

A process for suspension crystallisation

The present invention relates to a process for the separation of crystallisable organic compounds from a liquid mixture of compounds by suspension crystallisation.

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In view of their synthesis process, organic compounds are generally obtained in the form of a mixture of compounds which contains, in addition to the desired organic compounds, substantial or preponderant proportions of other compounds such as solvents, starting compounds, by-products and/or isomers of the organic compound.

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In many cases, the desired organic compound can be separated from the mixture by crystallisation. A characteristic of many crystallisable organic compounds is the low solid phase solubility of foreign substances, so crystallisation is often the means of choice for the separation.

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Conventional processes of the prior art are, inter alia, solution crystallisation or static crystallisation from the mixture of compounds itself, in which the compound to be isolated is precipitated on fixed cooled surfaces, then separated from the mother liquor and melted again.

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Both crystallisation processes require the use of large amounts of energy since the mass to be cooled and reheated for crystallisation exceeds considerably the mass of the reactants actually to be separated.

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Generally speaking, crystallisation processes in suspension can be carried out using less energy and with better efficiency than static crystallisation processes if so-called wash columns according to US-A 3 777 892 and US-A 3 872 009 are used for the separation and as the melting crystal phase.

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In principle, such suspension crystallisation processes, particularly for aqueous systems, such as e.g. the removal of water from foodstuff liquids, are known from US-A 4 004 886, US-A 4 316 368, US-A 4 430 104 and US-A 4 459 144.

Moreover, suspension crystallisation processes for purifying chemicals in several stages have already been proposed according to US-A 4 787 985.

5 A common feature of all said processes is that they have a crystallisation vessel (for each stage in the case of multi-stage crystallisation) in which crystals are frozen out by the removal of heat, a recrystallisation vessel in which larger crystals grow at the expense of smaller ones, and a filter in which the crystals are separated from the mother liquor. At least the filter of the final stage takes the form of a wash column.

10 The function of the wash column is to completely separate the pure crystal phase obtained from the mother liquor. In this case, the crystal slurry is fed into the column from below, compacted by a stamper which takes the form of a sieve plate, the mother liquor flowing downwards through the sieve plate, and a compacted crystal block forming above the sieve plate. Above the crystal block, crystals freed from the
15 mother liquor are scraped off the crystal block by means of a scraper, melted and expelled. In this case, the liquid pressure of the melted crystals above the crystal block is maintained at a level such that a small quantity of the liquid is pressed through the crystal block for washing out adhering mother liquor. The purity of the separated crystal phase depends to a large extent on the temperature difference
20 between the melting temperature of the crystals and the temperature of the crystal slurry fed to the wash column. Consequently, such wash columns may be operated advantageously only up to temperature differences of 5 to max. 10 °C between crystal suspension fed in and melted pure phase.

25 Mixtures of organic compounds, on the other hand, are obtained in mixing ratios which, in so far as they are at all accessible to separation by crystallisation, cause considerably larger temperature differences between crystal suspension and melting temperature of the pure compound to be separated, on account of the liquidus curve.

30 Although it is possible to increase the concentration in the liquid phase of the crystal suspension in the final stage before the wash column by multi-stage crystallisation

processes to the extent that the liquidus temperature of the mother liquor reached corresponds approximately to the liquidus temperature of the starting mixture, this gives rise to a considerable outlay in terms of equipment, thereby offsetting the advantages of suspension crystallisation over static processes.

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Organic compounds generally exhibit a very low solid phase solubility in one another, so inherently single-stage suspension crystallisation processes are suitable for the separation.

10 The object of the present invention is to provide a process in which the required number of crystallisation stages in suspension crystallisation can be reduced.

The present invention provides a process for the separation of organic compounds by single-stage or multi-stage suspension crystallisation, wherein each stage
15 comprises a crystalliser, optionally a recrystallisation vessel and a filter for separating liquid phase from the crystal slurry, wherein the liquid phase separated in the filter is returned to the relevant crystallisation stage, the crystal slurry is transferred to the succeeding stage or from the final stage into the wash column for complete separation of the mother liquor, and liquid phase depleted in the compound to be
20 crystallised is expelled from the first stage, the starting compound mixture being fed behind the final crystallisation stage, which is characterised in that the mother liquor of the crystal slurry from the final crystallisation stage is exchanged gradually, at least in part, for the starting compound mixture.

25 The exchange may take place stepwise in at least two stages.

In preference, the exchange takes place gradually and continuously, i.e. constantly in infinitesimal steps. This may take place in a flow channel with walls which take the form of sieves on both sides, wherein starting compound mixture flows in from
30 one side through one sieve and mother liquor is drawn off on the other side through the other sieve.

According to a particularly preferred embodiment, the flow channel has an annular flow channel which is formed by concentric sieve pipes. A preferred exchange device comprises three concentric pipes, the two inner pipes taking the form of sieves. The crystal slurry emerging from the final crystallisation stage flows through the central pipe, the starting compound mixture being fed into the outer pipe and mother liquor being drawn off from the innermost pipe.

In a particularly advantageous manner, provision is made for the feed of starting compound mixture and the withdrawal of mother liquor to be interchangeable by reversing valves. In this way, the direction of flow through the sieve apertures may be reversed and any blockages effectively prevented.

The exchange takes place preferably in such a way that the mother liquor conveying the crystal slurry is undersaturated with the crystallised compound i.e. a part of the crystal phase is redissolved in the mother liquor. Undersaturation is preferably chosen such that 2 to 5% of the crystal phase are redissolved. This prevents crystal caking occurring in the exchange device.

The mother liquor drawn off by the exchange is returned to the crystalliser in single-stage crystallisation processes. In multi-stage crystallisation processes, the exchange mother liquor is returned preferably to the previous crystallisation stage. In particular preference, it is used for the corresponding exchange of mother liquor in the preceding stage.

The process according to the invention is carried out preferably with only one crystallisation stage.

In particular preference, the process according to the invention is used for the separation of isomers of isocyanates, particularly for obtaining pure isomers of 2,4-toluylene diisocyanate and 4,4'-diphenylmethane diisocyanate from the isomer mixtures with 2,6-toluylene diisocyanate and 2,4'-diphenylmethane diisocyanate.

Toluylene diisocyanate is obtained as an isomer mixture containing 80% 2,4-TDI and 20% 2,6-TDI. The liquidus temperature of the mixture is 13.5 °C. The melting point of the pure 2,4-TDI is 22 °C. In view of the differing reaction behaviour when TDI is used in the polyaddition reaction for the production of polyurethanes, varying use is made of the pure isomer 2,4-TDI on the one hand and an isomer mixture of 65 to 69% 2,4-TDI and 35 to 31% 2,6-TDI on the other hand. The liquidus temperature of the isomer mixture with 65% 2,6-TDI is about 6.3 °C. The crystal slurry of the single-stage suspension crystallisation process consequently has a temperature of 6.3 °C. For an effective separation of the pure crystal phase in a wash column, a crystal suspension at a temperature of at least 12 °C would have to be fed to the wash column allowing for the melting temperature of the pure 2,4-TDI phase. According to the liquidus curve, this corresponds to a content of 77% 2,4-TDI in the mother liquor. Allowing for the additional requirement of a pumpable mixture which preferably has a crystal content of not more than 30%, such a concentration can be obtained by adding the starting isomer mixture to the crystal slurry only by accepting uneconomically high redissolution of at least 50% of the crystal phase, or by multi-stage crystallisation.

As a result of the continuous-gradual exchange of mother liquor by the starting isomer mixture according to the invention, on the other hand, it is readily possible, by accepting only a favourable redissolution rate in terms of the process of 2.5 to 5%, to provide the necessary starting mother liquor concentration and temperature for the wash column. If the product desired is a phase depleted in 2,4-TDI with 67% 2,4-TDI, it is sufficient to exchange only part of the starting isomer mixture with the mother liquor and to mix the remainder of the starting isomer mixture with the crystal slurry. If a product with 69% 2,4-TDI is desired, it is sufficient to carry out the exchange of starting isomer mixture and mother liquor in two stages, wherein a part of the starting isomer mixture and the crystal slurry are mixed continuously and mother liquor is then expelled with a filter before the remaining starting isomer mixture is mixed with the crystal slurry in a further vessel. Excess mother liquor may

be expelled from the final exchange stage by means of a separate filter or directly in the wash column.

The invention is explained below in more detail on the basis of the Figures attached.

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Fig. 1 shows a single-stage crystallisation process according to the invention with two-stage exchange.

Fig. 2 shows a single-stage crystallisation process with gradual exchange.

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Fig. 3 shows a two-stage crystallisation process according to the invention.

Fig. 4 shows a two-stage crystallisation with mother liquor exchange in both stages.

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Fig. 5 shows a preferred exchange device according to the invention.

Fig. 1 shows diagrammatically a crystalliser 1 in which, via the cooling jacket 2, heat is removed from the crystal suspension situated therein. The cooling jacket 2 is cooled by means of the cooling unit 3. The crystal suspension is fed via line 4 to an exchange vessel 5 which acts as the first exchange stage for the mother liquor. A part of the starting compound mixture, preferably about 40-60%, is fed to the exchange vessel 5 via line 6a. Exchange mother liquor is returned via line 8 to crystalliser 1 by means of filter 7. A crystal suspension is drawn off from the exchange vessel 5 via line 9, the mother liquor of which suspension has a higher concentration of the compound to be crystallised than the crystal suspension leaving crystallisation vessel 1 via line 4. The mass flow through line 8 is controlled such that a readily pumpable crystal suspension is present in line 9, i.e. the crystal suspension in line 9 has a solids content of 25-35%. The starting substance mixture fed via line 6a is fed at a temperature such that, after being mixed with the crystal suspension fed via line 4, the mixture is slightly undersaturated. The remaining part of the starting compound

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mixture is fed via line 6b into the mixing vessel 10 into which the crystal suspension from the exchange vessel 5 is also fed via line 9. The mixing vessel 10 acts as the second stage for the gradual mother liquor exchange. A filter may be provided at the outlet of mixing vessel 10 by means of which excess mother liquor is separated and returned to crystalliser 1. In the embodiment shown, the function of the filter is taken over by wash column 20. The crystal suspension is fed into said wash column via line 11 and the hollow axis of the reciprocating pump 12 above the sieve plate 13 of wash column 20. Reciprocating pump 12 moves sieve plate 13 periodically upwards, the mother liquor flowing downwards through sieve plate 13. In view of the movement of the sieve plate, a compacted crystal block is formed above sieve plate 13. Above the crystal block, pure crystals are scraped off the crystal block by means of the scraper 14, melted at least partially in the heat exchanger 15 and expelled as pure crystallisable compound via valve 16 in the direction of arrow 17. Part of the melted pure crystallisable compound is returned to the top of wash column 20 by means of the pump 18 as a transport medium for the scraped crystals. By means of an appropriate adjustment of valve 16, the pressure maintained at the top of the wash column is such that part of the pure crystallisable compound is pressed as wash liquor against the compacted crystal block.

The mother liquor separated in the wash column is returned to crystalliser 1 via line 19. Mother liquor depleted in crystallisable compound is expelled from the crystalliser via filter 22 and line 21. The device according to Fig. 1 is suitable for separating 2,4-TDI from a starting isomer mixture containing 80% 2,4-TDI whilst obtaining a depleted isomer mixture still containing 69% 2,4-TDI, as described above. In Fig. 2, the exchange vessel 5 of Fig. 1 is replaced by the exchange column 5 for continuous gradual mother liquor exchange. The exchange column 5 is described in more detail below. The device shown according to Fig. 2 is suitable for obtaining 2,4-TDI from a starting isomer mixture containing 80% 2,4-TDI whilst simultaneously obtaining a depleted isomer mixture with 65% 2,4-TDI (removal via line 21). The entire starting isomer mixture is preferably fed into the exchange column via line 6a.

In the two-stage crystallisation process according to Fig. 3, the exchanged mother liquor flowing out of the exchange column 5 is returned via line 8 to the first stage (I) and mixed in mixing vessel 40 with the crystal suspension leaving the crystalliser 31 of the first stage. In filter 47, excess mother liquor (with regard to pumpability) is separated from the mother liquor leaving the mixing vessel 40 via line 41 and returned to crystalliser 31. The crystal suspension is fed to crystalliser 1 of the first stage. The mixture of compounds depleted in the crystallisable compound is expelled via line 51 from crystalliser 31 of the second stage.

The process according to Fig. 3 is particularly suitable for the separation of isomers of diphenylmethane diisocyanate (MDI). In view of the production process, MDI is obtained as a starting isomer mixture with 90% 4,4'-MDI and 10% 2,4'-MDI, wherein minor quantities of 2,2'-MDI may still be present. The liquidus temperature of the starting isomer mixture is about 36 °C. The pure 4,4'-MDI has a melting point of 40 °C. The isomer mixture to be expelled, depleted in 4,4'-MDI, still contains 55 wt.% of 4,4'-MDI with a liquidus temperature of 18 °C. Accordingly, the crystal suspension leaving crystalliser 31 has a temperature of 18 °C. The second crystallisation stage 1 is operated at a temperature of 27°C. This corresponds to a mother liquor containing 72% 4,4'-MDI. The mother liquor is fed into the exchange column 5 via line 4. The starting isomer mixture with 90% 4,4'-MDI having a temperature of 40 °C is fed into the exchange column 5 via line 6. An exchanged mother liquor with 76% 4,4'-MDI flows out via line 8. The crystal suspension leaving exchange column 5 via line 9 has a mother liquor with 80% 4,4'-MDI corresponding to a liquidus temperature of 32 °C. For every 100 parts of starting isomer mixture fed via line 6, 77.8 parts of pure 4,4'-MDI are expelled via line 17 and 22.2 parts of an isomer mixture still containing 55% 4,4'-MDI are expelled via line 51. A solids content of 30% in lines 4, 9 and 11 is obtained by controlling the mass flows in line 8 and line 49. The solids content of the crystal suspension leaving crystalliser 31 of the first stage is only 23%. In the embodiment of the invention according to Fig. 4, an exchange column 5 and 35 is provided in the two stages I and II respectively. As a result, the mother liquor concentration in the mixing vessel 40

and line 41 may be increased such that the solids content in lines 34 and 41 is also increased, i.e. the mass flows during the isomer separation of MDI are reduced. Moreover, with a device according to Fig. 4, it is possible to separate mixtures of compounds in two stages wherein an even greater depletion of the mixture to be expelled via line 51 takes place than that described for the isomer separation of MDI. The dashed lines 6b, 8b and 49 denote only minor mass flows which serve to control the process or adapt the way the process is conducted to specific problems to be solved.

Fig. 5 shows a mother liquor exchange pipe 5 which can be used according to the invention, which pipe comprises three concentric pipes 61, 62 and 63, wherein the inner pipes 61 and 62 take the form of sieve pipes. The crystal suspension coming from the crystalliser flows through the annular channel 64 between the two sieve pipes 61 and 62. The starting isomer mixture is fed into the outer annular channel 65 in the direction of arrow 6, which mixture enters annular channel 64 through the sieve pipe 62. At the same time, mother liquor is forced into the inner sieve pipe 61 and expelled via line 8. The direction of flow through sieve pipes 61 and 62 can be reversed by means of the simultaneously reversible valves 66 and 67 so that a blockage of the sieve apertures can be counteracted by periodical reversal, or a blockage of the sieve apertures can be counteracted by means of reversals initiated by a pressure change detected in lines 6 or 8. The change in the mother liquor concentration in the annular channel 64 brought about in each case by the reversal is evened out in the downstream mixing vessel 10 in each case.

**Patent claims**

1. A process for the separation of organic compounds by single-stage or multi-stage suspension crystallisation, wherein each stage comprises a crystalliser,
5 optionally a recrystallisation vessel and a filter for separating liquid phase from the crystal slurry, wherein the liquid phase separated in the filter is returned to the relevant crystallisation stage, the crystal slurry is transferred to the succeeding stage and from the final stage into the wash column for complete separation of the mother liquor, and liquid depleted in the isomer
10 to be crystallised is expelled from the stage, the starting compound mixture being fed behind the final crystallisation stage, characterised in that the mother liquor of the crystal slurry from the final crystallisation stage is exchanged gradually, at least in part, for the starting compound mixture.
- 15 2. A process according to claim 1, characterised in that the exchange takes place in a flow channel with walls which take the form of sieves on both sides, wherein starting compound mixture flows in from the side through the sieve and mother liquor is drawn off on the other side through the sieve.
- 20 3. A process according to claim 2, characterised in that the flow channel has an annular cross-section which is formed by concentric sieve pipes.
4. A process according to claim 2 or 3, characterised in that, in order to avoid blockages of the sieves, reversing valves are provided for exchanging the
25 sides of feed of starting compound mixture and withdrawal of mother liquor.
5. A process according to claim 1, characterised in that the starting compound mixture used is an isomer mixture of organic compounds.
- 30 6. A process according to one of claims 1 to 5, characterised in that the starting isomer mixture used is a mixture of 80% 2,4-toluylene diisocyanate and 20%

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2,6-toluylene diisocyanate, and only one crystallisation stage is used to obtain pure 2,4-toluylene diisocyanate.

- 5 7. A process according to one of claims 1 to 5, characterised in that the starting isomer mixture used is a mixture of 90% 4,4'-diphenylmethane diisocyanate and 10% 2,4'-diphenylmethane diisocyanate, and pure 4,4'-MDI and a mixture containing 55% 4,4'-MDI is expelled, two crystallisation stages being used.

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