 kg/h of a bottoms product stream 16 composed of 0.07% by weight of p-dichlorobenzene, 76.42% by weight of o-dichlorobenzene, 18.25% by weight of trichlorobenzene and 5.26% by weight of tars; and 4700 kg/h of a side-draw product stream 10 composed of 90.33% by weight of p-dichlorobenzene, 7.25% by weight of m-dichlorobenzene, 2.42% by weight of o-dichlorobenzene, which stream was withdrawn at the 19th stage from the top in the main fractionating zone 20 and fed to the melt crystallization system 22 to obtain the virtually pure p-dichlorobenzene product stream 24 having a purity of over 99.98% by weight. The purge stream 25 containing about 35% by weight of p-dichlorobenzene was discharged from the melt crystallization system 22 and fed to a subsequent m-dichlorobenzene purification system. About 8 kg/h of uncondensed vapor stream 5 mainly composed of benzene and chlorobenzene was fed to the second condenser (not shown in FIG.1).

The energy consumption was as low as 2.9 MW for the said divided wall column. A comparative example was tested by a method of using the conventional two-column distillation system to obtain the concentrated p-dichlorobenzene with the similar purity as that for the said divided wall column. The total energy consumption for the two conventional distillation columns was about 3.4 MW.

Example 2

A distillation stage of a divided wall column according to an embodiment of the invention as shown in FIG. 1 was performed. Structured packings with a specific surface area of $404 \text{ m}^2/\text{m}^3$ were used as mass exchange elements in the divided wall column. 48% by weight of the liquid was introduced to the pre-fractionating zone 18 and 52 % by weight of the liquid to the main fractionating zone 20. The rectifying zone 19 had 9 theoretical stages and the stripping zone 21 had 64 theoretical stages. The pre-fractionation zone 18 had 45 theoretical stages above and 15 theoretical stages below the feeding point for the feed stream 1 into the pre-fractionation zone. The main fractionation zone 20 had 9 theoretical stages above and 51 theoretical stages below the withdrawal point of the side-draw product stream 10 in the main fractionating zone. The overhead pressure was 510 mbar. The reflux ratio at the withdrawal point of the overhead product stream was 14.5:1. The pressure and temperature at the bottom of the divided wall column were 570 mbar and 163°C , respectively.

8041 kg/h of a feed stream 1 composed of 48.19% by weight of p-dichlorobenzene, 3.37% by weight of m-dichlorobenzene, 23.20% by weight of o-dichlorobenzene, 4.63% by weight of benzene, 15.39% by weight of chlorobenzene, 3.88% by weight of trichlorobenzene, 0.04% by weight of water, 1.30% by weight of tars and 0.01% by weight of hydrogen chloride was fed to the divided wall column, at the 56th stage from the top in the pre-fractionation zone 18. Three product streams were withdrawn from the divided wall column: 1609 kg/h of an overhead product stream 9 composed of 0.03% by weight of p-dichlorobenzene, 22.98% by weight of benzene, 76.77% by weight of chlorobenzene, 0.19% by weight of water and 0.02% by weight of hydrogen chloride; 2128 kg/h of a bottoms product stream 16 composed of 0.07% by weight of p-dichlorobenzene, 80.36% by weight of o-dichlorobenzene, 14.65% by weight of trichlorobenzene and 4.92% by weight of tars; and 4300 kg/h of a side-draw product stream 10 composed of 90.07% by weight of p-dichlorobenzene, 6.31% by weight of m-dichlorobenzene, 3.62% by weight of o-dichlorobenzene, which stream was withdrawn at the 19th stage from the top in the main fractionating zone 20 and fed to the melt crystallization system 22 to obtain the virtually pure p-dichlorobenzene product stream 24 having a purity of over 99.98% by weight. The purge stream 25 containing about 35% by weight of p-dichlorobenzene was discharged from the melt crystallization system 22 and fed to a subsequent m-dichlorobenzene purification system. About 4 kg/h of uncondensed vapor stream 5 mainly composed of benzene and chlorobenzene was fed to the second condenser (not shown in FIG.1).

The energy consumption was as low as 3.0 MW for the said divided wall column. A comparative example was tested by a method of using the conventional two-column distillation system to

obtain the concentrated p-dichlorobenzene with the similar purity as that for the said divided wall column. The total energy consumption for the two conventional distillation columns was about 3.5 MW.

Example 3

A distillation stage of a divided wall column according to an embodiment of the invention as shown in FIG. 1 was performed. Structured packings with a specific surface area of $404 \text{ m}^2/\text{m}^3$ were used as mass exchange elements in the divided wall column. 28% by weight of the liquid was introduced to the pre-fractionating zone 18 and 72 % by weight of the liquid to the main fractionating zone 20. The rectifying zone 19 had 10 theoretical stages and the stripping zone 21 had 42 theoretical stages. The pre-fractionation zone 18 had 42 theoretical stages above and 14 theoretical stages below the feeding point for the feed stream 1 into the pre-fractionation zone. The main fractionation zone 20 had 14 theoretical stages above and 42 theoretical stages below the withdrawal point of the side-draw product stream 10 in the main fractionating zone. The overhead pressure was 360 mbar. The reflux ratio at the withdrawal point of the overhead product stream was 1.5:1. The pressure and temperature at the bottom of the divided wall column were 410 mbar and 157°C , respectively.

8674 kg/h of a feed stream 1 composed of 8.88% by weight of p-dichlorobenzene, 0.54% by weight of m-dichlorobenzene, 3.53% by weight of o-dichlorobenzene, 83.28 % by weight of chlorobenzene and 3.77% by weight of trichlorobenzene was fed to the divided wall column, at the 54th stage from the top in the pre-fractionation zone 18. Three product streams were withdrawn from the divided wall column: 7221 kg/h of an overhead product stream 9 composed of 0.01% by weight of p-dichlorobenzene and 99.99 % by weight of chlorobenzene; 620 kg/h of a bottoms product stream 16 composed of 0.03% by weight of p-dichlorobenzene, 47.22% by weight of o-dichlorobenzene and 52.75% by weight of trichlorobenzene; and 830 kg/h of a side-draw product stream 10 composed of 92.64% by weight of p-dichlorobenzene, 5.67% by weight of m- dichlorobenzene, 1.68% by weight of o-dichlorobenzene, which stream was withdrawn at the 25th stage from the top in the main fractionating zone 20 and fed to the melt crystallization system 22 to obtain the virtually pure p-dichlorobenzene product stream 24 having a purity of over 99.98% by weight. The purge stream 25 containing about 35% by weight of p-dichlorobenzene was discharged from the melt crystallization system 22 and fed to a subsequent m-dichlorobenzene purification system. About 3 kg/h of uncondensed vapor stream 5 mainly composed of benzene and chlorobenzene was fed to the second condenser (not shown in FIG.1).

The energy consumption was as low as 1.8 MW for the said divided wall column. A comparative example was tested by a method of using the conventional two-column distillation system to obtain the concentrated p-dichlorobenzene with the similar purity as that for the said divided wall column. The total energy consumption for the two conventional distillation columns was about 2.8 MW.

The invention claimed is:

1. A continuous method for the concentration of p-dichlorobenzene from a mixture composed of at least chlorobenzene and dichlorobenzene isomers by a distillation stage, in which method the distillation stage is performed using a divided wall column, wherein a side-draw product having a purity of at least 90% by weight of p-dichlorobenzene is obtained.

2. The method of claim 1, wherein the divided wall column comprises:

a divided wall provided vertically inside the column shell, defining a divided wall section between an upper undivided section as a rectifying zone for concentrating lower-boiling components of having a lower-boiling point than m-dichlorobenzene and a lower undivided section as a stripping zone for concentrating o-dichlorobenzene and higher-boiling components of having a higher boiling point than p-dichlorobenzene,

a divided wall section located between the rectifying zone and the stripping zone having a vertical dividing wall dividing the inner space of the divided wall section into a pre-fractionation zone at one side of the divided wall and a main fractionation zone at the other side of the divided wall, and

an inlet for the feed of the mixture containing at least chlorobenzene and dichlorobenzene isomers in the pre-fractionation zone, a side-draw outlet for the concentrated p-dichlorobenzene product stream in the main fractionation zone, an overhead product stream drawn off from the rectification zone, and a bottoms product stream removed from the stripping zone.

3. The method of claim 1, wherein the said distillation stage does not include any other distillation column in addition to the divided wall column.

4. The method of claim 1, wherein a pressure and a temperature at the top of the divided wall column are in the ranges of 150 to 700 mbar and 75 to 120° C, respectively.

5. The method of claim 1, wherein a pressure and a temperature at the bottom of the divided wall column are in the ranges of 210 to 760 mbar and of 132 to 180° C, respectively.

6. The method of claim 1, wherein the concentrated p-dichlorobenzene product steam withdrawn from the side-draw outlet of the divided wall column is subjected subsequently to a further purification step, which comprises at least one melt crystallization.

7. The method of claim 6, wherein the melt crystallization is preferably performed by a suspension melt crystallization, a static crystallization, a falling film crystallization or a combination thereof.

8. The method of claim 1, wherein the mass transfer elements are selected from the group consisting of random packings, structured packings and any combinations thereof.