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(54) **LOW-ENERGY CONSUMPTION PROCESS WITH REDUCED AMMONIA CONSUMPTION, FOR THE PRODUCTION OF HIGH-PURITY MELAMINE THROUGH THE PYROLYSIS OF UREA, AND RELATIVE PLANT**

NIEDRIGENERGIEVERFAHREN MIT REDUZIERTEM AMMONIAKVERBRAUCH ZUR HERSTELLUNG VON HOCHREINEM MELAMIN MITTELS HARNSTOFFPYROLYSE UND ENTSPRECHENDE AUSRÜSTUNG

PROCEDE DE PREPARATION DE FAIBLE CONSOMMATION ENERGETIQUE PRESENTANT UNE CONSOMMATION D'AMMONIAC REDUITE, POUR LA PRODUCTION DE MELAMINE DE GRANDE PURETE PAR PYROLYSE DE L'UREA ET EQUIPEMENT ASSOCIE

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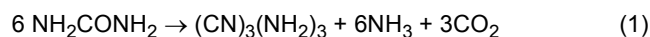
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Description

[0001] The present invention relates to a low-energy consumption process with reduced ammonia consumption for the preparation of high-purity melamine through the pyrolysis of urea and the relative plant.

[0002] To better understand the object of the present invention, reference is made to the state of the art as described hereunder. It is known that the transformation of molten urea into melamine is described by the following overall reaction (1):



urea melamine ammonia carbon dioxide

wherein 1.86 kg of NH_3 and CO_2 , as a whole called off-gases, are formed for each kg of melamine.

[0003] A particularly widespread industrial process, based on the high-pressure pyrolysis of urea, is described in patent EP2385043. In order to clearly appreciate the improvements and advantages of the process according to the present invention, figure 1 of the present patent application is representative of the state of the art and shows a simplified block-diagram of an embodiment of the production process of melamine described in EP2385043.

[0004] According to the scheme of figure 1, the process of EP2385043 comprises the following steps:

a) producing melamine by the pyrolysis of urea in a specific reactor and separating a biphasic liquid/gas effluent produced in the pyrolysis reaction of urea into a liquid stream of raw melamine and into a first stream of anhydrous off-gases comprising NH_3 , CO_2 and melamine vapour;

b) putting the above-mentioned liquid stream of raw melamine in contact with a stream of anhydrous gaseous NH_3 in a specific post-reactor, forming a liquid stream of raw melamine impoverished in CO_2 and a second stream of anhydrous off-gases comprising NH_3 , CO_2 and melamine vapour;

c) putting said first and second stream of anhydrous off-gases in contact with at least one aqueous washing stream to form an aqueous stream comprising melamine, NH_3 and CO_2 and a stream of wet off-gases comprising NH_3 , CO_2 and water vapour;

d) removing from said aqueous stream comprising melamine, NH_3 and CO_2 , at least a part of the CO_2 contained therein, forming a stream comprising the CO_2 removed and an aqueous stream comprising melamine impoverished in CO_2 ;

e) recovering the melamine contained in said liquid stream of raw melamine impoverished in CO_2 and the melamine contained in said aqueous stream comprising melamine impoverished in CO_2 through crystallization by cooling and separation, with the formation of a stream of crystallized melamine and a stream of mother liquor.

[0005] The block diagram of figure 1 shows the main sections of a plant for the production of melamine and the main streams of materials, according to the process of EP2385043, represented at the inlet by the stream of liquid urea (stream 1), the stream of liquid ammonia (stream 2) and the stream of make-up water (stream 32) and the outgoing streams represented by the stream of off-gases (stream 13), the stream of melamine produced (stream 31), the stream of carbonate (stream 27) and the stream of purified water (stream 29) if not reused within the plant.

[0006] The stream 1 of liquid urea is fed to the reaction section R, at a temperature higher than the melting temperature (equal to about 133°C) and the stream 3 of anhydrous gaseous NH_3 . The section R comprises a reactor equipped with a suitable heating system which keeps the reagent system at a temperature of about $360\text{--}420^\circ\text{C}$; the pressure is maintained at a value higher than 70 bar.

[0007] The liquid/gas biphasic effluent produced by the pyrolysis reaction of urea, is separated, inside the reactor R, or in one or more separators positioned downstream (not shown in Figure 1), into a liquid stream 6 of raw melamine comprising unreacted urea, NH_3 , CO_2 and impurities such as OATs and polycondensates, and a first stream of anhydrous off-gases 7 comprising NH_3 , CO_2 saturated with melamine vapour. The liquid stream 6 of raw melamine and the stream 7 of anhydrous off-gases are subjected to two different treatments for the recovery of melamine contained therein.

[0008] The liquid stream 6 of raw melamine is sent to a post-reaction section PR, which preferably operates under the same temperature and pressure conditions as the section R, wherein the same is put in contact with a stream of anhydrous gaseous NH_3 . The mass ratio between said stream 4 and said stream 6 can vary from 0.06 to 0.6. The stream of anhydrous gaseous NH_3 flows in close contact with the liquid stream of raw melamine and extracts the CO_2 dissolved therein, increasing the partial pressure of ammonia.

[0009] Furthermore, the permanence of raw melamine under the post-reactor conditions has some advantageous secondary effects:

a) it almost completely advances the conversion of the unreacted urea into melamine, resulting in an increase in the yield and reducing, in the sections downstream, the formation of CO_2 due to a possible decomposition of residual

urea;

b) it advances the conversion of OATs into melamine. The conversion degree of OATs into melamine is a function of the residence time of the stream 6 in contact with the stream 4 in the PR section;

c) increasing the partial pressure of NH_3 , it favours the reconversion of the polycondensates into melamine, lowering the concentration by over 20%.

[0010] From the above, it is clear that the greater the amount of ammonia that is fed to the post-reactor, the greater the effect of the CO_2 removal and the greater the partial pressure of the ammonia in liquid phase inside the post-reactor, will be. It is also clear, however, that the greater the amount of NH_3 , the greater will be the melamine coming out in vapour phase with the stream 9 and that will have to be absorbed and solubilized in the following section Q, and the quantity of wet off-gases to be sent to the urea plant.

[0011] Consequently, in fact, in the process according to EP238504, in order to reduce the amount of off-gas, there is the tendency to send the smallest possible amount of ammonia to the Post-Reactor which is necessary for a satisfactory but still not complete transformation of the by-products.

[0012] A liquid stream of partially purified melamine (stream 8) therefore exits from the PR section, having a low CO_2 content, with a low content of unreacted urea and reduced quantities of OATs and polycondensates. A second stream of anhydrous off-gases (stream 9) also exits from the PR section, mainly comprising NH_3 , a small amount of CO_2 and a certain quantity of melamine vapour. The streams of anhydrous off-gases coming from the sections R and PR, joined in a single stream 10, are subjected to a recovery treatment of the melamine by washing with water, in a single washing section Q. The stream 10 can contain melamine vapour up to 10% by mass of the overall melamine produced in the section R. In the section Q this melamine is recovered by putting the stream 10 in contact with an aqueous washing stream, preferably consisting of one or more streams collected from suitable points of the melamine plant (in figure 1, these streams are represented by a single stream 11), with the formation of an aqueous stream (stream 12) comprising melamine, NH_3 and CO_2 . The section Q operates at temperatures within the range of 125-190°C and pressures within the range of 20-30 barrel; the mass ratio between the stream 11 and the stream 10 ranges from 0.3 to 2.0.

[0013] The gaseous stream leaving the section Q after the washing (stream 13), consists of wet off-gases substantially comprising NH_3 , CO_2 and the saturation water vapour; it is sent to the urea plant as such or after being subjected to treatment (not shown in figure 1), such as, for example, condensation by absorption in aqueous solution. There is therefore a wet stream of off-gases consisting of $\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$ which is sent to the urea plant with negative effects due to the presence of water.

[0014] The aqueous stream leaving the section Q (stream 12) is sent to a CO_2 separation section STR, where a part of the CO_2 contained therein is removed by means of stripping with vapour, produced for example by a reboiler at the bottom of the same stripper. A gaseous stream rich in CO_2 (stream 14), which is sent to a point of the process in which it can no longer contribute to lowering the pH in the crystallization, and an aqueous stream comprising melamine impoverished in CO_2 (stream 15), are recovered from the section STR.

[0015] As already mentioned, the liquid stream of melamine 8, substantially free of CO_2 , also exits from the post-reaction section PR. It is sent to a quench-ammonolysis section QAL, where the quench treatment (dissolution in water of the raw melamine) and ammonolysis (elimination of the polycondensates) are effected.

[0016] The section QAL can be composed of one or more stationary apparatuses, preferably a single apparatus. The stream 8 enters the bottom of this equipment, kept under vigorous stirring, and is put in close contact with an aqueous ammonia solution (stream 16), in which the same is totally dissolved at a temperature of 160-180°C. The aqueous stream 16 is formed by the combination of an aqueous stream (stream 17) coming from the subsequent steps of the melamine process, and a stream of NH_3 (stream 19) formed, in turn, by the combination of the stream of NH_3 (stream 18) also coming from the subsequent steps of the melamine process and the make-up stream of NH_3 5; a direct recycling aqueous stream of the crystallization mother liquor (stream 25) is also sent to the quench-ammonolysis section.

[0017] At the inlet of the quench-ammonolysis section, the mass ratios between the combination of streams 16 and 25 and the stream of molten melamine 8, are selected so as to have mass concentrations of NH_3 at the outlet ranging from 10% to 17% in the aqueous ammonia solution comprising purified melamine (stream 20).

[0018] In the quench-ammonolysis equipment, the residence time is sufficient for almost completely eliminating the polycondensates present in the stream 8, mainly transforming the same into melamine.

[0019] The stream 15 coming from the section STR is preferably joined with stream 20 leaving the quench-ammonolysis section to form the stream 21; from this point, the melamine leaving the reaction section R and post-reaction section PR in vapour phase, is joined with the melamine that has left the same sections in liquid phase, and is subjected to the same treatment.

[0020] The stream 21 is sent to the filtration section F, composed of finisher filters which also complete the ammonolysis treatment. The stream leaving the section F (stream 22) is sent to the crystallization section Cr, where the melamine is crystallized by decreasing the temperature to a value of about 40-50°C, obtaining an aqueous suspension of high-purity melamine (stream 23).

[0021] The low content of CO₂ in stream 15, obtained by means of the section STR and the low content of CO₂ in stream 8 obtained through the section PR, allow the pH to be kept high in crystallization, thus operating under less favourable conditions for the precipitation of OATs. These advantageous conditions for the crystallization of pure melamine are obtained in the section STR, by separating the CO₂ from the melamine stream recovered from the off-gases (stream 12) and in the section PR, by stripping the CO₂ with NH₃ leaving the urea plant (stream 4) and is returned to the same together with the wet off-gases (stream 13).

[0022] The stream 23 leaving the section Cr is subjected to a solid/liquid separation in the section SLS, where the melamine crystals (stream 31) are separated from the crystallization mother liquor (stream 24) and sent to the drying and packaging sections (not shown in figure 1).

[0023] The stream 24 leaving the separator SLS is divided into two streams (stream 25 and 26): the stream 25 is recycled directly to the quench-ammonolysis section QAL, whereas the stream 26 is sent to the ammonia recovery section RA.

[0024] The fraction of mother liquor not directly recycled (stream 26) is subjected to deammoniation in the section RA, which separates three streams: a stream of NH₃ substantially free of CO₂, to be recycled to the ammonolysis section QAL (stream 18); a stream rich in CO₂ and ammonia (stream 27); an aqueous stream comprising melamine, OATs and substantially free of CO₂ and NH₃ (stream 28).

[0025] The stream of NH₃ 18 is extracted from the section RA, preferably in the gaseous state and then mixed, after joining with the ammonia make-up stream 5, with the aqueous stream 17, coming from the subsequent phases of the melamine process, in the ammonia absorption section (AA); in this way, the condensation enthalpy of NH₃ heats the resulting stream 16, with a positive effect on the thermal balance of the section QAL and therefore on the vapour consumption of the whole plant. The stream 27 containing CO₂, ammonia and water, normally called side stream, is sent directly to the urea plant, thus eliminating CO₂ from the plant, but also eliminating the ammonia contained in the solution forming stream 27. This ammonia must be reintegrated by means of make-up or reintegration (stream 5). The melamine plant therefore requires a total quantity of ammonia equal to the sum of streams 3-4-5 (stream 2).

[0026] The stream of deammoniated mother liquor 28 is sent to a section EO for elimination of the OATs and to obtain an aqueous solution (stream 30) to be recycled to the quench-ammonolysis section QAL (stream 17) and off-gas washing section Q (stream 11).

[0027] The section EO can be implemented in many different ways. In EP2385043, the whole stream 28 is sent for decomposition in order to recover the organic compounds in the form of NH₃ and CO₂, obtaining a stream of water (stream 29) substantially free of impurities, which can be discharged or re-used in a suitable point of the plant, and a stream of water 30 to be recycled to the sections QAL and Q (streams 17 and 11). The section EO also receives the make-up water (stream 32) in order to reintegrate the exits of water with the off-gases (stream 13), side stream (stream 27) and with the stream 29 if discharged and not recycled to the plant.

[0028] The process and plant according to the prior art, more specifically according to EP2385043, have been further improved, however, obtaining, in a completely surprising way, a process and plant which, maintaining all the advantages previously described, are more efficient in terms of reduction of the need for fresh ammonia from the battery limits, energy consumptions and the quantity of wet off-gases at the outlet which must be reconverted to urea.

[0029] As previously pointed out, in fact, in the process according to EP2385043, the melamine that exits in vapour phase with the stream 9, is absorbed and solubilized in the section Q, therefore the greater the quantity of anhydrous gases in stream 9, the greater the quantity of wet off-gases produced in Q which must be treated and reconverted to urea in the urea production plant, and the greater the quantity of water necessary for solubilizing the melamine contained therein.

[0030] Furthermore, as the solution containing melamine (stream 12) is fed to a stripping section STR, another drawback linked to the quantity of ammonia fed to the post-reactor is therefore represented by the amount of vapour necessary for carrying out the stripping of CO₂.

[0031] In order to reduce as much as possible the drawbacks linked to the amount of ammonia fed to the post-reactor indicated above, in the processes according to the state of the art, there is consequently the tendency to feed the minimum possible amount of ammonia necessary for reaching a satisfactory degree of transformation of the by-products, but not sufficient, however, for guaranteeing the complete transformation of the same.

[0032] The objective of the present invention is therefore to provide a process and plant which overcome the drawbacks of the state of the art described above and which are characterized by a reduced consumption of ammonia, an improved efficiency and, at the same time, with reduced production costs of melamine.

[0033] An object of the present invention therefore relates to a process for the production of melamine by the pyrolysis of urea which comprises the following steps:

- a) producing melamine by the pyrolysis of urea in a specific reactor and separating a biphasic liquid/gas effluent produced in the pyrolysis reaction of urea into a liquid stream of raw melamine and into a first stream of anhydrous off-gases comprising NH₃, CO₂ and melamine vapour;

b) putting said liquid stream of raw melamine in contact with a stream of anhydrous gaseous NH_3 in a specific post-reactor and forming a liquid stream of melamine impoverished in CO_2 and partially purified and a second stream of anhydrous gas comprising NH_3 , CO_2 and melamine vapour;

c) putting the first stream of anhydrous gas coming from step a) in contact with at least one aqueous washing stream, forming an aqueous stream, comprising melamine, NH_3 , CO_2 and a gaseous stream of wet off-gases comprising NH_3 , CO_2 and water vapour;

d) mixing the second stream of anhydrous gases coming from step b) with a stream of recycled water and forming an aqueous ammonia solution in which the melamine contained in the stream of anhydrous gases is dissolved, recovering the sensible heat and condensation heat of the gases;

e) removing, from the aqueous stream of step c), comprising melamine, NH_3 , CO_2 , at least a part of the CO_2 contained therein and forming a gaseous stream comprising the CO_2 removed and an aqueous stream comprising melamine, NH_3 and impoverished in CO_2 ;

f) subjecting the liquid stream of melamine impoverished in CO_2 and partially purified, leaving the post-reactor, to a quench-ammonolysis treatment by contact with the aqueous ammonia solution obtained in step d), and the formation of an aqueous ammonia stream comprising purified melamine;

g) recovering the melamine contained in the aqueous ammonia stream comprising purified melamine coming from step f) and the melamine contained in said aqueous stream comprising melamine and impoverished in CO_2 coming from step (e) by means of a crystallization step by cooling and separation, with the formation of a stream of crystallized melamine and a stream of mother liquor.

[0034] A second object of the present invention relates to a plant for the application of the above-mentioned process, comprising:

i) a separation section for separating a biphasic liquid/gas effluent produced in a pyrolysis reaction of urea into a liquid stream of raw melamine and a first stream of anhydrous off-gases comprising NH_3 , CO_2 and melamine vapour, said separation section being connected to a reaction section for the pyrolysis of urea from which it receives said biphasic liquid/gas effluent, said separation section being inside or outside said reaction section;

ii) a stripping section or post-reactor for putting said liquid stream of raw melamine coming from said reaction section in contact with a stream of anhydrous gaseous NH_3 and forming a liquid stream of melamine impoverished in CO_2 and partially purified and a second stream of anhydrous gases comprising NH_3 , CO_2 and melamine vapour, said stripping section being connected to said reaction section from which it receives said liquid stream of raw melamine;

iii) a washing section for putting said first stream of anhydrous off-gases in contact with an aqueous washing stream and forming an aqueous stream comprising melamine, NH_3 , CO_2 and a stream of wet off-gases comprising NH_3 , CO_2 and water vapour, said washing section being connected to said separation section from which it receives said first stream of anhydrous off-gases;

iv) a removal section of the CO_2 for removing from said aqueous stream comprising melamine, NH_3 , CO_2 , at least a part of the CO_2 contained therein and comprising the CO_2 removed and an aqueous stream, comprising melamine, NH_3 and impoverished in CO_2 , said removal section of the CO_2 being connected to said washing section from which it receives said aqueous stream, comprising melamine, NH_3 and CO_2 ;

v) a mixing and heat recovery section for mixing said second stream of anhydrous gases with a stream of recycled water and forming an aqueous ammonia solution in which the melamine contained in the stream of anhydrous off-gases is dissolved, and for recovering both the sensible heat and the condensation heat of the gases, by absorption of the ammonia, said mixing and heat recovery section being connected to the stripping section or post-reactor from which it receives said second stream of anhydrous gases and said quench-ammonolysis section to which the aqueous ammonia solution is fed;

vi) a quench-ammonolysis section for subjecting the liquid stream of melamine impoverished in CO_2 and partially purified, leaving the post-reactor, to a quench-ammonolysis treatment by contact with the aqueous ammonia solution coming from the mixing and heat recovery section, and forming an aqueous ammonia stream, comprising purified melamine, said quench-ammonolysis section being connected to said stripping section or post-reactor from which it receives said liquid stream of melamine impoverished in CO_2 and partially purified;

vii) at least one recovery section of the melamine for recovering both the melamine contained in said aqueous ammonia stream comprising purified melamine and also the melamine contained in said aqueous stream comprising melamine, NH_3 and impoverished in CO_2 through crystallization by cooling and separation, with the formation of a stream of crystallized melamine and a stream of mother liquor, said recovery section of the melamine being connected to both said quench-ammonolysis section from which it receives the aqueous ammonia stream comprising purified melamine and to said removal section of the CO_2 from which it receives said aqueous stream comprising melamine, NH_3 and impoverished in CO_2 .

[0035] In its essence, the process object of the present invention provides for the collection and purification in aqueous solution of the melamine produced in the pyrolysis reactor and its separation by crystallization. More specifically, the invention relates to the recovery of the gases leaving the post-reactor within the process for the production of melamine.

[0036] Even more specifically, the gases leaving the post-reactor are absorbed and condensed in recycled water, recovering the melamine contained therein, thus obtaining the ammonia solution necessary for the purification of melamine and, at the same time, recovering both the sensible heat and the condensation heat of the ammonia.

[0037] More specifically, the process according to the present invention, by sending the gases leaving the post-reaction section to the mixing and heat recovery section, i.e. to the ammonia absorption section, and no longer to the off-gas washing section, overcomes the drawbacks of the state of the art, i.e. the fact of having to run with the minimum possible flow-rate of ammonia to the post-reactor to reduce the off-gases and consequently not completing the transformation of the by-products.

[0038] The process according to the present invention is therefore characterized by the recovery of the anhydrous off-gases leaving the post-reactor and by their condensation by mixing with recycled water, also guaranteeing an optimization of the use of make-up ammonia and a reduction in the total water leaving the plant, both that contained in the off-gases and also that contained in the solution to be treated in the urea plant, with the contemporaneous recovery within the melamine plant, of the discharge water, thus implementing a process without liquid discharges towards the outside.

[0039] In the present description, "*washing aqueous stream*", unless otherwise specified, refers to a stream of make-up water or it can consist of one or more aqueous streams taken from suitable points of the melamine plant itself.

[0040] In the present description, "*aqueous stream comprising melamine and impoverished in CO₂*" refers to a stream leaving a step of the process with a lower CO₂ content with respect to the stream fed to said process step, whereas "*liquid stream of melamine impoverished in CO₂ and partially purified*" refers to a stream leaving a step of the process with a lower content of CO₂ and impurities with respect to the stream fed to said process step.

[0041] In step d) of the process according to the present invention, the second stream of anhydrous gases coming from step b) is preferably mixed with the stream of recycled water and with a stream obtained by combining a stream of make-up ammonia and a stream of recycled ammonia to form said aqueous ammonia solution.

[0042] The process according to the present invention can comprise feeding the make-up ammonia stream to a subsequent deammoniation treatment of the portion of the stream of mother liquor not directly recycled.

[0043] At least a part of said stream of mother liquor obtained in step g) can be preferably used as aqueous stream in step f) for the quench-ammonolysis treatment of said liquid stream of melamine impoverished in CO₂ and partially purified, leaving the post-reactor, and at least a part of said stream of mother liquor obtained in step g) can be subjected to deammoniation treatment with the formation of a gaseous stream of NH₃ substantially free of CO₂, a stream comprising CO₂, ammonia and water and an aqueous stream of deammoniated mother liquor.

[0044] Said stream comprising CO₂, ammonia and water, coming from the deammoniation treatment, can be joined with a further stream, containing H₂O, CO₂ and NH₃ coming from a subsequent decomposition step carried out on said aqueous stream of deammoniated mother liquor, to form a single stream to be recycled to a plant for the production of urea either directly or after treatment which reduces the water content, or said stream containing CO₂, ammonia and water is sent to the washing step (c) of the anhydrous off-gases.

[0045] The aqueous stream of deammoniated mother liquor can be subjected to a decomposition treatment with the recovery of NH₃ and CO₂ and the production of an aqueous stream which is partially recycled as aqueous washing stream to said step c) and partially recycled as aqueous stream to contribute to forming the aqueous ammonia stream (step d)) fed to the quench-ammonolysis treatment (step f)) and a stream containing H₂O, CO₂ and NH₃ which is combined with the stream comprising CO₂, ammonia and water coming from the deammoniation treatment.

[0046] The gaseous stream of NH₃, substantially free of CO₂, coming from the deammoniation treatment, can be mixed with a part of said aqueous stream in order to recover the condensation heat in step d).

[0047] The aqueous stream comprising melamine, coming from step e), can be joined with said aqueous ammonia stream comprising purified melamine coming from the quench-ammonolysis step f), with the formation of a single stream to be subjected to said step g). In step e) the removal of CO₂ from the aqueous stream comprising melamine, NH₃ and CO₂, is effected by means of depressurization or by stripping. The stream comprising the removed CO₂ obtained in step e), is recycled to a step of the same process subsequent to said recovery step g) for the recovery of melamine through crystallization by cooling.

[0048] The stream of wet off-gases comprising NH₃, CO₂ and water vapour obtained in step c) is preferably recycled to a plant for the production of urea, as such or after being subjected to a condensation treatment by absorption in aqueous solution or another type of treatment.

[0049] The process according to the present invention and the advantages deriving therefrom can be better understood from the following description of a first possible embodiment, illustrated in figure 2 and from two further embodiments shown in figure 3 and figure 4. In order to facilitate the description and comparison with the prior art, the same abbreviations and numbers as in figure 1 representing the state of the art have been retained in figures 2-4.

[0050] The block diagram of figure 2 shows the main sections of a plant for the production of melamine and the main streams of materials according to a first embodiment of the process of the present invention.

[0051] The stream 1 of liquid urea is fed to the reaction section **R**, at a temperature higher than the melting point (equal to about 133°C) together with the stream 3 of anhydrous gaseous NH₃. The section **R** comprises a reactor equipped with a suitable heating system, which keeps the reagent system at a temperature of about 360-420°C; the pressure is maintained at a value higher than 70 barrel.

[0052] Inside the reactor **R**, or in one or more separators positioned downstream (not shown in figure 2), the liquid/gas biphasic effluent produced by the pyrolysis reaction of urea is separated into a liquid stream 6 of raw melamine comprising unreacted urea, NH₃, CO₂ and impurities such as OATs and polycondensates, and a first stream of anhydrous off-gases 7 comprising NH₃ and CO₂ saturated with melamine vapour. The liquid stream 6 of raw melamine and the stream 7 of anhydrous off-gases are subjected to two different treatments for the recovery of melamine contained therein.

[0053] The stream 7 of anhydrous gases is sent to the washing section **Q** in order to absorb the melamine contained therein bringing it into solution; two streams therefore exit from the section **Q**, stream 13 of off-gases composed of NH₃ and CO₂ saturated with water in vapour phase, which leave the melamine production plant and are sent to subsequent treatment at the urea plant, and stream 12, composed of water, NH₃, CO₂ and melamine in solution, which is fed to the vapour stripping section **STR** to remove the CO₂ from said solution.

[0054] The liquid stream 6 of raw melamine is sent to a post-reaction section **PR**, which preferably operates under the same temperature and pressure conditions as the section **R**, or at a slightly lower pressure. The post-reaction section **PR** therefore receives stream 6 of raw melamine and stream 4 of overheated anhydrous gaseous melamine which enters into close contact with the stream 6 of raw melamine. The mass ratio between said stream 4 and said stream 6 ranges from 0.06 to 0.6.

[0055] The anhydrous gaseous NH₃ stream 4, flows in close contact with the liquid stream of raw melamine 6, extracting the CO₂ dissolved therein, increasing the partial pressure of ammonia in proportion to the quantity of ammonia fed. The increase in the partial pressure of ammonia and the permanence of the raw melamine under the conditions of the post-reactor offer advantageous secondary effects:

- a) they almost completely advance the conversion of the unreacted urea to melamine, resulting in an increase yield;
- b) they advance the conversion of OATs into melamine. The degree of conversion of the OATs into melamine is in relation to the residence time of the stream 6 in contact with the stream 4 having an increased partial pressure of NH₃, in the section **PR**;
- c) they favour the reconversion of polycondensates to melamine until the concentration is reduced by about 50%.

[0056] A first stream in gas phase composed of NH₃ and CO₂, saturated with melamine in vapour phase (stream 9) and a second stream in liquid phase (stream 8), composed of partially purified liquid melamine, impoverished in CO₂, leave the post-reaction section **PR**.

[0057] From the above it is evident that the greater the amount of ammonia fed to the post reactor, the greater the effect will be of the CO₂ removal and the greater the partial pressure of ammonia in the liquid phase inside the post reactor will be, with the above-mentioned benefits. It is also clear however that the greater the amount of NH₃ fed (stream 4), the greater the amount will be of anhydrous gases composed of NH₃ and CO₂ saturated with melamine in vapour phase exiting from the post reactor **PR** (stream 9).

[0058] As previously indicated, according to the state of the art, the melamine which exits in vapour phase with stream 9 is absorbed and solubilized in the subsequent section **Q**, consequently, the greater the amount of the anhydrous gases of stream 9, the greater will be the amount of wet off-gases produced by **Q**, which must be treated and reconverted to urea at the urea production plant, and the greater will be the amount of water necessary for solubilizing the melamine contained therein.

[0059] As the solution containing melamine (stream 12) is fed to a stripping section **STR**, there is therefore also another drawback linked to the quantity of ammonia fed to the post-reactor which is the quantity of vapour necessary for effecting the stripping of CO₂.

[0060] In order to reduce as much as possible the drawbacks linked to the amount of ammonia fed to the post-reactor described above, in the processes according to the state of the art, there is the tendency to feed the minimum possible amount of ammonia sufficient for reaching a satisfactory degree of transformation of the by-products.

[0061] In order to remedy these drawbacks, it has been surprisingly found that by treating the gases leaving the post-reaction section **PR** (stream 9) in the ammonia absorption section **AA**, i.e. the mixing and heat recovery section, the drawbacks of the state of the art are overcome, obtaining the following advantages:

- i) the sensible heat and condensation heat of the gases are completely recovered, obtaining an equal reduction in the heat necessary for heating the ammonia solution (stream 16), to be fed to the quench-ammonolysis section **QAL**;
- ii) all the ammonia fed to the post-reactor **PR** is completely recovered within the melamine production plant, reducing

the make-up ammonia required from the outside in an equal amount (stream 5);

iii) the wet off-gases produced by the process decrease in proportion to the same quantity of anhydrous gases which, in the process according to the state of the art, were sent from the post-reactor PR to the washing section with water Q where they exited saturated with water in stream 13;

iv) the quantity of solution be sent to the stripping section STR is reduced, with a proportional reduction in the vapour necessary.

[0062] Furthermore, as the stream 9 of anhydrous gases leaving the post-reaction section is no longer sent to the washing section Q, no longer contributing to the quantity of wet off-gases produced nor giving rise to the other negative effects previously described, the quantity of anhydrous ammonia 4 fed to the section PR can be increased, thus obtaining a greater efficiency of the section, with a higher conversion of polycondensates into melamine and with the almost complete transformation of OATs into melamine.

[0063] As there are fewer polycondensates, this also allows a reduction in the temperature and residence time in the purification section, with a reduction in the hydrolysis phenomena of melamine to form OATs, thus reducing the volume of the equipment and consequently also the investment costs.

[0064] A liquid stream of melamine therefore leaves the section PR (stream 8) which is not only practically free of CO₂, but is also partially purified, as it is practically free of urea and does not contain or contains quantities further reduced in OATs and polycondensates.

[0065] As indicated above, stream 7 of anhydrous gases leaving the section R is sent to the washing section Q for absorbing the melamine contained therein, bringing it in solution; this melamine is recovered in the section Q by putting stream 7 in contact with an aqueous washing stream, preferably consisting of one or more streams taken from suitable points of the melamine plant (in figure 2, these streams are represented by a single stream 11), with the formation of an aqueous stream (stream 12) comprising melamine, NH₃ and CO₂. The section Q operates at temperatures within the range of 125 - 190°C, preferably 160 - 175°C, and at pressures ranging from 20 to 30 bar_{rel}, preferably about 25 barrel; the mass ratio between stream 11 and stream 7 ranges from 0.3 to 2.0, preferably from 0.4 to 0.7.

[0066] The gaseous stream leaving section Q after the washing (stream 13) consists of wet off-gases substantially comprising NH₃, CO₂ and the saturation water vapour; it is sent to the urea plant as such or after being subjected to treatment (not indicated in figure 2) such as condensation by absorption in aqueous solution.

[0067] The aqueous stream leaving the section Q (stream 12) is sent to a section STR for the separation of CO₂, where a part of the CO₂ contained therein is removed by stripping with vapour, produced for example by a reboiler at the bottom of the stripper itself. A gaseous stream rich in CO₂ (stream 14) is recovered from the section STR and is sent to a point of the process where it can no longer contribute to lowering the pH in crystallization, together with an aqueous stream comprising melamine, NH₃ and impoverished in CO₂ (stream 15).

[0068] As already indicated, the liquid stream 8 of melamine, impoverished in CO₂ and partially purified, also leaves the post-reaction section PR. It is sent, as shown in figure 2, to a quench-ammonolysis section QAL, wherein the quench (dissolution in water of raw melamine) and ammonolysis (elimination of the polycondensates) treatment takes place.

[0069] On the basis of what is indicated above, the solution according to the present invention allows this section to be resized as the almost complete transformation of OATs and polycondensates already takes place in the PR, thanks to the increased quantity of NH₃ fed.

[0070] The section QAL can be composed of one or more stationary apparatuses, preferably a single piece of equipment. The stream 8 enters the bottom of this equipment, maintained under vigorous stirring, and is put in close contact with an aqueous ammonia solution (stream 16), in which it is completely dissolved at a temperature of 160-180°C, preferably 165-172°C, even more preferably 165-168°C.

[0071] The aqueous ammonia solution 16 comes from the ammonia absorption section AA, to which an aqueous stream (stream 17) coming from the subsequent steps of the melamine process, is fed together with stream 9 in gas phase composed of NH₃ and CO₂ saturated with melamine in vapour phase coming from the section PR and a stream (19) obtained by combining the stream of NH₃ preferably gaseous (18), also coming from the subsequent steps of the melamine process and the liquid make-up stream of NH₃ 5; a direct recycling aqueous stream of crystallization mother liquor (stream 25) is also sent to the quench-ammonolysis section.

[0072] At the inlet of the quench-ammonolysis section, the mass ratios between the combination of streams 16 and 25 and the molten melamine stream 8 are selected so as to have concentrations of NH₃ at the outlet ranging from 10% to 17% by mass (preferably from 12% to 15% by mass) in the aqueous ammonia solution comprising purified melamine (stream 20).

[0073] The residence time in the quench-ammonolysis equipment is sufficient for almost completely eliminating the possible residual polycondensates present in stream 8, mainly transforming them into melamine.

[0074] Stream 15 coming from section STR is preferably joined with stream 20 coming from the quench-ammonolysis section to form stream 21; from here on, the melamine that left the reaction R and post-reaction PR sections in vapour phase, joins the melamine which left the same sections in liquid phase, and is subjected to the same treatment.

[0075] The stream **21** is sent to the filtration section **F**, composed of finisher filters which also complete the ammonolysis treatment. The stream leaving the section **F** (stream **22**) is sent to the crystallization section **Cr**, where the melamine is crystallized by decreasing the temperature to a value of about 40-50°C, obtaining an aqueous suspension of high-purity melamine (stream **23**).

[0076] The low content of CO₂ in stream **15**, obtained through the section **STR**, allows the pH in crystallization to be kept at a high value, thus being able to operate under less favourable conditions for the precipitation of **OATs**. These advantageous conditions for the crystallization of pure melamine are obtained in the section **STR**, by separating the CO₂ from the melamine stream recovered from the off-gases (stream **12**). The stream **23** leaving the section **Cr** is subjected to a solid/liquid separation in the section **SLS**, where the melamine crystals (stream **31**) are separated from the crystallization mother liquor (stream **24**) and sent to the drying and packaging sections (not shown in figure 2). The stream **24** leaving the separator **SLS** is divided into two streams (streams **25** and **26**): stream **25** is recycled directly to the quench-ammonolysis section **QAL**, whereas stream **26** is sent to the ammonia recovery section **RA**.

[0077] The fraction of mother liquor not directly recycled (stream **26**) is subjected to deammoniation in the section **RA**, which separates three streams: a stream of NH₃ substantially free of CO₂, to be recycled to the ammonolysis section **QAL** (stream **18**); a stream rich in CO₂ and ammonia (stream **27**); an aqueous stream comprising melamine, OATs and substantially free of CO₂ and NH₃ (stream **28**).

[0078] The stream of NH₃ **18** is extracted from the section **RA**, preferably in the gaseous state, combined with the liquid make-up stream of NH₃ **5**, thus forming stream **19**, and then mixed in the ammonia absorption section (**AA**) with a part of the aqueous stream **17**, coming from the subsequent phases of the melamine process and with stream **9** in gas phase, saturated with melamine in vapour phase and mainly composed of NH₃ and CO₂ coming from **PR**; in this mixing and heat recovery section **AA**, the aqueous ammonia solution **16** is formed, in which the melamine contained in the stream of anhydrous gas **9** is dissolved, and both the sensible heat and the condensation heat of the gases is recovered; in particular, the condensation enthalpy of NH₃ also serves for heating the resulting stream **16**, with a positive effect on the thermal balance of the section **QAL** and therefore on the vapour consumption of the whole plant.

[0079] The stream **27** leaving the section **RA** and containing CO₂, ammonia and water, is combined with stream **33** containing H₂O, CO₂ and NH₃ coming from the section **EO** to form stream **34**, normally called side-stream, which is sent directly to the urea plant, thus eliminating CO₂ from the plant, but also eliminating the ammonia contained in the solution which forms stream **34**. This ammonia must be reintegrated by reintegration or make-up (stream **5**). The melamine plant therefore requires a total amount of ammonia equal to the sum of streams 3-4-5 (stream **2**).

[0080] The stream of deammoniated mother liquor **28** is sent to a section **EO** for the elimination of the OATs and to obtain an aqueous solution (stream **30**) to be recycled to the ammonia absorption section **AA** (stream **17**) and off-gas washing section **Q** (stream **11**).

[0081] In the section **EO**, the whole stream **28** is sent for decomposition in order to recover the organic compounds in the form of CO₂ and NH₃, obtaining a stream of water (stream **29**) substantially without impurities, which can be discharged or reused in a suitable point of the plant, and a stream of water **30** to be recycled to the sections **QAL** and **Q** (streams **17** and **11**) and a stream **33** containing H₂O, CO₂ and NH₃ which is joined with stream **27** coming from the section **RA**, forming stream **34**. The section **EO** also receives the make-up or reintegration water (stream **32**) in order to reintegrate the water outlets with off-gases (stream **13**), side stream (stream **34**) and with the stream of water **29** if discharged and not recycled to the plant.

[0082] A second embodiment of the process according to the present invention is schematically represented in figure 3. The block diagram of figure 3 shows the main sections of a plant for the production of melamine and the main streams of materials in accordance with a second embodiment of the process according to the present invention of which only the different aspects with respect to the first embodiment shown in figure 2 will be described hereunder.

[0083] In the embodiment represented in figure 3, the make-up ammonia **5** is fed as reflux ammonia to the section **RA**, thus reducing the consumption of cooling water for the condensation of the part of ammonia vapour, leaving the head of the section **RA**, necessary for the internal reflux of said section.

[0084] The stream of NH₃ **18** is extracted from the section **RA**, preferably in the gaseous state, and sent to the ammonia absorption section (**AA**) where it is mixed with a part of the aqueous stream **17**, coming from the subsequent steps of the melamine process and with stream **9** in gas phase, saturated with melamine in vapour phase, mainly composed of NH₃ and CO₂ coming from **PR**.

[0085] The indication of stream **19** is not present in figure 3 as stream **18** is fed to the section **AA** directly from the section **RA**, whereas the make-up ammonia **5** is sent directly to the section **RA**.

[0086] In addition to the advantages already indicated for the embodiment of figure 2, the solution represented in figure 3 therefore allows a reduction in the quantity of cooling water necessary for the condensation of part of the ammonia vapour, leaving the head of the section **RA**, necessary for the internal reflux of said section, with a consequent further energy advantage, at the same time avoiding the mixing of liquid ammonia and gaseous ammonia.

[0087] In the embodiment represented in figure 4, in addition to what has already been described for the embodiment of figure 3, the stream **34** containing CO₂, ammonia and water, normally called side stream, is sent to the washing

section Q of anhydrous off-gases.

[0088] In this way, the total amount of H₂O leaving the melamine plant with the off-gases (stream **13**) and with the side stream (stream **34**) is reduced when these are discharged separately.

[0089] The stream of water (stream **29**) substantially free of impurities, coming from the section **EO**, can be sent to a section **RF** i.e. a cooling section, where it is cooled to be used as make-up water.

[0090] It leaves the section **RF** as stream **29bis**, is combined with the make-up or reintegration water (stream **32**), fed to **EO** for reintegrating the outlets of water with the off-gases (stream **13**) and to obtain a plant for the production of melamine completely free of liquid discharges.

EXAMPLE 1 (comparative)

[0091] In a melamine plant having a nominal capacity of 40,000 t/y (5,000 t/h), according to the state of the art represented in figure 1 of patent EP2385043, 16.0 t/h of molten urea and 1.0 t/h of gaseous NH₃ (stream **3**) were sent to the reaction section **R**. The reactor operated at 380°C and 80 barrel.

[0092] 11.8 t/h of anhydrous off-gases (stream **7**) comprising melamine vapour and 5.2 t/h of liquid raw melamine (stream **6**) were separated from the reactor.

[0093] This liquid melamine was treated in the section **PR** with 1.1 t/h of anhydrous gaseous NH₃ (stream **4**), under the same conditions as the reaction section **R**, obtaining 5.1 t/h of liquid melamine (stream **8**) and 1.2 t/h of anhydrous off-gases (stream **9**) comprising melamine vapour which, combined with the off-gases leaving the section **R**, formed stream **10** of 13.0 t/h, comprising 3.8% by mass of melamine vapour.

[0094] Stream **8** of liquid melamine leaving the bottom of the section **PR** was sent to the quench-ammonolysis section **QAL**, where the quench (dissolution in water of the raw melamine) and the ammonolysis (elimination of the polycondensates) treatments were effected.

[0095] More specifically, stream **8** was kept under vigorous stirring and was put in close contact with an aqueous ammonia solution (stream **16**) in which it was completely dissolved at a temperature of 172°C and a pressure of 25 barrel..

[0096] More specifically, the aqueous stream **16** was obtained by combining an aqueous stream (stream **17**) coming from the section **EO** and a stream of NH₃ (stream **19**), in turn formed by combining the stream of NH₃ (stream **18**) coming from the section **RA** and the make-up stream of NH₃ (stream **5**): stream **5** fed proved to be equal to 1.9 t/h.

[0097] A direct recycling aqueous stream of the crystallization mother liquor (stream **25**) was also sent to the quench-ammonolysis section **QAL**.

[0098] The melamine plant was then fed with a quantity of ammonia equal to the sum of streams 3-4-5, equal to 4-0 t/h (stream **2**).

[0099] The mass ratios between the combination of streams **16** and **25** and the stream of molten melamine, stream **8**, at the inlet of the quench-ammonolysis section **QAL**, were selected so as to have concentrations of NH₃ at the outlet, equal to about 14% by mass in the aqueous ammonia solution comprising purified melamine (stream **20**).

[0100] In the quench-ammonolysis equipment, the operating conditions indicated and the residence time were such as to almost completely eliminate the polycondensates present in stream **8**, largely transforming them into melamine.

[0101] The gaseous stream **10**, obtained by joining the anhydrous streams of off-gases from the reactor and from the stripper (stream **9**), was sent to a washing section **Q** which operated at 169°C and 25 bar_{rel.}, where it was put in contact in countercurrent with 7.0 t/h of a recycled aqueous solution (stream **11**).

[0102] The washed off-gases leaving the head of the washing column (stream **13**), containing 18% by mass of water and substantially free of melamine, were sent to the adjacent urea plant to recover the NH₃ and CO₂ contained therein.

[0103] 6.4 t/h of an aqueous solution (stream **12**) comprising 0.5 t/h of melamine entering as vapour with the off-gases, and 4.5% by mass of CO₂, left the bottom of the washing column. This stream was sent to a vapour stripping column, which operates at the bottom at 160°C and 7 bar_{rel.}. 4.6 t/h of an aqueous solution (stream **15**) left the bottom of the stripping column where the CO₂ was reduced to 0.2% by mass.

[0104] This solution (stream **15**) was joined with the solution leaving the quench-ammonolysis section (stream **20**) and the whole mixture was sent to the filters from which a solution was discharged (stream **22**) with less than 100 ppm by mass of polycondensates; this latter solution (stream **22**) was then sent to the crystallizer, which operates at a temperature of 45°C and a pressure of 0.5 bar_{rel.}, with a concentration of CO₂ of about 0.15% by mass and a pH of about 11.5.

[0105] The suspension (stream **23**) leaving the crystallizer was sent to a solid/liquid separator (centrifuge), which separated the crystallization mother liquor (stream **24**) from the high-purity melamine (titer of over 99.9% by mass with respect to the dry material).

[0106] The amount of about 62.6 t/h of mother liquor (stream **24**) was divided into two streams.

[0107] One stream of 7.5 t/h (stream **25**) was recycled directly to the quench-ammonolysis section without being subjected to any treatment; the remaining 55.1 t/h (stream **26**) was sent to the deammoniation section to recover the NH₃ dissolved therein.

[0108] The deammoniation section (RA) consists of a distillation column from whose head gaseous, almost anhydrous NH₃ exits.

[0109] A liquid stream of CO₂, NH₃ and water, which was recycled in a suitable point of the process, exits from an intermediate plate of the column.

[0110] The aqueous solution leaving the bottom of the column (stream **28**) was sent to treatment for the elimination of the OATs by thermal decomposition alone. An aqueous solution (stream **30**) was thus separated, which was recycled to the quench-ammonolysis (stream **17**) and off-gas washing (stream **11**), together with another aqueous stream (which can be discharged or reused as water for utilities, for example make-up water at the cooling towers or as process water).

[0111] A part of the solution recycled to the quench-ammonolysis section (stream **17**) was mixed with the gaseous NH₃ leaving the head of the distillation column of the deammoniation section (stream **19**), condensing it and recovering the condensation heat.

[0112] The consumptions of urea, ammonia and vapour of the whole process according to the state of the art represented in figure 1 and object of the present comparative example 1, proved to be equal to 3.2 t/t, 0.80 t/t and 4.3 t/t respectively of melamine produced.

Example 2

[0113] A synthesis process of melamine was carried out according to the present invention in the embodiment described in figure 2, in a melamine plant having a nominal capacity of 40,000 t/y (5,000 t/h), wherein the gases leaving the post-reaction section PR (stream 9) were treated in the mixing and heat recovery section AA.

[0114] The subsequent steps of the process were carried out as indicated in comparative example 1.

[0115] The treatment of stream 9 in the section AA had, as first effect, a reduction in the flow-rate of the make-up ammonia (stream 5). In order to keep the concentration of ammonia constant in stream 20 leaving the quench-ammonolysis section QAL, stream 5 of make-up ammonia was in fact reduced.

[0116] More specifically, the stream of make-up ammonia 5 was reduced by an amount equal to the ammonia contained in stream 9, i.e. by a quantity equal to 1.1 t/h which is equal to the ammonia fed to the section **PR** (stream 4). The quantity of make-up ammonia therefore proved to be lower than that necessary according to comparative example 1 (1.9 t/h).

[0117] The total amount of NH₃ which must be fed to the melamine plant therefore proved to be equal to the sum of streams **3-4-5** (stream **2**), i.e. equal to the sum of 1.0 t/h, 1.1 t/h and 0.8 t/h.

[0118] Stream 2 of ammonia fed to the melamine plant is therefore equal to 2.9 t/h which correspond to 0.58 t/t of melamine produced.

[0119] The total quantity of ammonia therefore also proved to be lower than the amount necessary according to comparative example 1 (4.0 t/h).

[0120] Furthermore, as stream **9** of anhydrous gases leaving the post-reaction section is no longer sent to the washing section **Q**, it no longer contributes to the quantity of wet off-gases produced, neither does it give rise to the other negative effects described above, and this allowed the quantity of anhydrous ammonia (stream **4**) fed to the section **PR**, to be increased, thus obtaining a higher efficiency of the section, with a higher conversion of polycondensates into melamine and with the almost complete transformation of OATs into melamine.

[0121] A further advantage of the process according to the present example which provides for the treatment of stream 9 in the section AA described above, is the complete recovery of the sensible heat and condensation heat of the gases, obtaining an equal reduction in the heat necessary for heating the ammonia solution (stream **16**), to be fed to the quench-ammonolysis section **QAL**.

[0122] The heat recovered in treating stream 9 in the section AA allowed a reduction equal to 450 kg/h in the quantity of saturated vapour used for heating the ammonia solution (stream **16**), with respect to the process according to comparative example 1

[0123] The ammonia and vapour consumptions of the process in accordance with the present invention according to the embodiment of Figure 2, proved to be equal to 0.58 t/t and 4.21 t/t respectively of melamine produced, against the corresponding values of 0.80 t/t and 4.3 t/t of melamine produced of the process according to comparative example 1.

Example 3

[0124] A synthesis process according to the present invention in the embodiment described in figure 3, was carried out in a melamine plant having a nominal capacity of 40,000 t/y (5,000 t/h), the make-up ammonia (stream **5**) was fed as reflux ammonia to the section **RA**, thus reducing the consumption of cooling water for the condensation of the part of ammonia vapour leaving the head of the section **RA**, necessary for the internal reflux of said section.

[0125] The other steps of the process were carried out as indicated in the previous example 2.

[0126] In addition to the reduction in the consumption of ammonia indicated in example 2 and the heat recovered in treating stream 9 in the section AA, which allowed a reduction of 450 kg/h in the quantity of saturated vapour used for

heating the ammonia solution (stream 16) according to example 2, the embodiment of the present example led to a reduction in the consumption of cooling water, with a temperature differential of 9°C, of 20 m³/h for a melamine plant having a nominal capacity of 40,000 t/y (5,000 t/h).

5 Example 4

[0127] A synthesis process according to the present invention in the embodiment described in figure 4, was carried out in a melamine plant having a nominal capacity of 40,000 t/y (5,000 t/h), stream 34 containing CO₂, ammonia and water, normally called side-stream, was recycled within the melamine plant to the washing section of anhydrous off-gases Q, instead of being sent to the urea plant.

[0128] In this way, the total quantity of H₂O leaving the melamine plant with the off-gases (stream 13) and with the side stream (stream 34), when these are discharged separately, was reduced.

[0129] The other steps of the process were carried out as indicated in the previous example 3.

[0130] By recycling stream 34 to the washing section of anhydrous off-gases Q, its water content was internally recovered at the melamine plant in stream 12, whereas the content of NH₃ and CO₂ was recycled to the urea plant with stream 13, containing all the off-gases generated in the reaction section R and in the post-reaction section PR and a water content of 18% by weight, corresponding to 2.75 t/h.

[0131] The stream of water (stream 29) substantially free of impurities, coming from the section EO, was sent to the cooling section RF, where it was cooled to be used as make-up water.

[0132] When stream 34 was entirely recycled within the melamine plant, together with said stream 29, the water content which had to be reintegrated at the melamine plant with stream 32, proved to be equal to the water content of the stream of off-gases 13.

[0133] In addition to the reduction in the consumption of ammonia, indicated in example 2, the heat recovered in treating stream 9 in the section AA, which allowed a reduction equal to 450 kg/h of the quantity of saturated vapour used for heating the ammonia solution (stream 16) again according to example 2, a reduction in the consumption of cooling water, with a differential of temperature of 9°C, of 20 m³/h for a melamine plant having a nominal capacity of 40,000 t/y (5,000 t/h), according to example 3, the embodiment of the present example allowed a reduction in the flow-rate of stream 32 by an amount equal to the quantity of water contained in stream 34 (1.6 t/h) and the quantity of water contained in stream 29 (11 t/h), obtaining a plant for the production of melamine completely free of liquid discharges.

Claims

1. A process for the production of melamine by the pyrolysis of urea which comprises the following steps:

a) producing melamine by the pyrolysis of urea in a specific reactor (R) and separating a biphasic liquid/gas effluent produced in the pyrolysis reaction of urea into a liquid stream of raw melamine (6) and into a first stream of anhydrous off-gases comprising NH₃, CO₂ and melamine vapour (7);

b) putting said liquid stream of raw melamine (6) in contact with a stream of anhydrous gaseous NH₃ (4) in a specific post-reactor (PR) and forming a liquid stream of melamine impoverished in CO₂ and partially purified (8) and a second stream of anhydrous gases comprising NH₃, CO₂ and melamine vapour (9);

c) putting the first stream of anhydrous gases (7) coming from step a) in contact with at least one aqueous washing stream (11), forming an aqueous stream (12), comprising melamine, NH₃, CO₂ and a gaseous stream of wet off-gases (13), comprising NH₃, CO₂ and water vapour;

d) mixing the second stream of anhydrous gases (9) coming from step b) with a stream of recycled water (17) and forming an aqueous ammonia solution (16) in which the melamine contained in the stream of anhydrous gases (9) is dissolved, recovering the sensible heat and condensation heat of the gases;

e) removing, from the aqueous stream (12) of step c), comprising melamine, NH₃, CO₂, at least a part of the CO₂ contained therein and forming a gaseous stream comprising the CO₂ removed (14) and an aqueous stream (15) comprising melamine, NH₃ and impoverished in CO₂;

f) subjecting the liquid stream of melamine impoverished in CO₂ and partially purified (8), coming from the post-reactor, to a quench-ammonolysis treatment by contact with the aqueous ammonia solution (16) obtained in step d), and the formation of an aqueous ammonia stream (20) comprising purified melamine;

g) recovering the melamine contained in the aqueous ammonia stream (20) comprising purified melamine coming from step f) and the melamine contained in said aqueous stream (15) comprising melamine and impoverished in CO₂ coming from step (e) by means of a crystallization step by cooling and separation, with the formation of a stream of crystallized melamine (31) and a stream of mother liquor (24).

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2. The process according to claim 1, wherein, in step d), the second stream of anhydrous gases (9) coming from step b) is mixed with the stream of recycled water (17) and with a stream (19) obtained by joining a make-up ammonia stream (5) and a stream of recycled ammonia (18) forming the aqueous ammonia solution (16).
- 5 3. The process according to claim 1, comprising feeding a make-up ammonia stream (5) to a subsequent deammoniation treatment of the portion of mother liquor stream (24) not directly recycled, stream (26).
- 10 4. The process according to claim 1, **characterized in that** at least a part of said mother liquor stream (24) obtained in step g) is used as aqueous stream (25) in the quench-ammonolysis treatment of said liquid melamine stream (8) impoverished in CO₂ and partially purified.
- 15 5. The process according to one or more of claims 3 and 4, **characterized in that** at least a part of said mother liquor stream (24) obtained in step g) is subjected to deammoniation treatment, with the formation of a gaseous stream of NH₃ substantially free of CO₂ (18), a stream (27) comprising CO₂ and an aqueous stream (28) of deammoniated mother liquor.
- 20 6. The process according to the previous claim, **characterized in that** said stream (27) comprising CO₂, ammonia and water is joined with a further stream (33), containing H₂O, CO₂ and NH₃ and coming from a following step of decomposition of the stream (28) to form a single stream (34) and recycled to a production plant of urea directly or after treatment which reduces its water content or said stream (27) containing CO₂, ammonia and water, is sent to the washing step c) of the anhydrous off-gases (7).
- 25 7. The process according to claim 5, **characterized in that** said aqueous stream (28) of deammoniated mother liquor is subjected to a decomposition treatment with the recovery of NH₃ and CO₂, and the production of an aqueous stream (30) which is partly recycled as aqueous washing stream (11) to said step c) and partly recycled as aqueous stream (17) to contribute to forming said aqueous ammonia stream (16) fed to step f) for the quench-ammonolysis treatment and a stream (33) containing H₂O, CO₂ and NH₃ that is joined with the stream (27) comprising CO₂, ammonia and water, coming from the deammoniation treatment.
- 30 8. The process according to claim 5, **characterized in that** said gaseous stream (18, 19) of NH₃ substantially free of CO₂, coming from the deammoniation treatment, is mixed with a part of said aqueous stream (17), to recover its condensation heat in step d).
- 35 9. The process according to one or more of the previous claims, **characterized in that** said aqueous stream (15) comprising melamine, NH₃ and impoverished in CO₂ coming from step e), is joined with said aqueous ammonia stream (20) comprising purified melamine, with the formation of a single stream (21) to be subjected to said step g).
- 40 10. The process according to one or more of the previous claims, **characterized in that** in step e), the removal of CO₂ from said aqueous stream (12) comprising melamine, NH₃ and CO₂ is effected by depressurization or by means of stripping.
- 45 11. The process according to one or more of the previous claims, **characterized in that** said stream (14) comprising removed CO₂, obtained in step e), is recycled in a step of the same process following said step g) for the recovery of melamine through crystallization by cooling and separation.
- 50 12. The process according to one or more of the previous claims, **characterized in that** said stream of wet off-gases (13), coming from step c), comprising NH₃, CO₂ and water vapour, is recycled to a plant for the production of urea, as such or after being subjected to a condensation treatment by absorption in aqueous solution or another type of treatment.
- 55 13. The process according to claim 5, **characterized in that** said aqueous stream (28) of deammoniated mother liquor is separated into:
 - i) an aqueous stream enriched in melamine which is partly recycled as aqueous washing stream (11) to said step c) and partly recycled as aqueous stream (17) to contribute to forming said aqueous ammonia stream (16) fed to step f) for the quench-ammonolysis treatment;
 - ii) an aqueous stream enriched in OATs, suitable for being decomposed with the recovery of NH₃ and CO₂.

14. A plant for the implementation of a process for the production of melamine by the pyrolysis of urea according to any of the claims from 1 to 13, comprising:

5 i) a separation section for separating a biphasic liquid/gas effluent produced in a pyrolysis reaction of urea into a liquid stream of raw melamine (6) and a first stream of anhydrous off-gases comprising NH₃, CO₂ and melamine steam (7), said separation section being connected to a reaction section (R) for the pyrolysis of urea from which it receives said biphasic liquid/gas effluent, said separation section being inside or outside said reaction section (R);

10 ii) a stripping section or post-reactor (PR) for putting said liquid stream of raw melamine (6) coming from said reaction section (R) in contact with a stream of anhydrous gaseous NH₃ (4) and forming a liquid stream of melamine impoverished in CO₂ and partially purified (8) and a second stream of anhydrous gases comprising NH₃, CO₂ and melamine steam (9), said stripping section (PR) being connected to said reaction section (R) from which it receives said liquid stream of raw melamine (6);

15 iii) a washing section (Q) for putting said first stream of anhydrous off-gases (7) in contact with an aqueous washing stream (11) and forming an aqueous stream comprising melamine, NH₃, CO₂ (12) and a stream of wet off-gases comprising NH₃, CO₂ and water vapour (13), said washing section (Q) being connected to said separation section from which it receives said first stream of anhydrous off-gases (7);

20 iv) a removal section of the CO₂ (STR) for removing from said aqueous stream comprising melamine, NH₃, CO₂ (12), at least a part of the CO₂ contained therein and comprising the CO₂ removed (14) and an aqueous stream (15), comprising melamine, NH₃ and impoverished in CO₂, said removal section of the CO₂ (STR) being connected to said washing section (Q) from which it receives said aqueous stream (12), comprising melamine, NH₃, CO₂;

25 v) a mixing and heat recovery section (AA) for mixing said second stream of anhydrous gases (9) with a stream of recycled water (17) and forming an aqueous ammonia solution (16) in which the melamine contained in the stream of anhydrous off-gases (9) is dissolved, and for recovering both the sensible heat and the condensation heat of the gases, by absorption of the ammonia, said mixing and heat recovery section (AA) being connected to the stripping section or post-reactor (PR) from which it receives said second stream of anhydrous gases (9) and said quench-ammonolysis section (QAL) to which the aqueous ammonia solution (16) is fed;

30 vi) a quench-ammonolysis section (QAL) for subjecting the liquid stream of melamine impoverished in CO₂ and partially purified (8), coming from the post-reactor (PR), to a quench-ammonolysis treatment by contact with the aqueous ammonia solution (16) coming from the mixing and heat recovery section (AA), and forming an aqueous ammonia stream (20), comprising purified melamine, said quench-ammonolysis section (QAL) being connected to said stripping section or post-reactor (PR) from which it receives said liquid stream of melamine impoverished in CO₂ and partially purified (8);

35 vii) at least one recovery section of the melamine (CR, SLS) for recovering both the melamine contained in said aqueous ammonia stream comprising purified melamine (20) and also the melamine contained in said aqueous stream comprising melamine, NH₃ and impoverished in CO₂ (15) through crystallization by cooling and separation, with the formation of a stream of crystallized melamine and a stream of mother liquor, said recovery section of the melamine (CR, SLS) being connected to both said quench-ammonolysis section (QAL) from which it receives the aqueous ammonia stream comprising purified melamine (20) and to said removal section of the CO₂ (STR) from which it receives said aqueous stream comprising melamine, NH₃ and impoverished in CO₂ (15).

45 Patentansprüche

1. Verfahren zur Herstellung von Melamin durch die Pyrolyse von Harnstoff, das folgende Schritte umfasst:

50 a) Herstellen von Melamin durch die Pyrolyse von Harnstoff in einem spezifischen Reaktor (R) und Trennen eines zweiphasigen Flüssig/Gas-Abflusses, der bei der Pyrolyse von Harnstoff erzeugt wird, in einen flüssigen Strom von Rohmelamin (6) und in einen ersten Strom von wasserfreien Abgasen, der NH₃, CO₂ und Melamindampf (7) umfasst;

55 b) Inkontaktbringen des flüssigen Stroms von Rohmelamin (6) mit einem Strom von wasserfreiem gasförmigem NH₃ (4) in einem spezifischen Nachreaktor (PR) und Bilden eines flüssigen Stroms von Melamin, der an CO₂ angereichert und teilweise gereinigt ist (8), und eines zweiten Stroms von wasserfreien Gasen, der NH₃, CO₂ und Melamindampf umfasst (9);

c) Inkontaktbringen des ersten Stroms wasserfreier Gase (7), der aus Schritt a) kommt, mit mindestens einem wässrigen Waschstrom (11) unter Bildung eines wässrigen Stroms (12), der Melamin, NH₃, CO₂ umfasst, und

eines gasförmigen Stroms feuchter Abgase (13), der NH₃, CO₂ und Wasserdampf umfasst;
 d) Mischen des zweiten Stroms wasserfreier Gase (9), der aus Schritt b) kommt, mit einem Strom von rückgeführten Wasser (17) und Bilden einer wässrigen Ammoniaklösung (16), in der das in dem Strom wasserfreier Gase (9) enthaltene Melamin gelöst wird, wobei die fühlbare Wärme und die Kondensationswärme der Gase zurückgewonnen wird;

e) Entfernen aus dem wässrigen Strom (12) von Schritt c), der Melamin, NH₃, CO₂ umfasst, von mindestens einen Teil des darin enthaltenen CO₂ und Bilden eines gasförmigen Stroms, der das entfernte CO₂ umfasst (14), und eines wässrigen Stroms (15), der Melamin, NH₃ umfasst und an CO₂ abgereichert ist;

f) Unterziehen des aus dem Nachreaktor kommenden, flüssigen, an CO₂ abgereicherten und teilweise gereinigten Melaminstroms (8) einer Quench-Ammonolyse-Behandlung durch Kontakt mit der in Schritt d) erhaltenen wässrigen Ammoniaklösung (16) und Bilden eines wässrigen Ammoniakstroms (20), der gereinigtes Melamin umfasst;

g) Rückgewinnung des Melamins, das in dem wässrigen Ammoniakstrom (20) enthalten ist, der gereinigtes Melamin umfasst, der aus Schritt f) kommt, und des Melamins, das in dem wässrigen Strom (15) enthalten ist, der Melamin umfasst und an CO₂ abgereichert ist, der aus Schritt (e) kommt, mittels eines Kristallisationsschritts durch Abkühlen und Trennen unter Bildung eines Stroms von kristallisiertem Melamin (31) und eines Mutterlaugestroms (24).

2. Verfahren gemäß Anspruch 1, wobei in Schritt d) der zweite Strom von wasserfreien Gasen (9), der aus Schritt b) kommt, mit dem Strom von rückgeführten Wasser (17) und mit einem Strom (19) gemischt wird, der durch Vereinigen eines Ammoniak-Zusatzstroms (5) und eines Stroms von rückgeführten Ammoniak (18), die die wässrige Ammoniaklösung (16) bilden, erhalten wird.

3. Verfahren gemäß Anspruch 1, umfassend das Zuführen eines Ammoniak-Zusatzstromes (5) zu einer nachfolgenden Deammonisierungsbehandlung des nicht direkt rückgeführten Anteils des Mutterlaugestromes (24), Strom (26).

4. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** mindestens ein Teil des in Schritt g) erhaltenen Mutterlaugestroms (24) als wässriger Strom (25) bei der Quench-Ammonolyse-Behandlung des flüssigen Melaminstroms (8), der an CO₂ abgereichert und teilweise gereinigt ist, verwendet wird.

5. Verfahren gemäß einem oder mehreren der Ansprüche 3 und 4, **dadurch gekennzeichnet, dass** mindestens ein Teil des in Schritt g) erhaltenen Mutterlaugestroms (24) einer Deammonisierungsbehandlung unterzogen wird, wobei ein gasförmiger NH₃-Strom, der im Wesentlichen frei von CO₂ (18) ist, ein Strom (27), der CO₂ umfasst, und ein wässriger Strom (28) deammonisierter Mutterlauge gebildet werden.

6. Verfahren gemäß dem vorhergehenden Anspruch, **dadurch gekennzeichnet, dass** der CO₂, Ammoniak und Wasser umfassende Strom (27) mit einem weiteren Strom (33) vereinigt wird, der H₂O, CO₂ und NH₃ enthält und aus einem folgenden Schritt der Zersetzung des Stroms (28) kommt, um einen einzigen Strom (34) zu bilden, und direkt oder nach einer Behandlung, die seinen Wassergehalt verringert, zu einer Produktionsanlage für Harnstoff rückgeführt wird, oder der CO₂, Ammoniak und Wasser enthaltende Strom (27) dem Waschschrift c) der wasserfreien Abgase (7) zugeführt wird.

7. Verfahren gemäß Anspruch 5, **dadurch gekennzeichnet, dass** der wässrige Strom (28) der deammonisierten Mutterlauge einer Zersetzungsbehandlung unterzogen wird, mit Rückgewinnung von NH₃ und CO₂, und Herstellung eines wässrigen Stroms (30), der teilweise als wässriger Waschstrom (11) zu Schritt c) und teilweise als wässriger Strom (17) rückgeführt wird, um zur Bildung des wässrigen Ammoniakstroms (16) beizutragen, der Schritt f) für die Quench-Ammonolyse-Behandlung zugeführt wird, und eines Stroms (33), der H₂O, CO₂ und NH₃ enthält, der mit dem Strom (27) vereinigt wird, der CO₂, Ammoniak und Wasser umfasst und aus der Deammonisierungsbehandlung kommt.

8. Verfahren gemäß Anspruch 5, **dadurch gekennzeichnet, dass** der gasförmige NH₃-Strom (18, 19), der im Wesentlichen frei von CO₂ ist, der aus der Deammonisierungsbehandlung kommt, mit einem Teil des wässrigen Stroms (17) gemischt wird, um seine Kondensationswärme in Schritt d) zurückzugewinnen.

9. Verfahren gemäß einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der wässrige Strom (15), der Melamin, NH₃ umfasst und an CO₂ abgereichert ist, der aus Schritt e) kommt, mit dem wässrigen Ammoniakstrom (20), der gereinigtes Melamin umfasst, unter Bildung eines einzelnen Stroms (21), der dem Schritt g) zu unterziehen ist, vereinigt wird.

10. Verfahren gemäß einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** in Schritt e) die Entfernung von CO₂ aus dem wässrigen Strom (12), der Melamin, NH₃ und CO₂ umfasst, durch Druckabbau oder durch Strippen erfolgt.
- 5 11. Verfahren gemäß einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der in Schritt e) erhaltene Strom (14), der entferntes CO₂ umfasst, in einem Schritt desselben Verfahrens nach Schritt g) zur Gewinnung von Melamin durch Kristallisation durch Abkühlen und Trennen rückgeführt wird.
- 10 12. Verfahren gemäß einem oder mehreren der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Strom von feuchten Abgasen (13), der aus Schritt c) kommt, der NH₃, CO₂ und Wasserdampf umfasst, zu einer Anlage zur Herstellung von Harnstoff als solchem oder nach Unterziehen einer Kondensationsbehandlung durch Absorption in wässriger Lösung oder einer anderen Art von Behandlung rückgeführt wird.
- 15 13. Verfahren gemäß Anspruch 5, **dadurch gekennzeichnet, dass** der wässrige Strom (28) der deammonisierten Mutterlauge in Folgendes getrennt wird:
- 20 i) einen mit Melamin angereicherten wässrigen Strom, der teilweise als wässriger Waschstrom (11) zum Schritt c) rückgeführt wird und teilweise als wässriger Strom (17) rückgeführt wird, um zur Bildung des wässrigen Ammoniakstroms (16) beizutragen, der Schritt f) für die Quench-Ammonolyse-Behandlung zugeführt wird;
- 20 ii) einen wässrigen Strom, der mit OAT angereichert ist, der geeignet ist, mit der Rückgewinnung von NH₃ und CO₂ zersetzt zu werden.
- 25 14. Anlage für die Durchführung eines Verfahrens zur Herstellung von Melamin durch Pyrolyse von Harnstoff gemäß einem der Ansprüche 1 bis 13, Folgendes umfassend:
- 30 i) einen Trennabschnitt zum Trennen eines zweiphasigen Flüssig/Gas-Abflusses, der bei einer Pyrolysereaktion von Harnstoff erzeugt wird, in einen flüssigen Strom von Rohmelamin (6) und einen ersten Strom von wasserfreien Abgasen, der NH₃, CO₂ und Melamindampf (7) umfasst, wobei der Trennabschnitt mit einem Reaktionsabschnitt (R) für die Pyrolyse von Harnstoff verbunden ist, aus dem er den zweiphasigen Flüssig/Gas-Abfluss erhält, wobei der Trennabschnitt innerhalb oder außerhalb des Reaktionsabschnitts (R) liegt;
- 35 ii) einen Stripp-Abschnitt oder Nachreaktor (PR), um den flüssigen Strom von Rohmelamin (6), der aus dem Reaktionsabschnitt (R) kommt, mit einem Strom von wasserfreiem gasförmigem NH₃ (4) in Kontakt zu bringen und einen flüssigen Melaminstrom, der an CO₂ abgereichert und teilweise gereinigt ist (8), und einen zweiten Strom von wasserfreien Gasen, der NH₃, CO₂ und Melamindampf umfasst (9), zu bilden, wobei der Stripp-Abschnitt (PR) mit dem Reaktionsabschnitt (R) verbunden ist, aus dem er den flüssigen Strom von Rohmelamin (6) erhält;
- 40 iii) einen Waschabschnitt (Q), um den ersten Strom wasserfreier Abgase (7) mit einem wässrigen Waschstrom (11) in Kontakt zu bringen und einen wässrigen Strom, der Melamin, NH₃, CO₂ (12) umfasst, und einen Strom feuchter Abgase, der NH₃, CO₂ und Wasserdampf (13) umfasst, zu bilden, wobei der Waschabschnitt (Q) mit dem Trennabschnitt verbunden ist, aus dem er den ersten Strom wasserfreier Abgase (7) erhält;
- 45 iv) einen Abschnitt zur Entfernung des CO₂ (STR), um aus dem wässrigen Strom, der Melamin, NH₃, CO₂ (12) umfasst, mindestens einen Teil des darin enthaltenen CO₂ zu entfernen, der das entfernte CO₂ (14) und einen wässrigen Strom (15) umfasst, der Melamin, NH₃ umfasst und an CO₂ abgereichert ist, wobei der Abschnitt zur Entfernung des CO₂ (STR) mit dem Waschabschnitt (Q) verbunden ist, aus dem er den wässrigen Strom (12) erhält, der Melamin, NH₃, CO₂ umfasst;
- 50 v) einen Misch- und Wärmerückgewinnungsabschnitt (AA) zum Mischen des zweiten Stroms von wasserfreien Gasen (9) mit einem Strom von rückgeführtem Wasser (17) und zum Bilden einer wässrigen Ammoniaklösung (16), in der das in dem Strom von wasserfreien Abgasen (9) enthaltene Melamin gelöst wird, und zum Rückgewinnen sowohl der fühlbaren Wärme als auch der Kondensationswärme der Gase, durch Absorption des Ammoniaks, wobei der Misch- und Wärmerückgewinnungsabschnitt (AA) mit dem Stripp-Abschnitt oder Nachreaktor (PR), aus dem er den zweiten Strom wasserfreier Gase (9) erhält, und dem Quench-Ammonolyse-Abschnitt (QAL) verbunden ist, dem die wässrige Ammoniaklösung (16) zugeführt wird;
- 55 vi) einen Quench-Ammonolyse-Abschnitt (QAL), um den aus dem Nachreaktor (PR) kommenden, flüssigen Melaminstrom, der an CO₂ abgereichert und teilweise gereinigt ist (8), einer Quench-Ammonolyse-Behandlung durch Kontakt mit der aus dem Misch- und Wärmerückgewinnungsabschnitt (AA) kommenden wässrigen Ammoniaklösung (16) zu unterziehen, und einen wässrigen Ammoniakstrom (20) zu bilden, der gereinigtes Melamin umfasst, wobei der Quench-Ammonolyse-Abschnitt (QAL) mit dem Stripp-Abschnitt oder Nachreaktor (PR) verbunden ist, aus dem er den flüssigen Melaminstrom erhält, der an CO₂ abgereichert und teilweise gereinigt

ist (8);

vii) mindestens einen Rückgewinnungsabschnitt des Melamins (CR, SLS) zur Rückgewinnung sowohl des Melamins, das in dem wässrigen Ammoniakstrom enthalten ist, der gereinigtes Melamin (20) umfasst, als auch des Melamins, das in dem wässrigen Strom enthalten ist, der Melamin, NH₃ umfasst und an CO₂ abgereichert ist (15), durch Kristallisation durch Abkühlen und Trennen unter Bildung eines Stroms von kristallisiertem Melamin und eines Mutterlaugenstroms, wobei der Rückgewinnungsabschnitt des Melamins (CR, SLS) sowohl mit dem Quench-Ammonolyse-Abschnitt (QAL), aus dem er den wässrigen Ammoniakstrom erhält, der gereinigtes Melamin (20) umfasst, als auch mit dem Abschnitt zur Entfernung des CO₂ (STR) verbunden ist, von dem er den wässrigen Strom erhält, der Melamin, NH₃ umfasst und an CO₂ abgereichert ist (15).

Revendications

1. Un procédé pour la production de mélamine par la pyrolyse d'urée qui comprend les étapes suivantes :

a) produire de la mélamine par la pyrolyse d'urée dans un réacteur spécifique (R) et séparer un effluent liquide/gaz biphasique produit dans la réaction de pyrolyse d'urée en un flux liquide de mélamine brute (6) et en un premier flux de gaz de dégagement anhydres comprenant du NH₃, du CO₂ et de la vapeur de mélamine (7) ;

b) mettre ledit flux liquide de mélamine brute (6) en contact avec un flux de NH₃ gazeux anhydre (4) dans un post-réacteur spécifique (PR) et former un flux liquide de mélamine appauvrie en CO₂ et partiellement purifiée (8) et un deuxième flux de gaz anhydres comprenant du NH₃, du CO₂ et de la vapeur de mélamine (9) ;

c) mettre le premier flux de gaz anhydres (7) venant de l'étape a) en contact avec au moins un flux de lavage aqueux (11), former un flux aqueux (12), comprenant de la mélamine, du NH₃, du CO₂ et un flux gazeux de gaz de dégagement (13), comprenant du NH₃, du CO₂ et de la vapeur d'eau ;

d) mélanger le deuxième flux de gaz anhydres (9) venant de l'étape b) avec un flux d'eau recyclée (17) et former une solution aqueuse d'ammoniaque (16) dans laquelle la mélamine contenue dans le flux de gaz anhydres (9) est dissoute, récupérer la chaleur sensible et la chaleur de condensation des gaz ;

e) retirer, du flux aqueux (12) de l'étape c), comprenant de la mélamine, du NH₃, du CO₂, au moins une partie du CO₂ contenu dans celui-ci et former un flux gazeux comprenant le CO₂ retiré (14) et un flux aqueux (15) comprenant de la mélamine, du NH₃ et appauvri en CO₂ ;

f) soumettre le flux liquide de mélamine appauvrie en CO₂ et partiellement purifiée (8), venant du post-réacteur, à un traitement par trempe-ammonolyse par contact avec la solution aqueuse d'ammoniaque (16) obtenue à l'étape d), et la formation d'un flux aqueux d'ammoniaque (20) comprenant de la mélamine purifiée ;

g) récupérer la mélamine contenue dans le flux aqueux d'ammoniaque (20) comprenant de la mélamine purifiée venant de l'étape f) et la mélamine contenue dans ledit flux aqueux (15) comprenant de la mélamine et appauvri en CO₂ venant de l'étape (e) au moyen d'une étape de cristallisation par refroidissement et séparation, avec formation d'un flux de mélamine cristallisée (31) et d'un flux de liqueur mère (24).

2. Le procédé selon la revendication 1, où, à l'étape d), le deuxième flux de gaz anhydres (9) venant de l'étape b) est mélangé avec le flux d'eau recyclée (17) et avec un flux (19) obtenu en joignant un flux d'ammoniaque d'appoint (5) et un flux d'ammoniaque recyclée (18) formant la solution aqueuse d'ammoniaque (16).

3. Le procédé selon la revendication 1, comprenant le fait d'alimenter en un flux d'ammoniaque d'appoint (5) un traitement par déammoniation ultérieur de la portion du flux de liqueur mère (24) non directement recyclée, flux (26).

4. Le procédé selon la revendication 1, **caractérisé en ce qu'**au moins une partie dudit flux de liqueur mère (24) obtenu à l'étape g) est utilisée en tant que flux aqueux (25) dans le traitement par trempe-ammonolyse dudit flux de mélamine liquide (8) appauvrie en CO₂ et partiellement purifiée.

5. Le procédé selon une ou plusieurs des revendications 3 et 4, **caractérisé en ce qu'**au moins une partie dudit flux de liqueur mère (24) obtenu à l'étape g) est soumise à un traitement par déammoniation, avec formation d'un flux gazeux de NH₃ substantiellement exempt de CO₂ (18), d'un flux (27) comprenant du CO₂ et d'un flux aqueux (28) de liqueur mère déammoniaquée.

6. Le procédé selon la revendication précédente, **caractérisé en ce que** ledit flux (27) comprenant du CO₂, de l'ammoniaque et de l'eau est joint à un autre flux (33), contenant du H₂O, du CO₂ et du NH₃ et venant d'une étape suivante de décomposition du flux (28) pour former un flux unique (34) et recyclé vers une installation de production d'urée directement ou après traitement qui réduit sa teneur en eau ou ledit flux (27) contenant du CO₂, de l'ammo-

niaque et de l'eau, est envoyé à l'étape de lavage c) des gaz de dégagement anhydres (7).

- 5 7. Le procédé selon la revendication 5, **caractérisé en ce que** ledit flux aqueux (28) de liqueur mère déammoniaquée est soumis à un traitement par décomposition avec récupération de NH₃ et de CO₂, et la production d'un flux aqueux (30) qui est partiellement recyclé en tant que flux de lavage aqueux (11) à ladite étape c) et partiellement recyclé en tant que flux aqueux (17) pour contribuer à la formation dudit flux aqueux d'ammoniaque (16) alimenté à l'étape f) pour le traitement par trempé-ammonolyse et un flux (33) contenant du H₂O, du CO₂ et du NH₃ qui est joint au flux (27) comprenant du CO₂, de l'ammoniaque et de l'eau, venant du traitement par déammoniation.
- 10 8. Le procédé selon la revendication 5, **caractérisé en ce que** ledit flux gazeux (18, 19) de NH₃ substantiellement exempt de CO₂, venant du traitement par déammoniation, est mélangé avec une partie dudit flux aqueux (17), pour récupérer sa chaleur de condensation à l'étape d).
- 15 9. Le procédé selon une ou plusieurs des revendications précédentes, **caractérisé en ce que** ledit flux aqueux (15) comprend de la mélamine, du NH₃ et appauvri en CO₂ venant de l'étape e), est joint audit flux aqueux d'ammoniaque (20) comprenant de la mélamine purifiée, avec formation d'un flux unique (21) à soumettre à ladite étape g).
- 20 10. Le procédé selon une ou plusieurs des revendications précédentes, **caractérisé en ce qu'**à l'étape e), le retrait du CO₂ dudit flux aqueux (12) comprenant de la mélamine, du NH₃ et du CO₂ est effectué par dépressurisation ou au moyen d'une revaporisation.
- 25 11. Le procédé selon une ou plusieurs des revendications précédentes, **caractérisé en ce que** ledit flux (14) comprenant du CO₂ retiré, obtenu à l'étape e), est recyclé à une étape du même procédé suivant ladite étape g) pour la récupération de mélamine par le biais d'une cristallisation par refroidissement et séparation.
- 30 12. Le procédé selon une ou plusieurs des revendications précédentes, **caractérisé en ce que** ledit flux de gaz de dégagement humides (13), venant de l'étape c), comprenant du NH₃, du CO₂ et de la vapeur d'eau, est recyclé vers une installation pour la production d'urée, en tant que tel ou après avoir été soumis à un traitement de condensation par absorption en solution aqueuse ou un autre type de traitement.
- 35 13. Le procédé selon la revendication 5, **caractérisé en ce que** ledit flux aqueux (28) de liqueur mère déammoniaquée est séparé en :
- 40 i) un flux aqueux enrichi en mélamine qui est partiellement recyclé en tant que flux de lavage aqueux (11) à ladite étape c) et partiellement recyclé en tant que flux aqueux (17) pour contribuer à la formation dudit flux aqueux d'ammoniaque (16) alimenté à l'étape f) pour le traitement par trempé-ammonolyse ;
- 45 ii) un flux aqueux enrichi en OAT, approprié pour être décomposé avec la récupération de NH₃ et de CO₂.
- 50 14. Une installation pour la mise en œuvre d'un procédé pour la production de mélamine par la pyrolyse d'urée selon l'une quelconque des revendications de 1 à 13, comprenant :
- 55 i) une section de séparation pour séparer un effluent liquide/gaz biphasique produit dans une réaction de pyrolyse d'urée en un flux liquide de mélamine brute (6) et un premier flux de gaz de dégagement anhydres comprenant du NH₃, du CO₂ et de la vapeur de mélamine (7), ladite section de séparation étant raccordée à une section de réaction (R) pour la pyrolyse d'urée à partir de laquelle elle reçoit ledit effluent liquide/gaz biphasique, ladite section de séparation étant à l'intérieur ou à l'extérieur de ladite section de réaction (R) ;
- ii) une section de revaporisation ou un post-réacteur (PR) pour mettre ledit flux liquide de mélamine brute (6) venant de ladite section de réaction (R) en contact avec un flux de NH₃ gazeux anhydre (4) et former un flux liquide de mélamine appauvrie en CO₂ et partiellement purifiée (8) et un deuxième flux de gaz anhydres comprenant du NH₃, du CO₂ et de la vapeur de mélamine (9), ladite section de revaporisation (PR) étant jointe à ladite section de réaction (R) à partir de laquelle elle reçoit ledit flux liquide de mélamine brute (6) ;
- iii) une section de lavage (Q) pour mettre ledit premier flux de gaz de dégagement anhydres (7) en contact avec un flux de lavage aqueux (11) et former un flux aqueux comprenant de la mélamine, du NH₃, du CO₂ (12) et un flux de gaz de dégagement humides comprenant du NH₃, du CO₂ et de la vapeur d'eau (13), ladite section de lavage (Q) étant raccordée à ladite section de séparation à partir de laquelle elle reçoit ledit premier flux de gaz de dégagement anhydres (7) ;
- iv) une section de retrait du CO₂ (STR) pour retirer dudit flux aqueux comprenant de la mélamine, du NH₃, du CO₂ (12), au moins une partie du CO₂ contenu dans celle-ci et comprenant le CO₂ retiré (14) et un flux aqueux

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(15), comprenant de la mélamine, du NH₃ et appauvri en CO₂, ladite section de retrait du CO₂ (STR) étant raccordée à ladite section de lavage (Q) à partir de laquelle elle reçoit ledit flux aqueux (12), comprenant de la mélamine, du NH₃, du CO₂ ;

5 v) une section de mélange et de récupération de chaleur (AA) pour mélanger ledit deuxième flux de gaz anhydres (9) avec un flux d'eau recyclée (17) et former une solution aqueuse d'ammoniaque (16) dans laquelle la mélamine contenue dans le flux de gaz de dégagement anhydres (9) est dissoute, et pour récupérer à la fois la chaleur sensible et la chaleur de condensation des gaz, par absorption de l'ammoniaque, ladite section de mélange et de récupération de chaleur (AA) étant raccordée à la section de revaporisation ou au post-réacteur (PR) à partir de laquelle/duquel elle reçoit ledit deuxième flux de gaz anhydres (9) et ladite section de trempe-ammonolyse (QAL) que la solution aqueuse d'ammoniaque (16) alimente ;

10 vi) une section de trempe-ammonolyse (QAL) pour soumettre le flux liquide de mélamine appauvrie en CO₂ et partiellement purifiée (8), venant du post-réacteur (PR), à un traitement par trempe-ammonolyse par contact avec la solution aqueuse d'ammoniaque (16) venant de la section de mélange et de récupération de chaleur (AA), et former un flux aqueux d'ammoniaque (20), comprenant de la mélamine purifiée, ladite section de trempe-ammonolyse (QAL) étant raccordée à ladite section de revaporisation ou au post-réacteur (PR) à partir de laquelle/duquel elle reçoit ledit flux liquide de mélamine appauvrie en CO₂ et partiellement purifiée (8) ;

15 vii) au moins une section de récupération de la mélamine (CR, SLS) pour récupérer à la fois la mélamine contenue dans ledit flux aqueux d'ammoniaque comprenant de la mélamine purifiée (20) et également la mélamine contenue dans ledit flux aqueux comprenant de la mélamine, du NH₃ et appauvri en CO₂ (15) par le biais d'une cristallisation par refroidissement et séparation, avec formation d'un flux de mélamine cristallisée et d'un flux de liqueur mère, ladite section de récupération de la mélamine (CR, SLS) étant raccordée à la fois à ladite section de trempe-ammonolyse (QAL) à partir de laquelle elle reçoit le flux aqueux d'ammoniaque comprenant de la mélamine purifiée (20) et à ladite section de retrait du CO₂ (STR) à partir de laquelle elle reçoit ledit flux aqueux comprenant de la mélamine, du NH₃ et appauvri en CO₂ (15).

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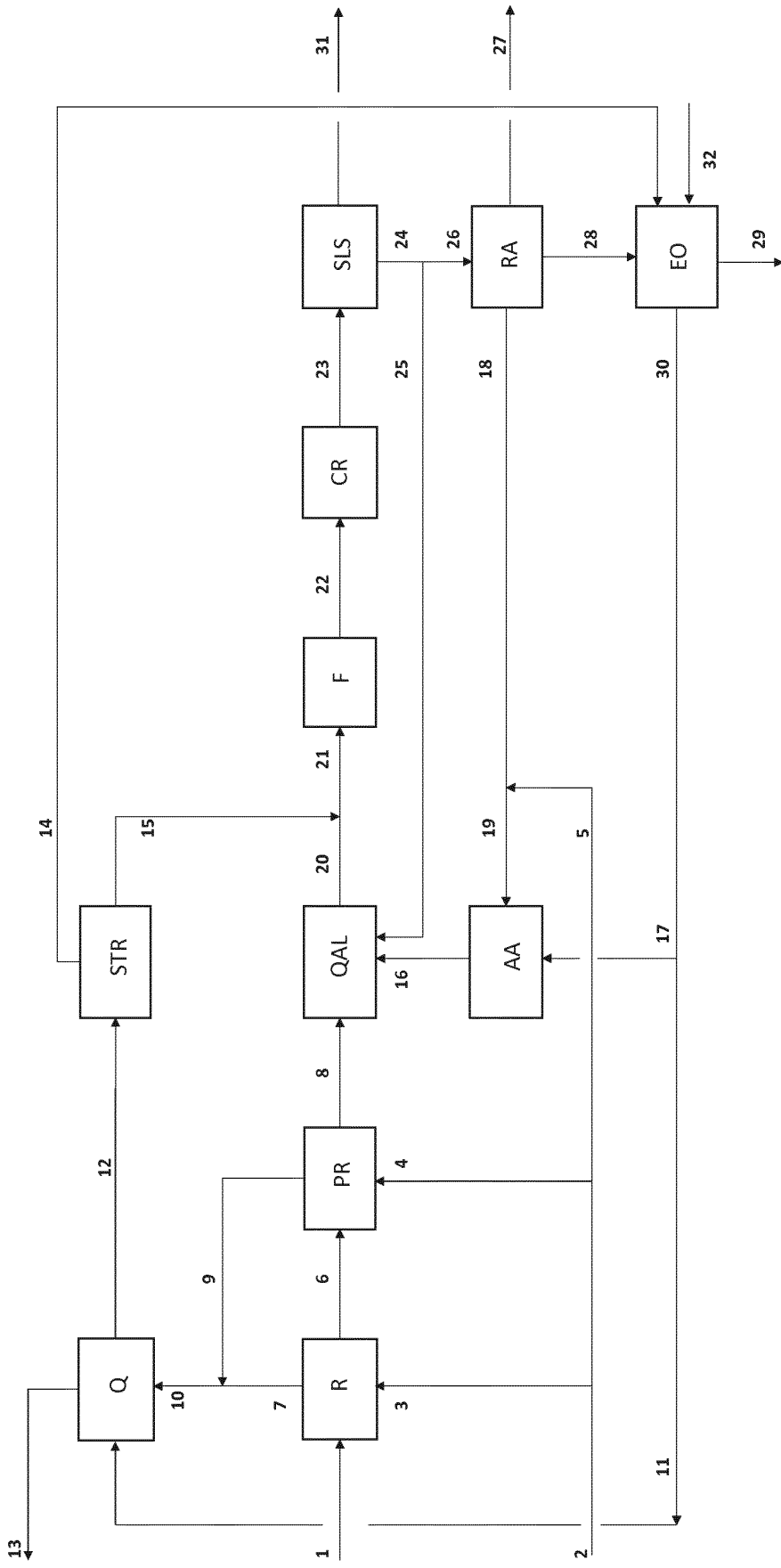


FIG. 1

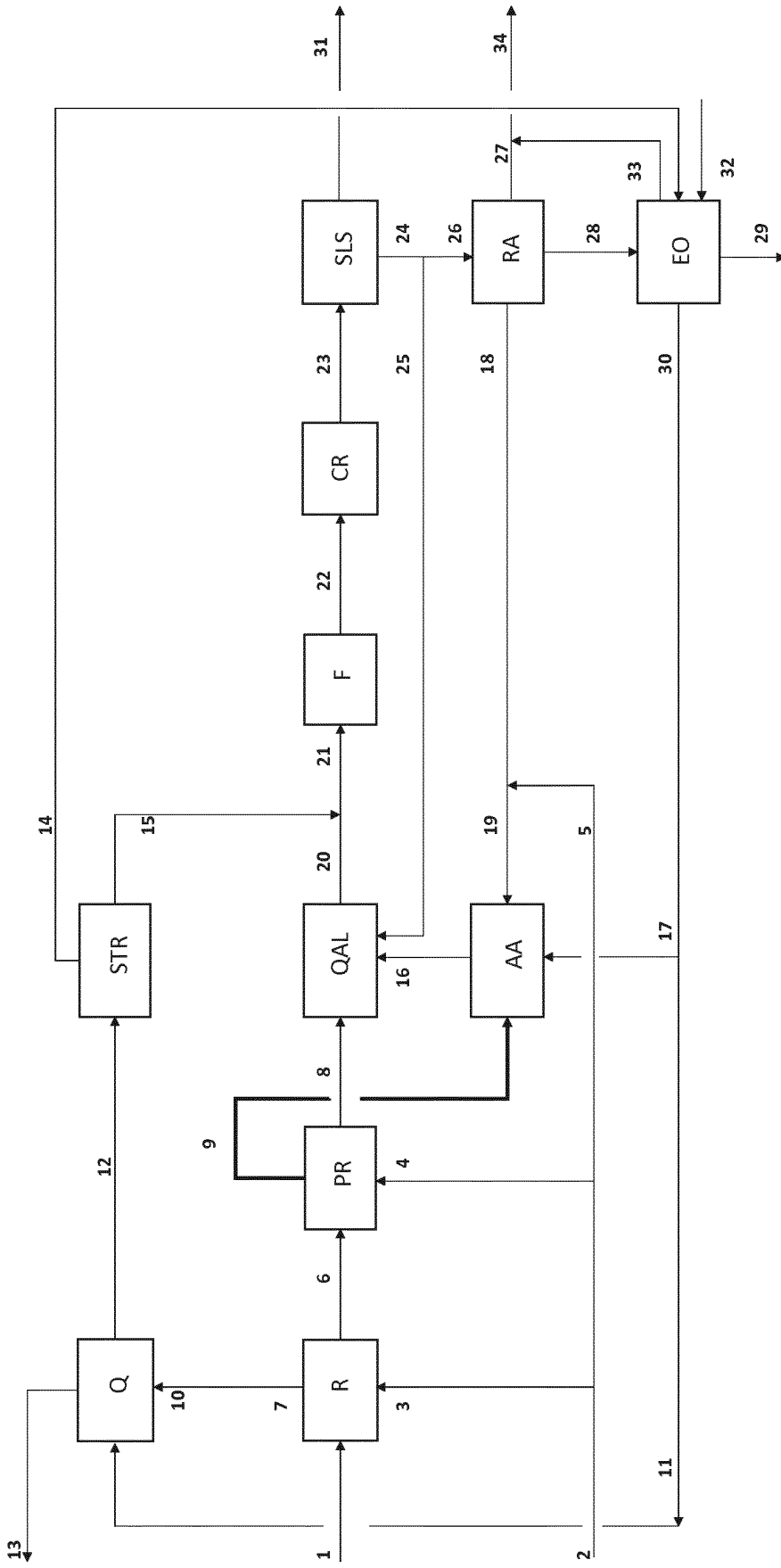


FIG. 2

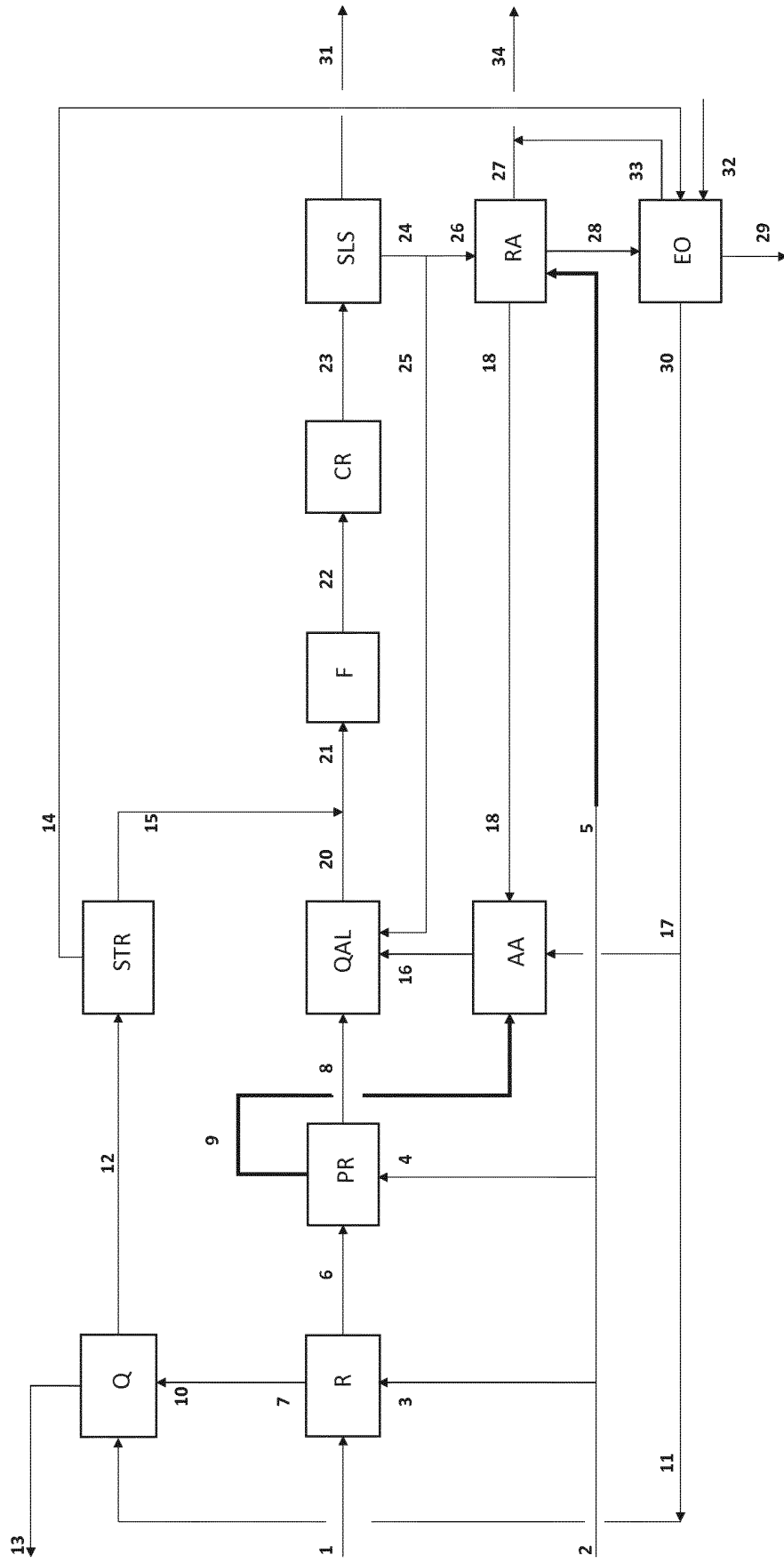


FIG. 3

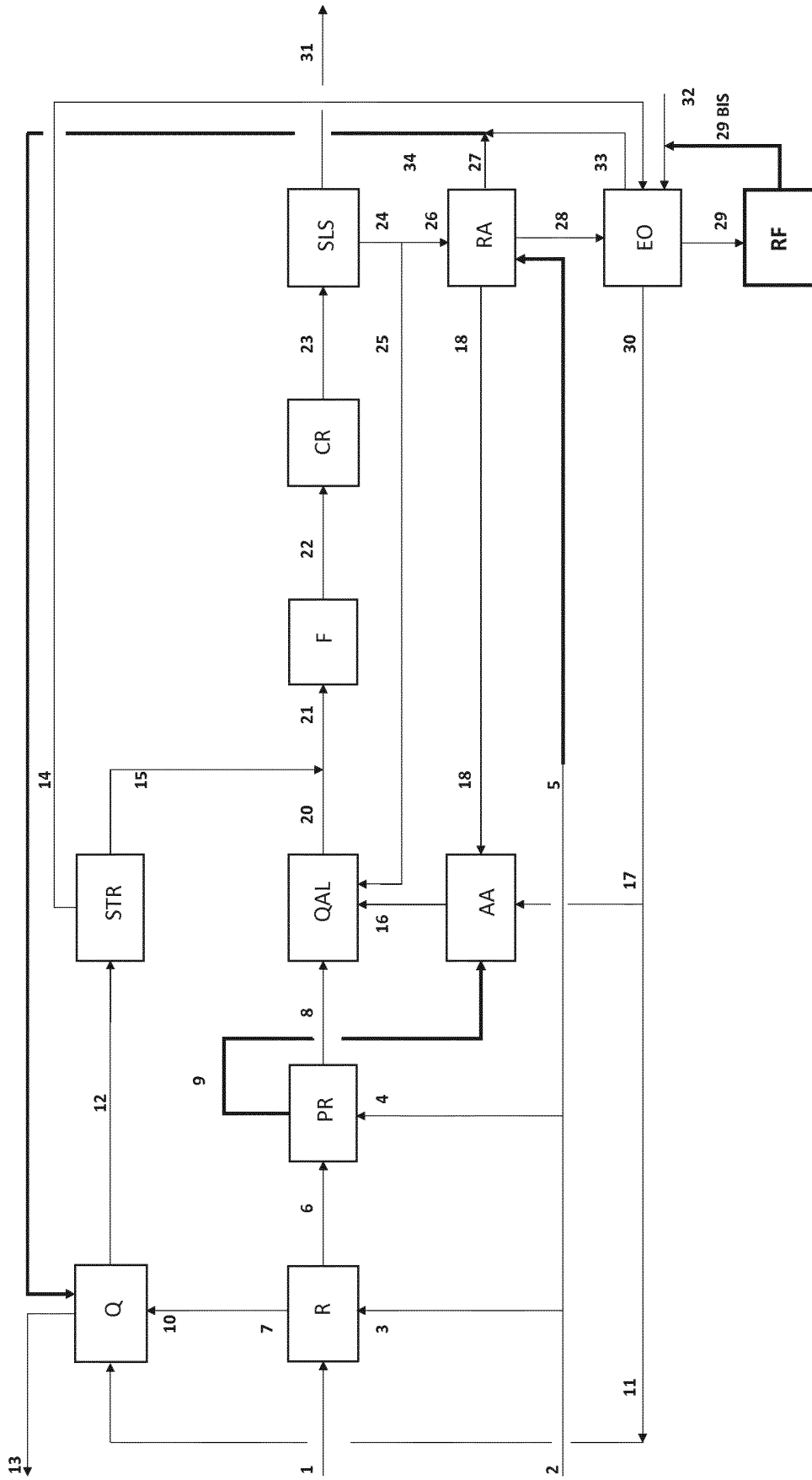


FIG. 4

REFERENCES CITED IN THE DESCRIPTION

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