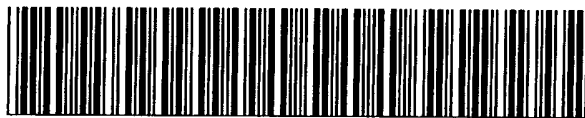


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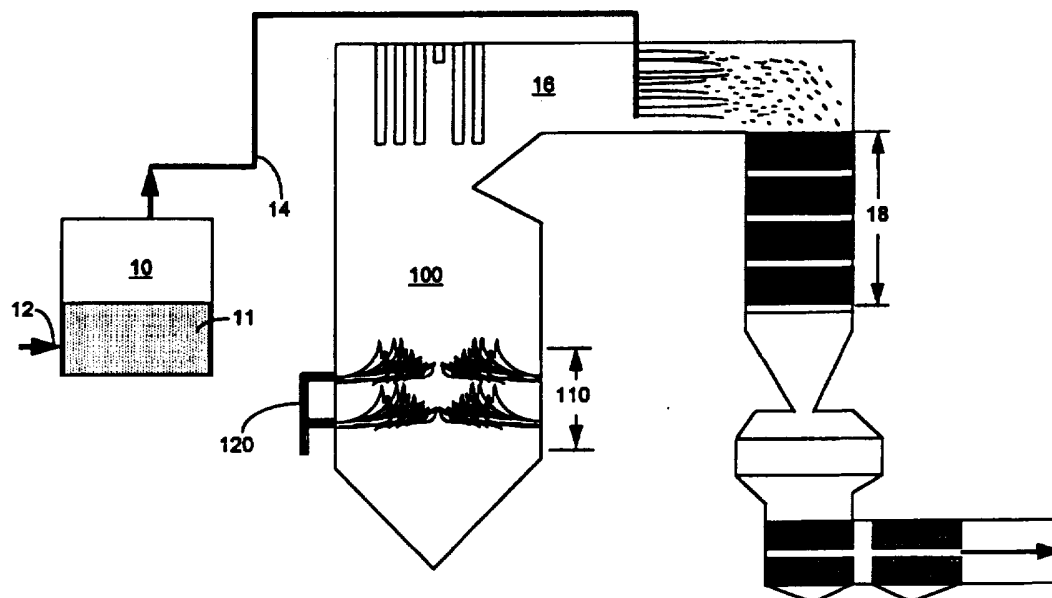
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(54) Title: PROCESS FOR THE SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES



(57) Abstract

Selective catalytic reduction of nitrogen oxides (NO_x) in combustion effluents utilizes ammonium carbamate to achieve the advantages of ammonia as an NO_x -reducing agent, while improving ease and safety of transportation, and economy of operation. The carbamate (11) can be transported dry or in aqueous solution in a sealed container (10) and water (12) is passed through the container to make up the solution prior to introduction to an SCR reactor (18). The convenience of urea is achieved without the need for hydrolysis of the urea or the problems of catalytic fouling which might occur if that were not accomplished.

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DESCRIPTION

PROCESS FOR THE SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES

Technical Field

5 The invention relates to selective catalytic reduction (SCR) of nitrogen oxides (NO_x) in combustion effluents. In particular, the invention provides a process which avoids problems with urea at low injection temperatures and achieves the advantages of ammonia as a NO_x -reducing agent without requiring its use. The invention eliminates reagent deposit on SCR catalysts
10 while enabling improved ease and safety of transportation.

 The problems with NO_x production during the combustion of carbonaceous fuels are well documented and have been the cause of regulations in many countries throughout the world. The processes for reducing NO_x can generally be segregated into two basic categories:
15 selective and nonselective. Among the selective processes, selective catalytic reduction (SCR) is sometimes preferred over selective noncatalytic reduction (SNCR) processes in installations where relatively high percentage NO_x reductions are required.

 SCR processes generally involve passing NO_x -laden effluent with
20 added ammonia across a catalyst bed, and are capable of achieving relatively high NO_x reductions, but require the use of ammonia.

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Ammonia is costly and can be dangerous. In some jurisdictions, ammonia is required to be transported and stored in the form of ammonia water, which in its most commonly utilized form is only about 25% ammonia and is sometimes as dilute as 10% ammonia. The use of ammonia water for providing ammonia to facilitate catalytic NO_x reduction can be impractical because of the increased costs of storage and transportation. In its anhydrous form, moreover, it requires pressure vessels and special handling. And, it is prudent to avoid the introduction of risk factors to facilities not familiar with them.

Urea is safer than ammonia, and has found wide acceptance in SNCR processes. Most SCR processes, however, operate at temperatures so low that the urea cannot enter the gas phase as either free radicals or simple gas molecules. It has been found that urea injected at low temperatures ahead of an SCR catalyst, can form deposits on the catalysts. These deposits reduce catalytic activity and can cause reduced NO_x-reducing activity and the creation of ammonia slip.

What is desired is a process for the selective catalytic reduction of nitrogen oxides which is able to economically achieve significant NO_x reductions with ease of reagent transportation and storage, no catalyst fouling, high chemical utilization, and practical safety.

Background Art

The art of selective gas phase NO_x reduction has greatly advanced in the last twenty years. There are now available a wide variety of SCR and

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SNCR processes with chemicals specific to each. Techniques have been developed, *inter alia*, for SCR using ammonia with a variety of catalysts (e.g., Kato *et al.* in U.S. Patent 4,138,469 and Henke in U.S. Patent 4,393,031), hybrids of SCR and SNCR (e.g., Hofmann, *et al.*, U.S. Patent 5,139,754), and multi-level SNCR injection (e.g., Epperly, *et al.*, U.S. Patent 4,777,024) utilizing urea. But, unlike SNCR which can effectively utilize either urea, a hydrolyzate of urea or ammonia, SCR processes have been limited as a practical matter to ammonia or ammonia water.

Among the chemicals found useful for SNCR, urea has been widely used since the disclosure by Arand, Muzio, and Sotter in U.S. Patent 4,208,386 and Arand, Muzio, and Teixeira in U.S. Patent 4,325,924. In addition, ammonia (Lyon, U.S. Patent 3,900,554), urea hydrolysates (e.g., von Harpe, *et al.*, U.S. Patent 5,240,688) and carbamate (Hofmann, *et al.*, U.S. Patent 4,997,631) and carbamate as an intermediate in urea hydrolysis (Jones in U.S. Patent 5,281,403) have been identified as SNCR agents.

For SCR processes, however, urea has not received acceptance because it tends to foul the catalysts at the low temperatures typically involved, presumably due to the production of polymeric species which deposit on the catalyst surface and decrease its activity. Carbamates, other than due to their presence in relatively dilute, aqueous solutions of urea hydrolysates, have not been mentioned for use in SCR processes. And, when carbamates are produced during urea hydrolysis contain large amounts of other by products and are quite costly as compared to ammonia which is a raw material in urea production.

The manufacture of urea followed by its hydrolysis adds significant expense over the cost of ammonia, and the cost disadvantage attributable to shipping and storing ammonia, is somewhat offset. Moreover, as the

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carbamates -- principally ammonium carbamate -- are now shipped and handled in the art, they add difficulty as compared to urea, evolving an off odor in the dry form in ambient storage and exhibiting relatively low solubility in water at the lower end of the temperatures normally encountered.

5 Thus, as the art now stands, the most suitable chemical for SCR processes remains ammonia -- just as it has for the past several decades -- whether in gaseous form as traditionally employed or as an aqueous solution prepared by the complete hydrolysis of urea (e.g., Ebina, JP HEI 2-191,528). Unfortunately, the requirement that catalytic reactions be conducted in the
10 presence of ammonia, means that a system for supplying ammonia gas safely to the effluent in the area of the catalyst must be developed and installed. This is not only expensive, but it does not eliminate the possibility of leakage and the associated health and safety problems.

 The art is in need of a system which provides better safety than
15 ammonia-SCR -- without the problems caused by urea when injected at low temperatures typical of SCR.

Disclosure of Invention

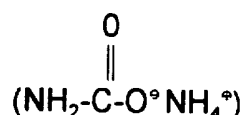
 It is an object of the invention to provide an improved NO_x-reduction process which achieves effectiveness similar to that of ammonia-SCR
20 processes, but without the need to ship either hazardous anhydrous ammonia or dilute aqueous solutions of it or other chemicals.

 It is a further object of the invention to provide an improved method for reducing NO_x by selective catalytic reduction, which eliminates the problems

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of ammonia and enables the use of a chemical as safe as urea without the problems of urea.

These and other objects are achieved by the invention which provides a process for the catalytic reduction of nitrogen oxides in a combustion effluent comprising: (a) directing the effluent through a passage including a catalysis zone containing a catalyst effective for reducing NO_x in the presence of ammonia and oxygen; (b) introducing into the passage, an aqueous solution of a NO_x-reducing agent consisting essentially of - ammonium carbamate, of the following formula



wherein the solution is introduced into the effluent at a temperature of less than 1300°F but sufficient to essentially completely dissociate the carbamate and form gaseous ammonia prior to entrance into the catalysis zone and the effluent containing the ammonia enters the catalysis zone at a temperature effective to reduce the concentration of nitrogen oxides by selective catalytic reduction.

In the preferred embodiment, the carbamate is produced in equipment conventional for urea synthesis, but under conditions effective to maximize the production of ammonium carbamate and minimize the production of urea. Desirably, the carbamate will consist essentially of ammonium carbamate and contain no more than minimal amounts of urea. Preferably, the combined amount of urea and other nitrogenous species such as ammonium carbonate, ammonium bicarbonate, and the double salt of ammonium carbonate (often called commercial ammonium carbonate, NH₄HCO₂·NH₂COONH₄), is maintained at a level of less than about 10%, more preferably less than 6%,

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and most preferably less than 2%. Also preferably, the carbamate is recovered from the process in the form of a solid. These and all parts and percentages in this description are on a weight basis and are based on the weight of the composition at the stage of processing referred to.

- 5 By the use of the process of the present invention, the catalytic destruction of nitrogen oxides can be effected in the presence of ammonia while reducing or eliminating the need for the undesirable storage, handling, and transport of ammonia, ammonia water or other dilute aqueous chemical.

Brief Description of the Drawing

- 10 The invention will be better understood and its advantages will be more apparent when the following detailed description is read in light of the accompanying drawings, wherein:

Figure 1 is a schematic representation of one embodiment of the invention wherein an aqueous solution of ammonium carbamate is introduced
15 into a NO_x-containing combustion effluent in a passage leading from a boiler and leading to a catalysis section; and

Figure 2 is an enlarged schematic view of a representative container means employed to transport the ammonium carbamate in dry or aqueous form, sealed from the atmosphere and to then receive make-up water and
20 deliver a solution of the desired concentration to the effluent.

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Best Mode for Carrying Out the Invention

The invention, which relates to the catalytic reduction of nitrogen oxides in a combustion effluent in the presence of ammonia by introducing into the NO_x-laden effluent an aqueous solution of ammonium carbamate, to
5 generate ammonia in the effluent, will be described with reference to the large utility boiler of the type shown as 100 in Figure 1 having a combustion zone 110 and a preferably skid-mounted container 10 as shown in Figure 2.

It will be understood by those skilled in the art, however, that the source of NO_x-containing effluent can be any combustor of any carbonaceous
10 fuel -- including an internal combustion engine such as those for fixed and mobile use powered by a suitable fuel such as gasoline, diesel fuel, heavy oil, alcohol, natural gas, or like fuel. The container is illustrative of one means for transporting ammonium carbonate, while other forms and constructions are possible. For example, the container can be a replaceable
15 cartridge which can be simply removably inserted in the supply line for NO_x-reducing chemical between a source of water and means for injecting the solution into the effluent.

In the preferred embodiment, ammonium carbamate is produced in equipment conventional for urea synthesis, but under conditions effective to
20 maximize the production of ammonium carbamate and minimize the production of urea and urea hydrolysis products other than the carbamate. Desirably, the carbamate will consist essentially of ammonium carbamate and contain no more than minimal amounts of urea. Preferably, the amount of urea and other nitrogenous species such as ammonium carbonate,
25 ammonium bicarbonate, and the double salt of ammonium carbonate (often called commercial ammonium carbonate, $\text{NH}_4\text{HCO}_2 \cdot \text{NH}_2\text{COONH}_4$), is

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maintained at a combined level of less than about 10%, more preferably less than 6%, and most preferably less than 2%.

In the preferred process, the carbamate is produced by combining liquid ammonia and liquid carbon dioxide at a pressure preferably above the critical pressure of ammonia, e.g., of from about 120 to about 200 atmospheres at a temperature of from about 135° to about 200°C, and then recovering the ammonium carbamate. Under these conditions, the reaction goes very rapidly and evolves large amounts of heat. When water is essentially excluded from the system, the production of urea and carbonates can be controlled to the low amounts preferred according to the invention.

It is an advantage of the invention that the ammonium carbamate can be shipped in dry form and, thereby, achieve savings in transportation costs because it is not necessary to ship it with large amounts of water. One particularly advantageous procedure is to store the ammonium carbamate in dry form, such as in sealed container 10 as shown in the drawings. At the site where the NO_x reduction is to be performed, water from a source 12 enters the container 10, preferably from the bottom, to take the carbamate 11 into solution for delivery via line 14 to passage 16.

The concentration of the solution can be controlled by suitable metering valves and, if desired, mixing elements within the container. The solubility of the carbamate in water increases with temperature, varying from about 35% at 0°C to about 75% at just under the boiling point. The relatively low solubility at low temperatures typically encountered in shipping, e.g., as low as -40°F, makes shipment in aqueous solution impractical in many instances; however, on the site of the NO_x reduction process, the water can be heated to the desired degree to obtain the concentration of solution required.

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The solution (aqueous solution) is introduced into the effluent at an effluent temperature wherein the ammonium carbamate readily converts to ammonia in order to facilitate the catalytic reduction of nitrogen oxides. Acceptable temperatures are those where the ammonium carbonate is not oxidized to NO_x, e.g., as high as about 1950°F, but are preferably lower. The effluent temperature is preferably less than 1300°F, and preferably within the range of from about 230° to about 1200°F at the point of introduction. More preferably, the effluent temperature is between about 500°F and about 1100°F. Most preferably, the effluent temperature at the point of introduction of the ammonium carbamate should be between about 550°F and about 950°F.

The point of introduction of the carbamate solution into the effluent should also be chosen so as to achieve essentially complete conversion of the ammonium carbamate to ammonia. This is assured by the provision of sufficient residence times and good mixing at the temperatures involved. Preferably, residence times of from about 0.5 to about 2 seconds are employed. If necessary, baffling or other structures can be added to assure good mixing.

The ammonia produced *in situ* is then utilized to selectively catalytically reduce the nitrogen oxides remaining in the effluent by passing the ammonia-containing effluent through a catalysis zone 18 comprising one or more catalyst sections 20 comprising a catalyst material effective for the reduction of nitrogen oxides in the presence of ammonia to further reduce the concentration of nitrogen oxides.

The ammonium carbamate solution may be at ambient temperature prior to introduction or, alternatively, it may be at or above its boiling point. In this way, the ammonium carbamate can flash off immediately upon

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introduction into the effluent, which might provide advantages in minimizing air requirements for atomization, etc.

Advantageously, the ammonium carbamate is introduced into the effluent in an amount sufficient to provide a molar ratio of the ammonia
5 generated to the baseline nitrogen oxides level (by which is meant the pre-treatment level of NO_x in the effluent) of about 0.8:1 to about 1.5:1. More preferably, treatment solution is introduced into the effluent to provide a molar ratio of ammonia to baseline nitrogen oxides of about 1:1 to about 1.2:1, most preferably about 1:1.

10 The catalyst used is one capable of reducing the effluent nitrogen oxides concentration in the presence of ammonia. These include, for instance, activated carbon, charcoal or coke, zeolites, vanadium oxide, tungsten oxide, titanium oxide, iron oxide, copper oxide, manganese oxide, chromium oxide, noble metals such as platinum group metals like platinum,
15 palladium, rhodium, and iridium, or mixtures of these. Other catalyst materials conventional in the art and familiar to the skilled artisan can also be utilized. These catalyst materials are typically mounted on a support such as a ceramic substance, a zeolite, or a homogeneous monolith, although other art known supports can also be used.

20 Among the useful catalysts are those described in the representative prior art processes below. Selective catalytic reduction processes for reducing NO_x are well known and utilize a variety of catalytic agents. For instance, in European Patent Application WO 210,392, Eichholtz and Weiler discuss the catalytic removal of nitrogen oxides using activated charcoal or
25 activated coke, with the addition of ammonia, as a catalyst. Kato *et al.* in U.S. Patent 4,138,469 and Henke in U.S. Patent 4,393,031 disclose the catalytic reduction of NO_x using platinum group metals and/or other metals such as

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titanium, copper, molybdenum, vanadium, tungsten, or oxides thereof with the addition of ammonia to achieve the desired catalytic reduction.

Another catalytic reduction process is disclosed by Canadian Patent 1,100,292 to Knight which relates to the use of a platinum group metal, gold, and/or silver catalyst deposited on a refractory oxide. Mori *et al.* in U.S. Patent 4,107,272 discuss the catalytic reduction of NO_x using oxysulfur, sulfate, or sulfite compounds of vanadium, chromium, manganese, iron, copper, and nickel with the addition of ammonia gas.

In a multi-phased catalytic system, Ginger, in U.S. Patent 4,268,488, discloses exposing a nitrogen oxides containing effluent to a first catalyst comprising a copper compound such as copper sulfate and a second catalyst comprising metal combinations such as sulfates of vanadium and iron or tungsten and iron on a carrier in the presence of ammonia.

The ammonia-containing effluent is most preferably passed over the catalyst while the effluent is at a temperature between about 230°F and about 950°F, preferably at least 550°F. In this manner, the ammonia present in the effluent by the introduction of the ammonium carbamate solution most effectively facilitates the catalytic reduction of nitrogen oxides. The effluent will preferably contain an excess of oxygen, e.g., from about 1 to about 10%.

Use of the present invention with any of the above catalysts (the disclosure of which are specifically incorporated by reference) reduces or eliminates the requirement for the transport, storage and handling of large amounts of ammonia or ammonium water. Even where the inventive process does not provide all of the ammonia required for the catalytic reduction of nitrogen oxides, the reduction of the amount needed still provides significant advantages in terms of both safety and cost.

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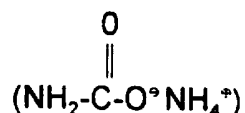
The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention and it is not intended to detail all of those obvious modifications and variations of it which will become apparent to the skilled worker upon reading the description. It is
5 intended, however, that all such obvious modifications and variations be included within the scope of the present invention which is defined by the following claims. The claims cover the indicated components and steps in all arrangements and sequences which are effective to meet the objectives intended for the invention, unless the context specifically indicates the
10 contrary.

CLAIMS

1. A process for reducing nitrogen oxides in a combustion effluent by selective catalytic reduction, comprising:

(a) directing the effluent through a passage including a catalysis zone containing a catalyst effective for reducing NO_x in the presence of ammonia and oxygen; and

(b) introducing into the passage, an aqueous solution of a NO_x -reducing agent consisting essentially of ammonium carbamate, of the following formula



wherein the solution is introduced into the effluent at a temperature sufficient to essentially completely dissociate the carbamate and form gaseous ammonia prior to entrance into the catalysis zone and the effluent containing the ammonia enters the catalysis zone at a temperature effective to reduce the concentration of nitrogen oxides by selective catalytic reduction.

2. A process according to claim 1 wherein the carbamate is produced in equipment conventional for urea synthesis, under conditions effective to maximize the production of ammonium carbonate and minimize the production of urea.

3. A process according to claim 2 wherein:

the carbamate consists essentially of ammonium carbamate and contains a combined amount of urea and other nitrogenous species of the group of ammonium carbonate, ammonium bicarbonate, and the double salt of ammonium carbonate, of less than about 10%.

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4. A process according to claim 3 wherein the combined level of urea and said nitrogenous species in said carbamate is less than 6%.
- 30 5. A process according to claim 2 wherein the carbamate is recovered from the process in the form of a solid.
6. A process of claim 1, wherein the ammonium carbamate is introduced into the effluent at an effluent temperature between about 550°F and about 950°F.
- 35 7. A process of claim 1, wherein the ammonium carbamate is introduced into the effluent in an amount sufficient to provide a molar ratio of ammonia to nitrogen oxides of about 0.8:1 to about 1.5:1.
8. A process according to claim 7 wherein the ammonium carbamate is introduced into the effluent at a point selected to provide a residence time of from about 0.5 to about 2 seconds prior to entrance into the catalysis zone.
- 40 9. A process of claim 7, wherein the effluent is at a temperature between about 230°F and about 950°F when the ammonia-containing effluent passes through said catalysis zone.
- 45 10. A process according to claim 1 wherein the carbamate is stored in a sealed container until utilized and then water is passed through the container to dissolve carbamate and prepare a solution of effective concentration.

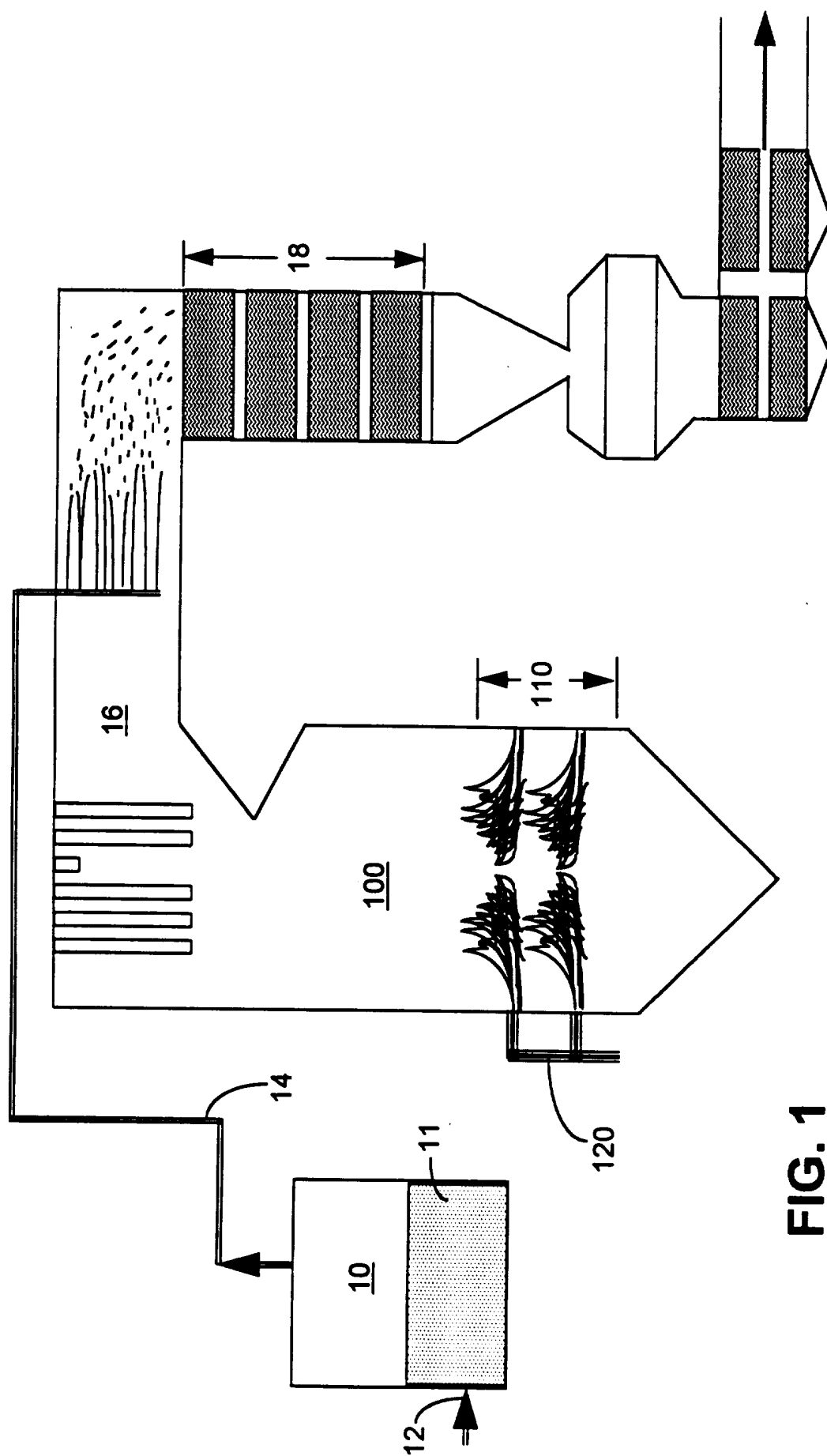


FIG. 1

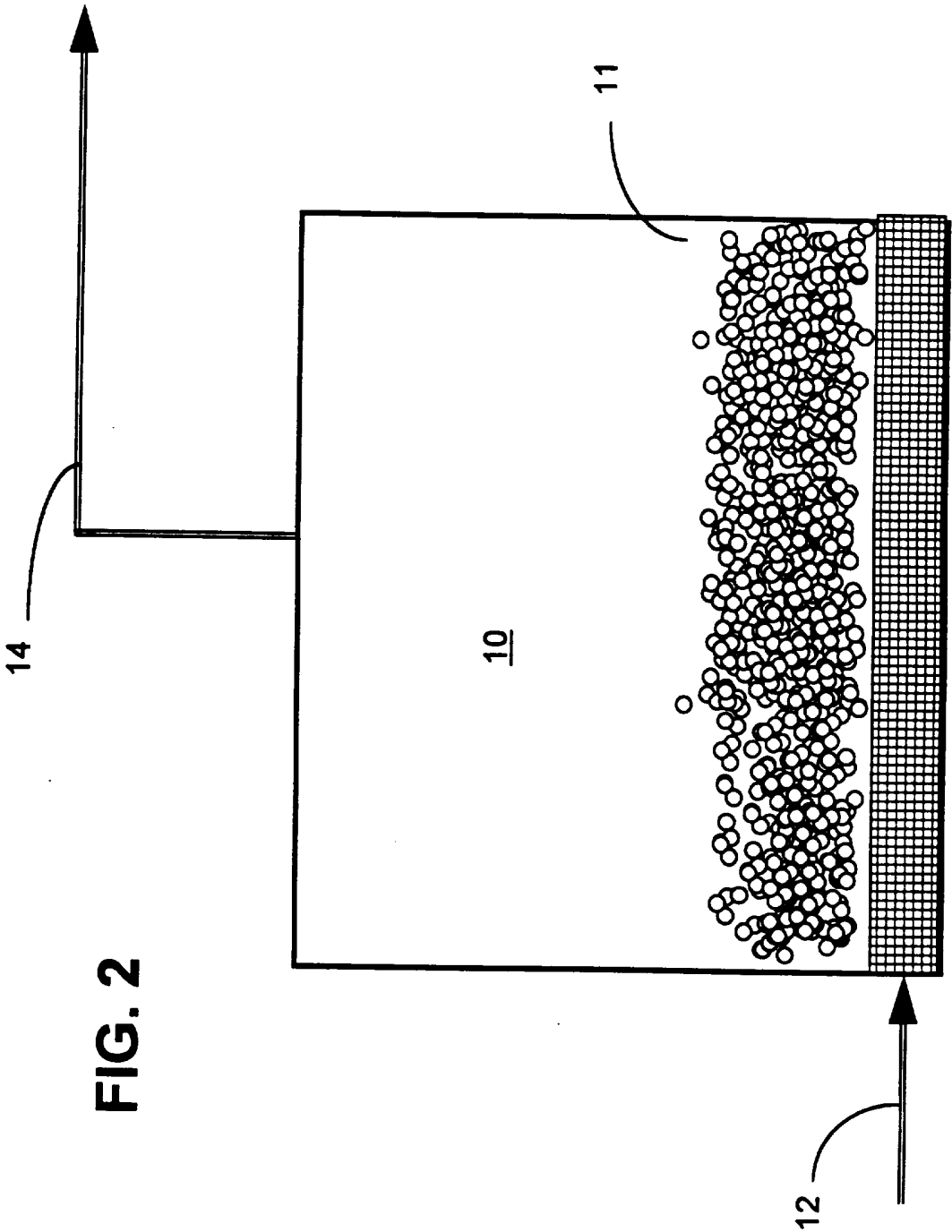


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/10585

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 8/00

US CL :423/235, 239.1

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/235, 239.1

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US, A, 5,139,754 (LUFTGLASS ET AL.) 18 AUGUST 1992, COLUMN 3, LINES 61-64; COLUMN 5, LINE 24; COLUMN 6, LINES 35-51.	1 ----- 1-10
Y	KIRK OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, VOLUME 23, OCTOBER 1983, PAGES 551-552.	2-6 AND 10
Y	GRANT AND HACKH'S CHEMICAL DICTIONARY, FIFTH EDITION, 1987, PAGE 612.	6



Further documents are listed in the continuation of Box C.



See patent family annex.

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

26 SEPTEMBER 1995

Date of mailing of the international search report

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