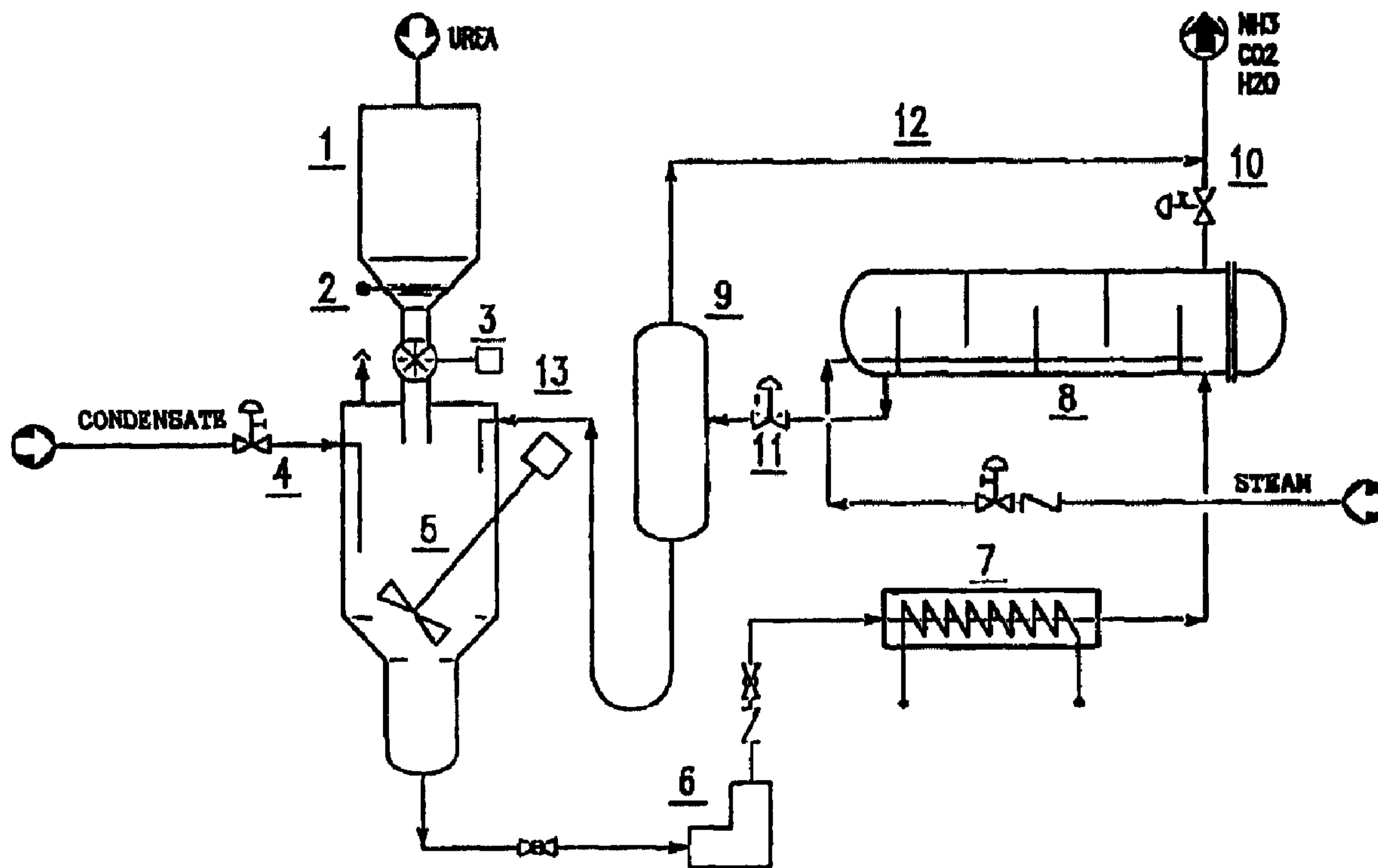




(86) Date de dépôt PCT/PCT Filing Date: 1999/05/14
 (87) Date publication PCT/PCT Publication Date: 1999/12/02
 (45) Date de délivrance/Issue Date: 2005/01/11
 (85) Entrée phase nationale/National Entry: 2000/11/03
 (86) N° demande PCT/PCT Application No.: IT 1999/000135
 (87) N° publication PCT/PCT Publication No.: 1999/061136
 (30) Priorité/Priority: 1998/05/25 (MI98A001155) IT

(51) Cl.Int.⁶/Int.Cl.⁶ B01D 53/56
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(54) Titre : PROCÉDE SERVANT A TRAITER DES GAZ DE COMBUSTION
 (54) Title: PROCESS FOR TREATING FLUE GAS



(57) Abrégé/Abstract:

Process for combustion flue gas conditioning, by injecting ammonia, in a very simple and viable way, in a stream of said combustion flue gas stream, characterized in that dissolved urea is hydrolyzed by heating under pressure to yield ammonia and carbon dioxide the hydrolysis product are stripped from the hydrolyzed solution by means of hot steam and injected into the flue gas stream while water coming out of the hydrolysed solution is reused to dissolve fresh urea to be fed to the plant.

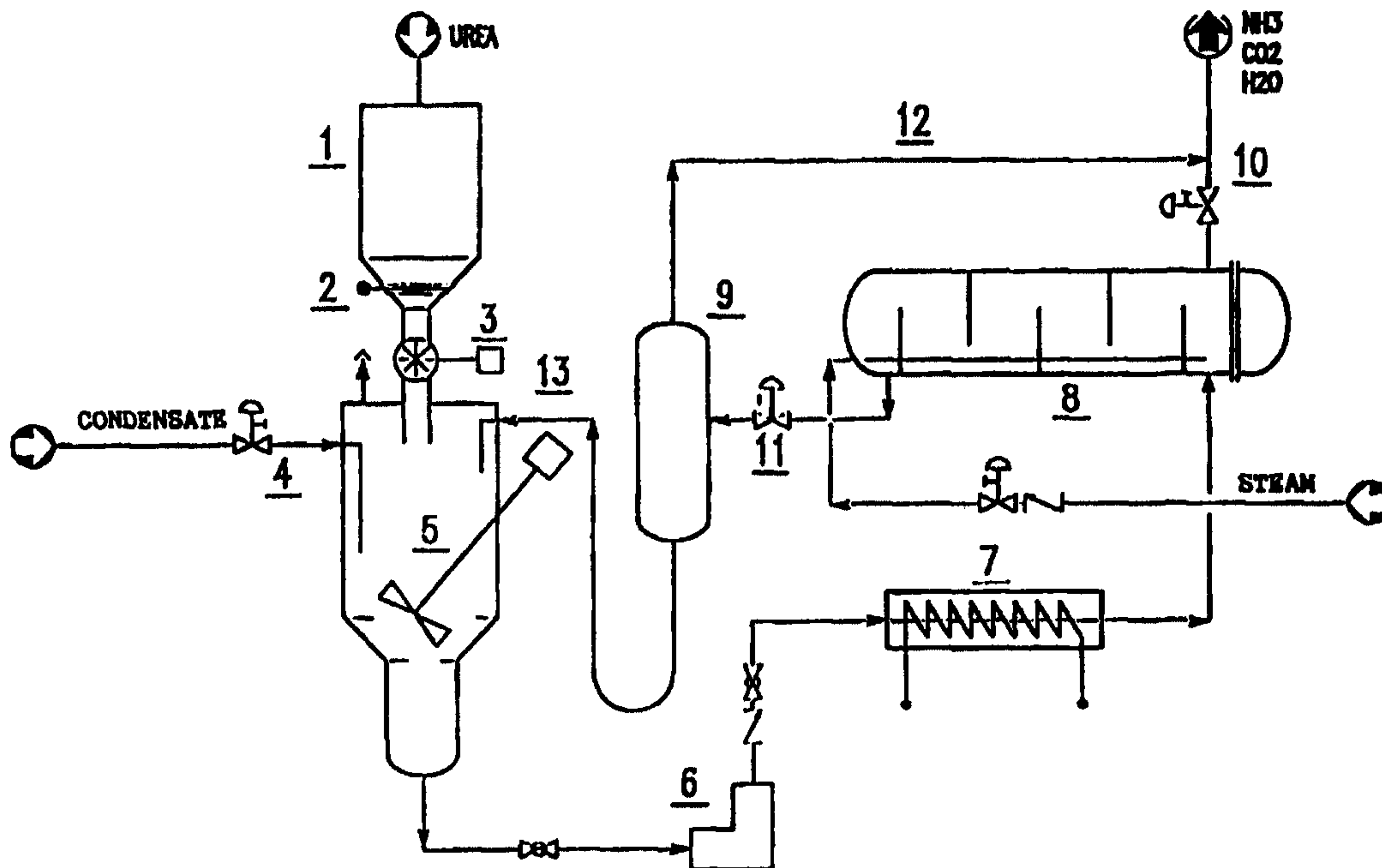
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WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01D 53/56	A1	(11) International Publication Number: WO 99/61136 (43) International Publication Date: 2 December 1999 (02.12.99)
<p>(21) International Application Number: PCT/IT99/00135</p> <p>(22) International Filing Date: 14 May 1999 (14.05.99)</p> <p>(30) Priority Data: MI98A001155 25 May 1998 (25.05.98) IT</p> <p>(71) Applicant (for all designated States except US): SI-IRTEC-NIGI S.P.A. [IT/IT]; Via Algardi, 2, I-20148 Milano (IT).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): LAGANA', Vincenzo [IT/IT]; Via Sismondi, 43, I-20133 Milano (IT).</p> <p>(74) Agent: CIONI, Carlo; Studio Cioni & Pipparelli, Viale Caldara, 38, I-20122 Milano (IT).</p>	<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	

(54) Title: PROCESS FOR TREATING FLUE GAS



(57) Abstract

Process for combustion flue gas conditioning, by injecting ammonia, in a very simple and viable way, in a stream of said combustion flue gas stream, characterized in that dissolved urea is hydrolyzed by heating under pressure to yield ammonia and carbon dioxide the hydrolysis product are stripped from the hydrolyzed solution by means of hot steam and injected into the flue gas stream while water coming out of the hydrolyzed solution is reused to dissolve fresh urea to be fed to the plant.

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PROCESS FOR TREATING FLUE GAS

Field of the invention

This invention refers to a process for treating flue gases and, more specifically, to a process for purifying (conditioning) such flue gases by ammonia addition. More particularly, this invention relates to a process for flue gas treatment by ammonia addition, whereby the ammonia is derived from hydrolysis of urea.

Description of prior art

It is well known to add ammonia to flue gases to remove, for instance, nitrogen oxides, which are formed in the course of combustion itself. Reaction between ammonia and nitrogen oxides, in the presence of oxygen, results in nitrogen and water formation in accordance with the following reaction:



Ammonia gas is injected into the flue gas stream to be treated by vapor obtained by stripping of the ammonia contained in an ammonia aqueous solution in which the ammonia concentration is roughly 30% by weight. The ammonia aqueous solution has to be transported from the production plant to the user plant, stored, sent to stripping plant to yield the desired ammonia, then the ammonia containing residual water has to be neutralized before its disposal.

Ammonia solutions are presently classified as toxic materials. Consequently, certain specific rules have to be followed for its handling, due to the high volatility and pollution level of ammonia.

In order to avoid the aforementioned problems, use of non-toxic, harmless compounds has been proposed which, under the reaction conditions, may yield ammonia. For this purpose, urea has been used to generate ammonia without the formation of any undesired by-product. Use of urea as conditioning agent of flue

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gases solved the problem connected with highly toxic material handling and storage; however, to obtain fine particles of solid urea and uniformly inject it into a flue gas stream still presents substantial problems.

In the US-520688 to Von Harpe, it has been also proposed to employ, as a source of ammonia, instead of solid urea, the products derived from the hydrolysis of urea. Such hydrolysis products are obtained by heating a urea solution. The overall hydrolysis products, namely ammonium carbonate, ammonium carbamate, ammonium bicarbonate and ammonia are used for NO_x reduction. However the simple heating of a concentrated urea solution does not allow to reach a satisfactory amount of hydrolysis products. The above Patent disclosed the use of a basic or acidic environment or addition of a catalyst. However the use of catalyst or acidic or basic products may lead to some problems due to the presence of said material both in the hydrolysis section and NO_x reduction section.

According to US-A-4168299 removal of urea hydrolysis products can be obtained by adsorbing pressurized CO₂ in a diluted urea solution then stripping-off the absorbed CO₂. This process employs a diluted urea solution and a source of a pressurized CO₂.

Summary of the invention

It is one object of the present invention to provide a process for flue gas conditioning by injection of ammonia, in a very simple and viable way, into a stream of said flue gases which avoids problems associated with hazardous material handling and storage.

It is a further object of the present invention to provide a process for *in-situ* production of gaseous ammonia, wherein said ammonia can be used without being subject to any particular safety rules and without any obligation to maintain, transport

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and store large volumes of ammonia solutions and toxic noxious material as required by conventional processes, nor to dispose any waste ammonia or ammonia precursor solution.

These and other objects of the present invention are achieved by a process for flue gas conditioning in which urea is dissolved in water to obtain a concentrated urea solution and the dissolved urea is hydrolyzed by heating the concentrated urea solution under pressure, yielding hydrolysis products of ammonia and carbon dioxide. The hydrolysis products are stripped from the solution using hot steam and injected into the flue gas stream while hydrolysis solution coming out of the stripping section, still containing some urea is reused in addition to fresh water, to dissolve fresh urea to be fed to the plant.

Urea solution to be hydrolyzed contains in the range of about 10% to 70% urea by weight. The urea hydrolysis is preferably carried out at a temperature in the range of about 100 to 233°C and a pressure in the range of about 0.1×10^3 KPa to 3.0×10^3 KPa. The hydrolysis solution, after stripping of the gaseous hydrolysis products still contains about 1% to 5% by weight of unhydrolyzed urea.

Brief description of the drawings

These and other objects and features of this invention will be better understood from the following detailed description taken in conjunction with the drawings wherein:

Fig. 1 is a schematic diagram of the process in accordance with one embodiment of this invention.

Description of preferred embodiments

This invention will now be described in more details with reference to Fig. 1 and the following experimental example. The drawing and example are provided to better illustrate the invention and are not to be construed as limiting of the scope thereof.

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As shown in Fig. 1, solid urea, in form of prills or crystals, is introduced into hopper 1 having a sufficient capacity for at least one day of continuous hydrolyze operations. Urea, through roll-type feeder 3, is introduced into dissolve 4 where a urea solution of a concentration of about 40% is formed using water condensate from plant battery limits and/or exhausted condensate recycle, which is also introduced into dissolver 4. Urea dissolving operations are facilitated by the action of stirrer 5. Slide valve 2 may be provided at the outlet of hopper 1, if necessary.

The urea/water solution thus obtained is compressed by pump 6 up to hydrolyzer operating pressure and preheated to hydrolysis temperature by means of preheater 7. In accordance with one embodiment of this invention, hydrolyzer operating conditions are as follows:

Pressure 1.9×10^3 KPa

Temperature 195°C

Residence time 40 minutes

Under these conditions, about 30%-40% by weight urea concentration in the feedstock decreases to about 1%-5% by weight in the hydrolyzed solution. Ammonia generated during the hydrolysis process is stripped out from the water solution by means of a defined amount of steam coming from battery limits and injected into bottom of hydrolyzer 8. Hydrolysis products comprising water-saturated ammonia and carbon dioxide are conveyed to reaction zone through line 10. Water is expanded through valve 11 and sent to separator 9, operating at atmospheric pressure, and then recycled to the dissolver 4. Vapors derived mainly from ammonia and water expansion through line 12 are added to the hydrolysis vapors in order to avoid any environmental pollution. Water from separator 9 is recycled through line 13 to the dissolver 4 at a temperature of about 100°C so that, after having supplied urea with

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the heat of solution, a solution is obtained at a temperature of about 40°C.

Example

To better illustrate the process of this invention, a quantitative example is given hereinafter based on an ammonia capacity of 100kg/h.

- 5 The amount of urea fed to the plant is 177 kg/h and the condensate amount coming from plant battery limits is 87kg/h. The water recycle amounts is 150kg/h including about 4.5kg/h of residual urea in the solution. The solution coming out of the dissolver 4 is at a temperature of about 40°C and a urea concentration of about 44% by weight is sent to pump 6, increasing the pressure up to about 1.6×10^3 KPa and,
- 10 through preheater 7, increasing the temperature of about 195°C. The solution enters hydrolyzer 8 resulting in the formation of hydrolysis products having the following characteristics:

Temperature	195°C		
Pressure	1.5×10^3 KPa		
15 Composition	NH ₃	100 kg/h	24.12% by weight
	CO ₂	129 kg/h	31.24% by weight
	<u>H₂O</u>	<u>185 kg/h</u>	<u>44.64% by weight</u>
	Total	414 kg/h	100.00

- Direct steam flow to hydrolyzer 8 required to maintain a constant hydrolysis
- 20 temperature and to strip reaction products is about 155kg/h.

- The result of the process of this invention is that the plant requires only storage facilities for urea, the most used nitrogen fertilizer, which is not subject to any strict regulation and therefore it does not require any special handling care. Other major advantages of the present invention are: safety plant operations, absence of any
- 25 storage by operating personnel of dangerous substances, absence of any polluting

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material, and investment cost reduction compared with the use of ammonia solutions according to the prior art.

CLAIMS

1. In a process for combustion flue gas conditioning in which ammonia is injected into a stream of said combustion flue gas stream, the improvement comprising:
 - 5 dissolving urea in water, forming a dissolved urea solution; heating and pressurizing said dissolved urea solution, forming a heated and pressurized dissolved urea solution; hydrolyzing the dissolved urea in said heated and pressurized dissolved urea solution, forming a hydrolysed solution
 - 10 comprising ammonia and carbon dioxide; stripping said ammonia and carbon dioxide from said hydrolysed solution by contacting said hydrolysed solution with steam, leaving behind a stripped hydrolysed solution; injecting said ammonia and carbon dioxide into said stream
 - 15 of said combustion flue gas; and recycling said stripped hydrolysed solution for dissolving said urea after having brought the pressure and temperature to values compatible to urea dissolving preparation.
2. A process in accordance with claim 1, wherein said dissolved
20 urea solution comprises a range of about 10 to about 70% by weight urea.
3. A process in accordance with claim 1, wherein said dissolved urea is hydrolyzed at a temperature in a temperature range of about 100°C to about 233°C.
- 25 4. A process in accordance with claim 1, wherein said dissolved urea is hydrolyzed at a pressure in a pressure range of about 0.1×10^3 KPa to about 3.0×10^3 KPa.
5. A process in accordance with claim 1, wherein said stripped
30 hydrolysed solution is expanded, forming hydrolysis vapors which are combined with said ammonia and carbon dioxide and injected into said stream of said combustion flue gas.

