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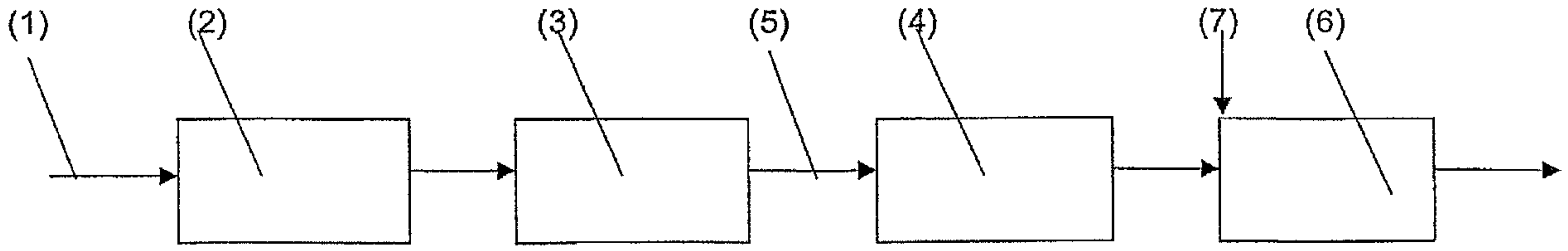
(54) **Titre : PROCEDE ET DISPOSITIF SERVANT A L'ELIMINATION DE NO_X ET DE N_2O**
(54) **Title: METHOD AND DEVICE FOR ELIMINATING NO_X AND N_2O**



(57) **Abrégé/Abstract:**

What is described is a process for removing N_2O and NO_x from offgases by catalytic decomposition of N_2O by means of iron-containing zeolite catalysts and catalytic reduction of the NO_x by means of reducing agents, the deNO_x stage connected downstream of the deN_2O stage being operated at inlet temperatures of T <= 400°C, and the inlet gas for the deN_2O stage comprising water and having a selected N_2O/NO_x ratio, and the operating parameters of temperature, pressure and space velocity of the deN_2O stage being selected so as to result in an N_2O degradation of 80 to 98%. Under these conditions, a degree of NO_x oxidation of 30-70% is established at the outlet of the deN_2O stage, which is defined as the ratio of the molar amounts of NO_2 to the total molar amount of NO_x. The result of this is that the downstream deNO_x stage can be operated under optimal conditions. The process can be operated in an apparatus which comprises the following elements: A) an apparatus (2) for adjusting the water content of the gas (1) comprising NO_x and N_2O, B) a deN_2O stage (3) arranged downstream of apparatus (2) for reducing the N_2O content of the gas stream comprising an iron- laden zeolite catalyst, C) a cooling apparatus (4) arranged downstream of the deN_2O stage (3) for cooling the gas stream (5) leaving the deN_2O stage, D) a deNO_x stage (6) arranged downstream of the cooling apparatus (4) and comprising an SCR catalyst for reducing the NO_x content of the gas stream, and E) a feed line (7) for introducing reducing agent for NO_x into the gas stream (5) leaving the deN_2O stage, which is arranged between the outlet of the deN_2O stage (3) and upstream of the catalyst of the deNO_x stage (6).

Abstract

Process and apparatus for eliminating NO_x and N_2O

What is described is a process for removing N_2O and NO_x from offgases by catalytic decomposition of N_2O by means of iron-containing zeolite catalysts and catalytic reduction of the NO_x by means of reducing agents, the deNO_x stage connected downstream of the deN_2O stage being operated at inlet temperatures of $T <= 400°C$, and the inlet gas for the deN_2O stage comprising water and having a selected N_2O/NO_x ratio, and the operating parameters of temperature, pressure and space velocity of the deN_2O stage being selected so as to result in an N_2O degradation of 80 to 98%. Under these conditions, a degree of NO_x oxidation of 30-70% is established at the outlet of the deN_2O stage, which is defined as the ratio of the molar amounts of NO_2 to the total molar amount of NO_x. The result of this is that the downstream deNO_x stage can be operated under optimal conditions.

The process can be operated in an apparatus which comprises the following elements:

A) an apparatus (2) for adjusting the water content of the gas (1) comprising NO_x and N_2O,

B) a deN_2O stage (3) arranged downstream of apparatus (2) for reducing the N_2O content of the gas stream comprising an iron-laden zeolite catalyst,

C) a cooling apparatus (4) arranged downstream of the deN_2O stage (3) for cooling the gas stream (5) leaving the deN_2O stage,

D) a deNO_x stage (6) arranged downstream of the cooling apparatus (4) and comprising an SCR catalyst for reducing the NO_x content of the gas stream, and

E) a feed line (7) for introducing reducing agent for NO_x into the gas stream (5) leaving the deN_2O stage, which is arranged between the outlet of the deN_2O stage (3) and upstream of the catalyst of the deNO_x stage (6).

Description

METHOD AND DEVICE FOR ELIMINATING NO_X AND N_2O

The invention relates to a process and to an apparatus for catalytic elimination of NO_x and N_2O.

Many processes, for example combustion processes, or industrial production of nitric acid or caprolactam, result in an offgas laden with nitrogen monoxide NO, nitrogen dioxide NO_2 (referred to collectively as NO_x) and dinitrogen monoxide N_2O. While NO and NO_2 have long been known to be compounds of ecotoxic relevance (acid rain, smog formation), and global limits have been fixed for the maximum permissible emissions thereof, dinitrogen monoxide too has become the subject of increasing attention in environmental protection in the last few years, since it contributes to a not inconsiderable degree to the degradation of stratospheric ozone and to the greenhouse effect. For reasons of environmental protection, there is therefore an urgent need for technical solutions for elimination of the dinitrogen monoxide emissions together with the NO_x emissions.

There are already numerous known options for elimination of N_2O on the one hand and NO_x on the other hand.

In the case of NO_x reduction, selective catalytic reduction (SCR) of NO_x by means of ammonia in the presence of vanadium-containing TiO_2 catalysts should be emphasized (cf., for instance, G. Ertl, H. Knözinger, J. Weitkamp: Handbook of Heterogeneous Catalysis, vol. 4, pages 1633-1668, VCH Weinheim (1997)). According to the catalyst, this can proceed at temperatures of approx. 150°C to approx. 450°C and is operated on the industrial scale preferably between 200°C and 400°C, especially between 250°C and 350°C. It is the variant usually used for reducing the NO_x level in offgases from industrial processes, and enables NO_x degradation of more than 90%.

There are also processes for reduction of NO_x based on zeolite catalysts, which proceed using a wide variety of different reducing agents. In addition to Cu-exchanged zeolites (cf., for example, EP-A-914,866), iron-containing zeolites in particular appear to be of interest for practical applications.

For instance, US-A-5,451,387 describes a process for selective catalytic reduction of NO_x with NH_3 over iron-exchanged zeolites, which operates preferably at temperatures between 200 and 550°C, especially around 400°C.

EP-A-756,891 describes a process for reduction of NO_x by means of NH_3 in the presence of honeycomb monoliths composed of iron-containing ZSM-5 zeolites. An advantage of the Fe zeolite catalysts over conventional V_2O_5-TiO_2-based deNO_x catalysts is likewise the extended temperature range from 200°C to 600°C.

However, a disadvantage of Fe zeolite catalysts for NO_x reduction is the availability and cost thereof. The latter is much higher compared to widespread and established V_2O_5-TiO_2-based deNO_x catalysts.

In contrast to the reduction of the NO_x level in offgases, which has been established in industry for many years, there exist only a few industrial processes for N_2O elimination, which are usually aimed at thermal or catalytic degradation of the N_2O. An overview of the catalysts which have been demonstrated to be suitable in principle for degradation and for reduction of dinitrogen monoxide is given by Kapteijn et al. (Kapteijn F. et al., Appl. Cat. B: Environmental 9 (1996) 25-64). The catalytic decomposition of dinitrogen monoxide to N_2 and O_2 gives the advantage over catalytic reduction with selected reducing agents, such as NH_3 or hydrocarbons, that no costs arise for the consumption of reducing agents. However, effective lowering of the N_2O level based on a catalytic decomposition, in contrast to N_2O or else NO_x reduction, can be achieved effectively only at temperatures greater than 400°C, preferably greater than 450°C.

Again, transition metal-laden zeolite catalysts appear to be particularly suitable for catalytic decomposition of N_2O to N_2 and O_2 (US-A-5,171,553).

Iron-laden zeolite catalysts are described as especially advantageous (for example in EP-A-955,080 or WO-A-99/34,901). The activity of the Fe zeolite catalysts for N_2O decomposition is enhanced considerably by the simultaneous presence of NO_x, as detailed scientifically, for example, by Kögel et al. in Catalysis Communications 2 273-276 (2001) or by Perez-Ramirez et al. in Journal of Catalysis 208, 211-223 (2003).

The combined elimination of NO_x and N_2O based on a catalytic reduction of the NO_x with NH_3 (in a $deNO_x$ stage) and a catalytic decomposition of N_2O to N_2 and O_2 over iron-containing zeolite catalysts (in a deN_2O stage) has also been described in the patent literature.

For example, DE 10 001 541 B4 claims a process for eliminating NO_x and N_2O from the residual gas of nitric acid production, wherein the offgas to be cleaned is passed first through a $deNO_x$ stage and then through a deN_2O stage with iron-laden zeolite catalysts. In the $deNO_x$ stage, the NO_x content is reduced to such an extent that an optimal NO_x/N_2O ratio of 0.001-0.5 is established, which leads to accelerated N_2O degradation in the downstream deN_2O stage.

The selected sequence of process stages is very advantageous from a process and chemical engineering point of view, since the process is arranged in the residual gas of the nitric acid production, between absorption tower and residual gas turbine in an ascending temperature profile; in other words, the residual gas at first, before entry into the $deNO_x$ stage, has a low inlet temperature which is < 400°C, preferably < 350°C, and so conventional $deNO_x$ catalysts based on V_2O_5-TiO_2 can also be used. The $deNO_x$ stage, before entry into the deN_2O stage, is then followed by a (single) heating of the residual gas to 350-500°C, such that effective catalytic N_2O decomposition is possible. The offgas is then supplied to a residual gas turbine in which the heat content of the offgas is recovered with decompression and cooling.

A reverse connection of the two process stages is also possible, i.e. in a sequence in which N_2O degradation is first provided and is then followed by NO_x degradation, as taught in WO-A-01/51181.

For this purpose, the offgas is passed at a homogeneous temperature of < 500°C through two reaction zones which comprise iron-laden zeolite catalysts and may be spatially separate from one another or connected to one another. In this case, the N_2O is decomposed in the deN_2O stage initially at an unreduced NO_x content, i.e. with full exploitation of the cocatalytic NO_x effect on the N_2O decomposition, and this is followed, after intermediate addition of ammonia, by the catalytic NO_x reduction. Since the NO_x reduction should preferably proceed at the same temperature as the N_2O decomposition, Fe zeolite catalysts are likewise used in the deNO_x stage, which, in contrast to conventional SCR catalysts, for example V_2O_5-TiO_2-based catalysts, can also be operated at higher temperatures > 400°C. Intermediate cooling of the process gas is thus not required.

If it were desired, for example for reasons of cost, to employ less expensive SCR catalysts, such as V_2O_5-TiO_2-based catalysts, in place of the Fe zeolite catalysts, cooling of the residual gas would thus always be required downstream of the deN_2O stage for operation of the deNO_x stage. This would be highly advantageous especially when, even in the case of use of other deNO_x catalysts, for example Fe zeolite-based catalysts, as a result of the specific application, for example in a plant for preparation of nitric acid by what is called the mono-medium pressure process or, for example, in a plant for preparation of caprolactam, a low exit temperature downstream of the denitrification unit is desired or required.

In this case, the person skilled in the art in the field of offgas cleaning is, however, confronted with the following problem, which makes the operation of a conventional deNO_x stage at a low temperature level downstream of a deN_2O stage comprising Fe zeolite catalysts appear to be technically and economically very disadvantageous.

For instance, Fe zeolite catalysts are known, as shown, for example, by Kögel et al. in Catalysis Communications 2 273-276 (2001) or by Perez-Ramirez et al. in Journal of Catalysis 208, 211-223 (2002), not only to accelerate N_2O decomposition but also, in the presence of NO_x, also to shift the NO/NO_2 ratio or the degree of NO_x oxidation in an accelerated manner. The latter is defined as the molar proportion of NO_2 in the total molar amount of NO_x (= sum of NO and NO_2); in other words, the higher the operating temperature of the deN_2O stage, the more rapidly and the greater the extent to which the NO/NO_2 ratio approaches the thermodynamically defined equilibrium position at the exit from the stage.

While the formation of NO_2 is predominant at low temperatures of < 400°C, preferential formation of NO takes place at higher temperatures of > 400°C or especially at T > 450°C (on this subject, see fig. 1, which shows the mole fractions of NO and NO_2 in thermodynamic equilibrium at 1 bar abs proceeding from 500 ppm of NO, 500 ppm of NO_2, 2% by volume of O_2 and remainder N_2).

The formation of NO_2 resulting from reaction of N_2O with NO at relatively low temperatures, according to reaction equation (1) below, becomes increasingly meaningless since NO_2 formed, according to reaction equation (2) below, is degraded again very rapidly to NO.

$$N_2O + NO \rightarrow NO_2 + N_2 \qquad (1)$$

$$NO_2 \leftrightarrow NO + \tfrac{1}{2} O_2 \qquad (2)$$

At the exit of the deN_2O stage, that degree of NO_x oxidation which corresponds to the thermodynamic equilibrium is thus established at high temperatures.

This relationship is well known to those skilled in the art and is described, for example, in the aforementioned articles by Kögel et al. and Perez-Ramirez et al. According to Perez-Ramirez et al., figure 5a on page 215, in a water-free test gas with 1.5 mbar of N_2O and 0.4 mbar of NO_x, in spite of intermediate formation of NO_2 according to reaction equation (1), an NO/NO_2 ratio which corresponds to the thermodynamic equilibrium position is established at temperatures of > 700 K (corresponding to > 427°C), even at a high space velocity of 60 000 h^{-1}. In the aforementioned article by Kögel et al., figure 1 shows that, proceeding from a water-containing test gas containing 1000 ppm of N_2O and 1000 ppm of NO, the thermodynamic NO_x equilibrium is attained from 400°C at a space velocity of 15 000 h^{-1}.

This means that, at the exit of a deN_2O stage, at T > 400°C and pressure 1 bar abs, a degree of oxidation of < 30% should be assumed, and at T > 450°C even a degree of oxidation of < 20%. However, such a degree of oxidation is generally extremely unfavorable for operation of a $deNO_x$ stage.

Thus, a $deNO_x$ stage is known to function at best when the ratio of NO/NO_2 = 1/1, i.e. the degree of oxidation is approx. 50%. In this case, the person skilled in the art refers to a “fast SCR” (cf. reaction equation 3 below), which proceeds several times faster than “standard SCR” (cf.

reaction equation 4 below) or “NO_2 SCR” (cf. reaction equation 5 below).

$$4\ NH_3 + 2\ NO + 2\ NO_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad (3)$$

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad (4)$$

$$4\ NH_3 + 3\ NO_2 \rightarrow 3.5\ N_2 + 6\ H_2O \qquad (5)$$

The dependence of the reaction rate on the degree of NO_x oxidation is especially important for the operation of a deNO_x stage at low temperatures. This is true both in the case of use of conventional SCR catalysts, such as V_2O_5-TiO_2-based deNO_x catalysts, as described, for example, by Koebel et al. in Catalysis Today 73, (2002), 239-247 (cf. fig. 3 therein), and, for example, of deNO_x catalysts based on iron zeolite.

It is evident from this that the operation of a deNO_x stage at low temperatures < 400°C, preferably < 350°C and especially < 300°C, downstream of an N_2O decomposition based on Fe zeolite catalysts, is exceptionally disadvantageous since the activity of the NO_x reduction, i.e. the performance of the deNO_x catalyst in the deNO_x stage, is greatly impaired by the unfavorable degree of NO_x oxidation.

This disadvantage can be counteracted only to a limited degree by an increase in the amount of catalyst in the deNO_x stage, since disproportionately large amounts of additional catalyst would be required to achieve high degradation rates of NO_x of, for example, > 80% or preferably > 90%, especially at high NO_x inlet concentrations. This would not only put into question the economic viability of the process due to excessive capital and operating costs, but it would also be unjustifiable in many cases for technical reasons, such as space required or permissible pressure drop.

It is thus an object of the present invention to provide a process for removing N_2O and NO_x from offgases by catalytic decomposition of N_2O by means of iron-containing zeolite catalysts and by catalytic reduction of the NO_x by means of reducing agents, wherein the deNO_x stage should be operated downstream of the deN_2O stage at inlet temperatures of $T < 400°C$, preferably < 350°C and especially of $T < 300°C$, and which overcomes the abovementioned disadvantages.

It is a further object of the present invention to provide an apparatus with which the aforementioned process can be operated and which enables a simple and economically favorable establishment of the operating parameters required for the deN_2O stage and deNO_x stage.

The object stated above is achieved by passing an offgas having a selected amount of water and a selected ratio of N_2O to NO_x through the deN_2O stage comprising iron zeolite catalysts. In the case of appropriate selection or establishment of the other operating parameters, the result is thus, at the outlet of the deN_2O stage, a higher proportion of NO_2 in the NO_x than corresponds to the thermodynamic equilibrium. As a result, the deNO_x stage which follows can be operated under conditions of a “fast SCR”.

This is because, in a kinetic modeling or simulation of the NO_x equilibrium and of the NO_x-assisted N_2O decomposition on iron zeolite catalysts, it has been found that, surprisingly, in the presence of large amounts of water in the offgas, or in the case of a high excess ratio of N_2O to NO_x in the offgas, or in the case of a combination of the two factors, the position of the NO_x equilibrium can be shifted or the speed of establishment of the NO_x equilibrium can be reduced significantly. This means that the NO_x equilibrium is firstly shifted constantly to the side of NO_2 by reaction of the NO with N_2O (according to reaction equation 1); secondly, the NO_2 formed as an intermediate (and any NO_2 present beforehand in the inlet gas stream) reacts much more slowly to give NO in the presence of appropriate amounts of water vapor than in the absence of water vapor. As a result, the establishment of the thermodynamic equilibrium position can also be delayed significantly at high temperatures, i.e. within the temperature range from 400°C to 650°C. By adjusting the residence time in the deN_2O stage, i.e. by selecting the space velocity, it is thus possible to establish an operating point at which high N_2O degradation rates and a high degree of NO_x oxidation of $> 30\%$, preferably of $> 40\%$, especially of $> 45\%$, are achieved at the same time.

As expected, there is not only an upper limit in the establishment of the space velocity arising from the minimum desired N_2O degradation of $> 80\%$, preferably of $> 90\%$, but surprisingly also a lower limit arising from a maximum N_2O degradation, which, in accordance with the invention, is $< 98\%$, preferably $< 97\%$, more preferably $< 95\%$. This means that the space velocity should have a lower limit such that a significant residue of N_2O always remains in the offgas at the exit of the deN_2O stage, which, according to reaction equation (1), results in constant formation of NO_2.

In interplay with the other operating parameters, the degree of oxidation of the NO_x at the exit from the deN_2O stage, in a departure from the thermodynamic equilibrium, can be adjusted to a value of 30-70%, preferably of 40-65% and more preferably of 45-60%, such that a deNO_x stage can be operated at a low temperature downstream of a deN_2O stage comprising Fe zeolite catalysts. The degree of NO_x oxidation is defined as the ratio of the molar amount of NO_2 to the molar total amount of NO_x.

The invention relates to a process for reducing the NO_x and N_2O contents in gases comprising NO_x and N_2O, comprising the steps of

a) passing a gas stream comprising N_2O, NO_x and water into a deN_2O stage comprising an iron-laden zeolite catalyst to reduce the N_2O content by decomposing the N_2O to nitrogen and oxygen, said gas stream comprising N_2O, NO_x and water on entry into the deN_2O stage having a water content between 1.0 and 10% by volume, the ratio of the molar amount of N_2O which enters the deN_2O stage to the molar amount of NO_x which leaves the deN_2O stage being at least 1.0, or said gas stream comprising N_2O, NO_x and water on entry into the deN_2O stage having a water content between 0.1 and less than 1.0% by volume, the ratio of the molar amount of N_2O which enters the deN_2O stage to the molar amount of NO_x which leaves the deN_2O stage being at least 1.5, the temperature of the gas stream in the deN_2O stage having been adjusted to a value between 400°C and 650°C, the pressure in the deN_2O stage having been adjusted to a value between 1 and 50 bar abs, and the space velocity in the deN_2O stage having been adjusted to such a value as to result in an N_2O degradation of 80% to 98% in the deN_2O stage, with the additional proviso that the degree of NO_x oxidation at the outlet of the deN_2O stage is at least 30%,

b) supplying the gas stream leaving the deN_2O stage to a cooling apparatus and cooling the gas stream, as it flows through this apparatus, to a temperature below 400°C,

c) supplying the gas stream leaving the cooling apparatus to a deNO_x stage for catalytic reduction of NO_x with a reducing agent in the presence of a deNO_x catalyst, with addition of such an amount of reducing agent which is sufficient to reduce the desired proportion of NO_x to the gas stream, viewed in flow direction, after it leaves the deN_2O stage and before it flows through the $deNO_x$ catalyst.

Preferably, the ratio of the molar amount of N_2O which enters the deN_2O stage to the molar amount of NO_x which leaves the deN_2O stage, irrespective of the water content of the offgas, is at least 1.5. Particular preference is given to N_2O/NO_x ratios of the gas comprising N_2O, NO_x and water of at least 2, especially of at least 5.

The N_2O/NO_x ratio can be found by determining the molar amount or the molar concentration of N_2O at the inlet of the deN_2O stage, and by determining the molar amount or the molar concentration of NO_x at the outlet of the deN_2O stage.

Gases suitable for the process according to the invention either already have the required ratio of N_2O and NO_x before entry into the deN_2O stage, or this ratio should be established by suitable measures.

The suitable N_2O/NO_x ratio is preferably established by chemical catalytic reduction of a portion of the NO_x present in the offgas stream in the deN_2O stage itself. For this purpose, a proportion of reducing agent corresponding to the proportion of the NO_x to be reduced is fed into the inlet gas stream to the deN_2O stage until the desired N_2O/NO_x ratio has been established. The presence of the reducing agent does not significantly influence the degradation of the N_2O since the rate of the NO_x reduction is several order of magnitude faster than the rate of N_2O decomposition. The amounts of reducing agent required for the establishment of the desired N_2O/NO_x ratio depend on the type of reducing agent and on the desired amount of NO_x to be degraded, and can be found by the person skilled in the art by routine experiments.

Just like the N_2O/NO_x ratio, the water content of the gas comprising N_2O, NO_x and water before entry to the deN_2O stage should also be adjusted to the inventive value by suitable measures, if the gas stream does not already contain sufficient water.

For instance, many offgases already have water contents of more than 0.1% by volume and can thus be used without any additional measures.

Preferably, the water content of the gas comprising N_2O and NO_x before entry into the deN_2O stage is adjusted to a value between 0.5 and 10% by volume. Particular preference is given to values between 1% by volume and 5% by volume, and very particular preference to values between 2% by volume and 5% by volume.

Experience has shown that an elevated water content, as used with preference in the process according to the invention, in the downstream $deNO_x$ stage is harmless; in other words, the performance of the $deNO_x$ stage is not significantly impaired. This is true both in the case of use of conventional SCR catalysts, for example of V_2O_5-TiO_2-based $deNO_x$ catalysts, and of Fe zeolite catalysts.

The water content of the gas comprising N_2O, NO_x and water can be adjusted in various ways before entry into the deN_2O stage. One option is to adjust it by addition of water vapor and/or by addition of water in liquid form. In addition, the water content should preferably be adjusted by introducing the offgases from a combustion stage in which hydrogen and/or hydrogen-containing compounds are combusted. Finally, the person skilled in the art has the option of conducting the gas stream comprising N_2O and NO_x through a loading device, which is, for example, a saturator or an absorption tower. This may be an absorption tower typically used in nitric acid plants or caprolactam plants for NO_x absorption. Also possible is a combination of different measures/apparatuses for adjusting the water content. In this context, a wide variety of different parameters in the water loading apparatus, such as the predominant pressure, the temperature and the flow rate of the loading medium and of the gas comprising N_2O and NO_x, are of significance. The person skilled in the art will select such parameters on the basis of his specialist knowledge according to the water content to be established.

According to the invention, iron-laden zeolite catalysts are used in the deN_2O stage. These are preferably zeolites selected from the group of the MFI, BEA, FER, MOR and MEL types, or mixtures thereof, preferably of the BEA or MFI type, more preferably a ZSM-5 zeolite. It is important that the zeolites used have a high hydrothermal stability. This property is a feature especially of the "high silica" zeolites, which are thus particularly preferred.

Specific details regarding the makeup or structure of the zeolites used with preference in accordance with the invention are given in the Atlas of Zeolite Structure Types, Elsevier, 4th revised Edition 1996, which is hereby explicitly incorporated by reference.

The process according to the invention also includes the use of those zeolites in which some of the lattice aluminum has been replaced by one or more elements selected from B, Be, Ga, Fe, Cr, V, As, Sb and Bi. Likewise included is the use of zeolites in which the lattice silicon has been replaced isomorphously by one or more elements, for example by one or more elements selected from Ge, Ti, Zr and Hf.

Most preferably, catalysts which have been treated with water vapor ("steamed" catalysts) are used in the deN_2O stage. Such a treatment dealuminates the lattice of the zeolite; this treatment is known per se to those skilled in the art. Preference is given to using hydrothermally treated zeolite catalysts in the deN_2O stage which have been laden with iron, and in which the ratio of extra-lattice aluminum to lattice aluminum is at least 1:2, preferably 1:2 to 20:1.

Catalysts used in accordance with the invention typically comprise further additives known to those skilled in the art, for example binders, for example aluminosilicates or boehmite. Catalysts used in accordance with the invention are based preferably on zeolites into which iron has been introduced by solid-state ion exchange. Typically, the starting materials for this purpose are the commercially available ammonium zeolites (e.g. NH_4-ZSM-5) and the appropriate iron salts (e.g. $FeSO_4 \times 7\ H_2O$), and these are mixed vigorously in a mechanical manner in a ball mill at room temperature (Turek et al.; Appl. Catal. 1984, (1999) 249-256; EP-A-0 955 080). These references are hereby explicitly incorporated by reference. The catalyst powders obtained are subsequently calcined in a chamber furnace under air at temperatures in the range from 400°C to 650°C. After the calcination, the iron-containing zeolites are washed vigorously in distilled water and, after filtering off the zeolite, dried. Finally, the suitable binders are added to and mixed with the iron-containing zeolites thus obtained and extruded, for example, to cylindrical catalyst bodies.

The catalyst may be present as a shaped body of any size and geometry, preferably in geometries which have a large ratio of surface area to volume, and which generate a minimum pressure drop in the course of flow through them.

Typical geometries are all of those known in catalysis, for example cylinders, hollow cylinders, multihole cylinders, rings, crushed pellets, trilobes or honeycomb structures.

The iron content of the iron-containing zeolites used in the deN_2O stage may vary within wide ranges based on the mass of zeolite, for example be up to 25%, but preferably be 0.1 to 10%, and especially 2 to 7%.

In the deN_2O stage, the temperature in the process according to the invention varies within the range from 400 to 650°C, preferably from 425 to 600°C and especially from 450 to 550°C.

In the deN_2O stage, the pressure in the process according to the invention varies within the range from 1 to 50 bar abs, preferably 1 to 25 bar abs, more preferably 4 to 15 bar abs. A higher operating pressure in the deN_2O stage reduces the amount of catalyst required for N_2O decomposition. An elevated pressure under otherwise identical operating parameters leads to a higher degree of NO_x oxidation at the outlet of the deN_2O stage.

The amount of catalyst in the deN_2O stage must be such that the desired degree of N_2O degradation is achieved, which in turn affects the desired degree of NO_x oxidation at the outlet of this stage.

The reactor bed of the deN_2O stage is preferably filled with catalysts such that – based on the entering gas stream – the result in each case is a space velocity of between 2000 and 50 000 h^{-1}, preferably a space velocity of between 2500 and 25 000 h^{-1}, and more preferably a space velocity of between 3000 and 20 000 h^{-1}, and most preferably a space velocity of between 4000 and 15 000 h^{-1}. In the context of this description, the term “space velocity” is understood to mean the quotient of parts by volume of gas mixture (measured at 273.15 K and 1.01325 bara) per hour based on one part by volume of catalyst. The space velocity can thus be adjusted via the volume flow rate of the gas and/or via the amount of catalyst.

In the process according to the invention, the process parameters in the deN_2O stage, i.e. space velocity, temperature and pressure, are selected within the above-specified ranges for these process parameters so as to result in, for a gas with a given water content and ratio of N_2O and NO_x at the outlet of the deN_2O stage, an N_2O conversion between 80% and 98%, preferably between 85% and 97%, and most preferably between 90% and 95%. Full degradation of the N_2O should not take place. Operation of the deN_2O stage under these conditions ensures that, at the outlet of this stage, the desired degree of NO_x oxidation is present, such that the downstream deNO_x stage can be operated with the desired efficiency in spite of lower operating temperatures.

In a preferred embodiment of the invention, the gas comprising N_2O, NO_x and water, before it enters the deN_2O stage, is heated by means of a heating apparatus, especially by means of a heat exchanger, to a temperature between 400°C and 650°C. The heating apparatuses usable also include electrical heaters or burners of any kind, especially catalytic burners. Burners offer an additional means of regulating the water content in the gas comprising N_2O and NO_x.

To remove the NO_x in the downstream deNO_x stage, the gas stream, after it leaves the deN_2O stage, must be cooled since the deNO_x stage is operated at lower temperatures. For this purpose, it is possible to use any cooling apparatuses known to those skilled in the art. The person skilled in the art preferably selects cooling apparatuses which permit the recovery of a portion of the heat withdrawn from the offgas stream, for example heat exchangers.

Advantageously, the resulting gas stream from the deN_2O stage is supplied to a cooling apparatus which permits the transfer of the heat released to the gas comprising N_2O, NO_x and water before it enters the deN_2O stage, this gas being heatable to a temperature between 400°C and 650°C. Very particular preference is given to using a recuperator for this purpose.

In a further preferred configuration of the invention, the heat exchanger is bypassed, such that a substream of the gas comprising N_2O, NO_x and water, or optionally even the entire gas stream, can be conducted past the heat exchanger. In this case, the amount of this (sub)stream is regulated by means of a valve. Thus, the temperature at the inlet into the deN_2O stage can also be adjusted in different modes of the plant in order to obtain the N_2O conversion which is optimal for the downstream deNO_x stage and hence the optimal degree of NO_x oxidation. Preferably, the resulting gas stream, before entry into the deN_2O stage, is supplied to a heating apparatus, which is especially a burner, and heated further by the latter before entry into the deN_2O stage, optionally with supply of water vapor.

In the case of operation of the process according to the invention in combination with some plants, for example with caprolactam plants, particular measures may be required for protection of the catalyst used in the deN_2O stage. In caprolactam plants, the absorption tower is frequently operated with a phosphate-containing buffer solution as an absorbent for the NO_x. In this case, it is possible that droplets of the absorbent are entrained by the residual gas stream which is to be cleaned by the process according to the invention. This results in the risk that entrained phosphoric acid or phosphates can be deposited on the downstream apparatuses, and also in the inventive system. There is thus the possibility of deactivation particularly of the catalyst of the deN_2O stage. In order to counter this risk, in a preferred embodiment, a guard bed consisting of random packings or structured packings of shaped bodies comprising alumina is connected upstream of the deN_2O stage. This guard bed binds the phosphoric acid or salts thereof and protects the iron zeolite catalyst of the deN_2O stage. This bed preferably consists of porous alumina pellets, for example an annular extrudate. The protective effect is ensured by the fact that alumina reacts with phosphoric acid or the corresponding ammonium salts of phosphoric acid to give aluminum phosphate, which is stable under the prevailing operating conditions.

In the region between the exit of the gas from the deN_2O stage and up to directly upstream of the catalyst bed of the $deNO_x$ stage, the N_2O-depleted gas is mixed with a reducing agent for NO_x. This may be any substance which is known to those skilled in the art and has a high activity for reduction of NO_x. This may, for example, be a nitrogen-containing reducing agent. The nitrogen-containing reducing agents employed may be any compounds provided that they are suitable for reduction of NO_x. Examples are azanes, hydroxyl derivatives of azanes, and also amines, oximes, carbamates, urea or urea derivatives. Examples of azanes are hydrazine and very particularly ammonia. One example of a hydroxyl derivative of azanes is hydroxylamine. Examples of amines are primary aliphatic amines, such as methylamine. One example of carbamates is ammonium carbamate. Examples of urea derivatives are N,N'-substituted ureas, such as N,N'-dimethylurea. Ureas and urea derivatives are preferably used in the form of aqueous solutions.

Particular preference is given to using ammonia as a reducing agent for NO_x.

The reducing agent is added in such amounts as required for reduction of the NO_x to the desired degree in the $deNO_x$ stage. The aim is a reduction in the NO_x content by > 80%, preferably > 90%, even more preferably > 95%, especially between 95% and 100%. The amounts of reducing agent required for that purpose depend on the type of reducing agent and can be determined by the person skilled in the art by routine experiments.

In the case of ammonia as a reducing agent for NO_x, typically 0.8 to 1.5, preferably 0.9 to 1.4 and more preferably 1.0 to 1.2 molar parts of ammonia are used, based on the molar proportion of NO_x to be reduced.

The way in which the reducing agents are introduced into the gas stream to be treated can be configured freely in the context of the invention. The reducing agent can be introduced in the form of a gas or else of a liquid or aqueous solution which evaporates in the gas stream to be treated. The feeding into the gas stream to be treated is effected through a suitable introduction apparatus, for example through an appropriate pressure valve or through appropriately configured nozzles. Preferably, a mixer can be provided downstream of the introduction apparatus in the line for the gas stream to be treated, and promotes the mixing of the gas stream to be cleaned with the reducing agent supplied. In the case of use of different reducing agents, supply and introduction into the gas to be cleaned may be separate or together.

The reducing agent is introduced, in flow direction, upstream of the $deNO_x$ stage or upstream of the catalyst bed of the $deNO_x$ stage and downstream of the deN_2O stage.

In the process variant in which a portion of the NO_x present is to be degraded as early as in the deN_2O stage in order to establish the desired N_2O/NO_x ratio in the deN_2O stage, the reducing agent is additionally introduced, in flow direction, upstream of the deN_2O stage or upstream of the (first) catalyst bed of the deN_2O stage.

In the deNO$_x$ stage, deNO$_x$ catalysts which promote the chemical reaction of NO$_x$ with reducing agents, and the performance of which depends on the degree of NO$_x$ oxidation of the entering gas stream, are used. Preference is given to conventional deNO$_x$ catalysts (SCR catalysts), especially those comprising transition metals and/or transition metal oxides, for example oxides of iron, nickel, copper, cobalt, manganese, rhodium, rhenium or vanadium, or metallic platinum, gold or palladium, or else mixtures of two or more of these compounds. Particular preference is given to using catalysts based on V_2O_5-TiO_2, or zeolite-based catalysts, especially copper- or iron-laden zeolites.

Like the deN$_2$O catalysts, the deNO$_x$ catalysts may also be present as shaped bodies of any size and geometry, and may have the preferred geometries mentioned for the deN$_2$O catalysts.

The design of the catalyst beds in the deN$_2$O and deNO$_x$ stage can be configured freely. These may be present, for example, in the form of a tubular reactor with axial flow or of a radial basket reactor with radial flow, or of a lateral flow reactor. It is also possible for several catalyst beds in series to be present in one stage.

In the deNO$_x$ stage, the temperature in the process according to the invention is less than 400°C, preferably between 180 and 380°C, more preferably between 200 and 350°C and especially preferably between 200 and 300°C.

In the deNO$_x$ stage, the pressure in the process according to the invention varies within the range from 1 to 50 bar abs, preferably 1 to 25 bar abs, more preferably 4 to 15 bar abs. A higher operating pressure in the deNO$_x$ stage reduces the amount of catalyst required for NO$_x$ reduction. An elevated pressure with otherwise identical operating parameters generally leads to increased degradation of NO$_x$ at the outlet of the deNO$_x$ stage.

The reactor bed of the deNO$_x$ stage is preferably filled with catalyst so as to result in each case in a space velocity – based on the entering gas stream – which brings about a reduction in the NO$_x$ content present at the inlet to this stage of at least 80% under the given temperature and pressure values in this stage. Typical space velocities in the deNO$_x$ stage vary within the range between 2000 and 200 000 h^{-1}, preferably between 5000 and 100 000 h^{-1} and more preferably between 10 000 and 50 000 h^{-1}. The space velocity can, as in the deN_2O stage too, be established via the volume flow of the gas and/or via the amount of catalyst.

In the process according to the invention, the process parameters in the $deNO_x$ stage, i.e. space velocity, temperature and pressure, are selected within the above-specified ranges for these process parameters so as to result in, for a gas with a given degree of NO_x oxidation and in the case of appropriate addition of reducing agent for NO_x, a reduction in the amount of NO_x of at least 80% at the outlet of the $deNO_x$ stage.

The invention also relates to a specially configured apparatus which can be used especially for performance of the process according to the invention.

This is an apparatus for reducing the NO_x and N_2O contents in gases comprising NO_x, N_2O and water, comprising the elements:

A) an apparatus (2) for adjusting the water content of the gas stream (1) comprising NO_x and N_2O,

B) a deN_2O stage (3) arranged downstream of apparatus (2) for reducing the N_2O content of the gas stream comprising an iron-laden zeolite catalyst,

C) a cooling apparatus (4) arranged downstream of the deN_2O stage (3) for cooling the gas stream (5) leaving the deN_2O stage,

D) a $deNO_x$ stage (6) arranged downstream of the cooling apparatus (4) and comprising a $deNO_x$ catalyst for reducing the NO_x content of the gas stream, and

E) a feed line (7) for introducing reducing agent for NO_x into the gas stream (5) leaving the deN_2O stage, which is arranged between the outlet of the deN_2O stage (3) and upstream of the $deNO_x$ catalyst of the $deNO_x$ stage (6).

In a preferred variant, the inventive apparatus comprises a cooling apparatus (4) for the gas stream (5) leaving the deN_2O stage which is thermally coupled to a heating apparatus (8) for the gas stream (1) comprising N_2O, NO_x and water, for the purpose of heating this gas stream (1) before it enters the deN_2O stage (3) and for the purpose of cooling the gas stream (5) leaving the deN_2O stage before it enters the $deNO_x$ stage (6). This is preferably a heat exchanger and most preferably a recuperator.

In a further preferred variant, the inventive apparatus comprises an apparatus for adjusting the water content of the gas stream (1) comprising NO_x, N_2O and water, which is a burner (9) in which combustion gas (10) comprising hydrogen and/or hydrogen-containing compounds is incinerated together with oxygen-containing gas (11), especially air, and the offgases (12) thereof are introduced into the feed line of the gas stream (1) comprising NO_x, N_2O and water to the deN_2O stage.

In a further particularly preferred variant, the inventive apparatus comprises a bypass (13) provided upstream of the heating apparatus (8) in the feed line for the gas stream (1) comprising N_2O, NO_x and water, with which a portion of the gas stream (1) or the entire gas stream (1) can be introduced directly into the deN_2O stage (3), said bypass (13) being provided with a valve (14) with which the proportion of the gas stream (1) passing through the heating apparatus (8) can be controlled, or can be regulated as a function of the temperature of the gas stream entering the deN_2O stage.

Yet a further particularly preferred variant relates to an inventive apparatus in which a feed line (7) arranged directly upstream of the catalyst of the $deNO_x$ stage (6) is provided for introduction of reducing agent for NO_x into the gas stream (5) leaving the deN_2O stage (3), preference being given to providing a mixer in the feed line of the gas stream into the $deNO_x$ stage downstream of the feed line (7).

Yet a further particularly preferred variant relates to an inventive apparatus in which a feed line (17) arranged directly upstream of the catalyst of the deN_2O stage (3) is provided for introduction of reducing agent for NO_x into the gas stream (1) comprising N_2O, NO_x and water, preference being given to providing a mixer in the feed line of the gas stream into the deN_2O stage downstream of the feed line (17).

The inventive plant is designed such that the at least one catalyst of the deN_2O stage is an iron-laden zeolite. The zeolites are preferably of the MFI, BEA, FER, MOR and/or MEL type, and more preferably ZSM-5.

Preference is given to an apparatus in which a guard bed connected upstream of the iron-laden zeolite catalyst of the deN_2O stage (3) consists of a structured packing or bed of alumina-containing shaped bodies.

Preference is likewise given to an apparatus in which the deNO$_x$ catalyst in the deNO$_x$ stage (6) is a transition metal-containing SCR catalyst or an iron- or copper-laden zeolite catalyst, especially an SCR catalyst based on V_2O_5-TiO_2.

The inventive system will be explained in detail by way of example hereinafter with reference to two figures, without any intention of a restriction thereby. The figures show:

Fig. 2:	an outline of the process according to the invention and of the plant for reducing the content of NO$_x$ and N_2O in gases, such as process gases or offgases
Fig. 3:	a preferred variant of the process according to the invention and of the inventive plant.

Figure 2 shows an outline of the process according to the invention / of the apparatus according to the invention. What is shown is an apparatus (2) for adjusting the water content of the gas (1) comprising NO$_x$ and N_2O. The water-laden offgas then enters a deN$_2$O stage (3) which comprises an iron-laden zeolite catalyst. After passing through the deN$_2$O stage (3), the gas stream (5) is passed through a cooling apparatus (4) and then enters a deNO$_x$ stage (6), and subsequently leaves the inventive cleaning plant. At the start of the deNO$_x$ stage (6), a feed line (7) is provided for introduction of reducing agent for NO$_x$ into the gas stream (5) leaving the deN$_2$O stage (3). In the outline, this feed line (7) is arranged immediately upstream of the deNO$_x$ stage (6); it may also be arranged in the region between the outlet of the deN$_2$O stage (3) and the position shown in figure 2. This feed line (7) may also open into the deNO$_x$ stage (6) itself, but upstream of the entry of the gas stream into the catalyst bed of the deNO$_x$ stage (6).

Figure 3 shows an outline of a preferred variant of the inventive system. A gas stream (1) comprising NO$_x$ and N_2O is passed into a heat exchanger (18). Heat is supplied to the gas stream (1) therein, resulting in a heated gas stream (21). A substream (13) of the gas stream (1) can bypass the heat exchanger (18) and is subsequently introduced together with the other substream of the gas stream (1) and with an offgas stream (15) from a burner (9) into a deN$_2$O stage (3). In burner (9), air (11) and hydrogen as combustion gas (10) are combusted. The hot offgas (15) heats the gas stream (1) further, and the water content in this gas stream (1) is also increased. The latter subsequently passes, as gas stream (12), into the deN_2O stage (3) which comprises an iron-containing zeolite preferably surrounded by an Al_2O_3 bed. The Al_2O_3 bed protects the iron-containing zeolite from, for example, phosphate which may additionally be present in the gas stream. At the start of the deN_2O stage (3) is a feed line (17) for introduction of NH_3, which serves as a reducing agent for partial degradation of the NO_x present in gas stream (12), which establishes an optimal N_2O/NO_x ratio. The gas stream (5) leaving the deN_2O stage (3), which has an optimal degree of NO_x oxidation of approximately $NO:NO_2 = 1:1$, is then passed through the heat exchanger (18) for heat exchange. At the same time, the gas stream releases the stored heat in the cooling apparatus (4) (here: part of the heat exchanger (18)) to the gas stream (1) which comprises NO_x and N_2O and is to be heated, and is itself cooled. In the next cleaning step, the gas stream thus cooled passes through the $deNO_x$ stage (6), into which NH_3 is introduced through line (7) in addition to the NO_x degradation. The gas stream which has thus been depleted of N_2O and NO_x leaves the unit (6), is passed into a turbine (19) and is then released to the environment (20).

In order to ensure optimal startup of the inventive apparatus, the substream (13) is provided in this illustrative embodiment. The volume of this substream can be controlled via the valve (14). This can ensure that the deN_2O stage (3) in particular is brought to the temperature of the NO_x- and N_2O-containing residual gas stream (1) within a short time. This eliminates the sluggishness of the system during startup.

In the case of startup from the cold state, the valve (14) is thus opened such that a substream bypasses the heat exchanger (18). As soon as a sufficient exit temperature of the deN_2O stage (3) has been attained, the burner (9) is lit in order to further raise the temperature of the gas stream to be cleaned in the deN_2O stage (3). The water concentration in the gas stream (12) also increases as a result of the supply of the offgas (15). When the optimal operating conditions for the deN_2O stage (3) have been attained, the valve (14) is closed and the bypassing of the heat exchanger (18) by the substream (13) is prevented. During operation, the opening of the valve (14) can also be adjusted so as to result in an optimal combination of inlet temperature and water content in the deN_2O stage.

In the case of restart of the inventive plant after a brief shutdown, which means that the plant is still in the warm state, the valve (14) is closed and the entire volume flow of the NO_x- and N_2O-containing residual gas stream (1) passes through the heat exchanger (18). In this case, the burner (9) is lit immediately since the temperature in the deN_2O stage (3) is already sufficiently high from the start. The water concentration increases in accordance with the water content of the offgas (15). The inlet temperature of the deN_2O stage (3) rises further due to the preheating in the heat exchanger (18) and in the burner (9) until the normal operating temperature has been attained.

In addition, the control of the volume of the substream (13) can allow optimal partial load operation to be ensured. Without the possibility of bypassing the heat exchanger (18), the temperature of the gas stream (1) would be too high in partial load operation, since the size of the heat exchanger (18) would be excessive. The burner output would have to be throttled, the energy recovery in the turbine (19) would become less, and NO_x slippage would additionally increase, which would be released to the environment. These are disadvantages which are eliminated by the system described by way of example here, by reducing the area of the heat exchanger (18) in operation with the substream (13).

The invention is illustrated by the examples which follow in tables 1 and 2. The data reproduced result from a kinetic simulation of the NO_x-assisted N_2O decomposition and of the NO_x equilibrium with the aid of the "Presto Kinetics" software from CiT GmbH for a catalyst bed of cylindrical pellets of Fe-ZSM-5 (diameter 2.6 mm, length 5.7 mm) in a flow tube reactor with axial flow. The reactor model used was developed on the basis of laboratory tests and verified by studies in a Mini-Plant, operated with the abovementioned catalyst extrudates on the liter scale.

Example	**1a**	**1b**	**1c**	**1d**	**1e**	**2**	**3**	**4a**	**4b**	**4c**	**5a**	**5b**	**5c**
P in bar abs	1	1	1	1	1	1	1	1	1	1	5	5	5
T in °C	480	480	480	480	480	480	480	480	480	480	480	480	480
$[N_2O]_{in}$ in ppm	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
$[NO]_{in}$ in ppm	100	100	100	100	100	-	200	500	500	500	500	500	500
$[NO_2]_{in}$ in ppm	100	100	100	100	100	200	-	500	500	500	500	500	500
$[NO_x]_{out}$ in ppm	200	200	200	200	200	200	200	1000	1000	1000	1000	1000	1000
$[H_2O]_{in}$ in % vol	3	3	3	3	3	3	3	3	3	3	3	3	3
$[O_2]_{in}$ in % vol	3	3	3	3	3	3	3	3	3	3	3	3	3
$[N_2]_{in}$ in % vol	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder
Space velocity in 1000 × h^{-1}	6.1	5.2	4.6	3.9	3.0	4.5	4.7	9.8	8.3	1.0	14.2	12.4	8.6
N_2O degradation	85%	90%	93%	96%	99%	93%	93%	80%	85%	90%	90%	93%	98%
Degree of NO_x oxidation at the inlet	50%	50%	50%	50%	50%	100%	0%	50%	50%	50%	50%	50%	50%
Degree of NO_x oxidation at the outlet	55.0%	46.4%	40%	32.1%	21.8%	40%	40%	38.6%	34.9%	30.5%	44.4%	41.4%	34.9%
Degree of NO_x oxidation at equilibrium	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	30.6%	30.6%	30.6%

Table 1

Example	**6a**	**6b**	**7a**	**7b**	**8a**	**8b**	**9a**	**9b**	**9c**	**10a**	**10b**	**10c**	**11a**	**11b**
P in bar abs	1	1	1	1	1	1	1	1	1	1	1	1	1	1
T in °C	480	480	480	480	480	480	480	480	480	480	480	480	430	430
$[N_2O]_{in}$ in ppm	1000	1000	1000	1000	1000	1000	1000	1000	1000	2000	2000	2000	1000	1000
$[NO]_{in}$ in ppm	500	500	1000	1000	-	-	500	500	500	100	100	100	100	100
$[NO_2]_{in}$ in ppm	500	500	-	-	1000	1000	500	500	500	100	100	100	100	100
$[NO_x]_{out}$ in ppm	1000	1000	1000	1000	1000	1000	1000	1000	1000	200	200	200	200	200
$[H_2O]_{in}$ in % vol	0.3	0.3	0.3	0.3	0.3	0.3	3	3	3	0.3	0.3	0.3	1	1
$[O_2]_{in}$ in % vol	3	3	3	3	3	3	3	3	3	3	3	3	3	3
$[N_2]_{in}$ in % vol	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder
Space velocity in 1000 × h^{-1}	11.8	10.3	11.8	10.3	11.6	10.1	10.1	8.6	6.3	9.1	8.0	5.8	2.6	3.0
N_2O degradation	90%	93%	90%	93%	90%	93%	80%	85%	93%	90%	93%	96%	85%	80%
Degree of NO_x oxidation at the inlet	50%	50%	0%	0%	100%	100%	50%	50%	50%	50%	50%	50%	50%	50%
Degree of NO_x oxidation at the outlet	23.2%	21.5%	19.8%	19.2%	26.7%	23.9%	30.3%	27.7%	22.9%	40.5%	35.0%	28.7%	36.7%	39.2%
Degree of NO_x oxidation at equilibrium	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	16.5%	27.6%	27.6%

Table 2

As evident in examples 1a-1d, inventive adjustment of the operating parameters of the deN_2O stage, especially of an N_2O/NO_x ratio of 2000/200 = 10, a water content of 3% by volume and suitable selection of the space velocity at the exit of the deN_2O stage, allows establishment of a degree of NO_x oxidation which differs significantly from the thermodynamic equilibrium position (of only 16.5%) and, in accordance with the invention, approaches the theoretical optimum of 50%.

When the space velocity, as shown in noninventive example 1e, is lowered to such an extent that the N_2O degradation is 99%, the degree of NO_x oxidation is only 21.8%, which would mean an inadequate starting position for operation of a downstream deNO_x stage.

The attainment of the desired degree of NO_x oxidation at the exit of the deN_2O stage depends, in a first approximation, on the degree of oxidation at the inlet of the deN_2O stage, as shown in examples 2 and 3.

Examples 5a-c show the positive influence of an increased operating pressure on the degree of NO_x oxidation.

The high water content of 3% by volume has a positive effect in accordance with the invention, as shown by a comparison of examples 1b-1d with examples 10a-10c. At a water content of 0.3% by volume, the N_2O conversion here should be limited to less than 96% in order to achieve a degree of NO_x oxidation of about 30%.

The lowering of the N_2O/NO_x ratio to a value of 2 under otherwise identical conditions in examples 4a-4c shows the influence of the N_2O/NO_x ratio, which, however, with a value of 2 is also still sufficient to achieve the inventive shift in the degree of NO_x oxidation.

If, in contrast, an N_2O/NO_x ratio of 1 is established (examples 6-9), the inventive effect can be achieved only when the input gas has a sufficiently high water content and, at the same time, a sufficiently high space velocity is established, such that a sufficiently low N_2O conversion is attained (ex. 9a). In noninventive examples 9b and 9c, the space velocity is not high enough, or the N_2O conversion achieved is too high and the desired degree of NO_x oxidation is not attained.

Claims

1. A process for reducing the NO_x and N_2O contents in gases comprising NO_x and N_2O, comprising the steps of
   a) passing a gas stream comprising N_2O, NO_x and water into a deN_2O stage comprising an iron-laden zeolite catalyst to reduce the N_2O content by decomposing the N_2O to nitrogen and oxygen, said gas stream comprising N_2O, NO_x and water on entry into the deN_2O stage having a water content between 1.0 and 10% by volume, the ratio of the molar amount of N_2O which enters the deN_2O stage to the molar amount of NO_x which leaves the deN_2O stage being at least 1.0, or said gas stream comprising N_2O, NO_x and water on entry into the deN_2O stage having a water content between 0.1 and less than 1.0% by volume, the ratio of the molar amount of N_2O which enters the deN_2O stage to the molar amount of NO_x which leaves the deN_2O stage being at least 1.5, the temperature of the gas stream in the deN_2O stage having been adjusted to a value between 400°C and 650°C, the pressure in the deN_2O stage having been adjusted to a value between 1 and 50 bar abs, and the space velocity in the deN_2O stage having been adjusted to such a value as to result in an N_2O degradation of 80% to 98% in the deN_2O stage, with the additional proviso that the degree of NO_x oxidation at the outlet of the deN_2O stage is at least 30%,
   b) supplying the gas stream leaving the deN_2O stage to a cooling apparatus and cooling the gas stream, as it flows through this apparatus, to a temperature below 400°C,
   c) supplying the gas stream leaving the cooling apparatus to a deNO_x stage for catalytic reduction of NO_x with a reducing agent in the presence of a deNO_x catalyst, with addition of such an amount of reducing agent which is sufficient to reduce the desired proportion of NO_x to the gas stream, viewed in flow direction, after it leaves the deN_2O stage and before it flows through the deNO_x catalyst.

2. The process as claimed in claim 1, wherein the ratio of the molar amount of N_2O which enters the deN_2O stage to the molar amount of NO_x which leaves the deN_2O stage is at least 1.5.

3. The process as claimed in claim 1, wherein the ratio of the molar amount of N_2O which enters the deN_2O stage to the molar amount of NO_x which leaves the deN_2O stage is at least 2.

4. The process as claimed in claim 1, wherein the ratio of the molar amount of N_2O which enters the deN_2O stage to the molar amount of NO_x which leaves the deN_2O stage is at least 5.

5. The process as claimed in any one of claims 1 to 4, wherein the molar ratio of N_2O and NO_x in the gas stream comprising NO_x, N_2O and water, even before it enters the deN_2O stage, is at least 1.5, or wherein a reducing agent for NO_x is added to the gas stream comprising NO_x, N_2O and water before or on entry thereof into the deN_2O stage in such an amount that the NO_x present in the gas stream is partly degraded, such that the molar ratio of N_2O and NO_x, immediately after the entry of the gas stream comprising NO_x and N_2O in the deN_2O stage, is at least 1.5.

6. The process as claimed in claim 5, wherein the water content of the gas stream comprising N_2O, NO_x and water, before it enters the deN_2O stage, is adjusted by addition of water vapor and/or by addition of water in liquid form.

7. The process as claimed in any one of claims 1 to 6, wherein the water content of the gas stream comprising N_2O, NO_x and water before it enters the deN_2O stage is adjusted by introducing an offgas stream from a combustion stage in which hydrogen and/or hydrogen-containing compounds are combusted, and/or wherein the water content of the gas stream comprising N_2O, NO_x and water is adjusted before it enters the deN_2O stage by passing it through a water loading apparatus selected from a group comprising saturators and absorption towers.

8. The process as claimed in any one of claims 1 to 7, wherein the gas stream comprising N_2O, NO_x and water, before it enters the deN_2O stage, is heated by means of a heating apparatus to a temperature between 400°C and 650°C.

9. The process of claim 8 wherein the gas stream comprising N_2O, NO_x and water, before it enters the deN_2O stage, is heated by means of a heat exchanger to a temperature between 400°C and 650°C.

10. The process as claimed in claim 8 or 9, wherein the resulting gas stream from the deN_2O stage is supplied to a cooling apparatus which is a recuperator, the heat released being transferred to the gas stream comprising N_2O, NO_x and water before it enters the deN_2O stage, thus heating it to a temperature between 400°C and 650°C.

11. The process as claimed in any one of claims 8 to 10, wherein the gas stream, viewed in flow direction, is divided into two substreams upstream of the heating apparatus, a first substream, after bypassing the heating apparatus, being combined again with the second substream which has passed through the heating apparatus, or wherein the gas stream bypasses the heating apparatus, the amount of the substreams being regulated by means of a valve.

12. The process as claimed in any one of claims 1 to 11, wherein the iron-laden zeolite catalyst of the deN_2O stage is based on a zeolite from the group of the MFI, BEA, FER, MOR and MEL types or mixtures thereof.

13. The process as claimed in any one of claims 1 to 11, wherein the iron-laden zeolite catalyst of the deN_2O stage is based on a zeolite from the group of the MFI or BEA, or mixtures thereof.

14. The process as claimed in any one of claims 1 to 11, wherein the iron-laden zeolite catalyst of the deN_2O stage is based on ZSM-5, or mixtures thereof.

15. The process as claimed in any one of claims 1 to 14, wherein the deN_2O stage has an upstream guard bed which comprises random packings or structured packings of shaped bodies comprising alumina.

16. The process as claimed in any one of claims 1 to 15, wherein the deNO$_x$ stage comprises a deNO$_x$ catalyst based on V_2O_5-TiO_2.

17. The process as claimed in any one of claims 1 to 16, wherein the process in the deN$_2$O stage is performed at space velocities of 2000 to 50 000 h^{-1}.

18. The process as claimed in any one of claims 1 to 16, wherein the process in the deN$_2$O stage is performed at space velocities of 2500 to 25 000 h^{-1}.

19. The process as claimed in any one of claims 1 to 16, wherein the process in the deN$_2$O stage is performed at space velocities of 3000 to 20 000 h^{-1}.

20. The process as claimed in any one of claims 1 to 19, wherein the reducing agent for NO$_x$ is ammonia.

21. The process as claimed in any one of claims 1 to 20, wherein space velocity, temperature and pressure in the deNO$_x$ stage are adjusted such that NO$_x$ conversions between 80% and 100%, are attained.

22. The process as claimed in any one of claims 1 to 20, wherein space velocity, temperature and pressure in the deNO$_x$ stage are adjusted such that NO$_x$ conversions between 90% and 100% are attained.

23. An apparatus for reducing the NO$_x$ and N$_2$O contents in gases comprising NO$_x$, N$_2$O and water, comprising the elements:
    A) an apparatus for adjusting the water content of the gas comprising NO$_x$ and N$_2$O,
    B) a deN$_2$O stage arranged downstream of the apparatus for adjusting the water content of the gas comprising an iron-laden zeolite catalyst,
    C) a cooling apparatus arranged downstream of the deN$_2$O stage for cooling the gas stream leaving the deN$_2$O stage,
    D) a deNO$_x$ stage arranged downstream of the cooling apparatus and comprising a deNO$_x$ catalyst for reducing the NO$_x$ content of the gas stream, and

E) a feed line for introducing reducing agent for NO_x into the gas stream leaving the deN_2O stage, which is arranged between the outlet of the deN_2O stage and upstream of the $deNO_x$ catalyst of the $deNO_x$ stage.

24. The apparatus as claimed in claim 23, wherein the cooling apparatus for the gas stream leaving the deN_2O stage is thermally coupled to a heating apparatus for the gas comprising N_2O, NO_x and water, for the purpose of heating this gas before it enters the deN_2O stage and for the purpose of cooling the gas stream leaving the deN_2O stage before it enters the $deNO_x$ stage.

25. The apparatus as claimed in claim 23, wherein the cooling apparatus for the gas stream leaving the deN_2O stage is thermally coupled to a heat exchanger for the gas comprising N_2O, NO_x and water, for the purpose of heating this gas before it enters the deN_2O stage and for the purpose of cooling the gas stream leaving the deN_2O stage before it enters the $deNO_x$ stage.

26. The apparatus as claimed in claim 23, wherein the cooling apparatus for the gas stream leaving the deN_2O stage is thermally coupled to a recuperator for the gas comprising N_2O, NO_x and water, for the purpose of heating this gas before it enters the deN_2O stage and for the purpose of cooling the gas stream leaving the deN_2O stage before it enters the $deNO_x$ stage.

27. The apparatus as claimed in any one of claims 23 to 26, wherein the apparatus A) is a burner in which combustion gas comprising hydrogen and/or hydrogen-containing compounds is incinerated together with oxygen-containing gas and the offgas thereof is introduced into the gas comprising N_2O, NO_x and water.

28. The apparatus as claimed in any one of claims 23 to 26, wherein the apparatus A) is a burner in which combustion gas comprising hydrogen and/or hydrogen-containing compounds is incinerated together with air, and the offgas thereof is introduced into the gas comprising N_2O, NO_x and water.

29. The apparatus as claimed in claim 24, wherein the entire gas stream or a portion of the gas stream can bypass the heating apparatus via a bypass provided upstream of the heating apparatus in the feed line for the gas stream comprising N_2O, NO_x and water, and this bypass is provided with a valve with which the portion of the gas stream which bypasses the heating apparatus can be controlled.

30. The apparatus as claimed in any one of claims 23 to 28, wherein the feed line for introduction of reducing agent for NO_x into the gas stream leaving the deN_2O stage is provided upstream of the catalyst of the deNO_x stage.

31. The apparatus of claim 30 further comprising providing a mixer downstream of the feed line in the feed line of the gas stream into the deNO_x stage.

32. The apparatus as claimed in any one of claims 23 to 31, wherein the feed line for introduction of reducing agent for NO_x into the gas stream comprising N_2O, NO_x and water is provided upstream of the catalyst of the deN_2O stage.

33. The apparatus of claim 32 further comprising providing a mixer downstream of the feed line in the feed line of the gas stream into the deN_2O stage.

34. The apparatus as claimed in any one of claims 23 to 33, wherein the catalyst in the deN_2O stage is selected from the group of the iron-laden zeolites of the MFI, BEA, FER, MOR and/or MEL type.

35. The apparatus as claimed in any one of claims 23 to 33, wherein the catalyst in the deN_2O stage is selected from the group of the iron-laden zeolites of an Fe-ZSM-5.

36. The apparatus as claimed in any one of claims 23 to 35, wherein a guard bed consisting of a structured packing or bed of alumina-comprising shaped bodies is provided upstream of the iron-laden zeolite catalyst of the deN_2O stage.

37. The apparatus as claimed in any one of claims 23 to 36, wherein the deNO$_x$ catalyst in the deNO$_x$ stage is a transition metal-comprising SCR catalyst or an iron- or copper-laden zeolite.

38. The apparatus as claimed in any one of claims 23 to 36, wherein the deNO$_x$ catalyst in the deNO$_x$ stage is a transition metal-comprising an SCR catalyst based on V_2O_5-TiO_2.

39. The apparatus as claimed in any one of claims 23 to 38, wherein different catalysts are provided in the deN$_2$O stage and in the deNO$_x$ stage.

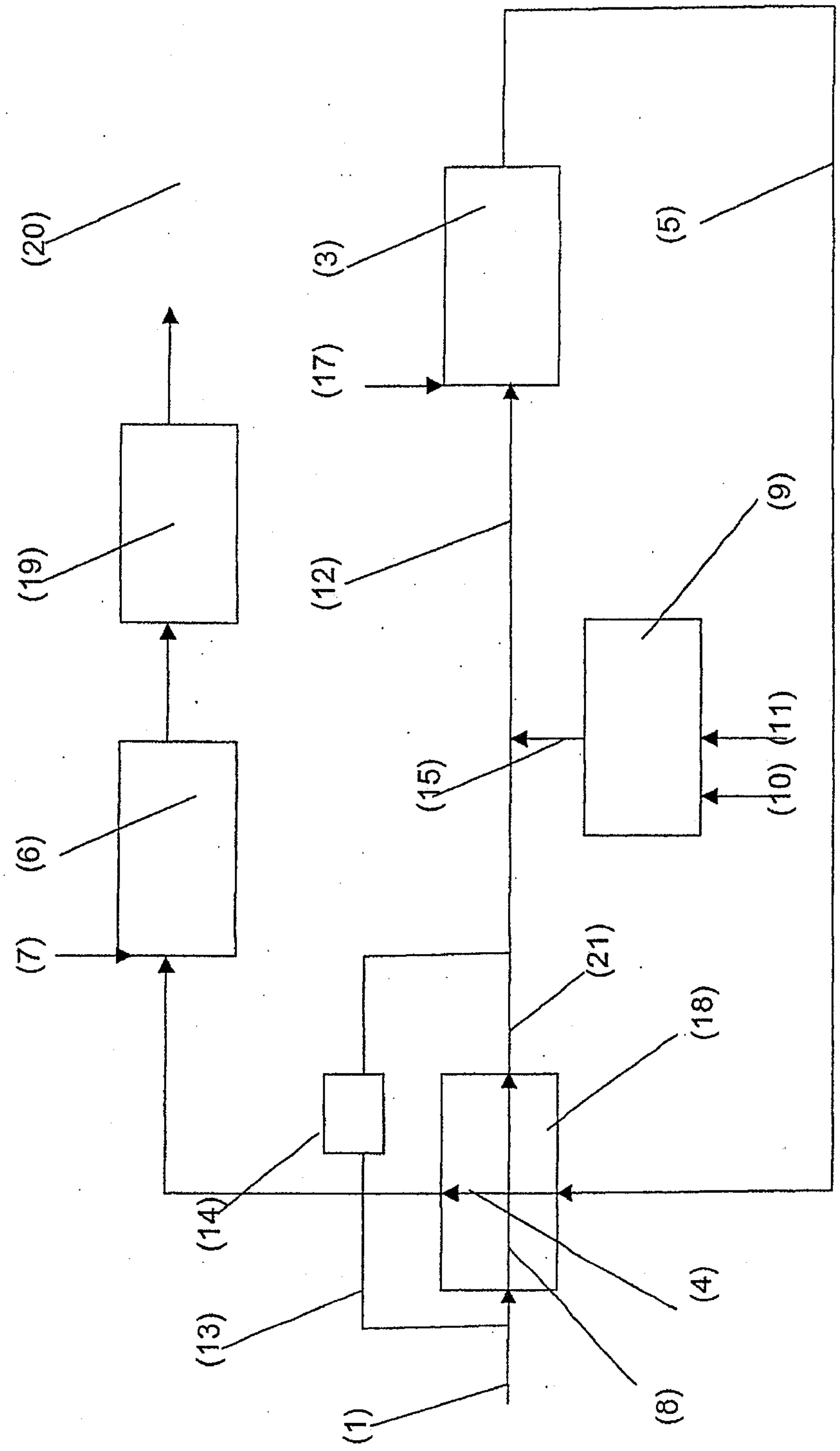


Figure 3

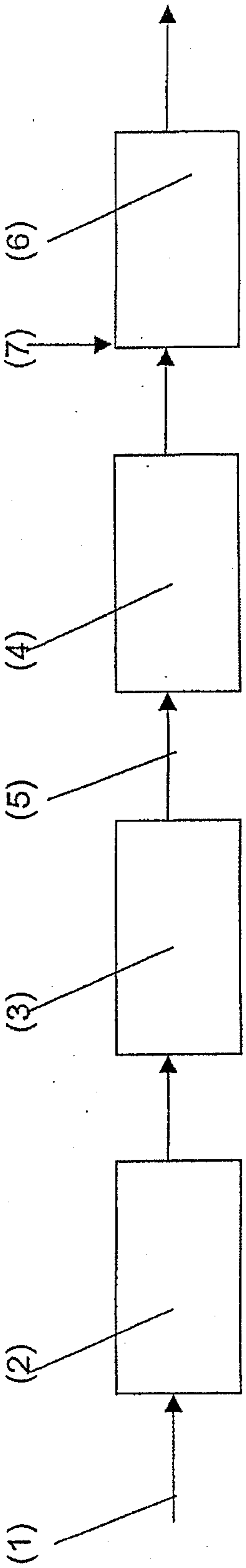


Figure 2

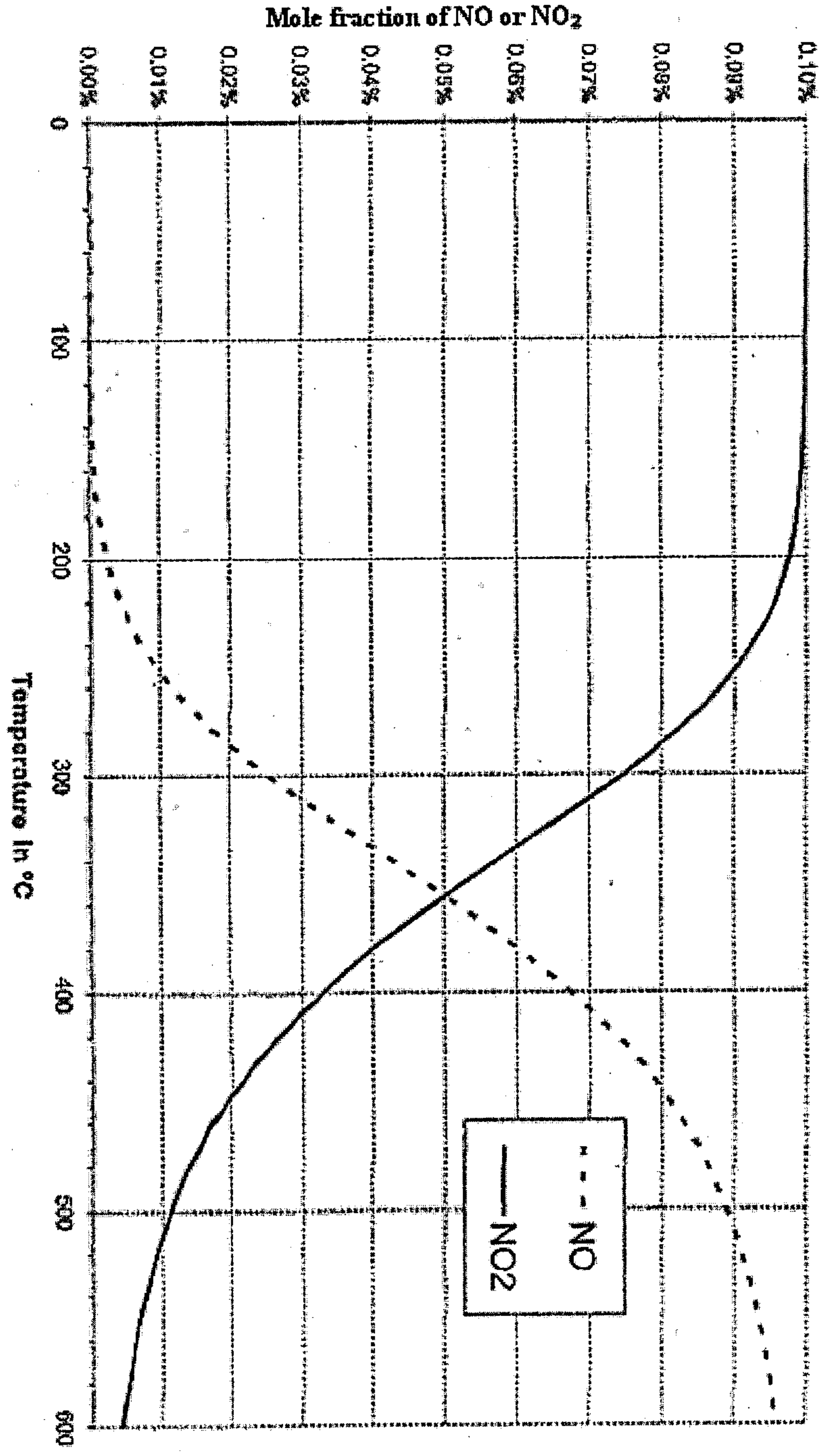

Mole fraction of NO or NO2
0.00%
0.01%
0.02%
0.03%
0.04%
0.05%
0.06%
0.07%
0.08%
0.09%
0.10%
0
100
200
300
400
500
600
Temperature in °C
NO
NO2

Figure 1


(1)
(2)
(3)
(5)
(4)
(7)
(6)