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(71) Applicant: **DSM IP ASSETS B.V.** [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors: **TINGE, Johan Thomas**; P.O. Box 4, NL-6100 AA Echt (NL). **OLZHEIM, Daniël Julius Maria**; P.O. Box 4, NL-6100 AA Echt (NL).

(74) Agent: **SCHMITT, Maja**; P.O. Box 4, NL-6100 AA Echt (NL).

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(54) Title: STEAM STRIPPING INORGANIC PROCESS LIQUID DISCHARGED FROM HPO® EXTRACTION SECTION AND UTILIZING HEAT OF CONDENSATION

(57) Abstract: A continuous process for preparing cyclohexanone oxime comprising steps including passing an extracted aqueous phase comprising organic solvent directly from the extraction zone to a water stripping zone; evaporating at least 5 % by weight of the water present in the extracted aqueous phase; passing the water vapour containing stream into a heat exchanger and transferring energy from the water vapour containing stream to an in-process liquid, thereby heating the in-process liquid and condensing at least part of water vapour containing stream.

STEAM STRIPPING INORGANIC PROCESS LIQUID DISCHARGED FROM HPO® EXTRACTION SECTION AND UTILIZING HEAT OF CONDENSATION

The invention relates to a process for preparing cyclohexanone oxime comprising extracting cyclohexanone oxime in an extraction zone with an organic solvent and passing an extracted aqueous phase into a combined stripping zone where in situ produced water vapour, organic solvent, cyclohexanone and at least 5 % by weight of the extracted aqueous phase is removed. The resultant water vapour containing stream is at least partially condensed and the energy released on condensation is used to heat in-process liquids.

The present invention relates to a continuous process for preparing caprolactam by Beckmann rearrangement of cyclohexanone oxime. The process of the invention is not limited to any particular form of lactam. The lactam preferably is ε-caprolactam. Such production processes for caprolactam include processes in which intermediates are made according the so-called (modified) Raschig technology, hydrogenation of nitric oxide based technology, ammoximation based technology and HPO® technology.

However, in order to do this a source of cyclohexanone oxime is required. There are several routes for preparing cyclohexanone oxime including the reaction of a buffered hydroxylammonium phosphate solution and cyclohexanone in presence of toluene (so-called HPO® technology), or where cyclohexanone oxime is prepared by reaction of cyclohexanone with ammonia in the presence of hydrogen peroxide (so-called ammoximation technology).

An important application of hydroxylammonium salts is in the preparation of oximes from ketones or aldehydes, in particular the preparation of cyclohexanone oxime from cyclohexanone. For this preparation method of an oxime, a cyclic process is known wherein an aqueous acid-buffered reaction medium is kept in circulation via a hydroxylammonium salt synthesis zone and an oxime synthesis zone. The reaction medium is acid-buffered by means of for instance phosphoric acid and/or sulphuric acid and the buffer salts derived from these acids, for instance alkali and/or ammonium salts. In the hydroxylammonium salt synthesis zone, nitrate ions or nitrogen oxides in a circulating inorganic liquid, are converted with gaseous hydrogen to hydroxylamine.

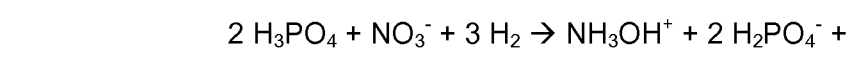
Fresh hydrogen is fed to the hydroxylammonium salt synthesis zone and a small amount of gas is regularly purged from the system to maintain a constant

partial hydrogen pressure. The purged gas comprises inert gaseous components that were in the fresh hydrogen and the produced gaseous by-products nitrogen (N_2) and nitrous oxide (N_2O).

The hydroxylamine reacts with free buffer acid to produce the corresponding hydroxylammonium salt, which is subsequently transferred to the oxime synthesis zone where it reacts with a ketone to the corresponding oxime with release of acid. After separation of the oxime from the reaction medium the reaction medium is recycled to the hydroxylammonium salt synthesis zone and fresh nitrate ions or nitrogen oxides are added to the reaction medium.

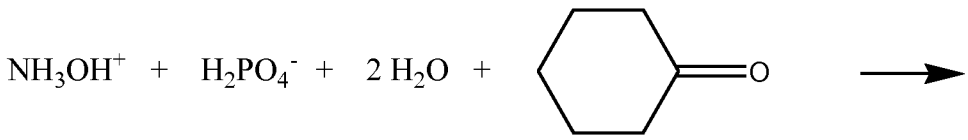
In the case where the hydroxylammonium salt synthesis starts from a solution of phosphoric acid and nitrate the above-mentioned chemical reactions are represented as follows:

Reaction 1) Preparation of the hydroxylammonium in the hydroxylammonium salt synthesis zone:

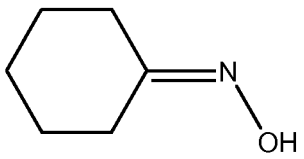


$$2\ H_3PO_4 + NO_3^- + 3\ H_2 \rightarrow NH_3OH^+ + 2\ H_2PO_4^- + 2\ H_2O$$

Reaction 2) Preparation of the oxime in the oxime synthesis zone:

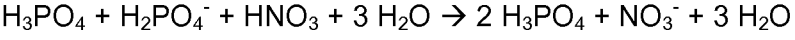


$$NH_3OH^+ + H_2PO_4^- + 2\ H_2O +$$



$$+ H_3PO_4 + 3\ H_2O$$

Reaction 3) Supply of HNO_3 to make up the depletion of the source of nitrate ions:



$$H_3PO_4 + H_2PO_4^- + HNO_3 + 3\ H_2O \rightarrow 2\ H_3PO_4 + NO_3^- + 3\ H_2O$$

The first reaction is catalysed heterogeneously. Preferably, the catalyst is present as finely divided solids as a disperse phase in a liquid reaction mixture.

The resulting mixture of the first reaction is an aqueous inorganic process liquid (IPL) comprising a suspension of solid catalyst particles in a hydroxylammonium salt solution.

As is clear from the reactions, the inorganic process liquid may comprise neutral species e.g. hydroxylamine or ammonia which may also be protonated e.g. hydroxylammonium or ammonium. This means that according to the present invention both hydroxylamine and hydroxylammonium may be read as hydroxylamine and/or hydroxylammonium, and that ammonia and ammonium may be read as ammonia and/or ammonium.

Before the aqueous inorganic process liquid (IPL) is transported to the oxime synthesis zone (Reaction 2), the solid catalyst particles are preferably separated from the aqueous inorganic process liquid. After filtration the inorganic process liquid is a hydroxylammonium salt solution filtrate.

Such processes include the HPO® process of DSM (see *e.g.* H.J. Damme, J.T. van Goolen and A.H. de Rooij, Cyclohexanone oxime made without by-product $(NH_4)_2SO_4$, July 10, 1972, Chemical Engineering; pp 54/55 or Ullmann's Encyclopedia of Industrial Chemistry (2005) at page 6/7 under the chapter Caprolactam.

Although, the preparation of hydroxylammonium has been known for many decades and ways to improve known preparation methods have been investigated thoroughly over the years, presently known industrial processes, which are generally of a continuous nature, still suffer from drawbacks.

US3940442 discloses a process for producing cyclohexanone oxime wherein a solution rich in hydroxylamine from the hydroxylamine synthesis zone is fed with cyclohexanone to said cyclohexanone oxime synthesis zone wherein the hydroxylamine and the cyclohexanone react with each other to form cyclohexanone oxime, separating the cyclohexanone oxime and unreacted cyclohexanone from said solution and recycling said solution back to said hydroxylamine synthesis zone. Then the solution being recycled from the cyclohexanone oxime synthesis zone to the hydroxylamine synthesis zone is stripped for a time sufficiently long enough so that any residual amount of cyclohexanone and cyclohexanone oxime, present in the solution after removal of the cyclohexanone oxime produced in the cyclohexanone oxime

synthesis zone, are substantially reduced to below about 0.02% by weight. This prevents the poisoning of palladium catalyst by adding nitrate ions to the stripped solution being recycled from the cyclohexanone oxime synthesis zone to the hydroxylamine synthesis zone after the stripping of the recycled solution.

US7309801 discloses a process for preparing cyclohexanone oxime, said process comprising passing an aqueous medium containing phosphate from a hydroxylammonium synthesis zone to a cyclohexanone oxime synthesis zone, extracting cyclohexanone and cyclohexanone oxime from said aqueous medium, prior to feeding the aqueous medium to the stripping zone from the cyclohexanone oxime synthesis zone to a stripping zone and from the stripping zone back to the hydroxylammonium synthesis zone and passing steam through the aqueous medium in the stripping zone; and discharging a vapour stream from said stripping zone; condensing the vapour stream to obtain a condensed aqueous fluid; and washing an organic product with the condensed aqueous fluid.

US7408081 discloses a process for preparing cyclohexanone oxime comprising passing an aqueous medium containing phosphate from a hydroxylammonium synthesis zone to a cyclohexanone oxime synthesis zone, from the cyclohexanone oxime synthesis zone to a stripping zone and from the stripping zone back to the hydroxylammonium synthesis zone, in said stripping zone, stripping the aqueous medium with steam; wherein said stripping is carried out at a pressure higher than 0.11 MPa. The resultant vapour stream may be discharged from the stripping zone and the heat of the vapour stream may be exchanged to a process liquid. Said extracting may be carried out by contacting the aqueous medium with any suitable solvent.

It was observed that in the process of US7408081 the aqueous medium containing phosphate stream after leaving the cyclohexanone oxime synthesis zone and after extracting cyclohexanone and cyclohexanone oxime from said aqueous medium with an organic solvent contains noticeable amounts of organic solvent. This organic solvent is not just present in a dissolved form, but is also present in entrained finely dispersed organic droplets. Although from US7408081 it is clear that the organic solvent is removed from the aqueous medium prior to it being fed to the stripping zone for removal of cyclohexanone and cyclohexanone oxime, no description is given in US7408081 as to how this is done.

The prior art processes are still not very economical due to high investments costs required for all separation units and the high variable costs due to additional energy consumption in the overall process.

Moreover, it is an object of the invention to provide an improved process while maintaining a target hydroxylammonium production rate compared to a conventional process operated in the same production facility. This will benefit in a more environmentally friendly process, and a cheaper process compared to a conventional process operated in the same production facility.

Surprisingly, it was found that by combining the removal of solvent from the aqueous medium with the removal of cyclohexanone and cyclohexanone oxime from the aqueous medium in one single stripping zone, the costs could be reduced, because the process according to the invention requires less equipment and less energy. An advantage is that the present invention does not require a separate liquid-liquid phase separating zone or an organic solvent stripping zone.

Therefore, according to the present invention there is provided a continuous process for preparing cyclohexanone oxime comprising steps:

I) preparing aqueous hydroxylammonium solution by catalytically reducing nitrate or nitrogen oxide with hydrogen in a hydroxylammonium synthesis zone;

II) preparing cyclohexanone oxime by reacting hydroxylammonium from step I) with cyclohexanone in a cyclohexanone oxime synthesis zone, resulting in an aqueous phase and first organic phase;

III) passing the resultant aqueous phase from step II) comprising water, salts, organic solvent, cyclohexanone oxime and cyclohexanone into an extraction zone;

IV) extracting cyclohexanone oxime and cyclohexanone with an organic solvent in the extraction zone to give an extracted aqueous phase and a second organic phase;

V) passing at least part of the second organic phase produced in step IV) back into the cyclohexanone oxime synthesis zone in step II);

VI) passing the extracted aqueous phase produced in step IV) into a water stripping zone;

VII) evaporating at least 5 % by weight of the water present in the extracted aqueous phase in the water stripping zone resulting in a stripped aqueous phase and a water vapour containing stream;

VIII) passing the water vapour containing stream produced in step VII) into a heat exchanger;

IX) transferring energy of the water vapour containing stream to an in-process liquid in an heat exchanger, thereby heating the in-process liquid;

X) returning at least part of the stripped aqueous phase obtained in step VII) to step I).

The present application further provide a continuous process for preparing cyclohexanone oxime comprising steps:

I) preparing aqueous hydroxylammonium solution by catalytically reducing nitrate or nitrogen oxide with hydrogen in a hydroxylammonium synthesis zone;

II) preparing cyclohexanone oxime by reacting hydroxylammonium from step I) with cyclohexanone in a cyclohexanone oxime synthesis zone, resulting in an aqueous phase and first organic phase;

III) passing the resultant aqueous phase from step II) comprising water, salts, organic solvent, cyclohexanone oxime and cyclohexanone into an extraction zone;

IV) extracting cyclohexanone oxime and cyclohexanone with an organic solvent in the extraction zone to give an extracted aqueous phase and a second organic phase;

V) passing at least part of the second organic phase produced in step IV) back into the cyclohexanone oxime synthesis zone in step II);

VI) passing the extracted aqueous phase produced in step IV) into a water stripping zone;

VII) evaporating at least 5 % by weight of the water present in the extracted aqueous phase in the water stripping zone resulting in a stripped aqueous phase and a water vapour containing stream;

VIII) passing the water vapour containing stream produced in step VII) into a heat exchanger;

IX) transferring energy of the water vapour containing stream to an in-process liquid in an heat exchanger, thereby heating the in-process liquid;

X) returning at least part of the stripped aqueous phase obtained in step VII) to step I);

wherein

a) the first organic phase produced in step II) contains more than 25 % by weight cyclohexanone oxime;

b) the extracted aqueous phase produced in step IV) also comprises organic solvent; and

c) during the transfer of energy in step IX) at least part of water vapour containing stream is condensed.

At least part of' is defined here in as more than 50% by weight, more preferably more than 75 % by weight and most preferably more than 85 % by weight.

Therefore, the process of the invention does not require a separate liquid-liquid phase separating zone.

Therefore, the process of the invention does not require an organic solvent stripping zone between step IV) and step VI).

In the process of the invention any suitable organic solvent may be used in which cyclohexanone and cyclohexanone oxime may be dissolved. Preferably the organic solvent is selected from the group consisting of benzene, toluene, xylene, methylcyclopentane, cyclohexane or mixtures thereof. Most preferably, the organic solvent is toluene.

Organic solvent is used for example in the oximation section and the extraction zone. The extraction zone may comprise one or more extraction devices, e.g. (pulsed) packed columns, rotating disc columns and/or mixer-settlers. The extraction zone preferably comprises a counter-current operated pulsed packed extraction column, in which cyclohexanone and cyclohexanone oxime are recovered from inorganic process liquid.

The inorganic process liquid (extracted aqueous phase from step IV) exiting the extraction zone may contain small amounts of cyclohexanone and cyclohexanone oxime and is saturated with the organic solvent and may contain entrained organic solvent droplets.

Preferably the weight fraction of organic solvent in the water vapour containing stream is at least 3 times higher than the weight fraction of organic solvent in the extracted aqueous phase.

Preferably the weight fraction of cyclohexanone in the water vapour containing stream ranges from 0.01 to 2 % by weight.

Preferably the content of organic solvent in the extracted aqueous phase obtained in step IV) ranges from 100 to 2000 ppm by weight. This is surprising

as it means a low level of organic solvent may be present without being detrimental to the process of the invention.

Preferably the extracted aqueous phase in step IV) is preheated before being passed into the water stripping zone. The preheating may be done by transferring heat from the stripped aqueous phase obtained in step VII) before reusing at least part of the stripped aqueous phase in step I) or alternatively the preheating may be done by transferring energy from the water vapour containing stream in step IX).

The inorganic process liquid is fed as such to the water stripping zone, in which steam is used as stripping agent. The stripping zone may comprise one more water strippers. Preferably, a single water stripper is used which provides a long residence time to the extracted aqueous phase.

The water stripper is equipped with a reboiler which uses high pressure externally supplied steam as energy source. This high pressure steam heats the liquid inside a column in the reboiler which is converted into steam which rises through the column. This is known as steam stripping. Because of this heat input a fraction of the extracted aqueous phase, at least 5 % by weight, more preferably 7 to 20 % by weight is evaporated as a water vapour containing stream and this will strip off (almost all) organic solvent and cyclohexanone. Cyclohexanone oxime has a too high boiling point and will not stripped off. However, cyclohexanone oxime at such temperatures is not stable and will decompose into cyclohexanone (and hyam).

The energy required for evaporating at least 5 % by weight of the water in step VII) may be introduced via an internal or an external reboiler by using an external energy source. The external energy source may a super-atmospheric water vapour containing stream.

The energy content of the water vapour containing stream (additionally comprising some organic components such as organic solvent and cyclohexanone) is at least partially recovered. The water vapour is at least partially condensed after leaving the water stripper in a heat exchanger. Furthermore, the organics in the water vapour are also recovered and reused in the process of the invention. Preferably both the organic solvent and cyclohexanone being present in the condensate obtained in step c) is at least partially reused in the process for preparing cyclohexanone oxime.

The energy released on condensation of the water vapour containing stream is used to heat for example in-process liquids via the use of heat exchangers.

A heat exchanger may be a reboiler of a distillation column, for instance a distillation column wherein cyclohexanone oxime is separated from an organic product comprising cyclohexanone and organic solvent, or a heat exchanger of a crystallizer, for instance a crystallizer wherein water is evaporated from an ammonium sulphate solution to effect crystallization of ammonium sulphate crystals; and organic flow entering extraction columns.

Examples include the released energy being used to drive reboilers of an oxime distillation column; to transfer heat in heat exchangers of ammonium sulphate crystallizers; to transfer heat to drive reboilers of concentrators of aqueous ammonium sulphate solution; to heat up organic flows entering extraction columns; or to transfer heat to a non-process liquid such as water to heat it up or to produce (low pressure) steam.

The water vapour stream may also be used as a stripping agent in a waste water stripper in a cyclohexanone oxime washing section.

According to the present invention there is also provided a process to prepare caprolactam comprising the process of the invention. In another embodiment of the invention there is also provided caprolactam obtained from a process according to the invention.

Figure 1 shows a comparative embodiment derivable from prior art processes which include an organic solvent stripper and a liquid-liquid phase separator.

Figure 2 shows an embodiment of the invention where there is no need for an organic solvent stripper or a liquid-liquid phase separator.

Figure 1.

A comparative embodiment derivable from prior art processes comprising a continuous inorganic process liquid (IPL) purification and concentration section is schematically illustrated in Figure 1.

An aqueous flow discharged from an oximation section (not shown in Figure 1) containing water, salts, organic solvent, cyclohexanone oxime and cyclohexanone is supplied to the top part of an extraction zone [E] via line [1] and organic solvent is introduced into bottom part of the extraction zone [E] via line [4]. In the extraction zone [E], cyclohexanone and cyclohexanone oxime being present in the aqueous phase (dissolved and / or entrained) are recovered via extraction with organic solvent. The obtained extracted aqueous flow is discharged via line [3]. The obtained second organic phase comprising organic solvent, cyclohexanone oxime and

cyclohexanone is discharged via line [2] and is preferably re-used in the cyclohexanone oxime synthesis zone (not shown in Figure 1).

The obtained extracted aqueous phase from the bottom of the extraction zone [E] is charged to the liquid-liquid phase separator [P] via line [3]. This obtained extracted aqueous phase contains some cyclohexanone oxime and cyclohexanone and at least 100 ppm organic solvent (dissolved and / or entrained). In separator [P] an aqueous phase and an organic phase are formed. The organic phase leaves the liquid-liquid phase separator [P] via line [5]. The aqueous phase (with some dissolved organic phase) of the liquid-liquid separator [P] is charged to organic solvent stripper [T] via line [7]. The stripping in the organic solvent stripper [T] is executed by introducing water vapour into the bottom section of the organic solvent stripper [T] via line [8]. The produced vapour in the organic solvent stripper [T] contains water and organic solvent. This vapour leaves the organic solvent stripper [T] from the top via line [6] and is after being condensed directed to the liquid-liquid separator [P].

The obtained aqueous bottom flow of the organic solvent stripper [T] is (almost) free of organic solvent and is discharged via line [9] and charged to the top of the water stripping zone [W]. In this water stripping zone [W] at least 5 % by weight of the water is removed via evaporation. In addition cyclohexanone is removed via stripping and cyclohexanone oxime is decomposed to cyclohexanone.

The thickening of the organic solvent stripped aqueous flow in water stripping zone [W] is executed by generating water vapour in the bottom of the water stripping zone [W] due to partial evaporation of the water (being present in the liquid phase) and/or by introducing water vapour to the bottom section of the water stripping zone [W] (line not shown in Figure 1).

This in-process water vapour production is done by partial evaporation of the water stripping zone content in an (internal or external) reboiler (not shown in Figure 1) by using an external energy source. The produced water vapour in the water stripping zone [W] contains water and cyclohexanone leaves the water stripping zone [W] from the top via line [10]. After condensation of the vapour flow cyclohexanone is recovered (not shown in Figure 1). The concentrated aqueous flow leaves the water stripping zone [W] via line [11].

Figure 2.

An embodiment of the invention comprising a continuous IPL purification and concentration section is schematically illustrated in Figure 2.

An aqueous flow discharged from a cyclohexanone oxime synthesis zone (step I and II) (not shown in Figure 2) containing water, salts, organic solvent, cyclohexanone oxime and cyclohexanone is supplied to the top part of an extraction zone [E] via line [1] (step III) and organic solvent is introduced into bottom part of the extraction zone [E] via line [4]. In the extraction zone [E], cyclohexanone and cyclohexanone oxime being present in the aqueous phase (dissolved and / or entrained) are recovered via extraction with organic solvent (step IV). The obtained second organic phase comprising organic solvent, cyclohexanone oxime and cyclohexanone is discharged via line [2] and is at least partially re-used in the cyclohexanone oxime synthesis zone (step V) (not shown in Figure 2).
The obtained extracted aqueous phase is discharged via line [3] from the bottom of the extraction zone [E] and is charged to the top of the water stripping zone [W] (step VI). This obtained extracted aqueous phase contains some cyclohexanone oxime and cyclohexanone and at least 100 ppm organic solvent (dissolved and / or entrained). In this water stripping zone [W] at least 5 % by weight of the water is removed via evaporation (step VII). In addition cyclohexanone is removed via stripping and cyclohexanone oxime is decomposed to cyclohexanone.

The thickening of the aqueous flow in water stripping zone [W] is executed by generating water vapour in the bottom of the water stripping zone [W] due to partial evaporation of the water (being present in the liquid phase) or by introducing water vapour to the bottom section of the of the water stripping zone [W] (line not shown).

This in-process water vapour production is done by partial evaporation of the water stripping zone content in an (internal or external) reboiler (not shown in Figure 2) by using an external energy source. The produced water vapour containing stream in the water stripping zone [W] contains water and cyclohexanone and leaves the water stripping zone [W] from the top via line [10]. This water vapour containing stream was fed to several heat exchangers (not shown in Figure 2) to heat-up various in-process liquids (step VIII and step IX), whereby the majority of the vapour was condensed. After condensation of the vapour flow cyclohexanone and organic solvent are recovered (not shown in Figure 2). The concentrated aqueous flow that is (almost) free of organic solvent leaves the water stripping zone [W] via line [11] and may be returned at least partially to step I) (step X) (not shown in Figure 2).

As is shown in Figure 2 there is no need for a separate organic solvent stripper and/or a liquid-liquid phase separator between the extraction zone [E] and the water stripping zone [W]. This simplifies the process and reduces the necessary investment without affection the quality of the final product.

The invention will be further elucidated by means of the following example without being limited thereto.

EXAMPLE

This example is performed in a commercial HPO® plant for the production of cyclohexanone oxime that is operated in a continuous mode.

In this plant nitrate was catalytically hydrogenated to hydroxylammonium in a hydroxylammonium reactor [step I) hydroxylammonium synthesis zone].

The obtained aqueous hydroxylammonium solution was after filtration fed together with toluene and fresh cyclohexanone to an oximation reactor (cyclohexanone oxime synthesis zone), in which cyclohexanone oxime was produced (step II). From the oximation reactor a first organic phase comprising approximately 42 wt% cyclohexanone oxime and the remainder being mainly toluene, was further worked up to almost pure cyclohexanone oxime. The work-up included removal of toluene by a 2-stage distillation. The reboiler of the first stage of this distillation was driven with a water vapour containing stream originating from the top of the stripping column, whereby the majority of the water vapour was condensed.

An aqueous phase comprising dissolved salts (including ammonium phosphate and ammonium nitrate), toluene, cyclohexanone and cyclohexanone oxime was discharged from the oximation reactor and fed to the top section of an extraction column [step III) extraction zone] that was operated in a counter-current mode. To the bottom section of this column almost pure toluene was fed for the extraction (step IV). From the top section of this extraction column a second organic phase comprising toluene, cyclohexanone and cyclohexanone oxime was discharged and was fed to the oximation reactor (step V).

From the bottom section of the extraction column an extracted aqueous phase comprising approx. 60 % by weight water, dissolved salts such as ammonium phosphate and ammonium nitrate, approximately 1800 ppm by weight of toluene, as well as cyclohexanone and cyclohexanone oxime was discharged. This aqueous phase was heated in a heat exchanger by condensing part of the water vapour that existed the top of the steam stripping column. The thus pre-heated aqueous phase was fed to the top section of a steam stripper column [(step VI) water stripping zone]. In this steam stripper column about 1/3 by weight of the water present in the aqueous feed was evaporated (step VII).

The energy required for the evaporation was introduced by a steam-driven external reboiler. The steam fed to this reboiler was sourced from a low pressure steam grid. As a result of the steam stripping a water vapour containing stream was present at the top of the steam stripper column that contained approximately 9000 ppm by weight of toluene and approximately 0.04 % by weight of cyclohexanone. This water vapour containing stream was fed to several heat exchangers to heat-up various in-process liquids (step VIII and step IX), whereby the majority of the vapour was condensed. The heated in-process liquids included the aqueous stream that was fed to the steam stripping column and the cyclohexanone oxime containing phase in the first stage of the cyclohexanone oxime distillation. The stripped aqueous phase that left the bottom section of the steam stripping column was returned to the hydroxylammonium reactor (step X).

CLAIMS

1. A continuous process for preparing cyclohexanone oxime comprising steps:
   I) preparing aqueous hydroxylammonium solution by catalytically reducing nitrate or nitrogen oxide with hydrogen in a hydroxylammonium synthesis zone;
   II) preparing cyclohexanone oxime by reacting hydroxylammonium from step I) with cyclohexanone in a cyclohexanone oxime synthesis zone, resulting in an aqueous phase and first organic phase;
   III) passing the resultant aqueous phase from step II) comprising water, salts, organic solvent, cyclohexanone oxime and cyclohexanone into an extraction zone;
   IV) extracting cyclohexanone oxime and cyclohexanone with an organic solvent in the extraction zone to give an extracted aqueous phase and a second organic phase;
   V) passing at least part of the second organic phase produced in step IV) back into the cyclohexanone oxime synthesis zone in step II);
   VI) passing the extracted aqueous phase produced in step IV) into a water stripping zone;
   VII) evaporating at least 5 % by weight of the water present in the extracted aqueous phase in the water stripping zone resulting in a stripped aqueous phase and a water vapour containing stream;
   VIII) passing the water vapour containing stream produced in step VII) into a heat exchanger;
   IX) transferring energy of the water vapour containing stream to an in-process liquid in the heat exchanger, thereby heating the in-process liquid;
   X) returning at least part of the stripped aqueous phase obtained in step VII) to step I).

2. A process according to claim 1 wherein
   a) the first organic phase produced in step II) contains more than 25 % by weight cyclohexanone oxime;
   b) the extracted aqueous phase produced in step IV) also comprises organic solvent; and

c) during the transfer of energy in step IX) at least part of water vapour containing stream is condensed.

3. A process according to claim 1 wherein the weight fraction of organic solvent in the water vapour containing stream is at least 3 times higher than the weight fraction of organic solvent in the extracted aqueous phase.

4. A process according to claim 1 wherein the weight fraction of cyclohexanone in the water vapour containing stream ranges from 0.01 to 2 % by weight.

5. A process according to claim 1 wherein the content of organic solvent in the extracted aqueous phase obtained in step IV) ranges from 100 to 2000 ppm by weight.

6. A process according to anyone of the preceding claims wherein the organic solvent is selected from the group consisting of benzene, toluene, xylene, methylcyclopentane, cyclohexane or mixtures thereof.

7. A process according to claim 1 wherein both the organic solvent and cyclohexanone being present in the condensate obtained in step c) is at least partially reused in the process for preparing cyclohexanone oxime.

8. A process according to claim 1 wherein the heat exchangers include reboilers in distillation columns, ammonium sulphate crystallisers and / or organic flow entering extraction columns.

9. A process according to claim 1 wherein the extracted aqueous phase in step IV) is preheated before being passed into the water stripping zone.

10. A process according to claim 9 wherein the preheating is done by transferring heat from the stripped aqueous phase obtained in step VII) before reusing in step I).

11. A process according to claim 9 wherein the preheating is done by transferring energy from the water vapour containing stream in step IX).

12. A process according to claim 1 wherein the energy required for the evaporating at least 5 % by weight of the water in step VII) is introduced via an internal or external reboiler by using an external energy source.

13. A process according to claim 12 wherein the external energy source is a super-atmospheric water vapour containing stream.

14. A process to prepare caprolactam comprising the process according to claim 1.

15. Caprolactam obtained from a process according to claim 1.

Figure 1

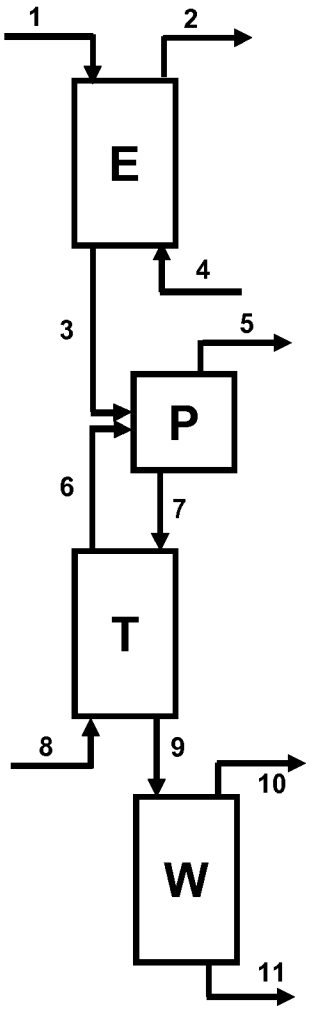
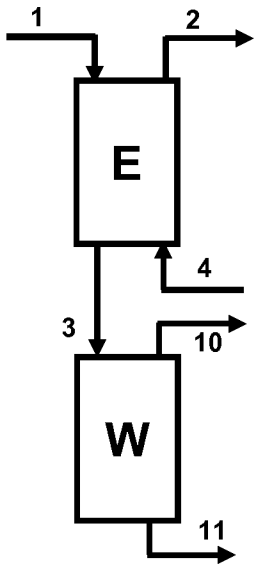


Figure 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/077057

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C249/08 C07C249/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/065375 A1 (BENNEKER ARNO [NL] ET AL) 24 March 2005 (2005-03-24) cited in the application the whole document -----	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 March 2014	28/03/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Tabanella, Stefania

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/077057

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