

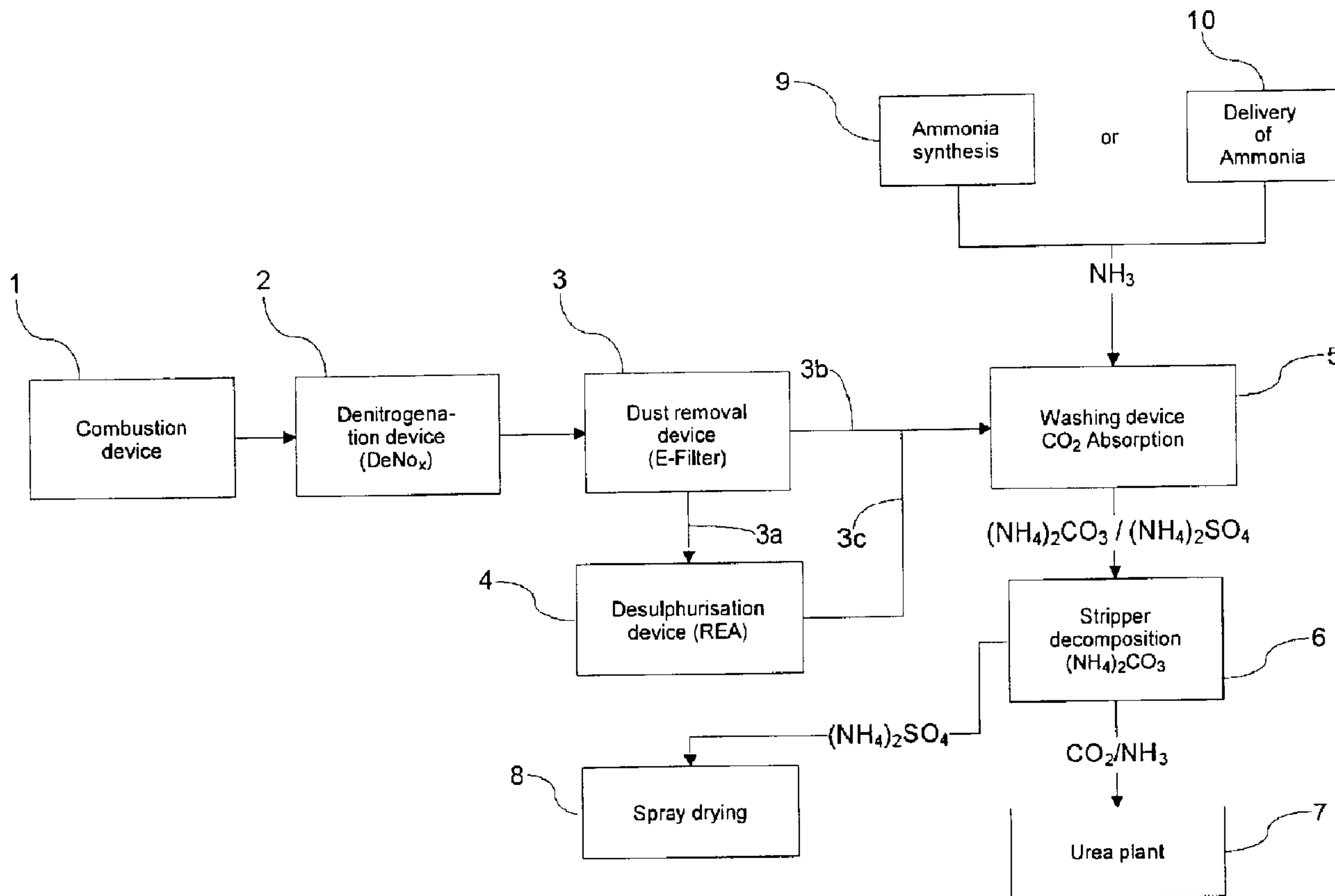


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(54) Titre : PROCEDE D'EPURATION DES GAZ DE COMBUSTION D'INCINERATEURS ET PRODUCTION  
ULTERIEURE D'UREE

(54) Title: METHOD OF CLEANING FLUE GASES FROM COMBUSTION PLANTS WITH THE SUBSEQUENT  
PRODUCTION OF UREA



(57) Abrégé/Abstract:

The invention relates to a method for removing carbon dioxide from flue gases of incinerators as well as an apparatus for carrying out said method. In a first step of said method, the flue gases are freed from dust (3) and nitric oxides (2), and in a subsequent step, the pre-purified flue gas is brought in contact (5) with an aqueous ammonia solution in the presence of an oxidant such that

(57) **Abrégé(suite)/Abstract(continued):**

the carbon dioxide of the flue gas reacts with the ammonia to produce ammonium carbonate. In a subsequent step, the ammonium carbonate present in the aqueous solution is thermally decomposed (6), and the gas flows generated during the decomposition process are fed to a urea generator (7).

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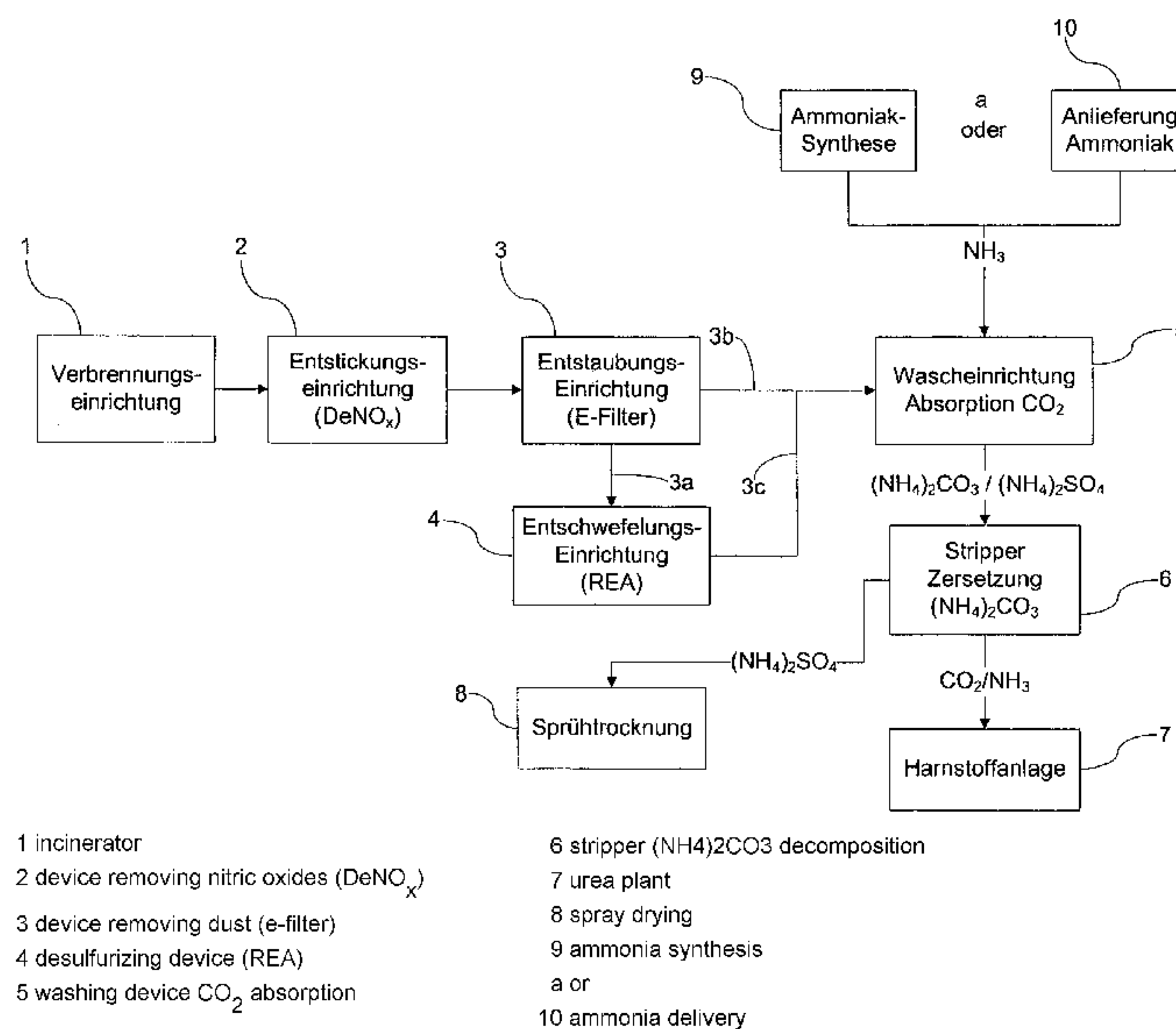
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[Fortsetzung auf der nächsten Seite]

(54) Title: METHOD FOR PURIFYING FLUE GASES FROM INCINERATORS AND THEN PRODUCING UREA

(54) Bezeichnung: VERFAHREN ZUM REINIGEN VON RAUCHGASEN AUS VERBRENNUNGSANLAGEN MIT ANSCHLIESSENDER HARNSTOFFERZEUGUNG



(57) Abstract: The invention relates to a method for removing carbon dioxide from flue gases of incinerators as well as an apparatus for carrying out said method. In a first step of said method, the flue gases are freed from dust (3) and nitric oxides (2), and in a subsequent step, the pre-purified flue gas is brought in contact (5) with an aqueous ammonia solution in the presence of an oxidant such that the carbon dioxide of the flue gas reacts with the ammonia to produce ammonium carbonate. In a subsequent step, the ammonium carbonate present in the aqueous solution is thermally decomposed (6), and the gas flows generated during the decomposition process are fed to a urea generator (7).

(57) Zusammenfassung: Die Erfindung betrifft ein Verfahren zum Entfernen von Kohlendioxid aus Rauchgasen von Verbrennungsanlagen sowie eine Vorrichtung zum Durchführen dieses Verfahrens. Bei einem ersten Verfahrensschritt werden die Rauchgase entstaubt (3) und entstickt (2) und bei einem nachfolgenden

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**Veröffentlicht:**

- mit internationalem Recherchenbericht
- vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen

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Verfahrensschritt wird das vorgereinigte Rauchgas in der Gegenwart eines Oxidationsmittels mit einer wäßrigen Ammoniaklösung in Kontakt gebracht (5), wobei sich das Kohlendioxid des Rauchgases mit dem Ammoniak zu Ammoniumcarbonat umsetzt. Bei einem nächsten Verfahrensschritt wird das in der wäßrigen Lösung vorliegende Ammoniumcarbonat thermisch zersetzt (6) und die bei der Zersetzung entstehenden Gasströme einem Harnstoffgenerator (7) zugeführt.

**METHOD OF CLEANING FLUE GASES FROM COMBUSTION  
PLANTS WITH THE SUBSEQUENT PRODUCTION OF UREA**

5           The present invention relates to a method of cleaning flue gases from combustion plants, particularly power stations, and to an apparatus for carrying out this method. The present invention relates in particular to a method and an apparatus for removing carbon dioxide from such flue gases.

10           Exhaust gases from combustion plants, so-called flue gases, include a number of contaminants which must be removed from them in accordance with the current environmental regulations. The contaminants to be removed include, for instance, sulphur oxides, nitrogen oxides and inorganic fluorine and chlorine compounds. New combustion plants are therefore equipped with flue gas cleaning devices, which remove the sulphur oxides, nitrogen oxides and  
15 inorganic fluorine and chlorine compounds from them. The flue gases are commonly also conducted through a series of filters in order to remove ash particles from the flue gases.

          Increased attempts have also been made recently also to remove a proportion of the carbon dioxide from the flue gases since carbon dioxide is a  
20 so-called greenhouse gas, which is partially responsible for the so-called greenhouse effect. One approach to reducing the CO<sub>2</sub> ground level concentration is to remove it from the flue gas flow and to store it deep in the earth or beneath the sea bed. This approach has, however, the disadvantage that there is no guarantee that the carbon dioxide thus stored will not be liberated  
25 again as a result of tectonic movement. This approach also has the disadvantage that extremely high costs are associated with it, on the one hand for the location of suitable storage sites and on the other hand for the actual

insertion into the storage sites. The high costs associated with known methods for reducing the CO<sub>2</sub> concentration prevent wide usage of this method or make it more difficult.

It is therefore the object of the invention to provide an alternative, economical method for removing carbon dioxide from flue gases and an apparatus suitable therefor.

This object is solved by a method of cleaning flue gases from combustion plants, including the steps of:

- a) removing dust and removing nitrogen from the flue gases,
- 10 b) bringing the flue gases into contact with an aqueous ammonia solution in the presence of an oxidising agent, whereby a reaction solution forms, which contains at least ammonium carbonate,
- c) heating the reaction solution such that ammonium carbonate decomposes and carbon dioxide and ammonia pass into the gas atmosphere; and
- d) reacting the gaseous carbon dioxide and the gaseous ammonia to form urea.

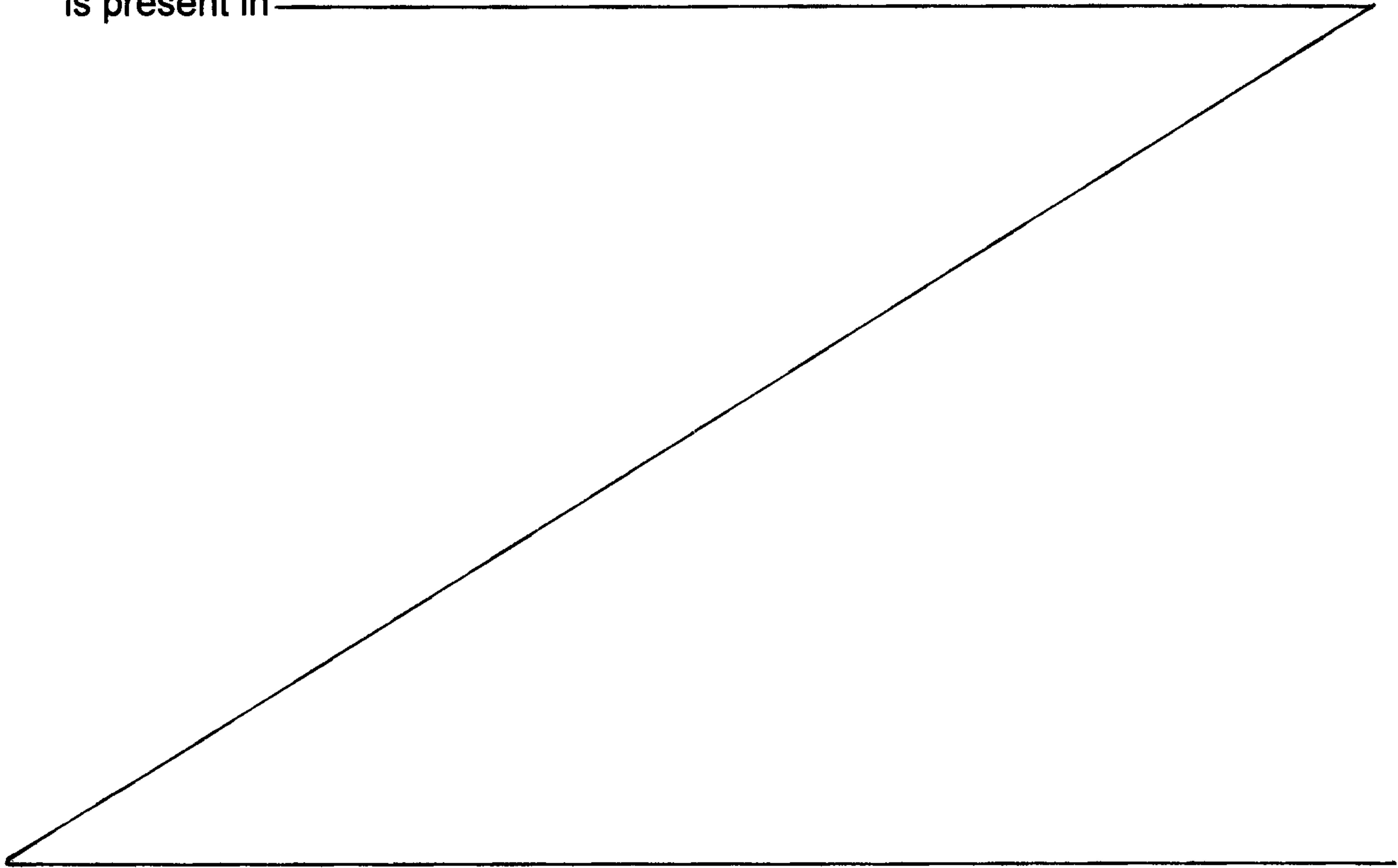
As can be appreciated, in a first method step, dust and nitrogen are removed from the flue gases, whereby the sequence of these two cleaning steps is not of importance to the invention. The removal of dust in the  
20 context of this invention includes the removal of fine ash, which is also referred to as dust, and the removal of coarse ash from the flue gases. Numerous methods and devices for removing dust or ash from flue gases are known from the prior art. These include centrifugal separators, filtration separators, electrostatic precipitators and wet scrubbers. The present invention is not limited to one of the aforementioned separation methods -

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depending on the field of application of the method in accordance with the invention any desire method can be used for the removal of dust.

In order to remove nitrogen from the flue gases, any method known from the prior art for  $\text{NO}_x$  separation can be used. Methods usable in the context of this invention may be grouped as follows: a) selective, non-catalytic reduction (SNCR), b) selective catalytic reduction (SCR), and c) different dry  $\text{NO}_x$  separation methods (e.g. electron beam methods (EBM)).

In a subsequent method step, at least a proportion of the flue gases is brought into contact with an aqueous ammonia solution in the presence of an  
10 oxidising agent. When this contact process occurs, the carbon dioxide from the flue gas reacts with the ammonia in the solution to form ammonium carbonate, whereby a reaction solution forms, in which ammonium carbonate is present in



dissolved form. The flue gases also contain sulphur dioxide, which react, when the flue gases are brought into contact with the aqueous ammonia solution, in the presence of an oxidising agent to form ammonium sulphate and is present after its formation in the reaction solution in dissolved form. Atmospheric  
5 oxygen is commonly used as the oxidising agent but other oxidising agents can, however, also be used in the context of this invention. In the event that the flue gases do not contain a sufficiently high concentration of oxygen in order to ensure oxidation of the sulphur dioxide, additional oxidising agent can be supplied, that is to say, for instance, directly into the flue gases before entry into  
10 the washing device or whilst they are brought into contact with the ammonia solution.

When the flue gases are brought into contact with the aqueous ammonia solution, the concentration of two gases in the flue gases is thus successfully reduced, namely the concentration of carbon dioxide and the concentration of  
15 sulphur dioxide. The contact process itself can, for instance, be effected by spraying in the aqueous ammonia solution. However, depending on the flow volume, numerous other variants known to the expert are also possible.

After bringing the flue gases into contact with the aqueous ammonia solution, the reaction solution thus produced is so heated in a suitable device  
20 that the ammonium carbonate contained in the reaction solution decomposes and carbon dioxide and ammonia pass into the gas phase but the ammonium sulphate remains in the reaction solution in an un-decomposed state. For this purpose, the reaction solution is heated under normal pressure to more than 58°C, the decomposition of ammonium carbonate begins at this temperature. In  
25 order to acceleration the decomposition, it is possible to perform the decomposition under a reduced pressure or in the presence of an appropriate catalyst.

It is thus possible with this method step to remove carbon dioxide in a targeted manner from the reaction solution which has previously been extracted from the flue gases by conversion to ammonium carbonate. After the heating process, the reaction solution contains primarily dissolved ammonium sulphate.

5 The carbon dioxide and ammonia obtained by the heating of the reaction solution are subsequently reacted to form urea in a suitable device in accordance with a method known from the prior art.

The technical production of urea from ammonia and carbon dioxide has been known for a long time. In order to provide the educt carbon dioxide,

10 natural gas is commonly burnt for this purpose. This process for providing the educt carbon dioxide has, however, the disadvantage that a valuable energy carrier (natural gas) is used in order to produce a comparatively low value product (carbon dioxide). In this respect, the invention goes down a completely different route - the waste product carbon dioxide which is abundantly present

15 in flue gases from combustion plants is removed from the flue gases with an aqueous ammonia solution and thus rendered usable. It is thus not necessary to burn a valuable energy carrier to provide an educt of the urea synthesis and instead exhaust gases from combustion plants are used for this purpose. This advantageously results in the avoidance of the combustion of a valuable energy

20 carrier at the same time as or in addition to a reduction in the CO<sub>2</sub> level, since at least a proportion of the carbon dioxide content of the flue gases is chemically bonded in the form of urea.

It is thus possible with the present invention to convert a considerable proportion of the "waste product" carbon dioxide present in flue gases into a

25 valuable material, namely urea. Urea is an important raw material for the bulk chemical industry, which is required in large volumes. The invention thus permits the ground level concentration of carbon dioxide to be considerably

reduced, whereby this occurs with the conversion of a waste product into a valuable product. This valuable product may be sold so that the method in accordance with the invention may thus be conducted economically as a whole. This synergy effect, on the one hand the reduction of the CO<sub>2</sub> and on the other hand the conversion of a waste product into a valuable product, renders an economical method possible, which may be used on a large technical scale.

In an advantageous embodiment of the method in accordance with the invention, step a) further includes the removal of sulphur from the flue gases. This is particularly advantageous if the flue gases from the combustion plants contain a high SO<sub>2</sub> concentration. As a result of the additional desulphurisation step, it is possible to adjust the sulphur dioxide concentration of the flue gas in a targeted manner and thus to influence the concentration of ammonium sulphate in the reaction solution. The method in accordance with the invention is not limited to a particular desulphurisation process - all methods known from the prior art can be used.

Modern combustion plants produce considerable volumes of carbon dioxide. Correspondingly large volumes of ammonia are necessary in order to convert at least a proportion of the carbon dioxide. The ammonia necessary for the aqueous ammonia solution is advantageously produced on site by ammonia synthesis. The complex and cost-intensive transport and the storage of the ammonia are avoided in this manner and there is always a sufficient amount of ammonia available.

In the method in accordance with the invention, ammonium sulphate is produced in the reaction solution in addition to ammonium carbonate. Ammonium sulphate is an important fertiliser additive and is used in the chemical industry, amongst other things, as a protein precipitant, as a floatation agent for the production of synthetic resin and for manufacturing fire

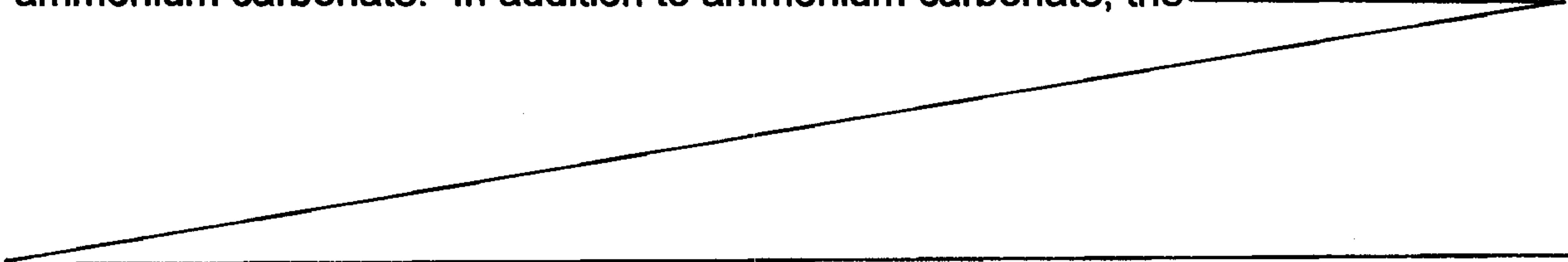
extinguishing powder and flame retardants. Ammonium sulphate is therefore preferably separated from the reaction solution after heating such that ammonium carbonate decomposes. The separation of the ammonium sulphate can be performed with a spray drying process in a particularly simple and thus advantageous manner.

In the reaction of sulphur dioxide to form ammonium sulphate, the sulphur must be oxidised. Air is preferably used as the oxidising agent. This is available in any desired amount and its handling does not constitute any problem at all.

10 In known methods of producing urea, an  $\text{NH}_3/\text{CO}_2$  educt ratio of 2.5 - 4 is used -  $\text{NH}_3$  is thus used in an excess with respect to  $\text{CO}_2$ . For the purpose of cost reduction and minimisation of the necessary amount of ammonia, it is therefore advantageous that the excess ammonia is recirculated for the urea synthesis or for producing the aqueous ammonia solution.

The object in accordance with the invention is also solved by an apparatus for cleaning flue gases from a combustion plant which includes devices for removing nitrogen and removing dust from the flue gases. These directly follow the combustion and can be operated in accordance with methods known from the prior art. The connection of the devices for the removal of nitrogen and the removal of dust may be as desired.

20 Connected downstream of the devices for the removal of nitrogen and the removal of dust is a washing device, in which at least a proportion of the flue gases is brought into contact with an aqueous ammonia solution in the presence of an oxidising agent, whereby a reaction solution forms, which contains at least ammonium carbonate. In addition to ammonium carbonate, the



reaction solution also contains ammonium sulphate, which is formed by the reaction of ammonia and sulphur dioxide in the presence of an oxidising agent.

Connected downstream of the washing device is a stripper, in which the reaction solution is treated such that the ammonium carbonate contained in the reaction solution decomposes into ammonia and carbon dioxide. In order to  
5 achieve such a decomposition, the reaction solution must be heated at normal pressure to above 58°C. The decomposition of ammonium carbonate can be promoted by numerous measures, such as a reduction in pressure.

Connected downstream of the stripper is a urea plant, in which ammonia  
10 and carbon dioxide are reacted to form urea. This reaction can be effected in accordance with methods for urea synthesis known from the prior art.

Further advantageous embodiments of the apparatus in accordance with the invention are given in the dependent claims.

The method in accordance with the invention and the apparatus in  
15 accordance with the invention will be described below with reference to a preferred exemplary embodiment in conjunction with the attached drawing, in which:

Figure 1 is a flow process diagram of a preferred embodiment of the method in accordance with the invention and the apparatus in accordance with  
20 the invention.

The apparatus shown in Figure 1 includes a combustion plant (1). The contaminated flue gas produced during combustion flows via a conduit into a denitrogenation device (2), in which nitrogen oxides are removed from the flue gas. In the apparatus in accordance with Figure 1, connected downstream of the  
25 denitrogenation device (2) is a dust removal device (3), in which solid components (ash) is separated from the flue gas flow.

Leading from the dust removal device (3) are conduits (3a, 3b) going to a

desulphurisation device (4) and a washing device (5), whereby the desulphurisation device (3) is in turn connected via a conduit (3c) to the washing device. In such an arrangement of the individual devices, it is possible to conduct any desired volumetric proportion of the flue gas flow through the desulphurisation device. In the event that the flue gas flow only has a low content of sulphur dioxide, the conduit through the separate desulphurisation device can be omitted. Traces of sulphur dioxide that are present can be removed in the washing device (5).

Connected downstream of the dust removal device (3) or the desulphurisation device (4) is a washing device (5), in which at least a proportion of the flue gases is brought into contact with an aqueous ammonia solution. When so brought into contact, carbon dioxide reacts to form ammonium carbonate, whereby a reaction solution containing it is produced. When the contact process occurs, sulphur dioxide contained in the flue gases also reacts in the presence of an oxidising agent to form ammonium sulphate, whereby atmospheric oxygen is commonly used as the oxidising agent. In the event that the atmospheric oxygen content of the flue gases is too low, additional atmospheric oxygen can be supplied. This can be supplied to the flue gas flow before the washing device or directly before or whilst bringing it into contact with the ammonia solution. After the reaction of the flue gases with the ammonia solution, the remaining flue gases are conducted away and, after optional further cleaning steps, discharged to the atmosphere. The ammonia necessary for the production of the aqueous ammonia solution can either be produced in an ammonia synthesis plant (9) on the site or delivered and supplied from appropriate supply tanks (10) to the washing device (5).

The reaction solution forming during the contact process is withdrawn from the washing device (5) and supplied via a conduit to a stripper (6), in

which this solution is so treated that the ammonium carbonate contained in it decomposes. This treatment can, for instance, be heating of the reaction solution to  $> 58^{\circ}\text{C}$  - above this temperature the ammonium carbonate decomposes into its educts - ammonia and carbon dioxide, which are withdrawn in the form of a rich gas flow and supplied via a conduit to the urea installation (7). Ammonia and carbon dioxide are reacted in the latter to form urea - optionally with the addition of further ammonia. The urea installation (7) itself can be operated in accordance with any desired process known from the prior art. Excess ammonia is re-circulated and can either be used to produce the aqueous ammonia solution or re-used directly in the urea synthesis.

The reaction solution remaining during the decomposition of ammonium carbonate includes a proportion of ammonium sulphate dependent on the sulphur dioxide concentration of the flue gases flowing into the washing device (5). In order to render this usable, the reaction solution is withdrawn from the stripper and supplied to a spray drying installation (8). An installation for purifying the ammonium sulphate can optionally additionally be connected to the spray drying installation (8).

**WHAT IS CLAIMED IS:**

1. A method of cleaning flue gases from combustion plants, including the steps of:
  - a) removing dust and removing nitrogen from the flue gases,
  - b) bringing the flue gases into contact with an aqueous ammonia solution in the presence of an oxidising agent, whereby a reaction solution forms, which contains at least ammonium carbonate,
  - c) heating the reaction solution such that ammonium carbonate decomposes and carbon dioxide and ammonia pass into the gas atmosphere; and
  - 10 d) reacting the gaseous carbon dioxide and the gaseous ammonia to form urea.
2. The method as claimed in Claim 1, wherein step a) further includes the removal of sulphur.
3. The method as claimed in Claim 1 or 2, wherein the ammonia necessary for the aqueous ammonia solution is produced on site by ammonia synthesis.
4. The method as claimed in any one of Claims 1 to 3, wherein ammonium sulphate is separated from the reaction solution from step c), after being heated such that ammonium carbonate decomposes.
5. The method as claimed in Claim 4, wherein the separation of the ammonium  
20 sulphate is performed by spray drying.
6. The method as claimed in any one of Claims 1 to 5, wherein air is used as the oxidising agent.
7. The method as claimed in any one of Claims 1 to 6, wherein excess ammonia from step d) is re-circulated for the urea synthesis or for producing the aqueous ammonia solution.

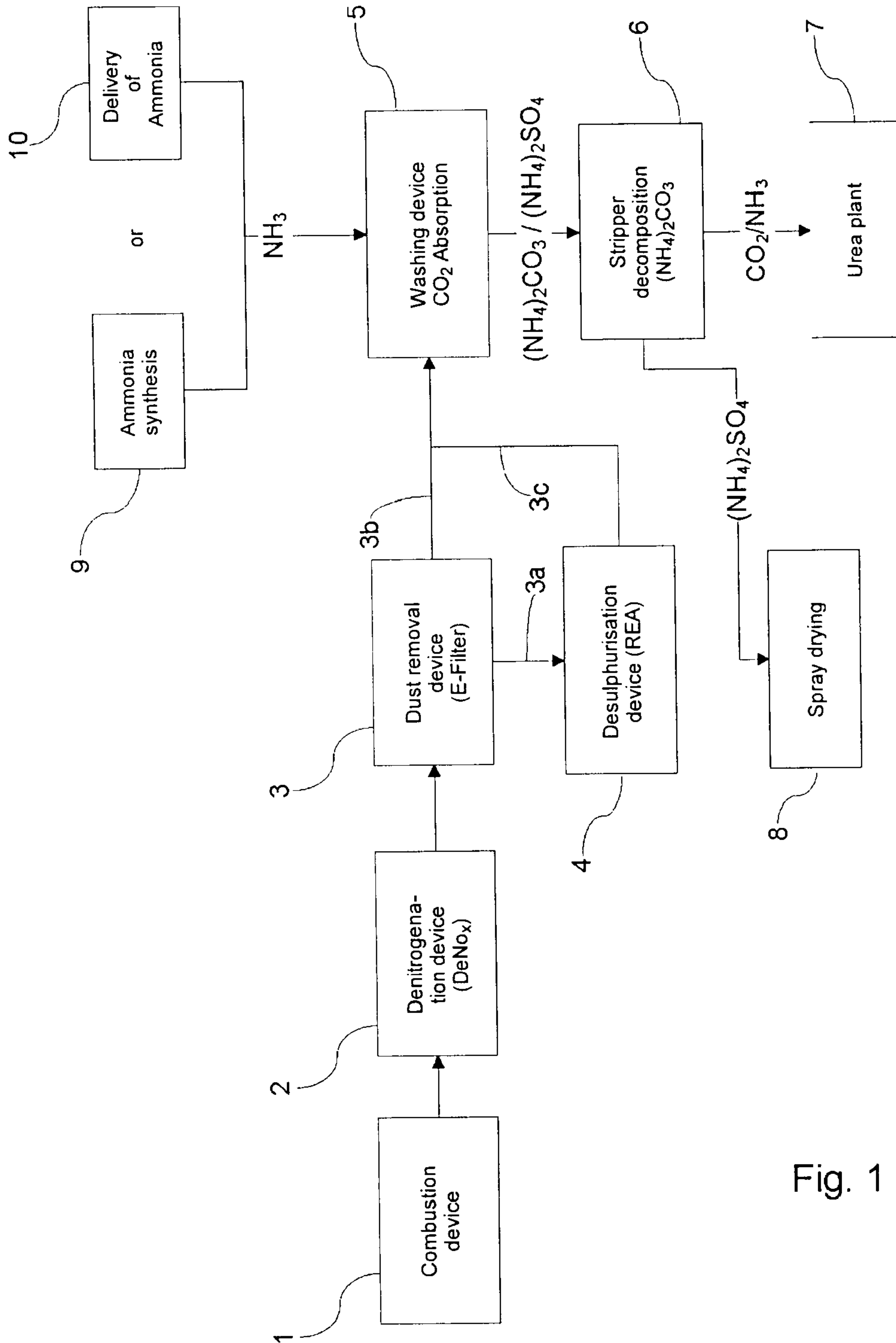


Fig. 1

