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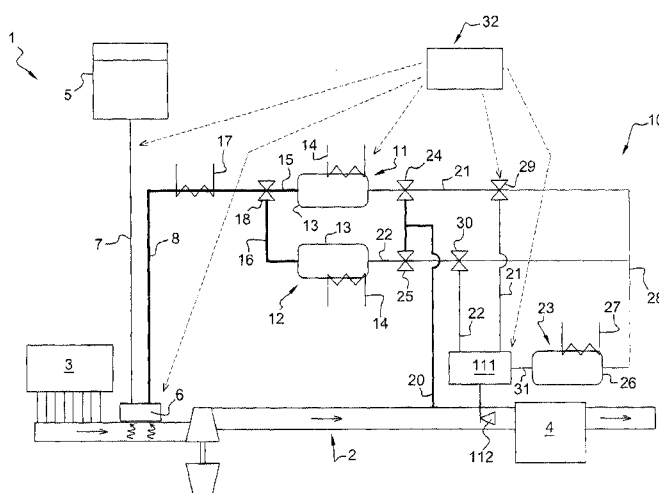
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**Fig. 1**

(57) Abstract: The system (1) comprises: - a source (5) of a precursor of ammonia; - a conversion device (6) for producing gaseous ammonia from said precursor; - a dosing device (111) for dosing gaseous ammonia to be introduced in the exhaust line (2) upstream from a selective catalytic reduction device (4); - an ammonia storage and release arrangement (10) comprising a first and a second unit (11, 12), each unit including a container (13) containing a material which, depending on the operating conditions, is capable of retaining gaseous ammonia supplied by the conversion device, in order to store gaseous ammonia, and of releasing previously retained gaseous ammonia towards the dosing device; - a control system (32) capable of operating each of the first and second units (11, 12) either in a storage mode or in a release mode.

## SYSTEM AND METHOD FOR TREATING NITROGEN OXIDES CONTAINED IN EXHAUST GASES

### Field of the invention

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The present invention relates to a system and a method for treating nitrogen oxides contained in exhaust gases flowing in an exhaust line of an engine, especially but not exclusively in a vehicle.

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### Technological background

Exhaust gases formed in the combustion of fuel in an internal combustion engine, in particular in industrial vehicles, may contain a proportion of undesirable components, in particular nitrogen oxides (NO<sub>x</sub>).

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A selective catalytic reduction (SCR) system has been a standard feature in engine arrangements for many years, in order to treat said nitrogen oxides and reduce air pollution. In such a system, exhaust gases, mixed with ammonia as a reducer, are treated in a specific catalytic converter where nitrogen oxides are converted into water and nitrogen which are both non-toxic substances.

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In a first arrangement of the prior art, ammonia may be introduced in the form of urea in aqueous solution from which ammonia is obtained through hydrolysis. The urea solution is usually nebulised in the exhaust gases upstream from the catalytic converter. To this end, a urea injection nozzle is fitted on the exhaust line upstream from the catalytic converter.

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One problem with this type of exhaust gases treatment is that, in some operating conditions of the engine, especially when the temperature of the exhaust gases is relatively low, for example around 200°C, urea can crystallize before it has transformed into ammonia. In concrete terms, the aqueous solution of urea which is sprayed through the nozzle inside the exhaust pipe, according to a direction which may be angled with respect to the exhaust gases flow direction, tends to form a solid deposit on the exhaust pipe wall, on the internal side thereof, for example opposite of the injection point. One consequence is that the cross section of the exhaust pipe is progressively reduced, which makes the engine efficiency decrease and which can seriously impair the engine operation in the long term.

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The aqueous solution of urea could also be vaporized into the exhaust line, i.e. introduced as a vapour rather than as a liquid. This solves the crystallization problem. However, with this implementation, urea is difficult to dose. Moreover, the lead time between the introduction of urea and the availability of ammonia in the exhaust line can be fairly high, which can result in poor efficiency of the system. Besides, by-products can be generated at low temperatures, which is not desirable.

In a second arrangement of the prior art, ammonia could be introduced in the exhaust line in the form of gaseous ammonia. However, this implementation is less preferred because of the safety issues related to the storage of ammonia in high pressure tanks.

According to a third arrangement of the prior art, there are provided containers containing a solid on which ammonia has been previously absorbed or adsorbed. In use, ammonia can be released under certain operating conditions, and directed towards the exhaust line upstream from the catalytic converter. This implementation is advantageous in that it avoids crystallization that occurs when injecting liquid urea solution. However, in practice, the containers need to be exchanged by the customer when all ammonia retained on the solid has been released, so as to meet legal requirements in terms of NOx emissions. This solution therefore proves inconvenient.

It therefore appears that, from several standpoints, there is room for improvement in the treatment of nitrogen oxides contained in exhaust gases.

## Summary

It is an object of the present invention to provide a system and a method for treating nitrogen oxides contained in exhaust gases that can overcome the drawbacks of the prior art.

More precisely, an object of the present invention is to provide such a system and method which can be effective, even at low temperatures, which avoids crystallization in the exhaust line and which is convenient for the vehicle operator.

According to a first aspect, the invention relates to a system to be fitted on an automotive vehicle for treating nitrogen oxides contained in exhaust

gases flowing in an exhaust line of an engine of the vehicle, wherein the system comprises:

- a source of a precursor of ammonia;
- a conversion device for producing gaseous ammonia from said precursor;
- a dosing device for dosing gaseous ammonia to be introduced in the exhaust line upstream from a selective catalytic reduction device;
- an ammonia storage and release arrangement ;

characterized in that:

- the ammonia storage and release arrangement comprises at least a first and a second unit, each unit including a container containing a material which, depending on the operating conditions, is capable of retaining gaseous ammonia supplied by the conversion device, in order to store gaseous ammonia, and of releasing previously retained gaseous ammonia towards the dosing device;
- in that the system comprises a control system capable of operating each of the first and second units:
  - either in a storage mode, in which ammonia is supplied to the unit to be stored in said unit;
  - or in a release mode, in which ammonia previously stored in said unit is released and sent towards the dosing device.

Therefore, the invention takes advantage of two complementary solutions, namely:

- by using a source of a precursor of ammonia – such as an aqueous solution of urea contained in a tank on-board the vehicle – and of the associated delivery circuit, which can be a standard feature in a vehicle, the invention does not require specific arrangement for this part of the system, nor does it involve the hazards related to the storage of liquid or gaseous ammonia;
- by injecting gaseous ammonia in the exhaust line, the invention avoids crystallization problems.

Moreover, by providing two containers which can alternatively and selectively be used to store and release ammonia in a gaseous form retained in a material, only a regular refill of the tank containing the precursor of ammonia is required. This can be done when also refilling the fuel tank of the vehicle.

- The containers can be fairly small, and can be used for a long period. An exchange of said containers is not needed between two normal

services of the vehicle. The containers can be made in various sizes and shapes, which makes their fitting on the vehicle easier.

With the system according to the invention, gaseous ammonia can always be available and ready to use, whatever the engine operating  
5 conditions, either in the first unit or in the second unit. Indeed, during the storage mode of one unit, gaseous ammonia can be released from the other unit.

A significant advantage of the invention over the prior art is that there is no need to provide a real time management of the converting process,  
10 i.e. of the production of ammonia, to always have available ammonia for treating the exhaust gases.

In practice, the first and second units can be arranged in parallel between the conversion device and the dosing device. In steady state phase, one unit can be operated in the storage mode while the other unit is operated in  
15 the release mode. At some point, the units can then be switched respectively to the release mode and the storage mode. Switching can occur for example when the unit in the storage mode reaches a certain high level of accumulated ammonia or when the unit in the release mode reaches a certain low level of remaining ammonia. However, in transient phases, it can be envisaged that  
20 both units be operated in the release mode, or in the storage mode. In the latter case, it may be preferred to provide gaseous ammonia to the dosing device through another device, so as to enable the continuous treatment of nitrogen oxides in the exhaust gases.

Another significant advantage of the invention is that the system  
25 performance is high even at low temperatures, insofar as gaseous ammonia is directly introduced in the exhaust line. Moreover, the dosing of gaseous ammonia proves simple and effective.

According to a second aspect, the invention relates to a method for treating nitrogen oxides contained in exhaust gases flowing in an exhaust line  
30 of an engine of an automotive vehicle, the method comprising:

- supplying a precursor of ammonia to a conversion device for producing gaseous ammonia;
- providing at least a first and a second unit, each unit including a container containing a material which, depending on the operating conditions,  
35 is capable of retaining gaseous ammonia supplied by the conversion device, in order to store gaseous ammonia, and of releasing previously retained gaseous

ammonia towards a dosing device which is intended for dosing gaseous ammonia to be introduced in the exhaust line upstream from a selective catalytic reduction device;

- operating one of the first and second units in a storage mode, in which ammonia is supplied from the conversion device to said unit in order to be stored in said unit;

- simultaneously operating the other one of the first and second units in a release mode, in which ammonia previously stored in said unit is released and sent towards the dosing device.

The method as above described corresponds to a steady state phase of the system operation. But, as previously mentioned, in transient phases, both units can be operated in the release mode, or in the storage mode.

These and other features and advantages will become apparent upon reading the following description in view of the drawings attached hereto representing, as non-limiting examples, embodiments of a system and method according to the invention.

### **Brief description of the drawings**

The following detailed description of several embodiments of the invention is better understood when read in conjunction with the appended drawings, it being however understood that the invention is not limited to the specific embodiments disclosed.

Figure 1 is a schematic representation of a system according to a first embodiment of the invention;

Figures 2 to 6 show the system of Figure 1 in various operating phases;

Figure 7 is a schematic representation of a system according to a second embodiment of the invention.

### **Detailed description of the invention**

Figure 1 schematically shows a first embodiment of a system for treating nitrogen oxides (NO<sub>x</sub>) contained in the exhaust gases produced by an automotive vehicle engine, especially by an internal combustion engine 3.

An exhaust line 2 carries exhaust gases from an engine 3 towards the atmosphere. In the exhaust line 2 is provided a selective catalytic reduction (SCR) device 4 in which NO<sub>x</sub> can be converted essentially into water and nitrogen by means of ammonia used as a reductant.

5           The system 1 comprises a tank 5 which contains a precursor of ammonia, i.e. a substance which is chemically separable into gaseous ammonia and possible other components. The tank can be considered a source of a precursor of ammonia. The conversion of the precursor into gaseous ammonia takes place in a conversion device 6 which is supplied with  
10 the precursor of ammonia from the tank 5 by a supply line 7 which may comprise a pump and a dosing system.

This conversion may require heat supply. To this end, the conversion device 6 can be thermally connected to the exhaust line 2, therefore using the thermal energy of hot exhaust gases to convert the precursor of  
15 ammonia into gaseous ammonia and other components. For example, the conversion device 6 may be located next to the exhaust line, and can be located upstream of a turbine driven by the exhaust gases so as to benefit from high temperature of the gases upstream of the turbine. In the shown example, the only interaction between the exhaust gases and the conversion device  
20 consists in a heat transfer. If necessary, an additional heating device, not relying on the heat generated by the engine, could also be provided to provide heat to the conversion device in certain operating conditions. Such heating device could include an electric heater, a fuel burner, etc...

In practice, the precursor of ammonia can comprise an aqueous  
25 solution of urea. Then, in the conversion device 6, both an evaporation and an hydrolysis of the aqueous solution of urea take place, resulting essentially in the production of gaseous ammonia, CO<sub>2</sub> and water vapour. It should be noted that the precursor of ammonia could be of a different chemical nature, for example aqueous ammonia. It could be in a different state such as in the case  
30 of urea in solid state, in the form of a block or in the form of pellets. The precursor could even comprise ammonium salts such as ammonium carbonate or ammonium carbamate. In such a case, the conversion device would be adapted accordingly.

At the outlet of the conversion device 6, a feed line 8 carries the  
35 gases resulting from the conversion of the precursor of ammonia towards an ammonia storage and release arrangement 10 which is intended to be able to

send gaseous ammonia towards a dosing device 111 substantially permanently in a steady state phase of the system. The dosing device 111 then doses gaseous ammonia to be introduced in the exhaust line 2 upstream from the SCR device 4. To this end, there may be provided a nozzle 112 capable of  
5 injecting gaseous ammonia in the exhaust line 2.

An embodiment of an ammonia storage and release arrangement 10 is now described.

The shown arrangement 10 comprises a first unit 11 and a second unit 12. Each unit comprises a container 13 having an inlet connected to the  
10 feed line 8 and an outlet connected to the dosing device 111. The container 13 of each unit contains a material which, depending on the operating conditions, is capable of retaining gaseous ammonia supplied by the conversion device 6, in order to store gaseous ammonia, and of releasing previously retained gaseous ammonia towards the dosing device 111. The supply line 8 may be  
15 equipped with a compressor to supply pressurized gases to the arrangement 10.

In a preferred embodiment ammonia is retained in the container by being absorbed and/or adsorbed by the material contained in the container and/or by forming a chemical complex with the material stored in the container.  
20 The material can be solid. It can take several forms, including that of a powder, of granules or pellets, of open-cell foam, of a block, etc.... Such type of storage and release units has several advantages over conventional pressurized tanks:

- the storage of ammonia is safe because the pressure level is very  
low;
- 25 - the amount ammonia which can be stored is quite important in a limited volume, without having pressurized ammonia;
- the gas which is stored is essentially pure ammonia which can be easily dosed when released and injected in the exhaust line.

In an implementation, said material can comprise a material which  
30 is capable of retaining gaseous ammonia under certain operating conditions, for example below a threshold temperature or in a low range of temperatures, and of releasing previously retained ammonia under different operating conditions, for example above said threshold temperature or in a high range of temperatures. For example, gaseous ammonia can be absorbed in the material  
35 or adsorbed at the material surface depending on the temperature of the material and/or of the ammonia and depending on the pressure of gaseous



ammonia. In such a case, operating the units in a storage mode or in a release mode can be controlled simply by controlling the temperature of said units.

Examples of suitable materials include materials based on  $\text{MgCl}_2$ ,  $\text{SrCl}_2$  or  $\text{CaCl}_2$  and may include ammine complexes such as calcium ammine chloride  $\text{Ca}(\text{NH}_3)_8\text{Cl}_2$  or Strontium ammine chloride  $\text{Sr}(\text{NH}_3)_8\text{Cl}_2$ . Suitable materials for retaining gaseous ammonia are described for example in US-6.387.336 and WO-2006/012903, which can also be referred to for a description of suitable preparation processes.

According to a non limitative embodiment of the invention, the materials contained in the containers 13 of the first and second units 11, 12 can have one and the same optimum ammonia release temperature. Said materials can furthermore be identical.

The range of temperatures at which the material or each of the materials releases gaseous ammonia can be comprised between 100 and 140°C, with an optimum of for example around 120°C. Such a temperature is fairly high, which means that there is no need to excessively cool the gaseous ammonia flowing from the conversion device 6 to maintain it in a low range of temperatures to allow it to be retained in the material, i.e. stored in the corresponding unit 11, 12. On the other hand, this release temperature is not too high, and therefore there is no need to excessively heat the material to allow gaseous ammonia to be released.

According to a preferred embodiment, as depicted in Figure 1, the units 11, 12 are similar, in particular contain the same material, and are arranged in parallel. This material may have an optimum release temperature of around 120°C. In the shown embodiment, both units have approximately the same capacity in terms of the amount of ammonia which can be retained. Nevertheless, it could be provided that one unit has a larger capacity than the other.

Each unit 11, 12 can further comprise a heater 14 which is capable of raising the temperature in the container 13 up to an optimum release temperature in order for the material to release gaseous ammonia. The heater is therefore intended to change the operating conditions of the corresponding unit 11, 12, so that the unit can be operated either in a storage mode or in a release mode.

The heater 14 can be operated by the heat generated by the engine 2, either directly or indirectly. For example, the heater 14 could take

advantage of the heat contained in exhaust gases, in an engine cooling fluid or in a lubrication fluid.

The arrangement 10 can comprise a cooler 17 located between the conversion device 6 and the units 11, 12. In concrete terms, said cooler 17 can be located in the feed line 8 before it divides into a first branch 15 and a second branch 16 respectively connected to the container inlet of the first and second unit 11, 12. The aim of the cooler 17 is to lower the temperature of gaseous ammonia down to an optimum storage range of temperatures, for example below the threshold temperature, before gaseous ammonia enters the container(s) 13, to enable the material to retain said gaseous ammonia. There could also be provided one cooler for each unit.

Preferably, a valve system is provided in order to direct the gas flow towards the appropriate unit(s) 11, 12. The valve system may comprise a three way valve 18 provided at the junction between the feed line 8 and the branches 15, 16. The valve system could alternatively comprise two valves, one in each branch 15, 16.

The outlet of the containers 13 of each of the first and second units 11, 12 come out into a respective release line 21, 22 connected to the inlet of the dosing device 111. The release lines 21, 22 can be distinct or, alternatively, could comprise common portions, in particular just upstream from the dosing device 111.

In an advantageous embodiment, the material of the first and second units 11, 12 can be capable of retaining essentially only gaseous ammonia among the gases produced in the conversion device 6. For example, if the precursor of ammonia is an aqueous solution of urea which converts into ammonia, CO<sub>2</sub> and water vapour, CO<sub>2</sub> and H<sub>2</sub>O are not retained by the material in the storage mode.

This makes it possible to send only gaseous ammonia to the dosing device 111 in the release mode, and therefore to properly dose the quantity of ammonia to be introduced into the exhaust line 2, insofar as the gas flow coming from the dosing device 111 is substantially entirely constituted of ammonia.

To that end, the ammonia storage and release arrangement 10 may comprise a purification or discharge line 20 connected to the outlet of each of the containers 13 of the first and second units 11, 12. The purification line 20 is used, when the corresponding unit is operated in the storage mode to carry

said gases produced in the conversion device 6 in addition to ammonia – and which have not been retained in the material of the unit – from said containers 13 towards the exhaust line 2, in the storage mode. The purification line 20 bypasses the dosing device 111.

5 A valve system ensures that the outlet of each unit 11, 12 is either connected to the purification line 20 or to the dosing device 111, depending on whether the unit is in the storage mode or in the release mode. For example, a three way valve 24, respectively 25, may be provided at the junction between the purification line 20 and the release line 21, 22 of the first unit 11,  
10 respectively the second unit 12.

According to a preferred embodiment, the ammonia storage and release arrangement 10 can comprise a third unit 23 including a container 26 containing a material which, depending on the operating conditions, is capable of retaining gaseous ammonia supplied by the conversion device 6, in order to  
15 store gaseous ammonia, and of releasing previously retained gaseous ammonia towards the dosing device 111. Preferably, said material has essentially the same properties as that of the first and second units 11, 12, and can comprise a material which is capable of retaining gaseous ammonia by absorption, and/or adsorption and/or formation of chemical complexes, under  
20 certain operating conditions, for example below a threshold temperature  $T_{th}$  or in a low range of temperatures, and of releasing previously retained ammonia under different operating conditions, for example above said threshold temperature or in a high range of temperatures.

One purpose of the third unit 23 is to more easily allow the release  
25 of gaseous ammonia for cold start of the engine 3.

To that end, it can be envisaged that an optimum release temperature or range of temperatures, or a threshold temperature, of the material of the third unit 23 be lower than an optimum release temperature or range of temperatures, or lower than a threshold temperature, of the material of  
30 at least one of the first and second units 11, 12. For example said optimum release temperature or range of temperatures of the third unit 23 could be comprised between 60 and 100°C, for example around 80°C if the optimum release temperature or range of temperatures of the material of the first and second units 11, 12 is comprised between 100 and 140°C, for example around  
35 120°C.

Such an optimum release temperature or range of temperatures is fairly low, which means that there is no need to provide a lot of heat to the material to allow gaseous ammonia to be released, which is advantageous during cold start of the engine 2.

5 In practice, the material of the third unit 23 can be  $\text{CaCl}_2$ , which has an optimum release temperature of around  $80^\circ\text{C}$ .

The third unit 23 can further comprise a heater 27 which is capable of raising the temperature in the container 26 above the optimum release temperature or range of temperatures (or above threshold temperature), in order  
10 for the material to release gaseous ammonia. The heater 27 is therefore intended to change the operating conditions of the unit 13 so that the unit is operated either in a storage mode or in a release mode. Preferably, the heater 27 is a heater which does not depend only on the heat generated by the engine 2, so as to be able to provide enough heat even during cold start. The heater  
15 27 may comprise for example an electric heater or a fuel burner.

In the embodiment depicted in Figure 1, the container 26 of the third unit 23 is connected to the outlet of the containers 13 of the first and second units 11, 12, and to the inlet of the dosing device 111.

In practice, there may be provided an additional line 28 branching  
20 from each release line 21, 22 and connected to the inlet of the container 26. Moreover, a valve system may be provided to selectively connect the inlet of container to the outlet of the containers 13 of the first and second units 11, 12. The valve system may comprise for example three way valves 29, respectively 30, provided at the junction of the additional line 28 and of the release line 21,  
25 respectively 22. An additional release line 31 connects the outlet of the container 26 to the inlet of the dosing device 111. Thus, the third unit 23 can be operated in a storage mode during the release mode of at least one of the first and second units 11, 12. A cooler (not shown) can be provided in the additional line 28 to lower the temperature of gaseous ammonia released from the first or  
30 second unit 11, 12. Indeed, said gaseous ammonia has been heated by heater 14 and its temperature when entering the container 26 of the third unit 23 could be too high to allow the material of the third unit 23 to retain it.

The third unit 23 could possibly be operated in a storage mode during the storage mode of at least one of the first and second units 11, 12,  
35 provided a dedicated purification line be provided for the third unit 23, in order

to remove the gases produced in the conversion device 6 in addition to ammonia from the gas flow before it enters the dosing device 111.

Alternatively, the third unit 23 could be arranged in parallel with the first and second units 11, 12, and therefore connected to the conversion device, to the dosing device and to a purification line through an adequate valve system.

As schematically shown in Figure 1, the system 1 further includes a control system 32 which can control cooler 17, heaters 14, 27, valves 18, 24, 25, 29, 30 as well as the supply of the precursor of ammonia towards the conversion device 6, in order to operate the system 1 according to the appropriate operating phases, as will now be explained.

The control system 32 can also control the dosing device 111 for introducing the appropriate quantity of gaseous ammonia in the exhaust line 2 depending on the quantity of NO<sub>x</sub> to be treated.

Therefore, the control system 32 is capable of operating each of the first and second units 11, 12, as well as the third unit 23 when present:

- either in a storage mode, in which ammonia is supplied to the unit 11, 12, or 23, to be stored in said unit,;

- or in a release mode, in which ammonia previously stored in said unit is released and sent towards the dosing device 111.

More precisely, when the first unit 11, for example, is in the storage mode: the precursor of ammonia is supplied to the conversion device 6 which makes the conversion into gaseous ammonia and other components, the cooler 17 may be set on to lower the gaseous ammonia temperature in order to allow the storage, and the valve 18 allows the gas flow to enter the container 13.

At that time, the heater 14 is in most cases set off, and the valve 24 is preferably set so as to direct the flow of other components, not retained in the material, only towards the purification line 20 and exhaust line 2.

To the contrary, when said first unit 11 is in the release mode, the valve 18 is preferably set so as to not allow a gas flow to enter the container 13. If said gas flow cannot be directed towards the second unit 12 for example because the second unit is fully loaded with ammonia, then, preferably, no gas flow is created in conversion device. To that end, no precursor of ammonia is supplied to the conversion device 6, and the conversion device 6 is not working. At that time, the heater 14 is set on in order to raise the temperature at

or above a minimum release temperature in order to allow the release of gaseous ammonia previously retained in the material, and the valve 24 is set to direct the flow of gaseous ammonia only towards the release line 21 and dosing device 111.

5 In Figures 2-7, a full line indicates that gas flows in said line, contrary to dotted lines. Dotted arrows indicate that gas can optionally flow in the corresponding line. Cooler or heaters are illustrated with thick lines when they are on, and with thin lines when they are off.

In order to simplify the following description, it will be considered  
10 that the precursor of ammonia is an aqueous solution of urea, bearing in mind that this embodiment shall not be considered as limitative. Similarly, the description will be made with first and second units 11, 12 having an optimum ammonia release temperature of around 120°C, and with a third unit 23 having an optimum ammonia release temperature of around 80°C. However, other  
15 embodiments are possible.

In Figure 2, the system 1 is depicted when the first unit 11 is in the storage mode and the second unit 12 is in the release mode.

Aqueous solution of urea is supplied through the supply line 7 from the tank 5 to the conversion device 6, where it is converted into gaseous  
20 ammonia and other components, especially CO<sub>2</sub> and H<sub>2</sub>O. The gases flowing in the feed line 8 are cooled by cooler 17 below 120°C, preferably well below, and are exclusively directed towards the first unit 11, the second unit 12 not being supplied with gases in this operating phase.

The heater 14 of the first unit 11 is set off, so that gaseous  
25 ammonia can be retained in the material. CO<sub>2</sub> and H<sub>2</sub>O go through the first unit 11 without being retained and are directed towards the purification line 20, no gas being sent from the first unit 11 neither towards the dosing device 111 nor towards the third unit 23.

In parallel, the heater 14 of the second unit 12 is set on, allowing  
30 ammonia to be released from the material and directed towards the dosing device 111 through release line 22.

It may be envisaged, during this phase, to send part of the gaseous ammonia released from the second unit 12 towards the third unit 23, in order to be stored in said third unit 23, if not the whole amount of released gaseous  
35 ammonia is required to treat the NO<sub>x</sub> contained in the exhaust gases. Indeed, as the third unit 23 is preferably used for cold start, it should preferably contain

enough retained ammonia when the engine 2 is started, which means that the third unit 23 should preferably be loaded with retained ammonia as soon as possible after the system has reached a steady state phase.

In case either the first unit 11 is nearly fully loaded with ammonia or the second unit 12 contains too little ammonia, the system 1 is operated in a transient phase, as depicted in Figure 3.

While the second unit 12 temporarily continues releasing gaseous ammonia, the operation of the first unit 11 is turned to the release mode.

In this operating configuration, it can be provided that no aqueous solution of urea is supplied and the conversion device 6 is then stopped. The cooler 17 is in such case set off and the valve 18 is shut, so that no gas is flowing towards any of the units 11, 12.

The heater 14 of the first unit 11 is set on and the valve 24 now directs the gas flow –containing essentially only ammonia – to the release line 21 and no more to the purification line 20.

The object of this transient phase is to ensure that ammonia is continuously provided to the dosing device 111, taking into account that the rate of delivery of ammonia by the first unit 11 is dependent on the temperature in the first unit 11, and that said temperature does not rise instantaneously to the optimum release temperature due to the thermal inertia of the unit.

As shown in Figure 4, when both the first and second units 11, 12 are releasing ammonia, at least part of said ammonia can be sent from one of said units or both units 11, 12 towards the third unit 23, through the additional line 28. Said ammonia is stored in the container 26, the heater 27 being set off. Indeed, insofar as two units 11, 12 can provide ammonia to the dosing device 111, there is generally more ammonia released than needed to treat the NO<sub>x</sub> in the exhaust line 2, which allows some ammonia to be stored in the third unit 23.

In Figure 5 is shown a steady state phase of the system 1 operation which is the equivalent of Figure 2 with the first unit 11 being in the release mode while the second unit 12 is in the storage mode.

Aqueous solution of urea is supplied through the supply line 7 from the tank 5 to the conversion device 6, where it is converted into gaseous ammonia and other components, especially CO<sub>2</sub> and H<sub>2</sub>O. The gases flowing in the feed line 8 are cooled by cooler 17 below 120°C and are exclusively directed towards the second unit 12, the first unit 11 not being supplied with gases in this operating phase.

The heater 14 of the second unit 12 is set off, so that gaseous ammonia can be retained in the material. CO<sub>2</sub> and H<sub>2</sub>O go through the first unit 11 without being retained and are directed towards the purification line 20, no gas being sent from the second unit 12 neither towards the dosing device 111 nor towards the third unit 23.

In parallel, the heater 14 of the first unit 11 is set on, allowing ammonia to be released from the material and directed towards the dosing device 111 through release line 21.

It may be envisaged, during this phase, to send part of the gaseous ammonia released from the second unit 12 towards the third unit 23, in order to be stored in said third unit 23, if not the whole amount of released gaseous ammonia is required to treat the NO<sub>x</sub> contained in the exhaust gases.

Figure 6 illustrates the system 1 during cold start of the engine 2.

In this phase, gaseous ammonia is mainly, or even exclusively at the very beginning, provided by the third unit 23. Indeed, first of all, the third unit 23 is designed for this purpose since it contains a material having a quite low ammonia release temperature. This material therefore does not require to be heated a lot before releasing previously retained ammonia. Moreover, the third unit 23 is preferably provided with a heater 27 which does only not use the heat provided by the engine operation. Therefore, the heater 27 can be effectively operated even if the engine temperature has not reached the threshold temperature yet.

In concrete terms, during this phase, gaseous ammonia flows from the container 26 of the third unit 23 towards the dosing device 111 through the additional release line 31.

At this stage, it can be provided that no aqueous solution of urea is sent towards the conversion device 6, the conversion device 6 is not working and does not supply gaseous ammonia to the first and second units 11, 12.

In order to prepare the transition to the steady state operating phase, at least one of the first and second units 11, 12 is progressively set on. To this end, the corresponding heater 14 is switched on and, when the temperature has reached the threshold temperature, gaseous ammonia begins to be released by the material and to be sent towards the dosing device 111 through the corresponding release line 21. When said unit 11 or 12 is fully operational, ammonia is preferably entirely provided by said unit and the third unit 23 is no more used. The system 1 is then operated as in Figure 2 or Figure



5, with a need in the short term to store ammonia in the third unit 23 in view of a subsequent cold start.

In case the amount of previously retained ammonia is not sufficient, the converting device 6 may be set on to provide ammonia to be stored in the first or second unit 11, 12. If the heat provided by the exhaust gases is not sufficient, an additional and dedicated heater may be provided for said converting device 6.

Figure 7 shows a second embodiment of the invention, where no third unit is provided, meaning that lines 28 and 31 are useless.

Because the third unit is no more present, another means is provided to allow the supply of gaseous ammonia during cold start of the engine 2. Thus, at least one of the first and second units – here the second unit 12 - comprises a main heater 14 operated by the heat generated directly or indirectly by the engine 2 and an additional heater 35 capable of supplying heat to the container 13 during the cold start of the engine.

The main heater 14 can be switched on from the beginning but it becomes effective only after a certain period of time, during which the additional heater 35 can allow the release of previously retained ammonia.

As in the previous embodiment, the two units can have a similar ammonia retaining material or can have different materials, especially having materials such that they start releasing ammonia at different temperature levels. Also the units could have the same capacity or be of different capacities.

It has to be noted that, alternatively, this embodiment could also include a third unit, if necessary.

The system according to the invention can be easily integrally fitted on-board an automotive vehicle, especially on a truck. It can be noted that the system according to the invention requires only a single dosing device for metering the reductant, here gaseous ammonia, which is effectively injected in the exhaust line.

The invention is of course not limited to the embodiments described above as examples, but encompasses all technical equivalents and alternatives of the means described as well as combinations thereof.

**CLAIMS**

1. A system to be fitted on an automotive vehicle for treating nitrogen oxides contained in exhaust gases flowing in an exhaust line (2) of an engine (3) of the vehicle, wherein the system (1) comprises:
- a source (5) of a precursor of ammonia;
  - a conversion device (6) for producing gaseous ammonia from said precursor;
  - a dosing device (111) for dosing gaseous ammonia to be introduced in the exhaust line (2) upstream from a selective catalytic reduction device (4);
  - an ammonia storage and release arrangement (10) characterized in that the ammonia storage and release arrangement comprises at least a first and a second unit (11, 12), each unit including a container (13) containing a material which, depending on the operating conditions, is capable of retaining gaseous ammonia supplied by the conversion device (6), in order to store gaseous ammonia, and of releasing previously retained gaseous ammonia towards the dosing device (111);
  - in that the system comprises a control system (32) configured to operate each of the first and second units (11, 12):
    - either in a storage mode, in which ammonia is supplied to the unit (11, 12), to be stored in said unit,
    - or in a release mode, in which ammonia previously stored in said unit (11, 12) is released and sent towards the dosing device (111).
2. The system according to claim 1, characterized in that the control system is configured to operate one unit in a storage mode and, simultaneously, the other unit in the release mode.
3. The system according to claim 1 or 2, characterized in that the material contained in a unit (11, 12) is capable of retaining gaseous ammonia by absorption and/or adsorption and/or formation of chemical complexes.
4. The system according to any preceding claim, characterized in that operating the units in a storage mode or in a release mode is controlled by controlling the temperature of said units.

5. The system according to any preceding claim, characterized in that each unit (11, 12) comprises a heater (14) controlled by the control system (32).

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6. The system according to any one of claims 1 to 5, characterized in that the ammonia storage and release arrangement (10) comprises a cooler (17) located between the conversion device (6) and the units (11, 12).

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7. The system according to any preceding claim in combination with claim 4, characterized in that the materials contained in the containers (13) of the first and second units (11, 12) have the same optimum ammonia release temperature.

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8. The system according to any one of claims 1 to 7, characterized in that the ammonia storage and release arrangement (10) comprises a purification line (20) connected to the outlet of each of the containers (13) of the first and second units (11, 12), said purification line (20) being capable of carrying gases from said containers (13) towards the exhaust line (2), by-passing the dosing device.

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9. The system according to any one of claims 1 to 8, characterized in that the material of the first and second units (11, 12) is capable of retaining gaseous ammonia while not retaining other gases produced in the conversion device in addition to gaseous ammonia.

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10. The system according to any one of claims 1 to 9, characterized in that at least one of the first and second units (11, 12) is associated to a main heater (14) operated by heat generated by the engine (3) and to an additional heater (35) capable of supplying heat to the container (13).

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11. The system according to any preceding claim in combination with claim 4, characterized in that the ammonia storage and release arrangement (10) comprises a third unit (23) including a container (26) containing a material which is capable of retaining gaseous ammonia supplied

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by the conversion device (6), in that the third unit (23) may be operated in a storage mode or in a release mode by controlling the temperature of said unit, and in that the third unit may release ammonia starting from a temperature which is lower than that of at least one of the first and second units (11, 12).

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12. The system according to claim 11, characterized in that an optimum ammonia release temperature of the material of the first and second units (11, 12) is comprised between 100 and 140°C, for example around 120°C, and in that an optimum ammonia release temperature of the material of the third unit (23) is comprised between 60 and 100°C, for example around 80°C.

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13. The system according to claim 11 or 12, characterized in that the container (26) of the third unit (23) is connected to the outlet of the containers (13) of the first and second units (11, 12), and to the dosing device inlet.

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14. The system according to any one of claims 1 to 13, characterized in that the precursor of ammonia comprises an aqueous solution of urea.

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15. The system according to any one of claims 1 to 14, characterized in that the conversion device (6) is thermally connected to the exhaust line (2).

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16. A method for treating nitrogen oxides contained in exhaust gases flowing in an exhaust line (2) of an engine (3) of an automotive vehicle, the method comprising:

- supplying a precursor of ammonia to a conversion device (6) for producing gaseous ammonia;

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- providing at least a first and a second unit (11, 12), each unit including a container (13) containing a material which, depending on the operating conditions, is capable of retaining gaseous ammonia supplied by the conversion device (6), in order to store gaseous ammonia, and of releasing previously retained gaseous ammonia towards a dosing device (111) which is

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intended for dosing gaseous ammonia to be introduced in the exhaust line (2) upstream from a selective catalytic reduction device (4);

5 - operating one of the first and second units (11, 12) in a storage mode, in which ammonia is supplied from the conversion device (6) to said unit in order to be stored in said unit,;

- simultaneously operating the other one of the first and second units (11, 12) in a release mode, in which ammonia previously stored in said unit is released and sent towards the dosing device (111).

10 17. The method according to claim 16, characterized in that it further comprises, during the storage mode, carrying the gases produced in the conversion device (6) in addition to ammonia and which are not retained in the material of the unit (11, 12) from the container (13) of said unit (11, 12) towards the exhaust line (2).

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18. The method according to claim 16 or 17, characterized in that it further comprises:

20 - providing a third unit (23) including a container (26) containing a material which, depending on the operating conditions, is capable of retaining gaseous ammonia supplied by the conversion device (6), in order to store gaseous ammonia, and of releasing previously retained gaseous ammonia towards the dosing device (111), the container (26) of the third unit (23) being connected to the outlet of the containers (13) of the first and second units (11, 12), and to the dosing device inlet;

25 - operating the third unit (23) in a storage mode, in which ammonia is supplied to the third unit (23) from the one of the first and second units (11, 12) which is operated in the release mode, so as to store ammonia in said third unit (23).

30 19. An automotive vehicle equipped with a system according to any of claims 1 to 15.

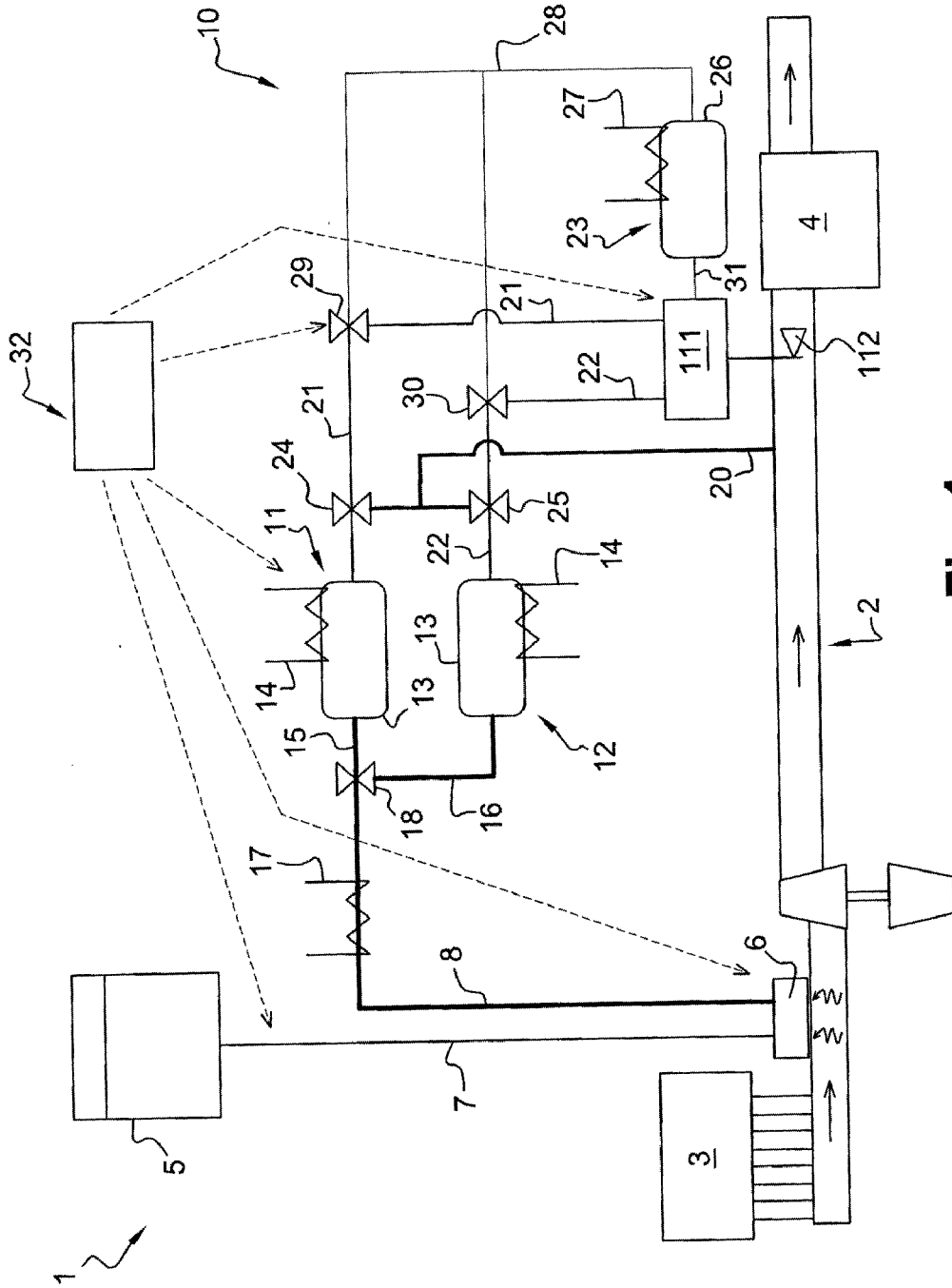


Fig. 1

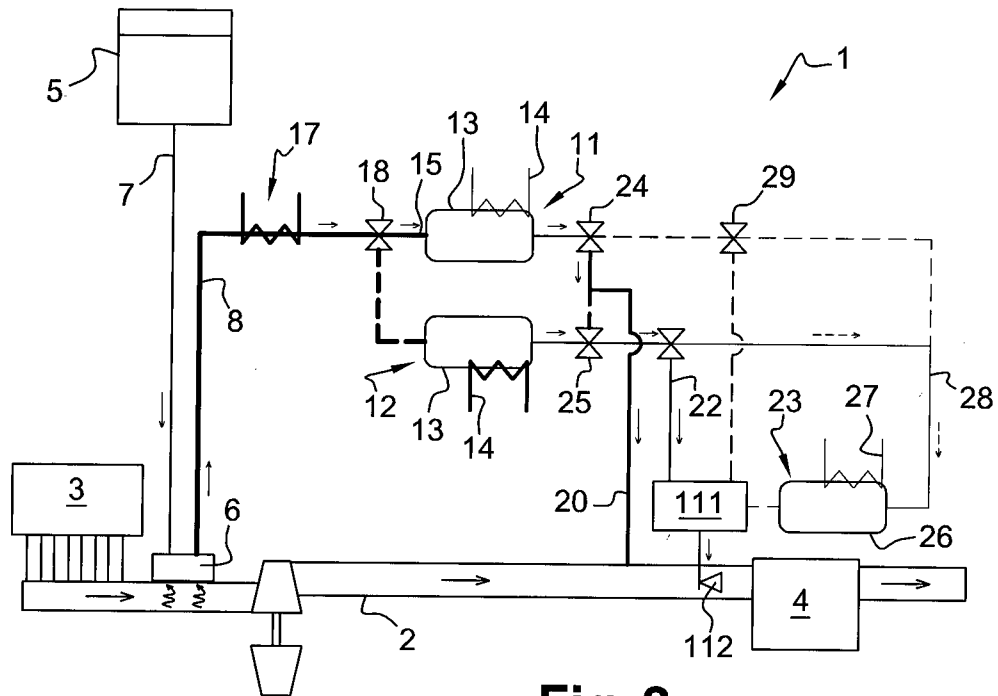


Fig. 2

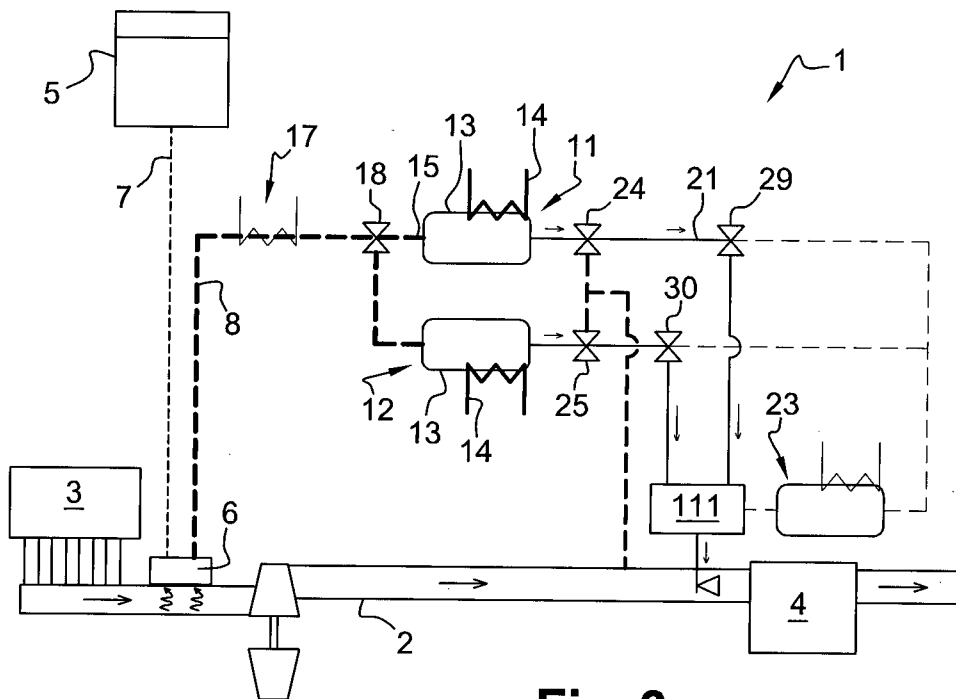


Fig. 3





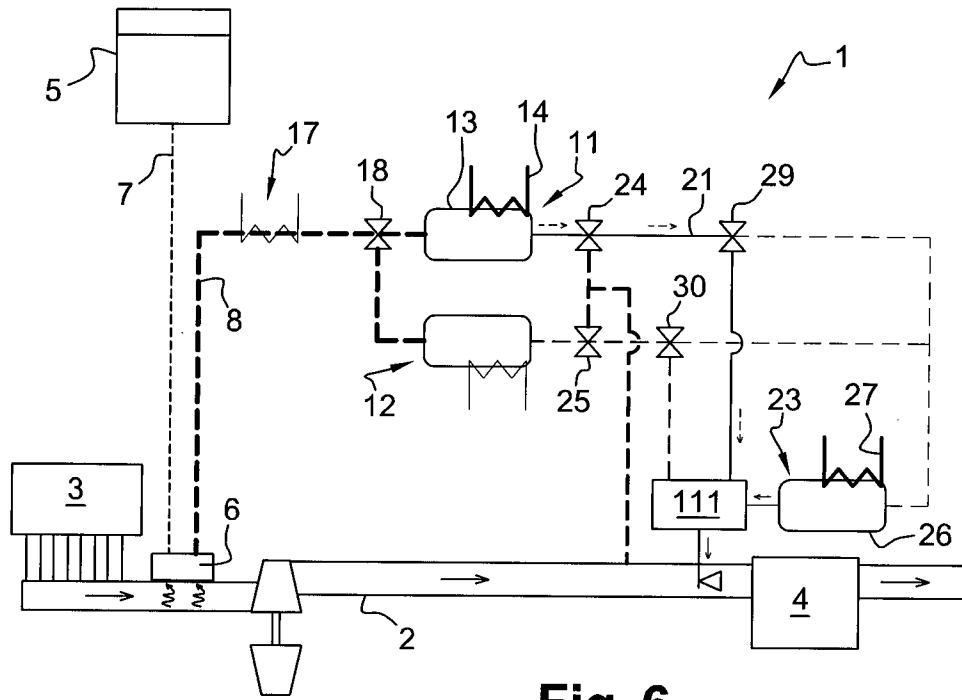


Fig. 6

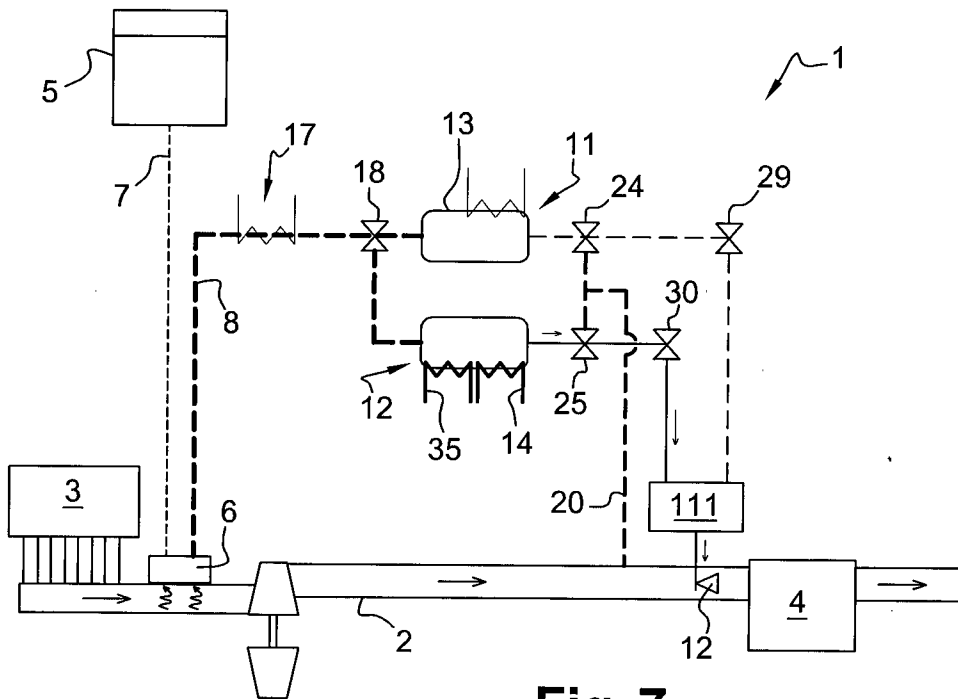


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2012/001024

A. CLASSIFICATION OF SUBJECT MATTER  
INV. F01N3/20  
ADD.  
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)  
F01N

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)  
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	----- US 6 361 754 B1 (PETER-HOBLYN JEREMY D [GB] ET AL) 26 March 2002 (2002-03-26) column 4, line 65 - column 5, line 38; figure 2	1,16,19
A	----- EP 2 333 262 A1 (IFP ENERGIES NOUVELLES [FR]) 15 June 2011 (2011-06-15) column 4, line 3 - line 55; figure 1	1,16,19
A	----- WO 2007/049042 A1 (IMI VISION LTD [GB]; COATES JAMES [GB]; BHIMANI ALAN [GB]) 3 May 2007 (2007-05-03) page 8, paragraph 8 - page 9, paragraph 1; figure 1	1,16,19

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

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- "&" document member of the same patent family

Date of the actual completion of the international search  14 January 2013	Date of mailing of the international search report  23/01/2013
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Zebst, Marc
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Information on patent family members

International application No

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