

Process for working up a stream comprising laurolactam for the recovery of all components of value present therein by combination of crystallization with downstream distillation

The present invention relates to a process for purifying laurolactam by means of integrated connection of distillation and crystallization. The crystallization can be performed here as a solution or melt crystallization. The stream to be worked up comprises, in addition to the laurolactam target component, at least one component other than laurolactam and having a lower or higher boiling point. The laurolactam removed in the crystallization already has a purity of >99%.

Laurolactam is typically purified by means of a multistage distillation in which secondary components with higher and lower boiling points are removed from laurolactam. For distillation, owing to the high boiling point of laurolactam, reduced pressure has to be applied. The thermal stress on the mixture in each evaporation step leads to partial thermal decomposition of the material of value. This leads to a reduction in the overall yield.

It is an object of the process according to the invention to develop a workup process as described in the claims, which meets the following boundary conditions:

- early removal of laurolactam in the workup process
- reduction in the thermal product stress by reducing the number of thermal separation steps necessary
- reduction in the thermal stress via lowering the process temperature needed
- recovery of all materials of value present in the stream, such as reactants and/or solvents
- removal and discharge of the components other than target product / reactants and solvents

The object was achieved by a process according to the claims, which are considered to form part of the description.

A process is claimed for working up a stream comprising lauro lactam for the recovery of all components present, characterized in that the stream which arrives from the synthesis and comprises lauro lactam and further components is first cooled such that, in a selective manner, by solution cooling crystallization, only the solubility limit of lauro lactam is exceeded and lauro lactam is selectively crystallized out and removed from the mother liquor in a downstream solid-liquid separation, and the mother liquor is subsequently sent to a multistage distillation sequence.

The crystallization can be performed as a solution crystallization, as a solution cooling crystallization or flash cooling crystallization.

For a stream consisting of lauro lactam and components different therefrom, the following workup sequence according to the claims has been found. By way of example, the process is described by the appended flow diagram (Figure 1) with the following stream composition:

LB – low boilers

LM –solvent

MB1 – medium boiler fraction 1

CDON – cyclododecanone as a reactant of the synthesis

MB2 – medium boiler fraction 2

HB – high boilers

LL- lauro lactam

The flow diagram (Figure 1) is merely illustrative and is not intended to restrict the process. The stream 1 which arrives from a synthesis sequence and consists of lauro lactam, solvent, CDON and components different therefrom is fed together with the mother liquor recycle stream 15 consisting of lauro lactam, solvent, CDON

and components different therefrom, and the distillate 22 of an evaporation apparatus K, comprising predominantly lauro lactam, to a flash cooling crystallization A with a temperature of at least 75°C, preferably at least 80°C and more preferably at least 85°C. The reduced vacuum in the flash cooling crystallization A establishes a corresponding boiling equilibrium. The amount of heat Q resulting from the temperature difference between inlet stream and boiling temperature leads to evaporation of the volatile constituents and to a lowering of the temperature according to the boiling equilibrium. As a result of the superimposition of the effects, the solubility limit of lauro lactam is exceeded and lauro lactam crystallizes out. At the crystallizer outlet, a temperature of not more than 70 °C, preferably lower, preferably a temperature of approx. 65°C, is established. The suspension 2 is conducted out of the flash cooling crystallization A to the solid-liquid separation B. The suspension is separated therein into mother liquor 5 and solid comprising predominantly lauro lactam 4. The moist solid 4 is freed of the adhering secondary components with condensed distillate 3 comprising predominantly solvent. The mother liquor obtained and the laden wash liquor are combined to give stream 5. A substream 15 is introduced back into the flash cooling crystallization A to increase the yield and adjust the solids content.

The washed moist solid 4 is fed to a melting unit C. The melting unit C is operated at a temperature above the melting point of lauro lactam. The molten stream 6 is sent to a flash stage D. At the top of the flash stage, a vapour stream 24 is removed and supplied to a distillative workup sequence which is not described any further at this point. The bottom stream 8 consisting of on-spec lauro lactam is removed and leaves the process.

Streams 16 and 24 are sent to distillative removal of solvent and secondary components, consisting of sequences I, J and K.

Detailed description

The crystallization A is performed as a flash cooling crystallization. This means that the amount of heat Q present in the feed stream 1+15+22 is used for partial evaporation of the solvent 3. In order that the solvent evaporates, according to the vapour pressure of the feed stream, a corresponding pressure and hence a corresponding internal crystallizer temperature are established. As a result of the controlled evaporation of the solvent 3 and the cooling of the solution, the solubility limit of lauro lactam is exceeded and it crystallizes out. An efficient connection allows the oversaturation needed for crystallization to be adjusted to a moderate level. The evaporative cooling allows direct heat exchange to be dispensed with completely in the crystallizer, such that encrustation tendencies of heat-transferring surfaces can be reduced significantly. The corresponding amount of heat is removed via the top condenser.

The solids obtained in the crystallization in stream 2 are removed from the mother liquor 5 by means of a downstream solid-liquid separation B. To remove the adhering mother liquor from the solid surface, it is washed with an appropriate wash liquid. To wash the solid, several wash liquids have been identified, which have a low solubility of lauro lactam. Ideally, a wash liquid which is already present in the process, dissolves the adhering components and can be worked up correspondingly should be used. In this context, one possible washing agent identified has been the solvent 3 removed in the crystallization step A.

The moist crystals 4 have to be freed of the adhering washing agent in a subsequent drying step C and D. It has been found that it is advantageous in apparatus terms to melt lauro lactam in a melter C and to remove it from the solvent 24 by means of a conventional flash evaporation D. It is known here from operating experience that entrainment of lauro lactam cannot be prevented. The entrainment leads to coverage of installed heat exchange surfaces and therefore requires a specific condensation system known to those skilled in the art for stream 24. The condensation system is not discussed at this point, and so the stream 24 leaves the process.

The installed medium boiler removal I and J can be configured in an integrated manner as a dividing wall column, the advantages of which are sufficiently well known to those skilled in the art. At the top of the column I/J, the medium boilers 17 are removed with a lower boiling point than the CDON product of value present. The installed dividing wall within the column I/J allows residual lauro lactam with the high boilers present to be removed via stream 21 at the bottom of the column. The CDON present and the medium boilers having a higher boiling point than CDON can each be removed within the permissible specification limits via two side draws 19 on the opposite side of the dividing wall column to the feed.

The bottom product 21 rich in lauro lactam and high boilers is sent from the medium boiler distillation I/J for removal of high boilers to a further workup step K. This consists of an evaporation apparatus for high-viscosity fluids which is sufficiently well known to a person skilled in the art. The high-boiling components are discharged here via the bottom stream 23. The condensed vapours 22 which comprise the majority of the lauro lactam originally present in the bottom product of the medium boiler distillation I/J are recycled into the workup sequence to increase the yield. The recycling is effected into the crystallization A.

The process detailed, according to the claims for working up lauro lactam and for recovering the components of value present, such as solvent and reactant, exhibits the following advantages over a conventional distillation process:

- A majority (greater than 80%, preferably greater than 85% and more preferably greater than 90%) of the material of value can be removed via the crystallization merely by cooling of the stream.
- The main fraction of the lauro lactam produced does not pass through any hot separation steps in which there may be thermal stress or decomposition.

- Reduction of the high boiler content (laurolactam) allows the bottom temperature of the dividing wall column to be operated at a moderate temperature level
- The combination of crystallization and distillation reduces the number of thermal separating operations necessary to a minimum.
- The low thermal stress on the laurolactam allows the formation of polymers from laurolactam to be reduced, such that the feedstock factor is improved over the workup sequence.
- The laurolactam removed in the crystallization has a purity of >99%.

Working example:

A laurolactam-containing stream is introduced at 1.5 kg/h at a temperature of 90°C into a stirred guide tube crystalliser with an internal temperature of 35°C and a liquid volume of 3.2 l. The pressure level of the crystalliser is approx. 0.05 bar abs. The stream comprises, as well as 20% by weight of laurolactam (LL) and approx. 77.5% by weight of solvent (LM), 2.5% by weight of secondary components other than LL and LM. The stream supplied is supplied to the crystalliser via a cross-sectional constriction with a pressure greater than the boiling pressure of solvent. As soon as the stream enters the liquid volume, an equienthalpic mass of solvent evaporates, approx. 0.25 kg/h. The evaporation enthalpy required is removed from the liquid system by lowering of the temperature. The evaporation of the solvent oversaturates the system with LL. The oversaturation is degraded by controlled crystal growth on the solid surface present. The mean residence time of the liquid-solid phase is approx. 2.5 h. The suspension obtained, approx. 1.25 kg/h, is removed batchwise in 10 min cycles.

The suspension is introduced via a conventional laboratory filter centrifuge. The mother liquor (approx. 0.85 kg/h) is separated therein from the solid moist target product (approx. 0.4 kg/h), the solid laurolactam. To raise the product quality, the solids are washed with cold (preferably with a temperature less than 65°C) solvent

(approx. 0.4 kg/h). This achieves washing of the solid surface, which removes undesired secondary components. The moist solid is dried at 90°C in a drying cabinet under reduced pressure (100 mbar). On completion of drying, 0.275 kg/h of solids remains. This corresponds to a yield of 91.7% laurolactam.

The workup of the liquid mother liquor does not require any reworking in the laboratory, since the basic connection is known from the "conventional" process.

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Cyclododecanol, Cyclododecanone, and Laurolactam

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Solvent selection

For the process detailed, preference is given to using hydrocumene as the solvent. Alternatively, it is also possible to use the solvents listed below. It is possible here to use different components or mixtures of components, for example hydrocumene (HC), cyclododecanone (CDON), cyclododecatriene (CDT), toluene, cycloheptane, cyclooctane (COA), cyclononane, cyclodecane, cyclododecane, vinylcyclohexane (VCH) or ethylcyclohexane (ECH), dimethylcyclohexane, tert-butylcyclohexane. In addition, combinations of the solvents listed are possible, since the eutectic behaviour, i.e. the melting point depression, of the mixtures can be exploited advantageously here. A lowering of the melting point of the dissolution medium (mixture of different solvents) reduces the apparatus complexity, since it would be possible to dispense with complex trace heating.

Claims:

1. A process for working up a stream comprising laurolactam for the recovery of all components present,
characterized in that
the stream which arrives from the synthesis and comprises laurolactam and further components is first cooled such that, in a selective manner, by solution cooling crystallization, only the solubility limit of laurolactam is exceeded and laurolactam is selectively crystallised out and removed from the mother liquor in a downstream solid-liquid separation, and the mother liquor is subsequently sent to a multistage distillation sequence.
2. A process according to claim 1,
characterized in that
the solution cooling crystallization is performed as a flash cooling crystallisation.
3. A process according to claim 1 or 2,
characterized in that
more than 80% of the laurolactam is already removed in the crystallization.
4. A process according to claim 1, 2 or 3,
characterized in that
the laurolactam removed in the crystallization is washed with a wash liquid to remove the adhering mother liquor.
5. A process according to any one of the preceding claims,
characterized in that
the laurolactam removed in the crystallization is washed with hydrocumene to remove the adhering mother liquor.

6. A process according to claim 4,
characterized in that
the wash liquid used may be hydrocumene (HC), cyclododecanone (CDON),
cyclododecatriene (CDT), toluene, cycloheptane, cyclooctane (COA),
cyclononane, cyclodecane, cyclododecane, vinylcyclohexane (VCH) or
ethylcyclohexane (ECH), dimethylcyclohexane, tert-butylcyclohexane or a
mixture thereof.
7. A process according to any one of the preceding claims,
characterized in that
the laurolactam removed in the crystallization is subject to a drying step.