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**Anmeldenummer Nr.**

**Application No**

**Demande de brevet n°**

PCT/EP2016/076152

Der Präsident des Europäischen Patentamts, i.A.  
For the President of the European Patent Office  
Le Président de l'Office européen des brevets, p.o.



V. Joseph



**Blatt 2 der Bescheinigung**  
**Sheet 2 of the certificate**  
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**Anmeldenummer - Application no. - Demande n°**

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A METHOD AND APPARATUS FOR REMOVING NOX AND N2O FROM A GAS

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A method and apparatus for removing NO<sub>x</sub> and N<sub>2</sub>O from a gas

## DESCRIPTION

### Field of the invention

- 5 The invention relates to systems for reducing the NO<sub>x</sub> and N<sub>2</sub>O content of a gas.

### Prior art

10 Many industrial processes discharge a gas containing nitrogen oxides (NO<sub>x</sub>) and nitrous oxide (N<sub>2</sub>O). In particular, any combustion process produces exhaust gases containing NO<sub>x</sub> and N<sub>2</sub>O. Another significant case is given by industrial production of nitric acid, which releases an offgas mainly consisting of nitrogen, Oxygen and unconverted NO<sub>x</sub> and N<sub>2</sub>O. The term nitrogen oxides or NO<sub>x</sub> collectively denotes nitrogen monoxide (NO) and dioxide (NO<sub>2</sub>).

- 15 NO<sub>x</sub> and N<sub>2</sub>O are known pollutants and the related emissions are subject to strict regulations. Hence a treatment of said combustion gas or offgas in a suitable de-NO<sub>x</sub> system is indispensable.

20 A prior art technique for removing NO<sub>x</sub> and N<sub>2</sub>O from a gas involves passing the gas over a sequence of two catalytic beds, wherein the first bed is to reduce the quantity of N<sub>2</sub>O and the second bed is to reduce the quantity of NO<sub>x</sub>. Elimination of NO<sub>x</sub> in the second bed is made possible by injection of ammonia as a reducing agent for NO<sub>x</sub> between the first bed and the second bed.

25 The above prior-art system is based on the finding that NO<sub>x</sub> accelerates the decomposition of N<sub>2</sub>O. Accordingly, ammonia for NO<sub>x</sub> abatement is only added after the passage in the first bed, so that the first step of de-N<sub>2</sub>O is

facilitated by the NO<sub>x</sub> contained in the source gas.

The removal of N<sub>2</sub>O basically follows the reaction:



while the removal of NO<sub>x</sub> follows:



Hence the prior art teaches first to convert N<sub>2</sub>O into NO<sub>x</sub> and, subsequently, to remove NO<sub>x</sub> by a catalytic reaction with ammonia.

This technique, however, requires a very accurate regulation of the added ammonia and intensive mixing between ammonia and the gas, otherwise  
10 the target concentration of NO<sub>x</sub> may not be reached or some ammonia may escape the second bed (ammonia slip). A fluctuation of the process may cause the release of NO<sub>x</sub> and/or ammonia outside the limit, which causes an environmental impact and may generate an additional cost. For example, some countries prescribe that the release of ammonia into  
15 atmosphere is subject to a penalty fee, making ammonia slip undesirable. The maximum ammonia which is permitted is generally very low, for example 5 ppm. A further reason why ammonia slip is undesirable is the possible formation of ammonium nitrite or nitrate which can lead to damage of equipment, for example of a downstream expander.

20 Typically, the flowrate of ammonia must be regulated with accuracy of 1-2% which is difficult to obtain. For example a system for reduction of NO<sub>x</sub> and N<sub>2</sub>O can be designed to process a gas current containing about 1000 ppm and be required to output a gas with no more than 25 ppm of NO<sub>x</sub> and 5 ppm of ammonia. As the quantity of ammonia required to reduce NO<sub>x</sub> is  
25 about the same of the NO<sub>x</sub>, this means that added ammonia shall be precisely regulated between 975 and 1005 ppm to meet both above requirements. The range of regulation is +/- 15 ppm, which means the required accuracy is 1.5% of the flowrate.

The above problem is more challenging as the requirement in terms of emissions of NO<sub>x</sub> and ammonia become more stringent in several countries.

#### Summary of the invention

- 5 The aim of the invention is to solve the above drawbacks of the prior art two-beds systems for abatement of NO<sub>x</sub> and N<sub>2</sub>O.

This aim is reached with a method and apparatus according to the attached claims. Preferred features of the invention are stated in the dependent claims.

- 10 The invention provides that nitrogen oxides NO<sub>x</sub> and nitrous oxide N<sub>2</sub>O are removed from an input gas by:

treating said input gas with a first amount of a NO<sub>x</sub> reducing agent in a first de-NO<sub>x</sub> catalytic bed;

- 15 treating the effluent of said first catalytic bed in a second catalytic bed for removal of N<sub>2</sub>O;

treating the effluent of said second catalytic bed with a second amount of a NO<sub>x</sub> reducing agent in a third de-NO<sub>x</sub> catalytic bed.

- 20 Preferably the NO<sub>x</sub> reducing agent is ammonia or contains ammonia. In the description, reference will be made to ammonia as a NO<sub>x</sub> reducing agent for simplicity.

- An aspect of the invention is that ammonia is added in two separate steps. A first amount of ammonia is added to the gas before admission into the first bed, and a second amount of ammonia is added after the passage over the second bed for removal of N<sub>2</sub>O, and before admission into the third de-  
25 NO<sub>x</sub> bed.

The majority of NO<sub>x</sub> are removed in the first bed, which means that the

majority of ammonia is added before said first bed. The first bed is designed to reach a low NOx content in the gas and, particularly, to ensure that no ammonia will remain in the effluent gas leaving said first bed. For example the effluent of the first bed may contain 50 to 200 ppm of NOx (as  
5 NO and NO<sub>2</sub>). The NOx content is preferably determined as the minimum required to provide the desired subsequent removal of N<sub>2</sub>O. Then, a relatively small amount of ammonia is added after the passage over the de-N<sub>2</sub>O bed, in order to remove the residual NOx and reach the target concentration, which may be for example 25 ppm.

10 In this description and in the attached claims, the term ppm denotes parts per million in volume.

The invention provides that a substantially ammonia-free and low-NOx gas is produced after treatment in a first catalytic bed, having a content of NOx which is as low as possible, taking into account the need of some NOx for  
15 subsequent N<sub>2</sub>O removal in a second bed. Then, residual NOx are removed in a third bed and with an addition of a second amount of ammonia which is smaller and easier to control than the first amount.

The second amount of ammonia is strictly determined by the amount of NOx in the effluent of the second bed. For example a residual amount of  
20 200 ppm NOx would require an addition of ammonia corresponding to 200 ppm. Assuming a setpoint of 190 ppm and maximum deviation of +/- 15 ppm, accuracy is 8% compared to 1.5% of the prior art. Accordingly, the control of the ammonia flow is easier. With a lower amount of ppm NOx in the gas, the accuracy becomes higher, namely easier to obtain. In the  
25 above example, 100 ppm of NOx would correspond to 16.7% accuracy of the ammonia flow control and 50 ppm would correspond to 37.5% accuracy.

Accordingly, the great advantage of the invention is the system being able

to reduce or eliminate the risk of excursion out of the limit and being able to operate under more stringent regulation. For example, the invention may obtain a final concentration of: less than 25 ppm of NO<sub>x</sub>, less than 30 ppm of N<sub>2</sub>O, less than 2 ppm of ammonia.

- 5 The three catalytic beds may have any suitable catalyst. Particularly, the two de-NO<sub>x</sub> catalytic beds may have the same or a different catalyst. According to preferred embodiments, the catalyst of the first bed (first de-NO<sub>x</sub>) is copper exchanged zeolite; the catalyst of the second bed (de-N<sub>2</sub>O) is iron exchanged zeolite; the catalyst of the third bed (second de-NO<sub>x</sub>) is
- 10 Vanadium oxide. In some embodiments, also an iron-based catalyst may be used for the first and/or the second de-NO<sub>x</sub> catalytic bed.

In a preferred embodiment the second de-NO<sub>x</sub> catalytic bed comprises a catalyst which is iron exchanged zeolite and the gas admitted into said second catalytic bed has a molar ratio of NH<sub>3</sub>/NO<sub>x</sub> greater than 1.33. Said

15 molar ratio NH<sub>3</sub>/NO<sub>x</sub> is understood as molar ratio of ammonia to the sum of NO and NO<sub>2</sub>. Even more preferably said ratio is greater than 1.4. A more preferred ratio is in the range 1.4 to 1.6. More preferably said ratio is 1.5 or about 1.5. Still more preferably, said iron exchanged zeolite catalyst of the second catalytic bed operates at a temperature around 430 °C.

- 20 In a preferred embodiment, both the first and second de-NO<sub>x</sub> catalytic beds comprise iron exchanged zeolite catalyst. More preferably, the first catalytic bed operates with NH<sub>3</sub>/NO<sub>x</sub> less than 1 to keep some NO<sub>x</sub> in the gas for subsequent removal of N<sub>2</sub>O.

The applicant has found that the above conditions of de-NO<sub>x</sub> bed result in a

25 virtually absent ammonia slip, typically less than 1 ppm. Also, a removal of almost all N<sub>2</sub>O (greater than 99%) is reached. Accordingly the invention allows meet the most stringent limits of NH<sub>3</sub> and NO<sub>x</sub>.

The three catalytic beds may be arranged in one or more separate pressure



vessels or in the same pressure vessel.

The catalytic beds, according to various embodiments, can be traversed axially or radially by the gas flow.

In a preferred embodiment, at least two catalytic beds are contained in a  
5 single pressure vessel. For example in one embodiment the first and the second bed are contained in the same pressure vessel; in another embodiment the second and the third bed are contained in the same pressure vessel; in another embodiment the three beds are all contained in the same pressure vessel.

10 According to some embodiments, the catalytic beds contained in a single pressure vessel can be arranged one above the other or, as an alternative, they can be arranged concentrically.

In some embodiments the first two catalytic beds traversed by the gas flow, namely the first de-NO<sub>x</sub> bed and the de-N<sub>2</sub>O bed, can be made of the  
15 same catalyst. In that case, there can be no physical separation between said two beds.

The invention will now be elucidated with reference to a non-limitative example of preferred embodiments.

#### Description of figure

20 Fig. 1 is a scheme of a method of removing NO<sub>x</sub> and N<sub>2</sub>O from a gas according to an embodiment of the invention.

Fig. 2 is a scheme of an apparatus to carry out the method of the invention, according to a preferred embodiment.

#### Detailed description

25 Referring to Fig. 1, a gas current 1 containing NO<sub>x</sub> and N<sub>2</sub>O is added with ammonia 2 and passed over a first de-NO<sub>x</sub> catalytic bed 3.

The majority of NOx contained in the input gas 1 are removed in the bed 3 by reaction with the added ammonia. The amount of ammonia 2 is determined in such a way that no ammonia remains in the effluent of the bed 3.

- 5 Then, a low-NOx and substantially ammonia-free gas 4 is collected from the first de-NOx bed 3. The content of NOx in the gas 4 is preferably determined as a function of the N2O in the input gas 1, namely the content of NOx in the gas 4 is the minimum content which is necessary or appropriate to allow a subsequent removal of N2O.
- 10 The gas 4 is then passed over a de-N2O catalytic bed 5. The effluent 6 of said de-N2O catalytic bed 5 is added with a second amount of ammonia 7 and is passed over a second de-NOx catalytic bed 8 for a further removal of NOx. The effluent 9 is a purified gas with a low content of NOx and N2O.

The second amount of ammonia 7, which is preferably smaller than the first  
15 amount 2, is controlled as a function of the NOx contained in the gas 6, and to match a target NOx content in the effluent 9.

Preferably, the content of NOx in the gas 6 is between 50 and 200 ppm and the ammonia 7 is determined accordingly. The target NOx in the gas 9 is generally determined by applicable law, for example less than 25 ppm may  
20 be prescribed.

The small amount of ammonia 7 can be precisely regulated to avoid ammonia slip in the effluent 9. Thanks to the invention, accuracy of the flow control of ammonia 7 (in percent) is less stringent than the prior art, for example around 10% or greater.

25 Fig. 2 is a simplified scheme of an apparatus 10 to carry out the method of the invention, wherein the three beds 3, 5 and 8 are contained in a single pressure vessel 11 and are traversed radially by the gas (radial-flow).

The catalytic beds are for example contained within baskets with gas

permeable walls, for example perforated or slotted walls. The path of the gas is shown by the arrows of Fig. 2.

More in detail, the Fig. 2 shows an embodiment where the first de-NO<sub>x</sub> bed 3 and the de-N<sub>2</sub>O bed 5 are arranged concentrically in an upper part of the apparatus 10 while the second de-NO<sub>x</sub> bed 8 is contained in a lower part of the same.

The flow of incoming gas 1 and ammonia 2 is distributed by a permeable wall 12 through the outer de-NO<sub>x</sub> bed 3 and traverses radially said bed 3 and the inner de-N<sub>2</sub>O bed 5. The effluent of said inner bed 5 (stream 6 of Fig. 1) is collected in a central collector 13 where the second amount of ammonia 7 is provided. Then, the gas mixture passes in the lower part of apparatus 10 and traverses the second de-NO<sub>x</sub> bed 8. The effluent 9 of said second de-NO<sub>x</sub> bed 8 is collected in a collector 14.

### Example

15 An off gas 1 from synthesis of nitrous acid has a flowrate of 4100 kmol/h and contains 700 ppm of NO<sub>x</sub> (NO+NO<sub>2</sub>) and 900 ppm of N<sub>2</sub>O. The gas 1 further contains 3% of oxygen.

The first de-NO<sub>x</sub> catalytic bed 3 has a copper exchanged zeolite catalyst and a space velocity of 15000 h<sup>-1</sup>. Ammonia 2 is added in an amount corresponding to 560 ppm in the gas 1. After a passage over said bed 3, the effluent gas stream 4 contains 145 ppm of NO<sub>x</sub> and 950 ppm of N<sub>2</sub>O.

The de-N<sub>2</sub>O catalytic bed 5 has an iron exchanged zeolite catalyst and has a space velocity of 5000 h<sup>-1</sup>. After a passage over said de-N<sub>2</sub>O bed 5, the effluent gas 6 still contains 145 ppm of NO<sub>x</sub> but only 20 ppm of N<sub>2</sub>O.

25 Said gas 6 is added with ammonia 7 and passed over the second de-NO<sub>x</sub> catalytic bed 8. The set point of the flowrate of ammonia 7 corresponds to 140 ppm in the gas, being a function of the NO<sub>x</sub> still contained in the gas.

The second de-NO<sub>x</sub> catalytic bed 8 preferably has a vanadium oxide catalyst and a space velocity of 15000 h<sup>-1</sup>.

The effluent 9 has NO<sub>x</sub> < 25 ppm and contains no or a negligible amount of ammonia, typically less than 2 ppm of ammonia.

## CLAIMS

1. A method for reducing the content of nitrogen oxides NO<sub>x</sub> and nitrous oxide N<sub>2</sub>O in an input gas (1), comprising the steps of:
  - 5 treating said gas (1) with a first amount of a NO<sub>x</sub> reducing agent (2) in a first de-NO<sub>x</sub> catalytic bed (3);
  - treating the effluent (4) of said first de-NO<sub>x</sub> catalytic bed (3) in at least one de-N<sub>2</sub>O catalytic bed (5) for removal of N<sub>2</sub>O;
  - 10 treating the effluent (6) of said at least one de-N<sub>2</sub>O catalytic bed (5) with a second amount of a NO<sub>x</sub> reducing agent (7) in a second de-NO<sub>x</sub> catalytic bed (8).
2. A method according to claim 1, comprising the steps of mixing the input gas with said first amount of NO<sub>x</sub> reducing agent before admission into the first de-NO<sub>x</sub> catalytic bed, and mixing the effluent gas of said at least  
15 one de-N<sub>2</sub>O catalytic bed with said second amount of NO<sub>x</sub> reducing agent before admission into the second de-NO<sub>x</sub> catalytic bed.
3. A method according to any of the previous claims, wherein the first amount of NO<sub>x</sub> reducing agent is completely reacted with NO<sub>x</sub> in the first de-NO<sub>x</sub> catalytic bed, so that the effluent of said first de-NO<sub>x</sub> catalytic  
20 bed is substantially free from said reducing agent.
4. A method according to any of the previous claims, wherein the majority of NO<sub>x</sub> contained in the input gas are removed in the first de-NO<sub>x</sub> catalytic bed, and the residual amount of NO<sub>x</sub> in the effluent of said catalytic bed is determined as a minimum content which is required for  
25 the subsequent treatment over said de-N<sub>2</sub>O catalytic bed.
5. A method according to any of the previous claims, wherein the second amount of NO<sub>x</sub> reducing agent is determined on the basis of the NO<sub>x</sub>

contained in the gas at the outlet of the first de-NO<sub>x</sub> catalytic bed or at the outlet of the De-N<sub>2</sub>O catalytic bed.

6. A method according to any of the previous claims, wherein said second amount of NO<sub>x</sub> reducing agent is smaller than the first amount.
- 5 7. A method according to any of the previous claims, wherein the concentration of NO<sub>x</sub> in the effluent of the first de-NO<sub>x</sub> catalytic bed is not greater than 200 ppm, preferably in the range 50 to 200 ppm.
8. A method according to any of the previous claims, wherein the NO<sub>x</sub> reducing agent is or contains ammonia.
- 10 9. A method according to any of the previous claims, wherein: the catalyst of the first de-NO<sub>x</sub> bed is copper exchanged zeolite, and/or the catalyst of the de-N<sub>2</sub>O bed is iron exchanged zeolite, and/or the catalyst of the second de-NO<sub>x</sub> bed is Vanadium oxide.
- 15 10. A method according to any of the previous claims, wherein: the first de-NO<sub>x</sub> bed has a copper exchanged zeolite catalyst and a space velocity of 15'000 h<sup>-1</sup>; the de-N<sub>2</sub>O bed has iron exchanged zeolite catalyst and a space velocity of 5'000 h<sup>-1</sup>; the second de-NO<sub>x</sub> bed has a Vanadium oxide catalyst and a space velocity of 15'000 h<sup>-1</sup>.
- 20 11. A method according to claim 8 wherein said second de-NO<sub>x</sub> catalytic bed comprises a catalyst which is iron exchanged zeolite and the gas admitted into said second catalytic bed has a molar ratio of NH<sub>3</sub>/NO<sub>x</sub> greater than 1.33.
12. A method according to claim 11, said ratio being greater than 1.4 and preferably in the range 1.4 to 1.6, more preferably about 1.5.
- 25 13. A method according to claim 11 or 12, wherein the first de-NO<sub>x</sub> catalytic bed comprises a catalyst which is iron exchanged zeolite and operates with a molar ratio of NH<sub>3</sub>/NO<sub>x</sub> less than 1.

14. A method according to any of the previous claims, wherein the effluent of the second de-NOx bed has NOx < 25 ppm; N2O < 30 ppm; NH3 < 2 ppm.
15. A method according to any of the previous claims, wherein the input  
5 gas is a combustion exhaust gas or a process gas, particularly an offgas of a process for making nitric acid.
16. An apparatus for reducing the content of NOx and N2O in a gas, comprising at least:
- 10 a first de-NOx catalytic bed and a device arranged to introduce a first amount of a NOx reducing agent in the input gas, so that the input gas is treated in the first de-NOx bed with the first amount of reducing agent;
- a de-N2O catalytic bed arranged to treat the effluent of said first de-NOx catalytic bed to remove N2O, and
- 15 a second de-NOx catalytic bed and a device arranged to introduce a second amount of a NOx reducing agent in the gas effluent from said de-NOx catalytic bed, so that said effluent is treated in the second de-NOx bed with the second amount of reducing agent.
17. An apparatus according to claim 16, wherein at least two of said catalytic beds are contained in a single pressure vessel.

ABSTRACT

Method for reducing the content of nitrogen oxides NO<sub>x</sub> and nitrous oxide N<sub>2</sub>O in an input gas, comprising the steps of: treating said gas with a first amount of a NO<sub>x</sub> reducing agent in a first de-NO<sub>x</sub> catalytic bed; treating the  
5 effluent of said first de-NO<sub>x</sub> catalytic bed in at least one de-N<sub>2</sub>O catalytic bed for removal of N<sub>2</sub>O; treating the effluent of said at least one de-N<sub>2</sub>O catalytic bed with a second amount of a NO<sub>x</sub> reducing agent in a second de-NO<sub>x</sub> catalytic bed.



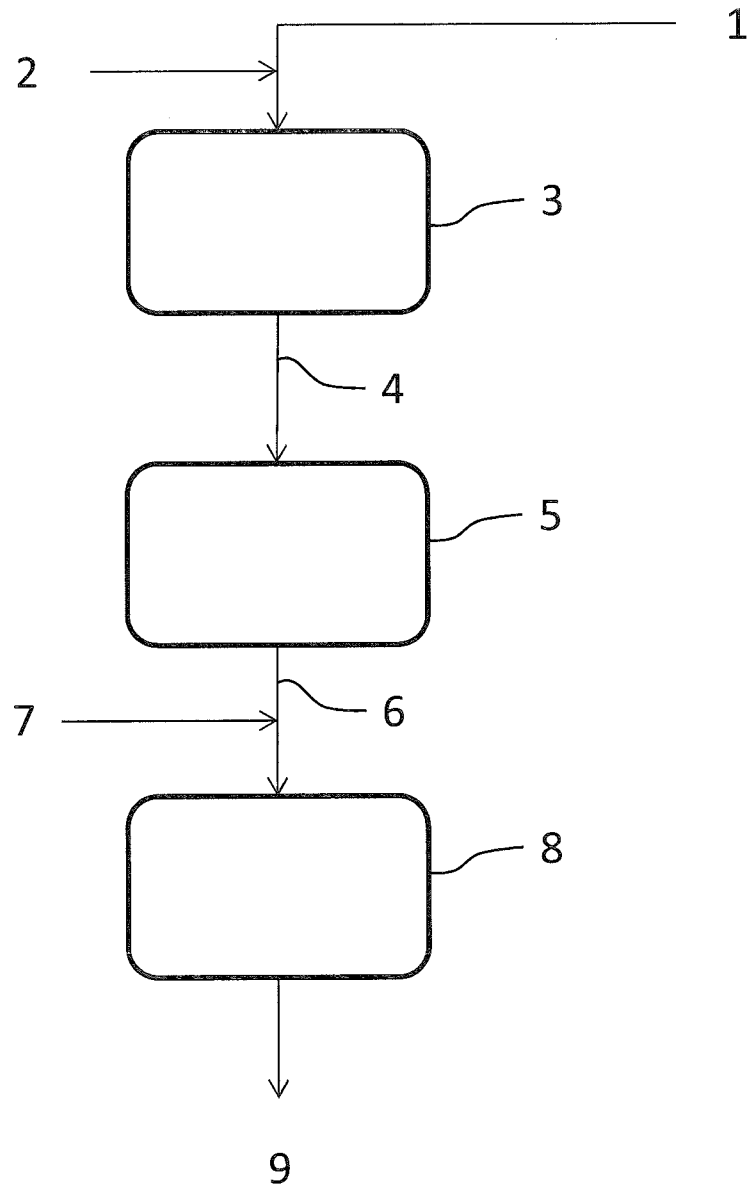


FIG. 1

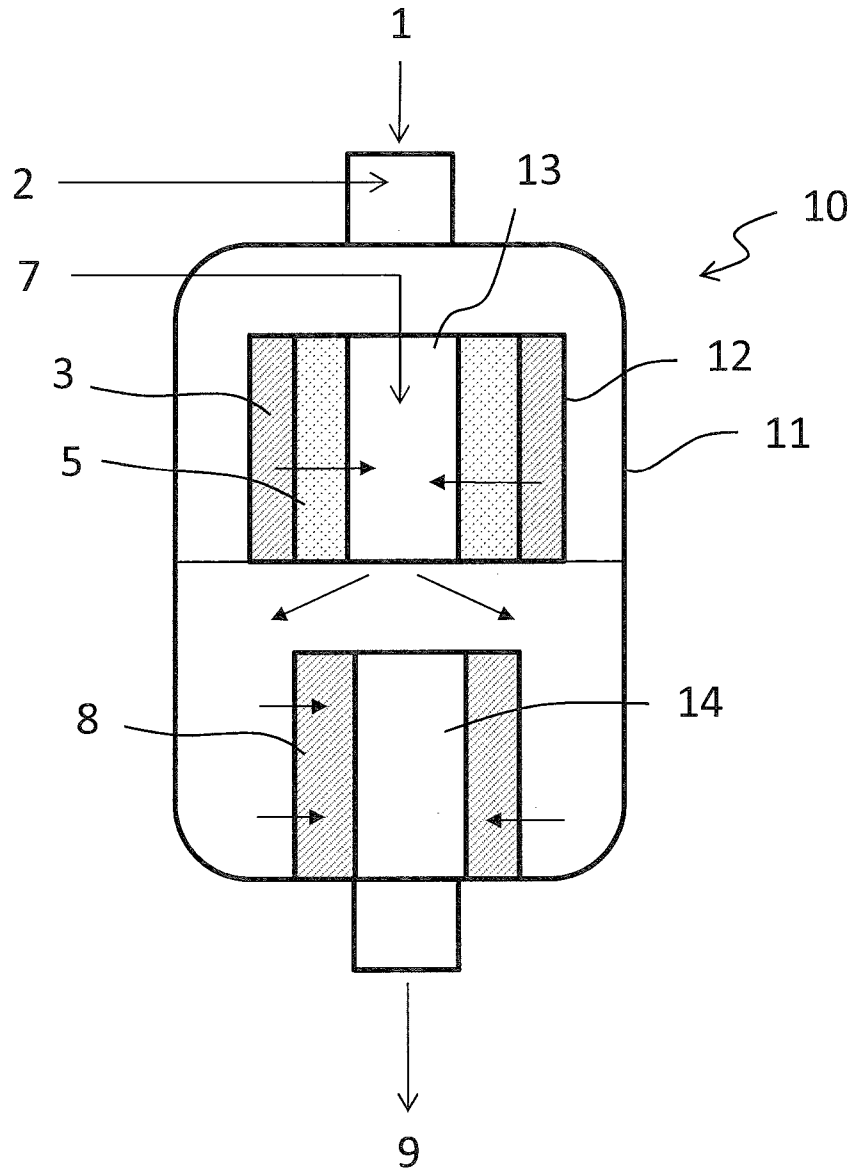


FIG. 2