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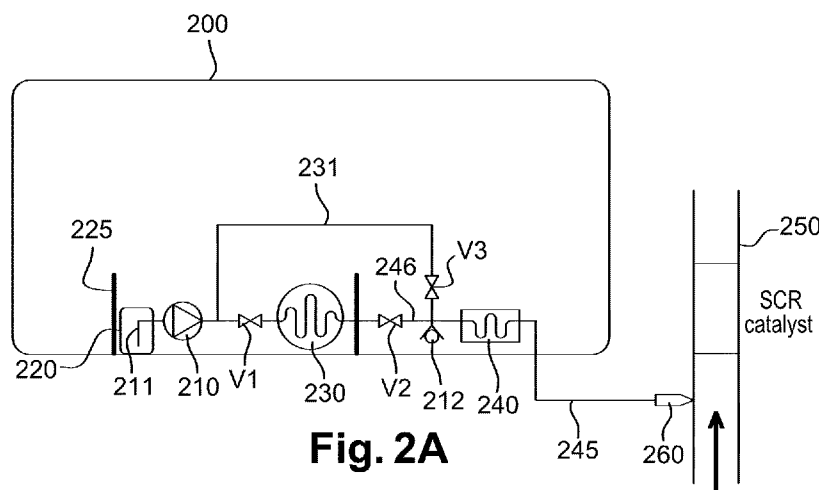


Fig. 2A

(57) Abstract: The invention relates to a system and method for generating ammonia on-board a vehicle. The system comprises: a tank (200) adapted for storing an ammonia precursor; a conversion unit (230) adapted for converting ammonia precursor into ammonia; a line (245) arranged for receiving ammonia from the conversion unit, said line optionally including a buffer (240); a fluid transfer device (210) located upstream of the conversion unit and configured for transferring ammonia precursor from the tank to the conversion unit; a controller configured for controlling said fluid transfer device such that a volume of said ammonia is pushed out of the conversion unit in the line, by ammonia precursor entering the conversion unit.



## Vehicle system and method for generating ammonia in batches

### Field of Invention

The invention relates to a system and method for use on-board a vehicle for the generation of ammonia solution for NOx control and to various components for use in such a system.

### Background

There exist prior art systems for supplying ammonia to an exhaust line of a vehicle in order to reduce the NOx emissions. A SCR (Selective Catalytic Reduction) process is used for converting nitrogen oxides of an exhaust gas coming from a vehicle engine into diatomic nitrogen and water. The SCR process enables the reduction of nitrogen oxides by injection of a reducing agent, generally ammonia, into the exhaust line. This ammonia may be obtained by using different techniques. One known technique is based on the use of an ammonia precursor, for example an aqueous urea solution. Generally, such urea solution is stored in a tank mounted on the vehicle. A catalyst is used to generate ammonia from an ammonia precursor solution. Such systems are disclosed in patent applications WO2015/032811 A1, EP 2 927 452 A1, and EP 2 746 548 A1 in the name of the Applicant, which are included herein by reference, and in US 2008/223021 A1.

PCT application with application number PCT/EP2014/068727 and publication number WO2015/032811 A1 in the name of the applicant describes an SCR system comprising a tank for the storage of an ammonia precursor solution, typically an aqueous urea solution; and a decomposition and storage unit located inside the tank.

The system also comprises a pump configured to transport the urea or the aqua ammonia to an injector. The injector injects the urea or the aqua ammonia in the exhaust gases for NOx removal. The pump may be connected to a first suction point located inside the decomposition and storage unit and to a second suction point located inside the tank. For example, in cold conditions, if at vehicle start-up the urea solution is not available (i.e. not enough urea in liquid state) because it is frozen or if it is desired to meter reducing agent very early while the exhaust pipe is still relatively cold, then the connection between the pump and the first suction point is opened to pump aqua ammonia stored in the decomposition and storage unit. The aqua ammonia is then injected into the exhaust gases. When the urea solution becomes available (after thawing), the connection between the pump and the second suction point is opened to inject urea solution in the exhaust pipe. The decomposition and storage unit may be surrounded by thermal isolation or by phase change materials (PCM), so that the ammonia precursor solution present in the unit at engine stop continues to be decomposed while the vehicle is at rest, so that aqua ammonia will be available for the next start-up of the engine.

The solution of PCT/EP2014/068727 is based on continuous generation of ammonia that is used for SCR at all times (at cold start and when the SCR catalyst is hot). The energy consumption for continuously converting urea is therefore high. Moreover, the volume of the conversion unit is significant, which is a drawback in a vehicle.

### Summary

The object of embodiments of the invention is to provide a method and system for use on-board a vehicle, allowing for the generation of ammonia solution for NO<sub>x</sub> control in an improved manner using a compact system.

According to a first aspect of the invention there is provided a method for generating ammonia on-board a vehicle. The method comprises:

- storing an ammonia precursor on-board a vehicle with a component requiring ammonia, e.g. an exhaust pipe or a component of a fuel cell such as a fuel cell conversion unit of a fuel cell subsystem;
- during a first period associated with a first operating event, e.g. a first driving event: converting stored ammonia precursor into ammonia in a conversion area;
- during a consecutive second period associated with a second operating event, e.g. a second driving event, said second period comprising a cold period in which the temperature of the component is below a predetermined first threshold: transferring, during said cold period, of a predetermined volume of ammonia from the conversion area to a fluid storage area downstream of the conversion area and upstream of the component such that it is available for injection/feeding into the component; and after said transferring, converting stored ammonia precursor to obtain a further volume of ammonia in the conversion unit.

Using the method of the invention, for each cold start (which corresponds with the second period mentioned above) a predetermined volume of ammonia is transferred to a fluid storage area, typically a line and/or a buffer, e.g. between the conversion area and an exhaust pipe or between the conversion area and a fuel cell, immediately or shortly after the cold start and before a first threshold temperature is reached in the component, e.g. in the exhaust pipe or in a component of the fuel cell. Following this transferring, the conversion of a further volume of ammonia is performed which further volume can then be used during a subsequent cold start period. In other words there is performed a batch processing which is started during the cold period, wherein the predetermined volume that may be needed for injection is transferred and a further volume for the next operating event, e.g. the next driving event is generated in the conversion area after said

transferring. In that way the conversion area may be small, whilst still allowing having the required volume available at a cold start. In other words, embodiments of the invention result in a compact ammonia precursor conversion system permitting to produce and store a small volume of ammonia solution to be used for NO<sub>x</sub> control at the next cold start.

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In a possible embodiment the fluid storage area is positioned upstream of an exhaust pipe of the vehicle, such that the predetermined volume of ammonia is available for injection into the exhaust pipe.

In another possible embodiment the fluid storage area is positioned upstream of a fuel cell of the vehicle, such that the predetermined volume of ammonia is available for feeding into the fuel cell.

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Embodiments of the invention permit to consume at each cold start the required amount of ammonia solution for NO<sub>x</sub> control (e.g. from 10 to 100 ml, allowing NO<sub>x</sub> control during about 20 km, and for instance 30 ml) or for fuel cell feeding, regenerate and store the same amount for the next cold start. The energy consumption for this conversion can be very low due to the limited volume to be converted (e.g. about 5 to 100 Wh), making it possible to use not only low temperature conversion techniques (biocatalysts, electrochemical conversion) but also high temperature conversion techniques such as pyrolysis, thermohydrolysis with or without heterogeneous catalysts. The conversion system may use energy available during driving and/or at key-off to prepare and store a new volume of ammonia for the next key-on.

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The strategy and associated setups of embodiments of the invention can ensure that the required volume of ammonia solution will be made available for the next cold start. This ammonia solution to be used for the next cold start is produced after the transferring of the predetermined volume of ammonia, preferably as soon as possible during the current driving operation, by starting the conversion operation and by vesting the (limited) required energy, preferably as soon as possible, while driving or during a limited period of time following key-off of the vehicle.

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When used for NO<sub>x</sub> control, embodiments of the invention are based inter alia on the inventive insight that the thermal inertia of the exhaust system can be used advantageously: on one hand this inertia leads to no injection of any reducing agent during the cold period just after a cold start, as the SCR catalyst is too cold. During this cold period the transferring can be done putting the required amount of ammonia ready for injection, and the conversion for the next cold start can be started.

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In an exemplary embodiment the cold period is defined as a period in which the temperature of the component, e.g. the exhaust pipe, is below a predetermined first threshold, wherein said first

threshold is between 110°C and 130°C, preferably between 115°C and 125°C. The length of this cold period, also called “cold start-up delay” ( $t_{\text{CSD}}$ ) may be determined empirically as a period after a cold start during which the first threshold will never be reached and during which ammonia solution is never needed because the component, e.g. the exhaust pipe is too cold. The “cold start-up delay” may be determined as a value which is lower than a minimum of all values at which the first threshold is reached for all possible operating events, e.g. all possible driving events.

In an exemplary embodiment the transferring of a predetermined volume of ammonia to the fluid storage area is performed by transferring stored ammonia precursor to the conversion area, such that said ammonia precursor pushes said predetermined volume out of the conversion area to the fluid storage area. In other words the transferring of the predetermined volume of the ammonia to the fluid storage area is performed simultaneously with the transferring of fresh ammonia precursor to the conversion area, such that the volume of the conversion area can be substantially equal to the volume of the fluid storage area.

In an exemplary embodiment the predetermined volume is between 10 and 100 ml, preferably between 10 and 90 ml, more preferably between 15 and 60 ml. In other words, the volume can be relatively small, and hence also the conversion area can be relatively small.

In an exemplary embodiment the further volume of ammonia generated during the second period is larger than or equal to the transferred predetermined volume of ammonia. In that manner, if the transferred volume is consumed during the second period, the required volume is available for the next cold start of the vehicle. Preferably, the further volume is smaller than 1.5 times the transferred predetermined volume in order to avoid that the conversion area is too big.

In an exemplary embodiment the method further comprises, during said consecutive second period: injecting the predetermined volume of ammonia when the temperature of the component, e.g. the exhaust pipe is above a predetermined second threshold ( $T_{\text{ammonia}}$ ), wherein the second threshold is higher than or equal to the first threshold. Preferably the second threshold is between 115°C and 125°C.

In an exemplary embodiment the predetermined volume of ammonia is such that the temperature of the component, e.g. the exhaust pipe is above a predetermined third threshold ( $T_{\text{urea}}$ ) after said predetermined volume has been injected; wherein the third threshold is higher than the second threshold. Preferably, the third threshold is associated with a temperature for which ammonia

precursor may be injected, e.g. a value above 170°C. In that manner ammonia precursor may be injected immediately after injecting ammonia.

In an exemplary embodiment after injecting of ammonia, ammonia precursor is injected, wherein  
5 said ammonia precursor flows through the fluid storage area immediately after the ammonia, on its way to the component, e.g. the exhaust pipe.

In an exemplary embodiment the first period and the second period correspond with a period of time between a key-on time of the vehicle and a key-off time of the vehicle, and optionally also an  
10 additional period of time after the key-off time. Especially, when the key-off is performed shortly after key-on, the energy available after key-off may be used to complete generating the further volume of ammonia for the next cold start.

According to another aspect there is provided a system for use on-board a vehicle, for performing a  
15 conversion from ammonia precursor into ammonia. The system comprises:

- a tank adapted for storing an ammonia precursor;
- a conversion unit adapted for converting ammonia precursor into ammonia;
- a fluid storage between an outlet of the conversion unit and a component requiring ammonia, e.g. an exhaust pipe or a component of a fuel cell;
- 20 - a controller configured for controlling during a period associated with an operating event, e.g. a driving event, said period comprising a cold period in which the temperature of the component is below a predetermined first threshold:
  - the transferring, during the cold period, of a predetermined volume of ammonia from said conversion unit to said fluid storage; and,
  - 25 - after said transferring, the converting of stored ammonia precursor to obtain a further volume of ammonia in the conversion unit.

The fluid storage may be a line and/or a buffer with a suitable volume adapted for containing the predetermined volume of ammonia before injection.

The fluid storage may be located e.g. between an outlet of the conversion unit and an inlet of an  
30 injector for injection of fluid in an exhaust pipe or between an outlet of the conversion unit and an inlet of a flow control means for feeding fluid to a component of a fuel cell, e.g. to a fuel cell conversion unit of a fuel cell subsystem.

According to yet another aspect of the invention, there is provided a system for generating  
35 ammonia on-board a vehicle. The system comprises a tank, a conversion unit, a line such as an injection line or a dosing line, a fluid transfer device and a controller. The tank is adapted for

storing an ammonia precursor. The conversion unit is adapted for converting ammonia precursor into ammonia. The line is arranged for receiving ammonia from the conversion unit. Optionally, the line includes a buffer. The fluid transfer device is located upstream of the conversion unit and is configured for transferring ammonia precursor from the tank to the conversion unit. In a preferred embodiment, the fluid transfer device is a pump. The controller is configured for controlling the fluid transfer device such that a volume of the ammonia is pushed out of the conversion unit in the line, by ammonia precursor entering the conversion unit. The line may be an injection line leading to an injector for injecting fluid in an exhaust pipe of the vehicle or a dosing line leading to a flow control means such as a valve for feeding a fuel cell with fluid, or more generally any line leading to a component requiring ammonia.

By having a fluid transfer device upstream of the conversion unit, it is prevented that the fluid transfer device is continuously in contact with ammonia which is more aggressive than ammonia precursor. Further fluid transfer device will allow to push the ammonia out of the conversion unit while fresh ammonia precursor enters in the conversion unit, leading to a compact and robust system.

According to an exemplary embodiment, the system further comprises a bypass line and a bypass flow regulating means. The bypass line is arranged for bypassing the conversion unit and arranged for transferring ammonia precursor from the tank to the line by means of the fluid transfer device. The bypass flow regulating device is arranged for regulating the flow through the bypass line. The controller is configured to control the bypass flow regulating device.

According to an exemplary embodiment, the system further comprises a first and a second flow regulating device for regulating the flow to and from the conversion unit. The first flow regulating device is arranged for regulating the flow of ammonia precursor from the tank to the conversion unit, and the second flow regulating device is arranged for regulating the flow of ammonia from the conversion unit to the line. The controller may then be configured to control the first and the second flow regulating device in order either to allow a flow of ammonia precursor into the conversion unit pushing ammonia out of the conversion unit, or to block a flow through the conversion unit, i.e. to isolate the conversion unit. When ammonia needs to be transferred to the line, the first and the second flow regulating device are controlled to allow a flow through the conversion unit, and when fresh ammonia precursor needs to be converted, the flow is blocked.

According to an exemplary embodiment, the controller is configured to control the fluid transfer device, the bypass flow regulating device, the first flow regulating device and the second flow

regulating device, in order to transfer first a predetermined volume of ammonia from the conversion unit to the line, and to transfer next ammonia precursor through the bypass line to the line.

5 According to an exemplary embodiment, the fluid transfer device is a pump.

According to an exemplary embodiment, the bypass flow regulating device, the first flow regulating device and the second flow regulating device each comprise a valve.

10 According to an exemplary embodiment, the controller is configured for controlling the fluid transfer device and the bypass flow regulating device such that the line and the bypass line are purged and filled with gas, typically gas from the exhaust line. Preferably, the controller is configured to perform the purging before the transferring of ammonia from the conversion unit to the line and of ammonia precursor from the bypass line to the line, such that an amount of gas  
15 present in the bypass line is inserted between the ammonia from the conversion unit and the ammonia precursor from the bypass line. By suitably sizing the bypass line, the volume of gas inserted between the ammonia and the ammonia precursor can be such that mixing between ammonia and ammonia precursor is reduced or avoided.

20 According to an exemplary embodiment, the conversion unit is configured for thermal hydrolysis of ammonia precursor at a temperature between 150°C and 400°C. The conversion unit may have a substantially spherical housing and may be located in the tank. Preferably, the conversion unit comprises a conversion chamber surrounded by a preconditioning chamber configured to use heat of the conversion chamber for preconditioning the ammonia precursor entering the conversion unit.

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According to another aspect of the invention, there is provided a method for generating ammonia on-board a vehicle. The method comprises the following steps. An ammonia precursor is stored on-board a vehicle. Ammonia precursor is transferred from the tank to a conversion unit. Ammonia precursor is converted into ammonia in the conversion unit. The transfer of ammonia precursor  
30 from the tank is controlled such that a volume of ammonia is pushed in a line, e.g. an injection line by ammonia precursor entering the conversion unit. Optionally, the line includes a buffer.

According to an exemplary embodiment, the method further comprises the steps of transferring ammonia precursor from the tank to the line through a bypass line bypassing the conversion unit;  
35 and controlling the transferring through the bypass line such that the ammonia previously pushed into the line is followed by ammonia precursor coming from the bypass line.

According to an exemplary embodiment, the method further comprises the steps of regulating a flow of ammonia precursor from the tank to the conversion unit; of regulating a flow of ammonia from the conversion unit to the line; of regulating a flow of ammonia precursor through the bypass line; and of controlling the regulating in order to transfer first a predetermined volume of ammonia from the conversion unit to the line, and next to transfer ammonia precursor through the bypass line to the line.

According to an exemplary embodiment, the method further comprises the steps of purging the line and the bypass line such that the line and the bypass line are filled with gas. The purging is performed before the transferring of ammonia from the conversion unit to the line and of ammonia precursor from the bypass line to the line, such that an amount of gas present in the purged bypass line is inserted between the ammonia from the conversion unit and the ammonia precursor from the bypass line. By giving the bypass line a suitable inner volume, the volume of gas inserted between the ammonia and the ammonia precursor can be such that mixing between ammonia and ammonia precursor is avoided, or at least reduced.

The urea conversion method and system may use any available technology to produce ammonia, for instance urea pyrolysis, or urea hydrolysis at high temperatures (above 150°C) with or without a heterogeneous catalyst, urea hydrolysis at low temperatures (below 60°C) with an enzymatic catalyst, or electrochemical conversion by applying a voltage to the urea solution at low temperatures (below 80°C). In a possible embodiment the enzymatic catalyst is a urease enzyme. Suitable examples of catalysts are given in EP 15162678.5 in the name of the applicant which is included herein by reference.

In a preferred embodiment the ammonia precursor is an aqueous urea solution, typically AdBlue®. It is noted that the ammonia precursor solution may be prepared, at least partly, within the retaining unit by dissolving ammonia precursor in solid form in the retaining unit; and/or, at least partly before arriving at the retaining unit, e.g. in a separate dissolving compartment in the tank. In exemplary embodiments it may be advantageous to dissolve ammonia precursor in solid form in the ammonia precursor liquid gradually, as the reaction proceeds. Such a gradual dissolving may be advantageous for the life time of the catalyst since an ammonia precursor solution having a high concentration of ammonia precursor may be unfavourable for the catalyst. In an embodiment with a dissolving compartment in the retaining unit, the liquid that is transferred from the tank to the retaining unit may be water or a liquid with a low ammonia precursor concentration, the ammonia precursor in solid form may be transferred (optionally together with the liquid) to the retaining unit

or may be stored in the retaining unit, and the ammonia precursor in solid form may be dissolved in the liquid in the retaining unit.

According to another aspect there is provided an SCR system for a vehicle comprising a system  
5 according to any one of the embodiments disclosed above.

The fluid transfer device may be e.g. a pump, a valve, a pump and a valve, gravity in combination with a valve, or a valve in combination with whatever system known by the person skilled in the art to transfer the fluid.

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Further, it is noted that embodiments of the invention may also be used in an ammonia precursor booster system comprising a storage compartment for storing ammonia precursor granules, and a dissolving compartment for storing an ammonia precursor solution, and for dissolving ammonia precursor granules in the ammonia precursor solution. An example of such a booster system is  
15 disclosed in European patent application EP 14177713.6 in the name of the Applicant, which is included herein by reference. The dissolving compartment may be included in the tank of embodiments of the present invention.

According to a further aspect, the invention relates to the use of a system according to any one of  
20 the embodiments above in a vehicle.

### **Brief description of the figures**

The accompanying drawings are used to illustrate presently preferred non-limiting exemplary embodiments of devices of the present invention. The above and other advantages of the features  
25 and objects of the invention will become more apparent and the invention will be better understood from the following detailed description when read in conjunction with the accompanying drawings, in which:

Figure 1A is a graph plotting the temperature in the exhaust pipe in function of time for two test situations;

30 Figure 1B is a graph plotting schematically the cumulative demand of ammonia solution at time  $t_{Conv}$ , the ammonia solution that can be generated at  $t_{Conv}$  and the available energy, respectively, in function of the key-off time  $t_{Key-off}$ ;

Figures 2A-2H illustrate exemplary embodiments of a vehicle system for generating and injecting ammonia and ammonia precursor;

35 Figures 3A-3F illustrate exemplary embodiments of a conversion unit for use in vehicle system for generating ammonia;

Figure 4 illustrates another exemplary embodiment of a vehicle system for generating and injecting ammonia and ammonia precursor; and

Figure 5 is a flow chart illustrating an exemplary embodiment of a method for generating and injecting ammonia and ammonia precursor in an exhaust; and

5 Figure 6 illustrates an exemplary embodiment of a vehicle system for generating ammonia for a fuel cell.

### Description of embodiments

Embodiments of the invention describe an ammonia precursor conversion system permitting to  
10 consume a small volume of ammonia to be used for NO<sub>x</sub> pollution control at a cold start of an automotive vehicle and produce and store an equivalent volume of ammonia for the next cold start. Ammonia is able to reduce harmful NO<sub>x</sub> emissions into nitrogen at lower temperatures than ammonia precursors such as urea, permitting an improved pollution control of the exhaust gases at cold start. The system can for instance be used in combination with the widely applied Selective  
15 Catalytic Reduction (SCR) technology consisting in the injection of a urea solution (AdBlue®/DEF) when the SCR catalyst temperature is above a certain value. In the latter case, the urea is first hydrolysed to ammonia on the SCR catalyst before the NO<sub>x</sub> reduction to nitrogen takes place. It is not possible to use urea SCR at cold start of a vehicle because urea does not decompose properly below 180-200°C, forming deposits that rapidly decrease the SCR catalyst performances.  
20 Ammonia and ammonia solutions can be used at temperatures as low as 120°C that are reached much faster after the cold start, allowing starting the NO<sub>x</sub> reduction much earlier, e.g. about 3 minutes after the cold start instead of 5 minutes and more.

Embodiments of the invention present a compact system permitting to convert a small volume of  
25 urea solution (or another ammonia precursor) to ammonia while driving or at key-off consecutive to the driving events following a cold start, and to store the produced ammonia for use at next key-on in cold start conditions. By “cold start”, we mean starting the engine (key-on) in conditions of temperature such that the SCR catalyst in the exhaust pipe does not reach a given temperature before a given time, for instance does not reach 120°C before 2 minutes; we will refer to this time  
30 as the Cold Start-up Delay ( $t_{CSD}$ ). The energy consumption for urea conversion will be very low since the volume of ammonia required to tackle NO<sub>x</sub> during the start-up period is very low too. For instance, the conversion of 10 to 100 ml of urea solution will allow controlling NO<sub>x</sub> emissions during approximately 20 km or more. The energy required for this conversion can for instance be  
35 less than 10 Wh if low temperature conversion techniques (biocatalyzed conversion, electrochemical conversion) are used and about 20 Wh if high temperature conversion techniques (pyrolysis, thermohydrolysis with or without a heterogeneous catalyst) are used; generally it is in

the range 5-100 Wh. This amount of energy is available without affecting other energy demanding applications during driving or at key-off (for instance from the vehicle battery), or during driving and the short period following key-off during which consumption of energy available in the car (typically electricity from batteries) is allowed. Moreover, the volume occupied by the present  
5 urea conversion system is very small, which is an advantage in vehicles where space is limited.

The urea conversion system may use any available technology to produce ammonia, for instance urea pyrolysis, or urea hydrolysis at high temperatures (above 150°C) without or with a heterogeneous catalyst, or urea hydrolysis at low temperatures (below 60°C) with an enzymatic  
10 catalyst such as urease for example, or electrochemical conversion by applying a voltage to the urea solution at low temperatures, typically below 80°C. Examples of urea hydrolysis at low temperatures (below 60°C) with an enzymatic catalyst such as urease for example are disclosed in patent applications EP 13182919.4, EP 12199278.8, EP 12199278.8 and EP 13182919.4 in the name of the Applicant, which are included herein by reference. Examples of electrochemical conversion by  
15 applying a voltage to the urea solution at low temperatures references are described in Fei Lu and Gerardine G. Botte, "Electrochemically Induced Conversion of Urea to Ammonia", ECS Electrochemistry Letters, 4 (10), E5-E7, 2015, which is included herein by reference.

Additionally, a sensor may be integrated within the urea conversion unit to monitor the progress of  
20 this conversion. The sensor will enable the detection of the end of the conversion process and will indicate that the produced ammonia may be stored. This sensor can for instance be based on electrical conductivity measurements or any other suited technology. The sensing of the evolution of this conversion operation can also be used for the monitoring of the quality of the urea solution. The electrical conductivity increases significantly (typically by a factor of at least 10) as the  
25 conversion of urea solution to ammonia solution (during which carbonates and hydrogen carbonates are also generated) progresses, what would not be the case with most other fluids; so discrimination of fluids can be based on this sensor.

In order to better understand features and advantages of embodiments of the invention, first it will  
30 be explained what happens in a vehicle fitted with an SCR system in the exhaust pipe when it is started in cold conditions. Figure 1A plots the evolution of the temperature of an SCR catalyst in the exhaust pipe as a function of time for two exemplary situations, see the first curve 110 and the second curve 120.

35 The first curve 110 corresponds to a situation where the engine is cold-started, and then stopped after it has been running for 4.5 minutes since the initial start-up, whereupon the engine is restarted

at 5.5 minutes and finally stopped at 8 minutes after the initial start-up of the engine. At a point in time  $t_{\text{Tammonia}}$ , here at 3.5 minutes, the temperature of the SCR catalyst reaches  $T_{\text{ammonia}}$ , in the example 120°C, ammonia solution may be injected in the exhaust pipe to reduce the NOx without damaging the exhaust system. Before the point in time  $t_{\text{Tammonia}}$ , preferably no ammonia solution is injected and ammonia solution is therefore not needed. After the engine is stopped at 4.5 minutes, the temperature of the SCR catalyst decreases, and when the engine is started again at 5.5 minutes, the temperature of the SCR catalyst increases and can reach  $T_{\text{urea}}$ , here 180°C, at which temperature urea solution (e.g. AdBlue®/DEF) can be directly injected in the exhaust pipe to reduce the NOx without damaging the exhaust system; at that time ammonia solution is also not needed.

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The second curve 120 corresponds to another cold start-up where the engine is stopped earlier, here after 4 minutes, and restarted much later, here at 13.5 minutes. In this case as well, no ammonia solution is needed before the point in time  $t_{\text{Tammonia}}$ , as the SCR catalyst is too cold. The difference between the first and the second curve between time = 0 and time = 4 minutes is due to the fact that depending on the conduct of the driver and specific itinerary, the temperature may increase in a different manner.

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From the first and second curve 110, 120 it can be derived that there is a “cold start-up delay”  $t_{\text{CSD}}$  after a cold start during which  $T_{\text{ammonia}}$  will never be reached and during which ammonia solution is never needed. The “cold start-up delay” is actually the minimum of all values of  $t_{\text{Tammonia}}$  at which the temperature  $T_{\text{ammonia}}$  is reached for all possible driving events. The cold start-up delay  $t_{\text{CSD}}$  may be determined empirically by choosing a value which is lower than all values of  $t_{\text{Tammonia}}$  as measured for various situations with extreme driving conditions, e.g. very high acceleration immediately after a cold start on a hot summer day.

25

The conversion of urea solution into ammonia solution cannot be performed instantaneously. Indeed, urea solution has to be fed to the reactor as well as energy (in the form of e.g. heat, electrical energy, etc.) in order to start the chemical reaction, and a certain time is then required to reach a complete conversion of the reactants due to the reaction kinetics. So, for a conversion unit of a given size, a delay  $t_{\text{Conv}}$  is needed after the cold start-up before ammonia solution can be produced. Embodiments of the invention consists in a system and associated strategy allowing to ensure that after a delay  $t_{\text{Conv}}$  following the initial cold start, enough ammonia solution has been generated so as to ensure that further needs of ammonia solution beyond  $t_{\text{Conv}}$  can be fulfilled, in particular for the next cold start, or optionally also for other driving conditions such as driving with low engine loads during which the temperature of the SCR catalyst could be too low for urea solution.

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Figure 1B shows the evolution of various parameters as a function of the time since the last stop of the engine  $t_{\text{Key-Off}}$  on a time interval going from the initial cold start-up to the delay  $t_{\text{Conv}}$ . Indeed it is not relevant to consider values of  $t_{\text{Key-Off}}$  exceeding  $t_{\text{Conv}}$  as ammonia solution will be renewed at this stage as explained above. The first parameter shown in figure 1B is the maximal envelope of the cumulative demand for ammonia solution at time  $t_{\text{Conv}}$  as a function of  $t_{\text{Key-Off}}$ . This cumulative demand corresponds with curve 130 in figure 1B. When the last key-off during the interval occurs before  $t_{\text{CSD}}$ , i.e. before any possible value of  $t_{\text{Tammonia}}$  of demand curves, ammonia solution is not needed, and the envelope stays at 0. When the last stop of the engine  $t_{\text{Key-Off}}$  occurs after  $t_{\text{CSD}}$ , ammonia may be required, and the envelope curve of the cumulative demand at time  $t_{\text{Conv}}$  increases up to time  $t_{\text{Conv}}$ , that corresponds to the maximum cumulative demand for ammonia solution  $D_{\text{conv}}$  that could be needed within the time interval going from the initial cold start-up up to  $t_{\text{Conv}}$ . So the system according to the invention should be sized so as to generate a quantity  $D_{\text{conv}}$  of ammonia solution within the time interval  $t_{\text{Conv}}$ .

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The second parameter on figure 1B is the available energy as a function of time  $t_{\text{Key-Off}}$ . Typically the heating of the conversion unit and of the other peripherals of the system will be fed by electrical power; so the energy made available will increase linearly as a function of the duration during which the power is applied, see curve 140. The energy curve 140 does not necessarily start at 0, as on some vehicle energy can be taken from the battery a few seconds after the stop of the engine, during the power shutdown procedure or before the start of the engine. It should also be noted that the system could also be served by additional energy sources such as specific batteries or capacitors that can be recharged during normal vehicle operation.

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The third parameter on figure 1B is the quantity of ammonia solution that can be generated at time  $t_{\text{Conv}}$  as a function of  $t_{\text{Key-Off}}$ , see curve 150. When  $t_{\text{Key-Off}}$  is very short (smaller than  $t_{\text{Preparation}}$ ), there is not enough time to fill the conversion unit and store enough energy in the system so as to complete the conversion at  $t_{\text{Conv}}$ . When the available energy (curve 140) reaches a certain value, the amount of ammonia solution that can be generated at  $t_{\text{Conv}}$  starts to increase – in figure 1B this takes place at time  $t = t_{\text{Preparation}}$ . When  $t_{\text{Key-Off}}$  is sufficient (larger than  $t_{\text{Preparation}}$ ), the conversion unit is filled completely and enough energy is stored in the system so as to complete the conversion at  $t_{\text{Conv}}$ ; this third parameter then jumps to the quantity of ammonia solution corresponding to the sizing of the conversion unit.

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In embodiments, the conversion unit and the associated system are sized so as to fill it and store enough energy within a time  $t_{\text{Preparation}}$  shorter than  $t_{\text{CSD}}$  so as to be able to generate a quantity of

ammonia solution exceeding  $D_{\text{conv}}$  at the end of the time interval  $t_{\text{conv}}$ . Indeed if  $t_{\text{Preparation}}$  was larger than  $t_{\text{CSD}}$ , the quantity of ammonia solution stored initially at the cold start could be progressively consumed if several successive trips would last a period of time between  $t_{\text{CSD}}$  and  $t_{\text{Preparation}}$ .

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It should be noted that heat can be stored in the reactants themselves and in the materials surrounding the reactants. The storage of this type of energy can be increased using phase change materials. It should also be noted that electrical energy can be stored as well using specific batteries, or capacitors or super-capacitors. This is especially important for systems based on electrochemical conversion. Such conversion system and strategy can be used for other applications than NO<sub>x</sub> reduction: for instance fuel cells relying on ammonia or ammonia solutions, fed directly or indirectly through additional conversion steps may have cumulative demand envelopes similar to the ones shown in figure 1B: for instance, the vehicle can be started using some energy accumulated in batteries, while the fuel cells are being conditioned prior to starting producing electric power; so in this case as well, there is a “cold start-up delay”  $t_{\text{CSD}}$  during which ammonia or ammonia solution is never needed. In this case also energy is available just after the cold start to store all materials and energies required so as to generate the required ammonia / ammonia solution for the next cold start.

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More generally, these system and strategies can be used for any on-board conversion system for which the chemical kinetics does not allow to perform the conversion fast enough to satisfy the demand, but for which the elements necessary to generate the required products can be prepared before the demand for these products starts. It is also attractive to reduce the amount of products stored on-board; this is especially important when these products are difficult to store or represent a particular risk as regards safety or risk of any other nature.

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Figure 2A shows an exemplary embodiment. A fluid transfer device, here a pump 210, e.g. a state-of-the-art AdBlue®/DEF pump, with its suction point 211 is located inside a tank 200, e.g. a state of the art AdBlue®/DEF tank 200. The suction point 211 can be located inside a retention reservoir 220, in which the fluid coming from the pump during the purge of the line can be accumulated. This retention reservoir 220 can also have a specific heating means (not drawn) so as to be able to start the pump 210 as soon as possible and to condition the fluids (either urea solution or ammonia solution) before they are delivered to a conversion unit 230 or directly to the exhaust pipe 250.

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The conversion unit 230 is located downstream the pump 210. The conversion unit 230 may be spherical to allow reduced heat losses from the conversion unit 230 to the tank 200, so as to reduce energy consumption and avoid premature degradation of the urea solution in the tank; such a shape may also shorten the warm-up time. In addition, a spherical shape has the advantage of having a good resistance to high internal pressures that can be encountered during the conversion operation. Optionally, the conversion unit 230 can be thermally isolated from the rest of the tank by an isolation layer (not represented). The conversion unit 230 may have other shapes than spherical: a cylinder with flat ends, a cylinder with ellipsoidal ends, an ellipsoidal shape, a box shape, etc. The conversion unit 230 may be equipped with a sensor for the monitoring of the conversion progress (not drawn). This sensor can for instance be a conductivity sensor, e.g. an electrical conductivity sensor.

The pump 210 may be included in a pump circuit equipped with a check valve 212 allowing pressure regulation thanks to a pressure sensor (not represented). A bypass line 231 allows to bypass the conversion unit 230 so as to send fluid (AdBlue®/DEF or a mixture of AdBlue®/DEF and ammonia solution) directly to the injector 260, when the appropriate temperature has been reached at the level of the SCR catalyst (i.e. a temperature higher than  $T_{urea}$ , typically higher than 180°C). Further flow regulating devices in the form of valves V1, V2, V3 are provided in the pump circuit for regulating the flows through the conversion unit 230 and through the bypass line 231.

An injection line 245 is arranged for receiving ammonia from the conversion unit 230. A small buffer 240 is located downstream the urea conversion unit 230. The buffer 240 and the injection line 245 going from the buffer 240 to the injector 260 create a fluid storage which allows hosting an amount of ammonia solution needed for the cold phase of the NO<sub>x</sub> reduction process, while the SCR catalyst is between  $T_{ammonia}$  and  $T_{urea}$  (typically between 120°C and 180°C), i.e. when the ammonia solution can be injected but not the urea solution. This buffer 240 may also act as a heat exchanger allowing the fluid to cool down or be heated up, using surrounding fluid from the tank 200 or using a heater (not drawn). Typically, this heat exchanger function allows cooling down the ammonia solution coming out of the conversion unit 230. The system further comprises a controller (not shown) configured for controlling the pump 210 such that a volume of ammonia is pushed out of the conversion unit 230 by ammonia precursor entering the conversion unit 230.

Bypass line 231 is arranged for bypassing conversion unit 230 and for transferring ammonia precursor from tank 200 to injection line 245 by means of pump 210. A bypass flow regulating device, here in the form of valve V3, is arranged for regulating the flow through bypass line 231. The controller (not shown) may be further configured to control valve V3.

A first flow regulating device, here in the form of a valve V1, is arranged for regulating the flow of ammonia precursor from tank 200 to conversion unit 230. A second flow regulating device, here in the form of a valve V2, is arranged for regulating the flow of ammonia from conversion unit 230 to injection line 245. The controller (not shown) may be configured to control valves V1, V2 such that either a flow through the conversion unit 230 is made possible, or no flow is possible. Preferably, the controller is configured to control pump 210, and valves V1, V2, V3 in order to transfer first a predetermined volume of ammonia from conversion unit 230 to injection line 245, and next to transfer ammonia precursor through bypass line 231 to injection line 245.

Now a possible strategy will be described. When the car is at rest with the engine stopped and no power on the system, all valves V1 to V3 are closed. Ammonia solution generated since the last cold start is present in the conversion unit 230, while the lines going from the pump 210 to the injector 260 via the by-pass line 231 are purged (including buffer 240). In case of a cold start, i.e. a start-up of the vehicle while the exhaust pipe is close to the ambient temperature, after a period of time exceeding  $t_{Conv}$  since the last stop of the engine, the heating of the conversion unit 230, and if necessary of the pump 210, the retention reservoir 220, the reservoir 225 and of the lines is started, so as to increase the temperature of the conversion unit 230 and if necessary thaw the ammonia solution and preheat it before sending it to the injector 260. The nature of the liquid contained in the conversion unit 230 may be checked e.g. using a conductivity sensor (not drawn). When the above elements are hot enough (typically 1 to 120 seconds after the cold start), the pump 210 is started and valves V1 and V2 are opened, while V3 is kept closed. The injector 260 can be opened as well to facilitate the filling of the lines. The urea solution coming out of the pump 210 is pushing the ammonia solution present in the conversion unit 230 up to the injector 260, at which time the injector 260 is closed in order to avoid overflowing the exhaust pipe 250 with ammonia solution while no ammonia solution should be injected. Lines 245, 246, buffer 240 and conversion unit 230 are sized in such a way that when the ammonia solution reaches the injector 260, the conversion unit 230 is filled with fresh urea solution. Valves V1 and V2 are then closed and V3 is opened, so that pump 210 continues pushing the ammonia solution present in the buffer 240 and in the line 245 between the buffer 240 and the injector 260. The positioning of the check-valve 212 between valve V3 and the buffer 240 may facilitate the evacuation of the gases present in the by-pass line 231. Once the temperature  $T_{ammonia}$  is reached, the injector 260 is opened, ammonia solution is consumed, and urea solution progresses inside the buffer 240 and the line 245 up to the injector 260. The system is sized in such a way that the SCR catalyst has reached or exceeded the temperature  $T_{urea}$  by the time the urea solution reaches the injector 260.

In other words, in the embodiment of figure 2A injection line 245 and buffer 240 create a fluid storage between an outlet of conversion unit 230 and an inlet of an injector 260 for injection of fluid in an exhaust pipe 250. The controller (not shown) is configured for controlling during a period associated with a driving event, said period comprising a cold period in which the temperature of the exhaust pipe is below a predetermined first threshold; the transferring, during the cold period, of a predetermined volume of ammonia from conversion unit 230 to the fluid storage 245, 240; and after said transferring, the converting of stored ammonia precursor to obtain a further volume of ammonia in the conversion unit. This controlling can be done by controlling valves V1, V2, V3 and pump 210. Preferably, the predetermined volume is between 10 and 100 ml, preferably between 10 and 90 ml, more preferably between 15 and 60 ml; and the further volume is larger than or equal to the transferred predetermined volume of ammonia and smaller than 1.5 times the predetermined volume. The controller (not shown) is further adapted for controlling the injecting by injector 260 of the predetermined volume of ammonia when the temperature of the exhaust pipe is above a predetermined second threshold ( $T_{\text{ammonia}}$ ). Typically, the first and second threshold lie between 110°C and 130°C, preferably between 115°C and 125°C. Controller 300 may be configured to control valves V1, V2, V3, pump 210 and injector 260 such that the injected predetermined volume of ammonia is such that the temperature of the exhaust pipe is above a predetermined third threshold ( $T_{\text{urea}}$ ) after said predetermined volume has been injected by the injector. The third threshold is higher than the second threshold, and the third threshold is preferably above 170°C.

When the engine is stopped, the pump 210, lines 245, 246 and buffer 240 along the by-pass line 231 are purged as in conventional AdBlue®/DEF systems, for instance by inverting the rotation of the pump 210 and opening the injector 260. Valves V1 and V2 stay closed and the solution present in the conversion unit 230 is kept there so as to reach the required level of conversion, if not yet reached at the time the engine is stopped. All valves V1, V2, V3 are closed at the shutdown of the vehicle so as to avoid any flow of urea or ammonia solution in the exhaust pipe 250. For performing the purging, the controller (not shown) is configured for controlling pump 210 and valves V1, V2, V3 such that injection line 245 and bypass line 231 are purged and filled with gas. This is done before a following cycle at the next start-up of the engine, i.e. before transferring of ammonia from conversion unit 230 to the injection line 245 and of ammonia precursor from bypass line 231 to injection line 245. In that manner, an amount of gas present in the bypass line can be inserted between the ammonia from the conversion unit and the ammonia precursor from the bypass line. By suitably sizing the bypass line 231, a suitable amount of gas can be inserted between the ammonia and the ammonia precursor which prevents or reduces mixing of the ammonia and the ammonia precursor.

Following the cold start the engine can also be stopped before the pump 210 has started. In this case, no other action is necessary and the system is stopped. Following the cold start the engine can also be stopped during the initial filling of the buffer 240 and lines 245, 246, or a short time after this filling. In this case, the filling is completed if not done yet, V1 and V2 are closed, V3 is opened and the line buffer 240 and by-pass line 231 are purged. The urea solution filled in the conversion unit 230 and the energy already stored in the conversion unit 230 together with the energy that can still be gained during the vehicle shutdown procedure will be sufficient so as to ensure the appropriate level of conversion at  $t_{Conv}$  for the next cold start. The ammonia solution that was sent to the buffer 240 and the lines 245, 246 is accumulated in the retention reservoir 220. If the engine is restarted in the following seconds or minutes (hot start, before  $t_{Conv}$ ; wherein T is higher than  $T_{ammonia}$ , but may be lower or higher than  $T_{urea}$ ), V1 and V2 will stay closed and V3 will be opened so that this ammonia solution will be sent to the injector 260 through the by-pass line 231, while the generation of ammonia solution for the next cold start is in progress in the conversion unit 230.

One can easily understand that in case several hot starts occur during the period  $0 - t_{Conv}$  following the cold start, some ammonia solution might be lost or mixed with urea solution in the successive filling-purging steps. This is the reason why the conversion unit is typically sized to produce some more ammonia solution than the amount  $D_{Conv}$ , typically at least 20% more. If the engine is restarted after  $t_{Conv}$ , the system can operate as described above in case of cold start. However if the temperature of the SCR catalyst is above  $T_{urea}$ , it can be started as in the case of the hot start above, keeping V1 and V2 closed so as to avoid spending energy in the generation of unnecessary ammonia solution.

It should also be noted that in the last seconds of the purge, it might be advantageous to shortly open V1 and V2 so as to release some ammonia solution (totally or partially converted) to the pump 210 and retention reservoir 220. This is advantageous as the freezing point of the resulting mixture will be lower than the freezing point of the AdBlue®/DEF in the tank 200, what could facilitate thawing at the next start-up. The same advantageous effect is also obtained when the system is purged while ammonia solution is still present in the buffer-line-injector area. It should also be noted that this system and its associated strategy allows using a single pump for two fluids and is therefore simple and low cost.

The exemplary embodiment of figure 2B is similar to the embodiment of figure 2A, but most components relative to the conversion (valves V1 to V3, by-pass line 231, conversion unit 230,

buffer 240) are assembled in a conversion module 235, while the pump 210 is integrated in a delivery module 215 which may be similar to currently available delivery modules for urea tanks. The outlet of the delivery module 215 is connected to the conversion module 235 through an external line 216. This architecture is particularly advantageous so as to upgrade existing system configurations to improved systems with a conversion unit 230. The valves V1, V2, V3 and the conversion unit 230 are integrated inside the conversion module 235. The conversion module 235 can also act as a reservoir as it may be filled by the excess flow from the check-valve 212. So all valves V1, V2, V3 and conversion unit 230 may be surrounded by urea solution, what makes the system very safe even in case of a leak of ammonia solution, as this ammonia solution would be directly mixed with urea solution. The overflow of this reservoir created by the conversion module 235 can also be connected to a reservoir created by the delivery module 215, so as to feed this reservoir created by the delivery module 215 as well. This helps avoiding cavitation in case of a low level of urea solution in the tank 200.

The exemplary embodiment of figure 2C is similar to the embodiment of figure 2B, with this difference that the outlet of the delivery module 215 is connected to the conversion module 235 through an internal line 217, allowing further simplification of the system, as less external connections are necessary.

The exemplary embodiment of figure 2D is similar to the embodiment of figure 2B. In addition the conversion is catalyzed thanks to the use of a biocatalyst, e.g. a biocatalyst in liquid form. The biocatalyst, typically a urease enzyme in a liquid formulation containing for example low molecular weight polyols (e.g. glycerol, sorbitol and mannitol) as additives, is filled in a small biocatalyst tank 270. The biocatalyst tank 270 is connected to the conversion unit 230 via a biocatalyst feeding line 276 which includes a dosing pump 275. The biocatalyst is dosed to the conversion unit 230 at the time of the conversion using a dosing pump 275. Alternatively the biocatalyst may also be dosed by liberating the content of a capsule (not drawn) containing the biocatalyst in liquid form. The quantity of biocatalyst in the capsule then corresponds to what is required to convert the urea solution contained in the conversion unit.

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Figure 2E illustrates another exemplary embodiment in which similar components have been indicated with the same reference numerals. In this embodiment the urea conversion unit 230 and the ammonia storage buffer 240 are located outside the urea solution tank 200. A fluid transfer device 210 inside the tank 200 can transfer urea via a three-way valve 213 to conversion unit 230 or to bypass line 231, depending on the position of the three-way valve 213. A second fluid transfer device 210' is located downstream of the conversion unit 230, between the conversion unit

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230 and the buffer 240. A third fluid transfer device 210'' is located downstream of the buffer 240, between buffer 240 and a further three-way valve 213'. The further three-way valve 213' connects a line 246' to the injector 260 either with the bypass line 231 or with the branch containing the buffer 240. At cold start, the ammonia stored in the buffer 240 is sent to the injector 260 for pollution control and no urea solution is used. Once the ammonia buffer 240 has been emptied completely, the SCR catalyst is hot enough for pollution control with the urea solution and therefore the urea solution is sent to the injector 260. The conversion of urea to ammonia in the urea conversion unit 230 can be performed either during driving or at key-off or can be started during driving and completed during the period consecutive to key-off. In the first and third cases, the urea conversion unit 230 may have been filled with urea during cold start, i.e. when ammonia from the buffer 240 was sent to the injector 260. In the second case, the urea conversion unit 230 may be filled at key-off. In all cases, at the end of the conversion procedure, the ammonia is sent to the buffer 240 via a fluid transfer device 210' and it is stored there until the next key-on at cold start. In the event that the next key-on is very close to the last key-off so that the SCR catalyst temperature is high enough for urea SCR, the urea solution can be directly dosed for NOx control and the stored ammonia can be kept available for the next key-on at cold start.

It should be noted that the urea conversion unit 230, the buffer 240, the fluid transfer devices 210' and 210'' as well as the by-pass line 231 may be positioned close to the injector 260, allowing fast switching between ammonia and urea solutions.

Figure 2F illustrates another exemplary embodiment in which similar components have been indicated with the same reference numerals. In this embodiment the urea conversion unit 230 and the ammonia storage buffer 240 are located inside the urea solution tank 200. A fluid transfer device 210 inside the tank 200 can transfer urea to conversion unit 230 and to bypass line 231. A second fluid transfer device 210' is located downstream of the conversion unit 230, between the conversion unit 230 and the buffer 240. A third fluid transfer device 210'' is located downstream of the buffer 240, between buffer 240 and a further three-way valve 213'. The further three-way valve 213' connects a line 246' to the injector 260 either with the bypass line 231 or with the branch containing the buffer 240 through three-way valve 213'. This embodiment has the advantage to prevent any leakage of ammonia in the external environment in case of a defect on the urea conversion unit 230 or on the ammonia buffer volume 240.

The exemplary embodiment of figure 2G is similar to the embodiment of figure 2B, with this difference that the conversion module 230 is positioned outside of the tank 200 and close to the injector 260. If the buffer 240 and the line from the conversion module 230 to the injector 260

have small inner volumes, such a system allows switching very fast from ammonia solution to urea solution or from urea solution to ammonia solution as long as ammonia solution is available in the conversion unit 230. Such switching can be interesting for instance when the temperature of the SCR catalyst decreases below  $T_{urea}$ , in case of low load of the engine. Such a position of the conversion unit 230 outside of the tank 200 is however more critical in terms of safety as regards the consequence of leaks of ammonia solution, that are more likely to affect the environment.

The exemplary embodiment of figure 2H is similar to the embodiment of figure 2D. Here the conversion unit 230 is positioned in the tank 200 as in figure 2D, but an additional switching unit 280 is located near the injector 260. This switching unit 280 is configured to allow fast switching from ammonia solution to urea solution or from urea solution to ammonia solution as long as ammonia solution is available in a second buffer 281 of the switching unit 280. Preferably the second buffer 281 can contain a volume similar to the volume of conversion unit 230. After cold start, during the initial filling, valves V4, V5 and V6 of the switching unit 280 are opened, valve V6 is closed once the line is filled, and ammonia solution is sent to the injector 260 through the second buffer 281. Once  $T_{urea}$  is reached, V4 and V5 are closed, and V6 is opened, so that some ammonia solution can be preserved in second buffer 281, while urea solution is injected through the by-pass line 231 and valve V6. If the temperature of the SCR catalyst decreases below  $T_{urea}$  in case of low load of the engine, V6 can be closed and V4 and V5 reopened so that ammonia solution will be supplied to the injector very quickly.

In the event that the amount of ammonia solution falls below some critical quantity in the second buffer 281 (this amount can be monitored e.g. by monitoring the amount of ammonia solution being consumed at the injector level), buffer 281 can be refilled by supplying ammonia solution from the conversion unit 230: valves V1 and V2 can be opened and V3 closed so as to release ammonia solution from the conversion unit 230. Whenever this ammonia solution arrives at the level of valve V6 (this can also be monitored e.g. by monitoring the amount of solution being consumed at the injector level), V6 is closed and V4 and V5 opened, so as to store ammonia solution in second buffer 281. When second buffer 281 has received enough ammonia solution, valves V4 and V5 are closed and V6 reopened to continue inject urea solution in the exhaust pipe while the temperature of the SCR catalyst is above  $T_{urea}$ .

When the system has to be purged, all valves V4, V5 and V6 are opened simultaneously or in sequence, for instance V6 is first opened, and then V4 and V5 so as to suck ammonia solution at last and have it available in the retention reservoir to facilitate thawing if necessary at the next cold start.

Figure 3A illustrates an exemplary embodiment of an enzymatic conversion unit 230 where the urea to ammonia conversion is carried out at low temperatures, typically below 60°C in presence of a catalyst 1001, typically an enzymatic catalyst, for instance urease. The enzymatic catalyst may be immobilized on a support, e.g. beads, for increased durability. The system can be heated by any heating means 1002, for instance electrical heating or heat exchange by circulation of any liquid or gas available at a suited temperature. Urea solution 1003 may enter the conversion unit 230 at a top part thereof, and flow through the enzymatic catalyst to a bottom part, such that ammonia solution 1004 may leave the conversion unit 230 at the bottom part thereof. Such an embodiment permits to convert 30 ml of AdBlue®/DEF into ammonia at 50°C with an energy consumption not exceeding 5Wh. Alternatively, the enzymatic catalyst may be added in the urea solution and dosed using a dosing system, e.g. as shown in figure 2D.

Figure 3B illustrates an exemplary embodiment of an electrochemical urea conversion unit 230 where the urea to ammonia conversion is carried out at low temperatures, typically below 80°C, by applying a certain voltage, typically less than 2 V, using a power supply 2005 between two electrodes 2001a, 2001b in contact with the urea solution 2003. A strong base such as potassium hydroxide can be added to the urea solution 2003 to increase the ionic conductivity of this solution, enabling an accelerated conversion process. The system can be heated by any available heating means 2002, such as in the embodiment of Figure 3A. Urea solution 2003 may enter the conversion unit 230 at a bottom part thereof, and gaseous ammonia 2004 may leave the conversion unit 230 at a top part thereof. The embodiment of Figure 3B permits to convert 30 ml of AdBlue®/DEF into ammonia at 70°C with an energy consumption not exceeding 10 Wh.

Figure 3C illustrates schematically a spherical conversion unit 230 suited for thermal hydrolysis (with or without a heterogeneous catalyst) of urea at high temperatures (150°C to 400°C, preferably 150°C to 250°C) and high pressures. The conversion unit 230 comprises a plurality of small tubular subunits CU1, CU2, CU3, CU4, CU5, CU6. The plurality of small tubular subunits CU1, CU2, CU3, CU4, CU5, CU6 are interconnected, see the arrows in figure 3C, and closed by plugs 3010 as needed for guiding the flow of urea solution 3003 through the plurality of small tubular subunits CU1, CU2, CU3, CU4, CU5, CU6. Several heating elements 3002 are positioned inside the unit so as to quickly reach the conversion temperatures. In addition heating fins 3008 may be provided, e.g. extending from a central portion to the wall of spherical housing 3007 of the conversion unit 230. Heating elements 3002 can be conventional electrical resistance or PTC (Positive Thermal Coefficient) elements, enabling very fast heat-up. Phase Change Materials 3006 melting at a temperature within the range of the conversion temperatures, for instance in a range between 160°C and 200°C, can be positioned around the subunits so as to accumulate heat before

$t_{\text{Preparation}}$  and reconstitute it later so as to complete the conversion at  $t_{\text{Conv}}$ . A layer of insulating material (not drawn) may be placed around the spherical housing 3007. Optionally, catalysts such as zirconium oxide, titanium oxide or aluminum oxide can be placed inside the conversion unit 230 so as to speed up the conversion (or limit the necessary temperatures and pressures). Urea solution 3003 enters the conversion unit 230 in tubular subunit CU1, passes through the respective subunits CU2, CU3, CU4, CU5, see the arrows in figure 3C, and ammonia solution 3004 leaves the conversion unit 230 after having passed through tubular subunit CU6.

Figures 3D and 3E show another possible design of a conversion unit 230 using thermal hydrolysis (with or without a heterogeneous catalyst) in a preconditioning chamber. Figure 3D shows a vertical cross-section through the middle of the spherical conversion unit 230, while figure 3E shows a horizontal cross-section through the middle of the same unit 230. A layer of insulating material (not drawn) can be placed all around the spherical housing 4007.

As can be observed on figure 3D, a conversion chamber 4010 of the conversion unit 230 is located in a centre portion and may have the shape of a cylinder with spherical domes at the top and at the bottom. The conversion chamber 4010 of the conversion unit 230 is surrounded on both sides by a preconditioning chamber 4015. The preconditioning chamber 4015 allows performing a partial conversion of urea solution to ammonia solution thanks to the heat losses coming from the conversion chamber 4010 and heating elements 4002a, 4002b located at the bottom of the cylindrical separating wall. This allows reducing the time  $t_{\text{Conv}}$ , and hence the minimum amount of ammonia solution to be generated  $D_{\text{conv}}$ , as suggested on figure 1B. Indeed, with a preconditioning chamber 4015, the volume of the buffer and line can be smaller, resulting in smaller values of  $t_{\text{Conv}}$  and  $D_{\text{Conv}}$ .

Baffles 4020 may be present in both the conversion chamber 4010 and the preconditioning chamber 4015 so to allow first-in-first-out filling of the chambers when control valves controlling the flow through the chambers 4015, 4010 are opened. These baffles 4020 can contain heating elements 4002a such as PTC (positive thermal coefficients) heating elements and/or PCM (phase change material) elements 4006. This layout is advantageous as it allows a fast heat transfer as these elements are directly in the reactants. Advantageously the walls of the housing 4007 can be made with low heat capacity materials so as to allow fast heating of the reactants. The internal layout of the chambers 4010, 4015 may be further optimized so as to avoid dead spots that could result in temperature inhomogeneity and partial conversion.

Urea solution 4003 enters the preconditioning chamber 4015, passes from the preconditioning chamber 4015 to the conversion chamber 4010, and ammonia solution 4004 leaves the conversion chamber 4010.

- 5 The preconditioning chamber 4015 allows recovering heat from the conversion chamber 4010, and does not necessarily reach temperatures as high as in the conversion chamber 4010. Advantageously, a catalyst such as zirconium oxide, titanium oxide or aluminum oxide can be put inside the preconditioning chamber 4015 to increase the level of conversion achieved in this chamber. The preconditioning chamber 4015 can be separated from the conversion chamber 4010  
10 by a check-valve (not drawn) preventing back-flow from the conversion chamber 4010 to the preconditioning chamber 4015. As the temperature in the preconditioning chamber 4015 is lower than in the conversion chamber 4010, and the level of conversion is also lower, the pressures prevailing in the preconditioning chamber 4015 will also be lower, at an intermediate value between the pressure in the conversion chamber 4010 and the pressure of the environment. This is  
15 advantageous from a structural point of view, as the walls of the housing 4007 are submitted to lower pressure differences.

The conversion system 230 displayed here shows a conversion chamber 4010 with one preconditioning chamber 4015. It is noted that two or more successive preconditioning chambers  
20 could be used, wherein the reactants may be moved from one to the following e.g. at each line filling. This would allow a further reduction of  $t_{\text{Conv}}$ .

Figure 3F shows a horizontal cross-section of another conversion unit 230 using thermal hydrolysis (with or without a heterogeneous catalyst) in a preconditioning chamber 5015. The layout of the  
25 baffles 5020 with heating elements 5002a and PCM 5006 may be such that a natural circulation is created thanks to convection while the system is heated, resulting in a good homogeneity. Urea solution 5003 enters the preconditioning chamber 5015, passes from the preconditioning chamber 5015 to the conversion chamber 5010, and ammonia solution 5004 leaves the conversion chamber 5010.

- 30 A layer of insulating material (not drawn) may be placed all around the sphere.

Now an example of an SCR application in a passenger's car in which an exemplary embodiment of the invention is used, will be described. Preferably the volume of ammonia solution stored will be between 5 and 150 ml, more preferably between 10 and 100 ml, most preferably between 20 and  
35 40 ml, e.g. about 30 ml. This value should be bigger than  $D_{\text{Conv}}$ , which is preferably between 5 and

30 ml, more preferably between 5 and 20 ml, most preferably between 10 and 15 ml, and e.g. 12 ml.

For the example of a stored volume of ammonia solution of 30 ml and  $D_{\text{conv}} = 12$  ml, typical values are:

- 5 - Ammonia precursor: about 30 ml of urea solution
- Energy: typically about 20 Wh
- Time  $t_{\text{Conv}}$ : typically 13 minutes.

10 In embodiments of the invention the tank 200 may be filled with the commercially available liquid ammonia precursor, known as AdBlue<sup>®</sup> and matching the ISO 22241 standard specifications. Such a fluid contains  $32.5 \pm 0.7$  weight % urea.

15 An example of a urea decomposition system is disclosed in patent applications EP 13182919.4 and EP 12199278.8 in the name of the Applicant, the contents of which are included herein by reference. In those applications the Applicant has proposed two new methods for generating ammonia on board a vehicle (passenger car, truck, etc.) based on a biological catalysis. Biological catalysis comprises all forms of catalysis in which the activating species (i.e. biological catalysts) is a biological entity or a combination of such. Included among these are enzymes, subcellular organelles, whole cells and multicellular organisms.

20

A heater may heat up a decomposition area at the appropriate temperature for the reaction, i.e. for the decomposition of the ammonia precursor into ammonia. In the event that the biological catalyst is urease, a suitable temperature would be from around 40 to 60°C. The heater can be of any type as known in the state of the art. Typically a resistive heater is well suited. However, it is also possible to provide, as a heater, a conduit through which the cooling liquid of the engine is circulated. A thermal conditioning element may contribute to the heating during the decomposition of the ammonia precursor solution, e.g. a urea solution. These conditioning elements can be e.g. Peltier effect devices, isolating elements, phase change materials, or combinations of thereof.

30

Embodiments of the invention may also be used in an ammonia precursor booster system comprising a storage compartment for storing ammonia precursor granules, and a dissolving compartment for storing an ammonia precursor solution, and for dissolving ammonia precursor granules in the ammonia precursor solution. An example of such a booster system is disclosed in European patent application EP 14177713.6 in the name of the Applicant, which is included herein by reference.

35

Figure 4 illustrates another exemplary embodiment of a system for generating ammonia on-board a vehicle. The system comprises a tank 200, conversion unit 230, an injection line 245 including a buffer 240, and a fluid transfer device in the form of a pump 210. Tank 200 is adapted for storing an ammonia precursor. Conversion unit 230 is adapted for converting ammonia precursor into ammonia. Injection line 245 is arranged for receiving ammonia from conversion unit 230. Pump 210 is located downstream of conversion unit 230 and configured for transferring ammonia precursor from tank 200 to conversion unit 230 when valves V1' and V2' are open. The system further comprises a controller 300 configured for controlling pump 210 such that a volume of ammonia is transferred out of conversion unit 230.

The system of the preceding further comprises a suction point 232 and a valve V3'. The suction point 232 is arranged for transferring ammonia precursor from tank 200 to injection line 245 by means of pump 210. Valve V3' is arranged for regulating the flow from tank 200 to injection line 245. Controller 300 is configured to control valve V3'.

A first valve V1' is arranged for regulating the flow of ammonia precursor from tank 200 to conversion unit 230. A second valve V2' is arranged for regulating the flow of ammonia from conversion unit 230 to injection line 245. The controller 300 is configured to control pump 210, and valves V1', V2' and V3', in order to transfer first a predetermined volume of ammonia from conversion unit 230 to injection line 245, and next to transfer ammonia precursor from suction point 232 to injection line 245.

In the embodiment of figure 4, injection line 245 and buffer 240 create a fluid storage between an outlet of conversion unit 230 and an inlet of an injector 260 for injection of fluid in an exhaust pipe 250. Controller 300 is configured for controlling during a period associated with a driving event, said period comprising a cold period in which the temperature of the exhaust pipe is below a predetermined first threshold; the transferring, during the cold period, of a predetermined volume of ammonia from conversion unit 230 to the fluid storage 245, 240; and after said transferring, the converting of stored ammonia precursor to obtain a further volume of ammonia in the conversion unit. This controlling can be done by controlling valves V1', V2', V3' and pump 210. Preferably, the predetermined volume is between 10 and 100 ml, preferably between 10 and 90 ml, more preferably between 15 and 60 ml; and the further volume is larger than or equal to the transferred predetermined volume of ammonia and smaller than 1.5 times the predetermined volume.

35

Controller 300 is further adapted for controlling the injecting by injector 260 of the predetermined volume of ammonia when the temperature of the exhaust pipe is above a predetermined second threshold ( $T_{\text{ammonia}}$ ). Typically, the first and second threshold lie between 110°C and 130°C, preferably between 115°C and 125°C. Controller 300 may be configured to control valves V1', V2', V3', pump 210 and injector 260 such that the injected predetermined volume of ammonia is such that the temperature of the exhaust pipe is above a predetermined third threshold ( $T_{\text{urea}}$ ) after said predetermined volume has been injected by the injector. The third threshold is higher than the second threshold, and the third threshold is preferably above 170°C.

10 Figure 5 is a flowchart illustrating an embodiment of a method for generating ammonia on-board a vehicle. The method comprises:

- storing an ammonia precursor on-board a vehicle, see step 6001;
- during a first period associated with a first driving event: transferring a first batch of ammonia precursor to a conversion area, see step 6002 and converting the first batch into ammonia in the conversion area, see step 6003;
- during a consecutive second period associated with a second driving event, checking whether it is a cold-start in which the temperature of the exhaust pipe is below a predetermined first threshold, see step 6004;
- if it is a cold start: transferring a predetermined volume (the first batch) of ammonia from the conversion area to a fluid storage area downstream of the conversion area and upstream of the exhaust pipe such that it is available for injection into the exhaust pipe; and transferring a second batch of ammonia precursor to the conversion area, see step 6005; it is noted that the transferring of the first batch to the fluid storage area may be performed simultaneously with the transferring of the second batch in the conversion area, e.g. because the second batch pushes the first batch out of the conversion area;
- converting the second batch of ammonia in the conversion area, see step 6007;
- checking if the temperature of the exhaust pipe is above a predetermined second threshold ( $T_{\text{ammonia}}$ ), see step 6006;
- injecting the predetermined volume of ammonia (the first batch) when the temperature of the exhaust pipe is above a predetermined second threshold (during said consecutive second period), see step 6008;
- injecting ammonia precursor in the exhaust when the temperature  $T$  is above a third threshold ( $T_{\text{urea}}$ ), see steps 6009 and 6010; preferably, the predetermined volume of ammonia (the first batch) is such that the temperature of the exhaust pipe is above the predetermined third threshold ( $T_{\text{urea}}$ ) after said predetermined volume has been injected.

When the engine is stopped, see step 6011, a purging of the lines is performed, see step 6012. This purging may be performed as described above in connection with any one of the exemplary embodiments. Next, the cycle starts again, see steps 6013, 6014, 6015 and 6016.

- 5 Preferably, each batch has a predetermined volume between 10 and 100 ml, preferably between 10 and 90 ml, more preferably between 15 and 60 ml. Preferably, the first threshold lies between 110°C and 130°C, preferably between 115°C and 125°C. Preferably, the second threshold lies between 115°C and 125°C. Preferably, the third threshold is above 170°C. Preferably the above mentioned first period and second period correspond with a period of time between a key-on time  
10 of the vehicle and a key-off time of the vehicle, and optionally also an additional period of time after the key-off time in order to allow that the conversion of the second batch is finished.

The strategy discussed and illustrated above is also usefully applied to fuel cells or fuel cell subsystems. Indeed some fuel cells such as Solid Oxide Fuel Cells (SOFC) need to be heated up to  
15 high temperatures (typically above 650°C). This is typically done by blowing hot air on the cathode side. During this heating-up operation, the anode could be deteriorated once it has reached an intermediate temperature (typically above 250°C) due to the diffusion of some oxygen through the electrolyte and the resulting oxidation of the anode. A convenient way to avoid this degradation is to feed the anode with some reducing agent, for instance hydrogen or ammonia once  
20 the temperature of the anode is above a first threshold value (e.g. 250°C for a SOFC), until the fuel cell reaches its operating temperature (e.g. 650°C for a SOFC), at which its anode can be fuelled with its nominal fuel to produce electricity.

The fuel cell subsystem may consist of a fuel cell conversion unit operating in continuous mode in  
25 direct contact with a fuel cell stack. When the SOFC operates at its nominal temperature ( $T > T_{\text{urea}}$ , for instance in the case of a SOFC  $T_{\text{urea}} = 650^\circ\text{C}$ ), the fuel cell conversion unit operating in continuous mode is also at its nominal temperature and converts ammonia precursor, in this case a urea solution into effluents containing ammonia, thanks to the heat generated by the fuel cell. The generated ammonia is used as a fuel by the SOFC.

30 During the heat-up phase of the SOFC however, the fuel cell conversion unit operating in continuous mode and located near the SOFC cannot deliver ammonia as it is not hot enough. The conversion unit containing ammonia converted during the previous operations can however play this role and release ammonia to the fuel cell subsystem while the subsystem is between  $T_{\text{ammonia}}$ ,  
35 for instance in the case of a SOFC 250°C and  $T_{\text{urea}}$ , for instance 650°C.

Figure 6 shows an exemplary embodiment of a vehicle system for generating ammonia for a fuel cell subsystem 290 having an anode 292 and a cathode 291, an air inlet 296, an air outlet 297, and a fuel outlet 298. A fluid transfer device, here a pump 210, e.g. a state-of-the-art AdBlue®/DEF pump, with its suction point 211 is located inside a tank 200, e.g. a state of the art AdBlue®/DEF tank 200. The suction point 211 can be located inside a retention reservoir 220, in which the fluid coming from the pump during the purge of the line can be accumulated. This retention reservoir 220 can also have a specific heating means (not drawn) so as to be able to start the pump 210 as soon as possible and to condition the fluid (either a urea solution or an ammonia solution) before it is delivered to a conversion unit 230 or directly to a fuel cell subsystem 290. The fuel cell within the fuel cell subsystem 290 has been sketched in figure 6 as a single cell, but several cells can be put in parallel as known by the person skilled in the art.

The conversion unit 230 is located downstream the pump 210. The conversion unit 230 may be spherical to allow reduced heat losses from the conversion unit 230 to the tank 200, so as to reduce energy consumption and avoid premature degradation of the urea solution in the tank; such a shape may also shorten the warm-up time. In addition, a spherical shape has the advantage of having a good resistance to high internal pressures that can be encountered during the conversion operation. Optionally, the conversion unit 230 can be thermally isolated from the rest of the tank by an isolation layer (not represented). The conversion unit 230 may have other shapes than spherical: a cylinder with flat ends, a cylinder with ellipsoidal ends, an ellipsoidal shape, a box shape, etc. The conversion unit 230 may be equipped with a sensor for the monitoring of the conversion progress (not drawn). This sensor can for instance be a conductivity sensor, e.g. an electrical conductivity sensor.

The pump 210 may be included in a pump circuit equipped with a check valve 212 allowing pressure regulation thanks to a pressure sensor (not represented). A bypass line 231 allows to bypass the conversion unit 230 so as to send fluid (AdBlue®/DEF or a mixture of AdBlue®/DEF and ammonia solution) directly to a flow control means 260, such as a dosing valve, and the fuel cell subsystem 290, when the appropriate temperature has been reached at the level of the fuel cell subsystem 290 (e.g. a temperature higher than  $T_{urea}$ , typically higher than 650°C). Further flow regulating devices in the form of valves V1, V2, V3 may be provided in the pump circuit for regulating the flows through the conversion unit 230 and through the bypass line 231.

A dosing line 245 is arranged for receiving ammonia from the conversion unit 230. A fluid storage area comprising a small buffer 240 is located downstream the conversion unit 230. The buffer 240 and the dosing line 245 going from the buffer 240 to the dosing valve 260 allow hosting an amount

of ammonia solution needed for the cold start-up phase of the fuel cell subsystem 290, while the fuel cell subsystem 290 is between  $T_{\text{ammonia}}$  and  $T_{\text{urea}}$  (typically between 250°C and 650°C), i.e. when the ammonia solution has to be delivered but not the urea solution. The system further comprises a controller (not shown) configured for controlling the pump 210 such that a volume of ammonia is pushed out of the conversion unit 230 by ammonia precursor entering the conversion unit 230.

Bypass line 231 is arranged for bypassing conversion unit 230 and for transferring ammonia precursor from tank 200 to dosing line 245 by means of pump 210. A bypass flow regulating device, here in the form of valve V3, is arranged for regulating the flow through bypass line 231. The controller (not shown) may be further configured to control valve V3.

A first flow regulating device, here in the form of a valve V1, is arranged for regulating the flow of ammonia precursor from tank 200 to conversion unit 230. A second flow regulating device, here in the form of a valve V2, is arranged for regulating the flow of ammonia from conversion unit 230 to dosing line 245. The controller (not shown) may be configured to control valves V1, V2 such that either a flow through the conversion unit 230 is made possible, or no flow is possible. Preferably, the controller is configured to control pump 210, and valves V1, V2, V3 in order to transfer first a predetermined volume of ammonia from conversion unit 230 to dosing line 245, and next to transfer ammonia precursor through bypass line 231 to dosing line 245.

Now a possible strategy will be described. When the fuel cell subsystem 290 is at rest and the temperature is below  $T_{\text{ammonia}}$ , all valves V1 to V3 are closed, the anode 292 of the fuel cell subsystem 290 does not need to be protected. Hot air is blown on the side of the cathode 291 of the SOFC so as to heat it up, see the air inlet 296 and the air outlet 297. Ammonia solution generated since the last cold start is present in the conversion unit 230, while the lines going from the pump 210 to the dosing valve 260 via the by-pass line 231 have been purged (including buffer 240) and contain ammonia generated by any one of the conversion unit 230 and the fuel cell conversion unit 295 during previous operations. In case of a cold start, i.e. a start-up of the fuel cell subsystem 290 while it is below its operating temperature, after a period of time exceeding  $t_{\text{Conv}}$  since the last stop of the fuel cell subsystem 290, the heating of the conversion unit 230, and if necessary of the pump 210, the retention reservoir 220, the reservoir 225 and of the lines is started, so as to increase the temperature of the conversion unit 230 and if necessary thaw the ammonia solution and preheat it before sending it to the dosing valve 260. The nature of the liquid contained in the conversion unit 230 may be checked e.g. using a conductivity sensor (not drawn). When the above elements are hot enough (e.g. 1 to 120 seconds after the cold start), the pump 210 is started

and valves V1 and V2 are opened, while V3 is kept closed. The dosing valve 260 can be opened as well to facilitate the filling of the lines. The urea solution coming out of the pump 210 is pushing the ammonia solution present in the conversion unit 230 up to the dosing valve 260, at which time the dosing valve 260 is closed in order to avoid overflowing the fuel cell subsystem 290 with ammonia solution while no additional ammonia solution should be delivered. Lines 245, 246, buffer 240 and conversion unit 230 are sized in such a way that when the ammonia solution reaches the dosing valve 260, the conversion unit 230 is filled with fresh urea solution. Valves V1 and V2 are then closed and V3 is opened, so that pump 210 continues pushing the ammonia solution present in the buffer 240 and in the line 245 between the buffer 240 and the dosing valve 260. The positioning of the check-valve 212 between valve V3 and the buffer 240 may facilitate the evacuation of the gases present in the by-pass line 231; these gases may contain ammonia, and the AdBlue® contained in the tank act as an ammonia trap. Once the temperature  $T_{\text{ammonia}}$  is reached, the dosing valve 260 is opened, ammonia is consumed, and urea solution progresses inside the buffer 240 and the line 245 up to the dosing valve 260. The system is sized in such a way that the fuel cell subsystem 290 has reached or exceeded the temperature  $T_{\text{urea}}$  (typically 650°C) by the time the urea solution reaches the dosing valve 260.

In other words, in the embodiment of figure 6 dosing line 245 and buffer 240 create a fluid storage between an outlet of conversion unit 230 and an inlet of a dosing valve 260 for dosing of fluid in a fuel cell subsystem 290. The controller (not shown) is configured for controlling during a period associated with a fuel cell operating event, said period comprising a cold period in which the temperature of the fuel cell is below a predetermined first threshold; the transferring, during the cold period, of a predetermined volume of ammonia from conversion unit 230 to the fluid storage 245, 240; and after said transferring, the converting of stored ammonia precursor to obtain a further volume of ammonia in the conversion unit 230. This controlling can be done by controlling valves V1, V2, V3 and pump 210. The controller (not shown) is further adapted for controlling the dosing by dosing valve 260 of the predetermined volume of ammonia when the temperature of the fuel cell subsystem is above a predetermined second threshold ( $T_{\text{ammonia}}$ ). Typically, the first and second threshold lie between 150°C and 350°C, preferably between 200°C and 300°C. The controller (not shown) may be configured to control valves V1, V2, V3, pump 210 and dosing valve 260 such that the dosed predetermined volume of ammonia is such that the temperature of the fuel cell subsystem is above a predetermined third threshold ( $T_{\text{urea}}$ ) after said predetermined volume has been fed by the dosing valve 260. The third threshold is higher than the second threshold, and the third threshold is preferably above 550°C.

When the fuel cell subsystem is stopped, the pump 210, lines 245, 246 and buffer 240 along the by-pass line 231 are purged, eventually after a conversion delay and filled with effluents containing ammonia coming from the fuel cell conversion unit 295 operating in continuous mode, for instance by inverting the rotation of the pump 210 and opening the dosing valve 260. Valves V1 and V2 stay closed and the solution present in the conversion unit 230 is kept there so as to reach the required level of conversion, if not yet reached at the time the engine is stopped. All valves V1, V2, V3 are closed at the shutdown of the vehicle so as to avoid any flow of urea or ammonia solution in the fuel cell subsystem 290. For performing the purging, the controller (not shown) is configured for controlling pump 210 and valves V1, V2, V3 such that dosing line 245 and bypass line 231 are purged and filled with effluents coming from the fuel cell conversion unit 295 operating in continuous mode; this can be easily done thanks to the overpressure of ammonia that can be generated in any one of the conversion units 230, 295 so as to avoid the suction of air on the side of the anode 292 of the fuel cell subsystem 290. This is done before a following cycle at the next start-up of the fuel cell subsystem, i.e. before transferring of ammonia from conversion unit 230 to the dosing line 245 and of ammonia precursor from bypass line 231 to dosing line 245.

Following the cold start, the fuel cell subsystem 290 can also be stopped before the pump 210 has started. In this case, no other action is necessary and the system is stopped. Following the cold start, the fuel cell subsystem 290 can also be stopped during the initial filling of the buffer 240 and lines 245, 246, or a short time after this filling. In this case, the filling is completed if not done yet, V1 and V2 are closed, V3 is opened and the line buffer 240 and by-pass line 231 stay filled with ammonia solution. The urea solution filled in the conversion unit 230 and the energy already stored in the conversion unit 230 together with the energy that can still be gained during the vehicle shutdown procedure will be sufficient so as to ensure the appropriate level of conversion at  $t_{\text{Conv}}$  for the next cold start. If the fuel cell subsystem 290 is restarted in the following seconds or minutes (hot start, before  $t_{\text{Conv}}$ ; wherein  $T$  is higher than  $T_{\text{ammonia}}$ , but may be lower or higher than  $T_{\text{urea}}$ ), V1 and V2 will stay closed and V3 will be opened so that this ammonia solution will be sent to the dosing valve 260 through the by-pass line 231, while the generation of ammonia solution for the next cold start is in progress in the conversion unit 230.

If the fuel cell subsystem 290 is restarted after  $t_{\text{Conv}}$ , the system can operate as described above in case of cold start. However if the temperature of the fuel cell subsystem 290 is above  $T_{\text{urea}}$ , it can be started as in the case of the hot start above, keeping V1 and V2 closed so as to avoid spending energy in the generation of unnecessary ammonia solution.

35

Whilst the principles of the invention have been set out above in connection with specific embodiments, it is to be understood that this description is merely made by way of example and not as a limitation of the scope of protection which is determined by the appended claims.

### Claims

1. A system for generating ammonia on-board a vehicle, said system comprising:
  - a. a tank (200) adapted for storing an ammonia precursor;
  - 5 b. a conversion unit (230) adapted for converting ammonia precursor into ammonia;
  - c. a line (245) arranged for receiving ammonia from the conversion unit, said line optionally including a buffer (240);
  - d. a fluid transfer device (210) located upstream of the conversion unit and configured for transferring ammonia precursor from the tank to the conversion unit;
  - 10 e. a controller configured for controlling said fluid transfer device such that a volume of said ammonia is pushed out of the conversion unit in the line (245), by ammonia precursor entering the conversion unit.
  
2. The system of the preceding claim, further comprising:
  - 15 a. a bypass line (231) arranged for bypassing the conversion unit and arranged for transferring ammonia precursor from the tank to the line by means of the fluid transfer device; and
  - b. a bypass flow regulating device (V3) arranged for regulating the flow through the bypass line; wherein the controller is configured to control the bypass flow  
20 regulating device.
  
3. The system of any preceding claim, further comprising:
  - a. a first flow regulating device (V1) arranged for regulating the flow of ammonia precursor from the tank to the conversion unit;
  - 25 b. a second flow regulating device (V2) arranged for regulating the flow of ammonia from the conversion unit to the line;  
wherein the controller is configured to control the first and the second flow regulating devices in order to allow or block a flow of ammonia precursor into the conversion unit pushing ammonia out of the conversion unit.  
30
  
4. The system of claim 2 and 3, wherein the controller is configured to control the fluid transfer device, the bypass flow regulating device (V3), the first flow regulating device (V1) and the second flow regulating device (V2) in order to transfer first a predetermined volume of ammonia from the conversion unit to the line, and next to transfer ammonia  
35 precursor through the bypass line to the line.

5. The system of any preceding claim, wherein the fluid transfer device is a pump.
6. The system of any one of the claims 2-4, wherein any one or more of the bypass flow regulating device, the first flow regulating device and the second flow regulating device comprises a valve.  
5
7. The system of claim 2, optionally in combination with any preceding claim, wherein the controller is configured for controlling the fluid transfer device and the bypass flow regulating device such that the line and the bypass line are purged and filled with gas.  
10
8. The system of claim 4 and 7, wherein the controller is configured to perform the purging before the transferring of ammonia from the conversion unit to the line and of ammonia precursor from the bypass line to the line, such that an amount of gas present in the bypass line is inserted between the ammonia from the conversion unit and the ammonia precursor from the bypass line.  
15
9. The system of any preceding claim, wherein the conversion unit is configured for thermal hydrolysis of ammonia precursor at a temperature between 150°C and 400°C.
10. The system of claim 9, wherein the conversion unit has a substantially spherical housing and is located in the tank.  
20
11. The system of claim 9 or 10, wherein the conversion unit comprises a conversion chamber surrounded by a preconditioning chamber configured to use heat of the conversion chamber for preconditioning the ammonia precursor entering the conversion unit.  
25
12. A method for generating ammonia on-board a vehicle, said method comprising:
  - a. storing an ammonia precursor on-board a vehicle;
  - b. transferring ammonia precursor from the tank to a conversion unit;
  - 30 c. converting stored ammonia precursor into ammonia in the conversion unit;
  - d. controlling said transferring such that a volume of ammonia is pushed in a line by ammonia precursor entering the conversion unit, said line optionally including a buffer.
- 35 13. The method of the preceding claim, further comprising:
  - a. transferring ammonia precursor from the tank to the line through a bypass line bypassing the conversion unit; and

- b. controlling the transferring through the bypass line such that the ammonia previously pushed into the line is followed by ammonia precursor coming from the bypass line.

- 5           14. The method of claim 13, further comprising:
- a. regulating the flow of ammonia precursor from the tank to the conversion unit;
  - b. regulating the flow of ammonia from the conversion unit to the line;
  - c. controlling the regulating in order to transfer first a predetermined volume of ammonia from the conversion unit to the line, and next to transfer ammonia
- 10           precursor through the bypass line to the line.

- 15           15. The method of claim 13 or 14, further comprising purging the line and the bypass line such that the line and the bypass line are filled with gas; wherein the purging is performed before the transferring of ammonia from the conversion unit to the line and of ammonia precursor from the bypass line to the line, such that an amount of gas present in the purged
- 15           bypass line is inserted between the ammonia from the conversion unit and the ammonia precursor from the bypass line.

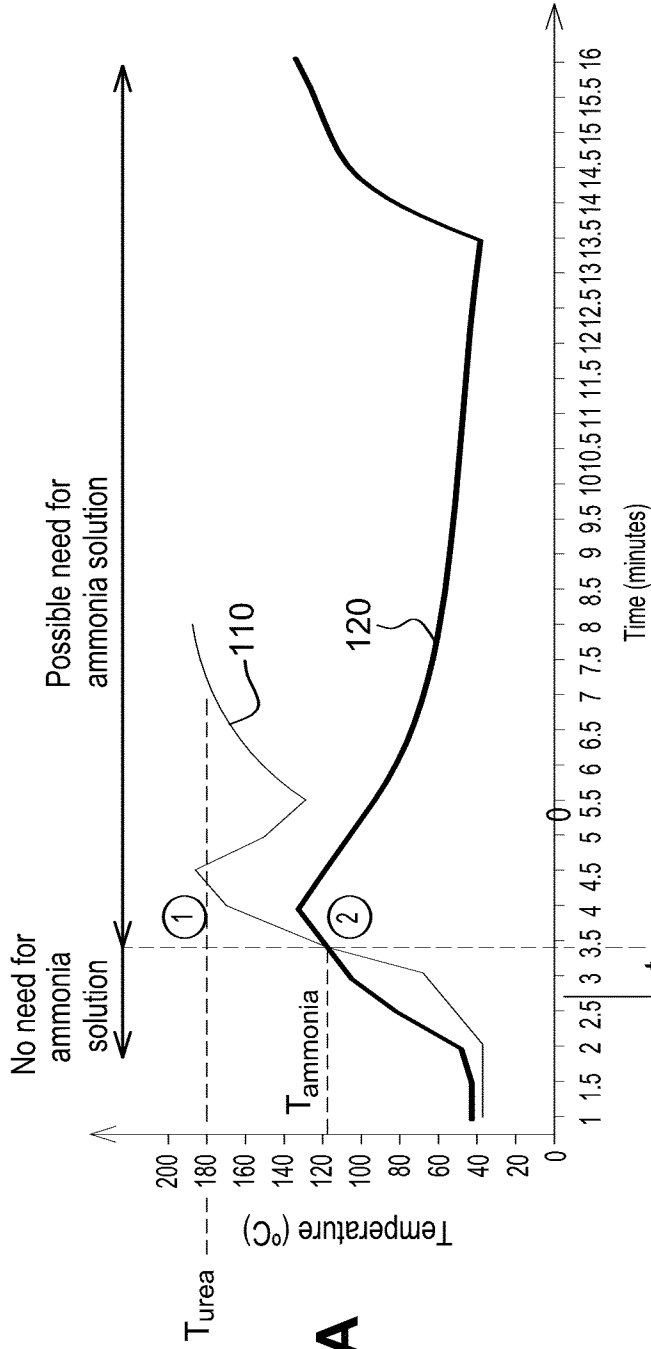


Fig. 1A

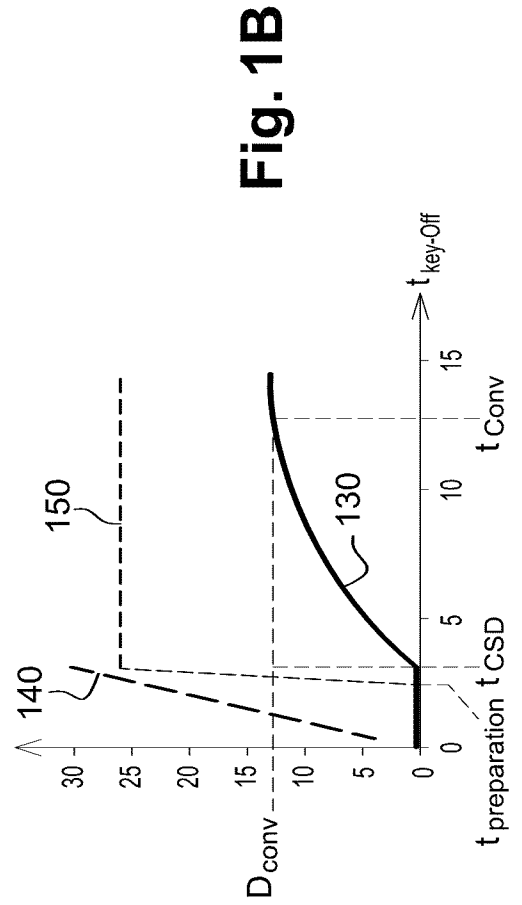
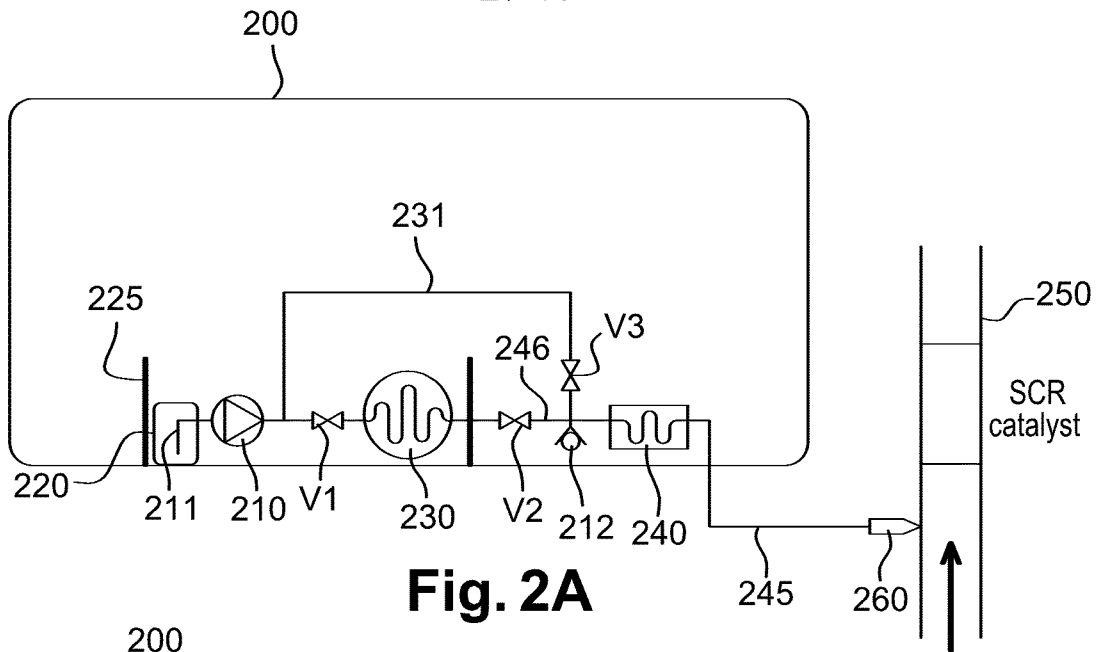
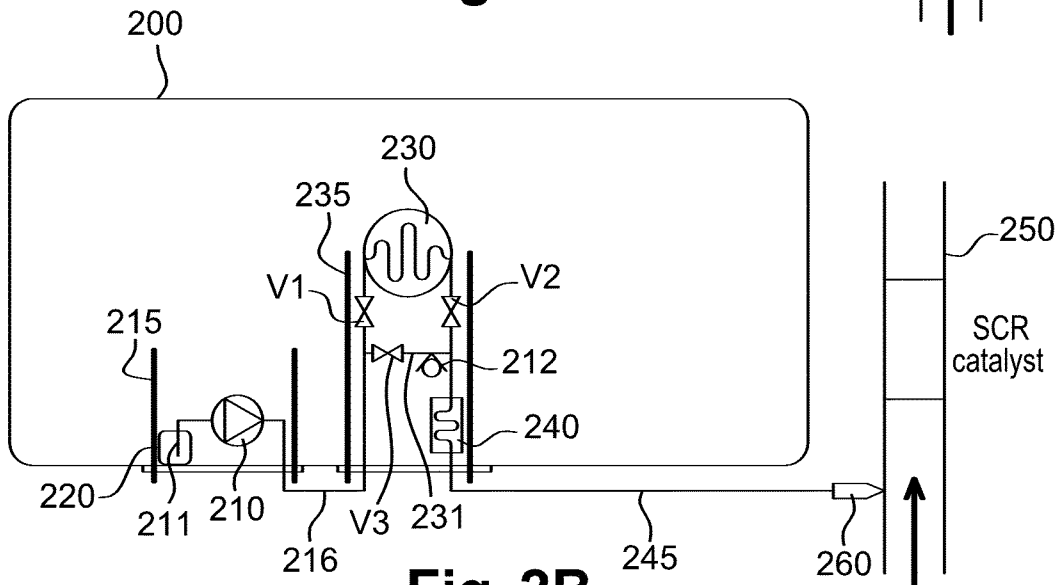


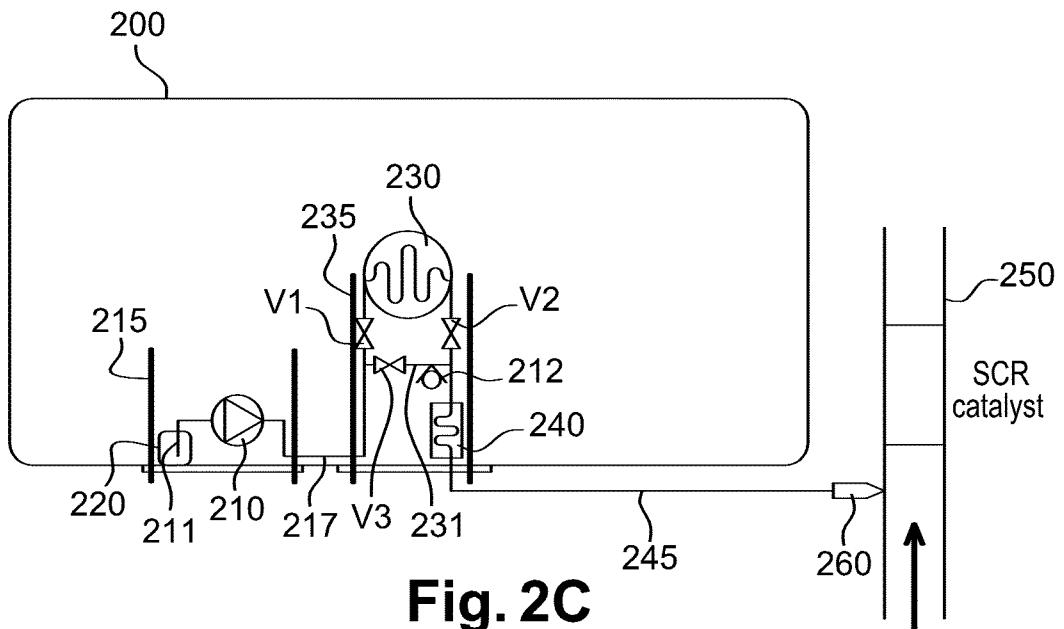
Fig. 1B



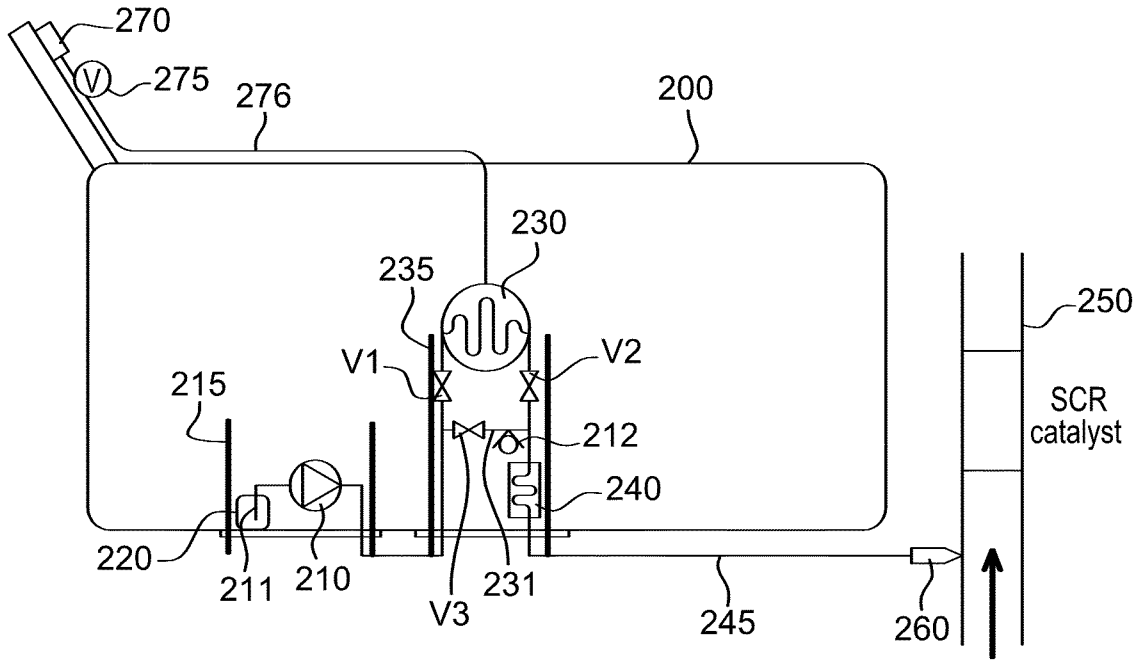
**Fig. 2A**



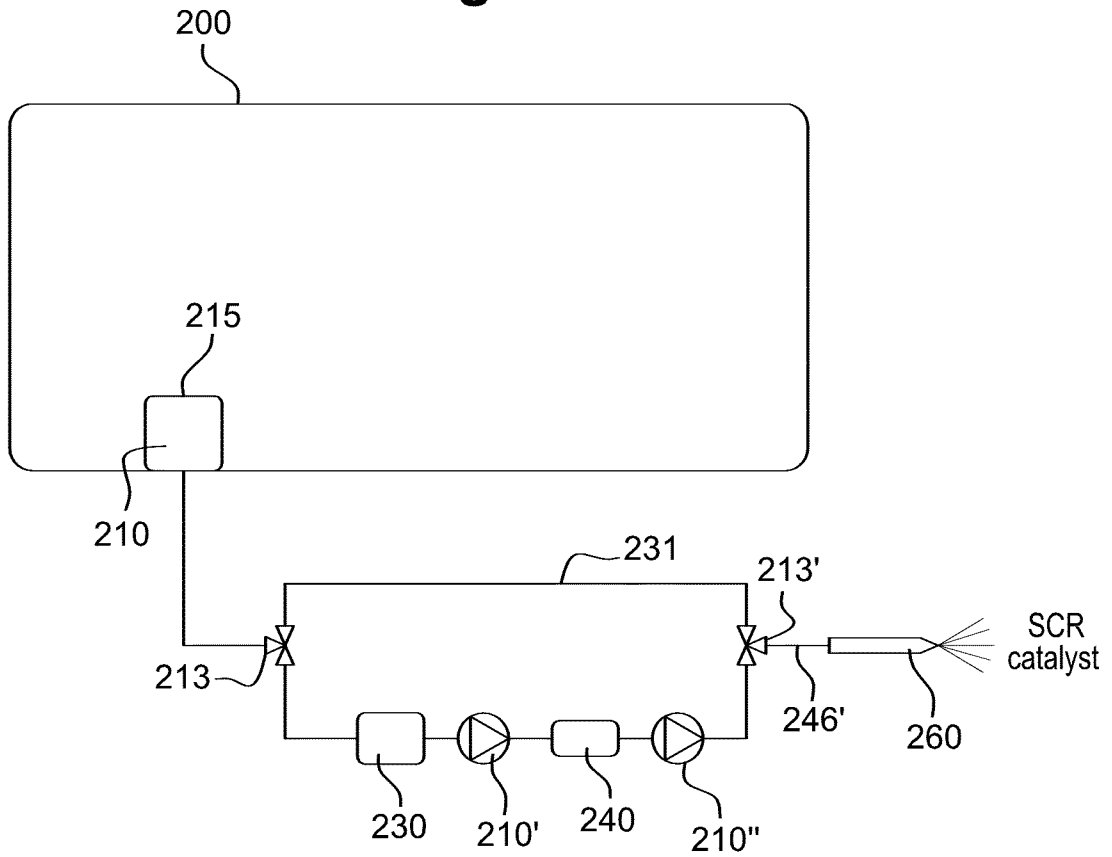
**Fig. 2B**



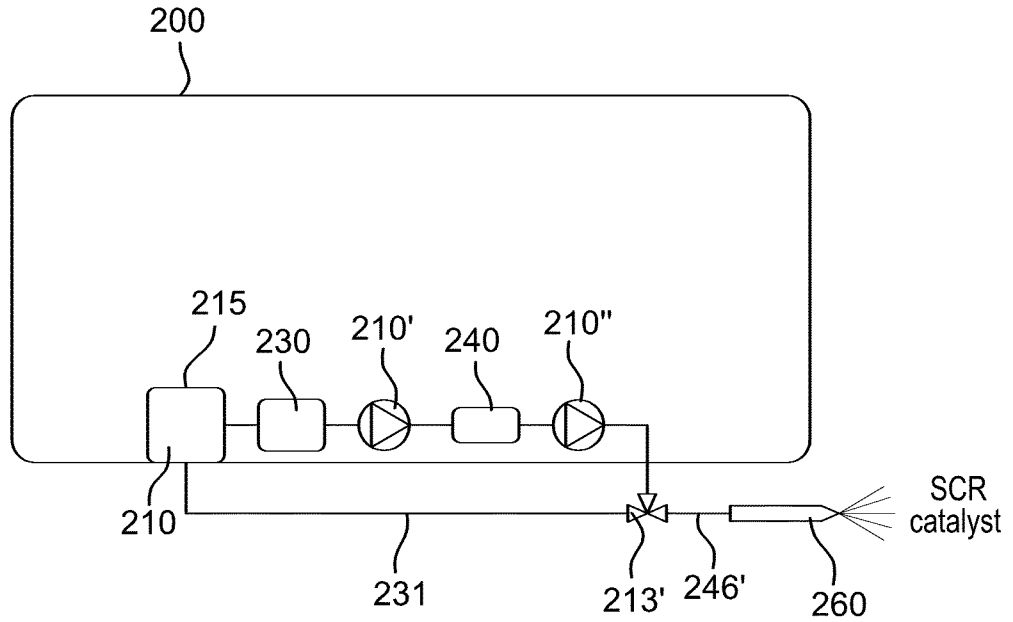
**Fig. 2C**



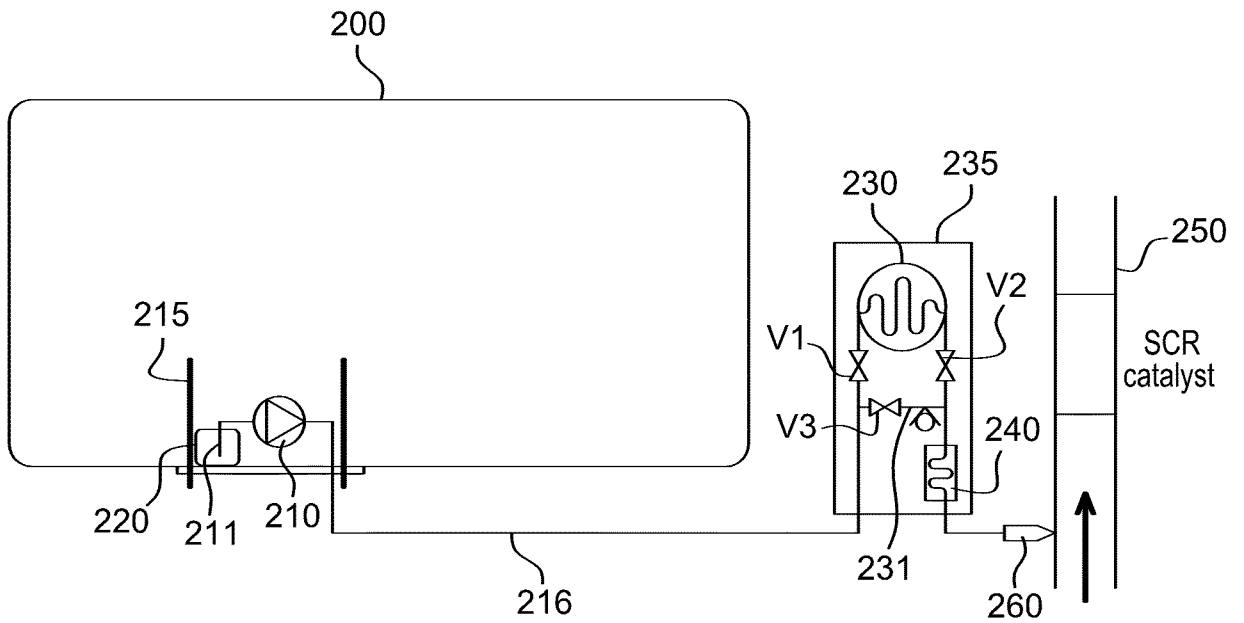
**Fig. 2D**



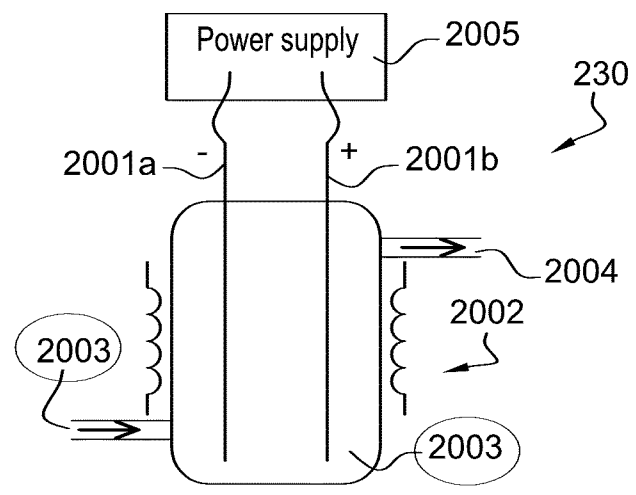
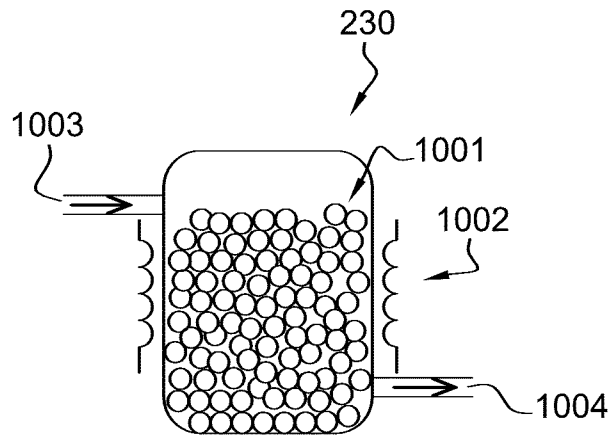
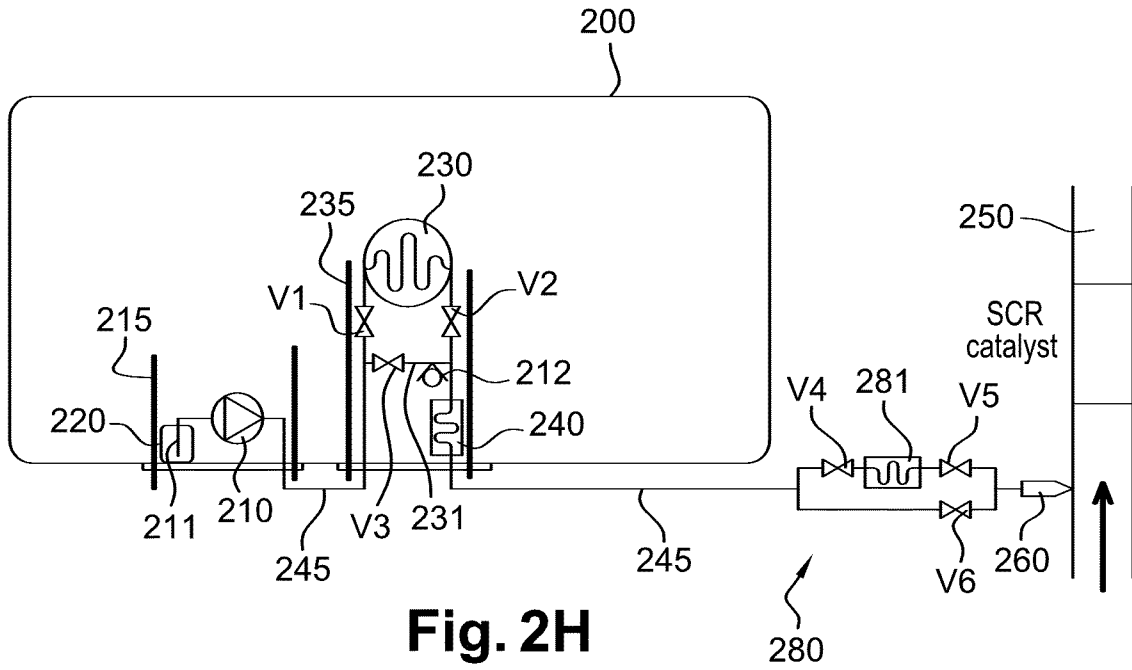
**Fig. 2E**



**Fig. 2F**



**Fig. 2G**



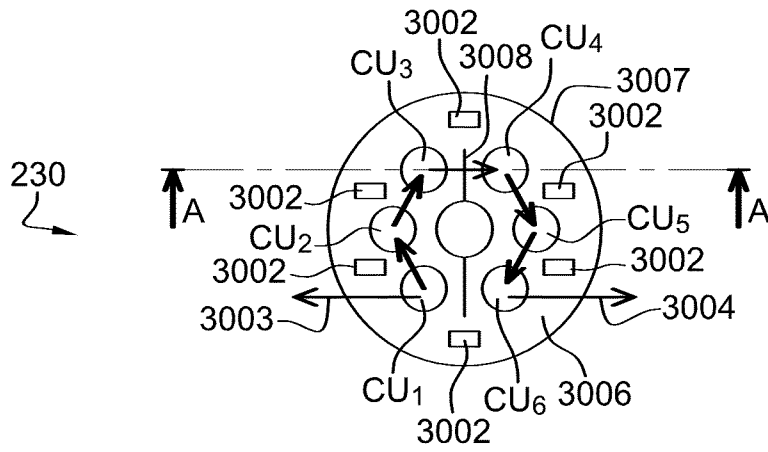


Fig. 3C

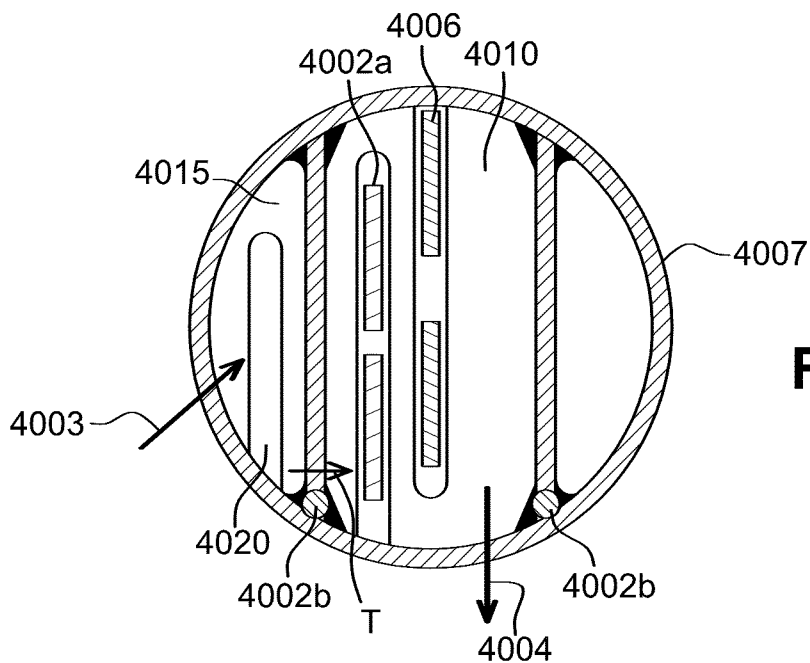
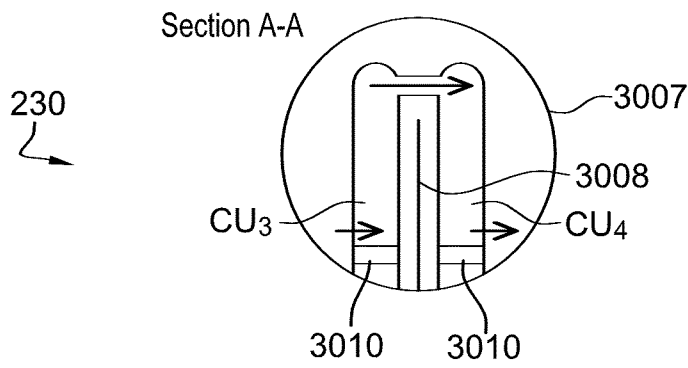
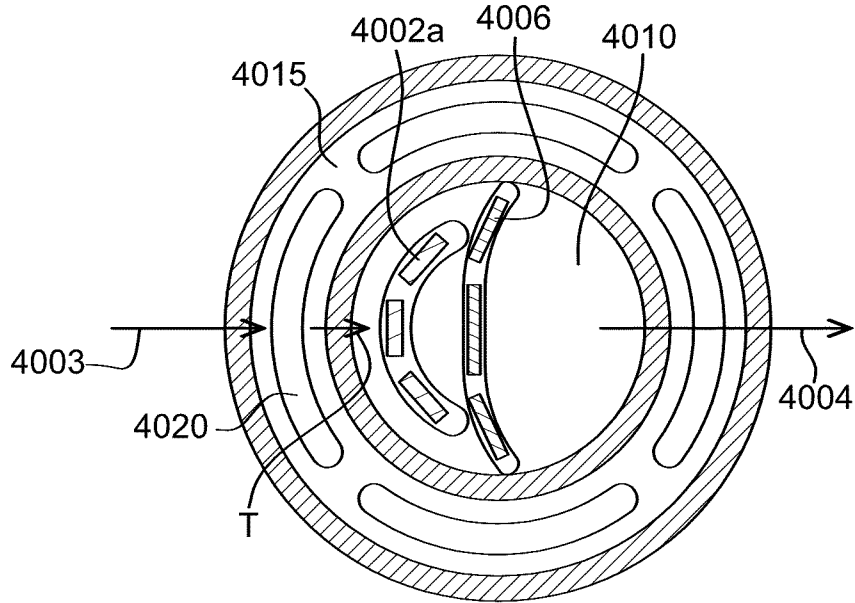
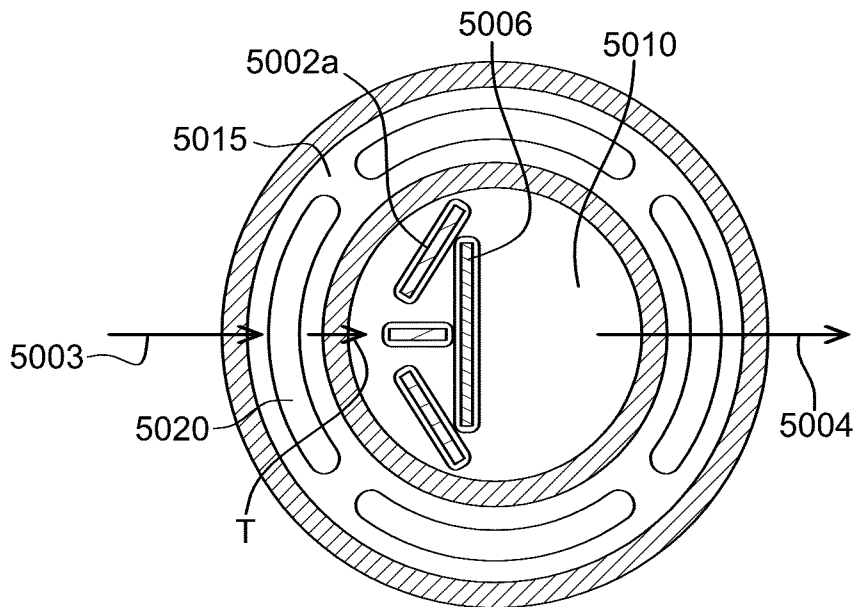


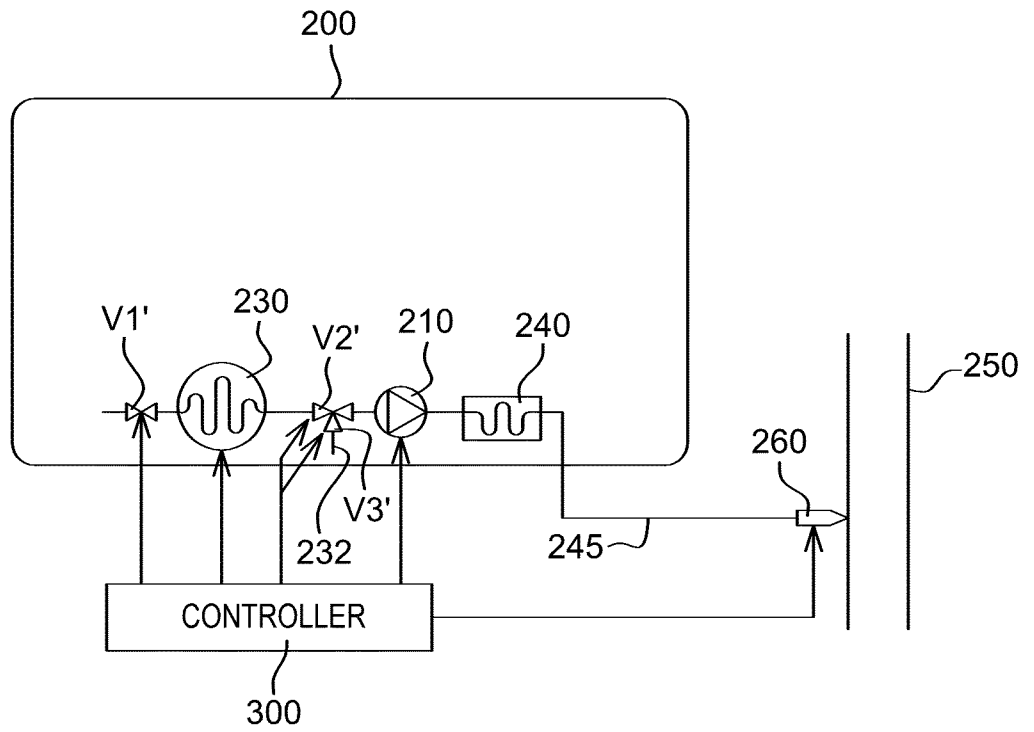
Fig. 3D



**Fig. 3E**



**Fig. 3F**



**Fig. 4**

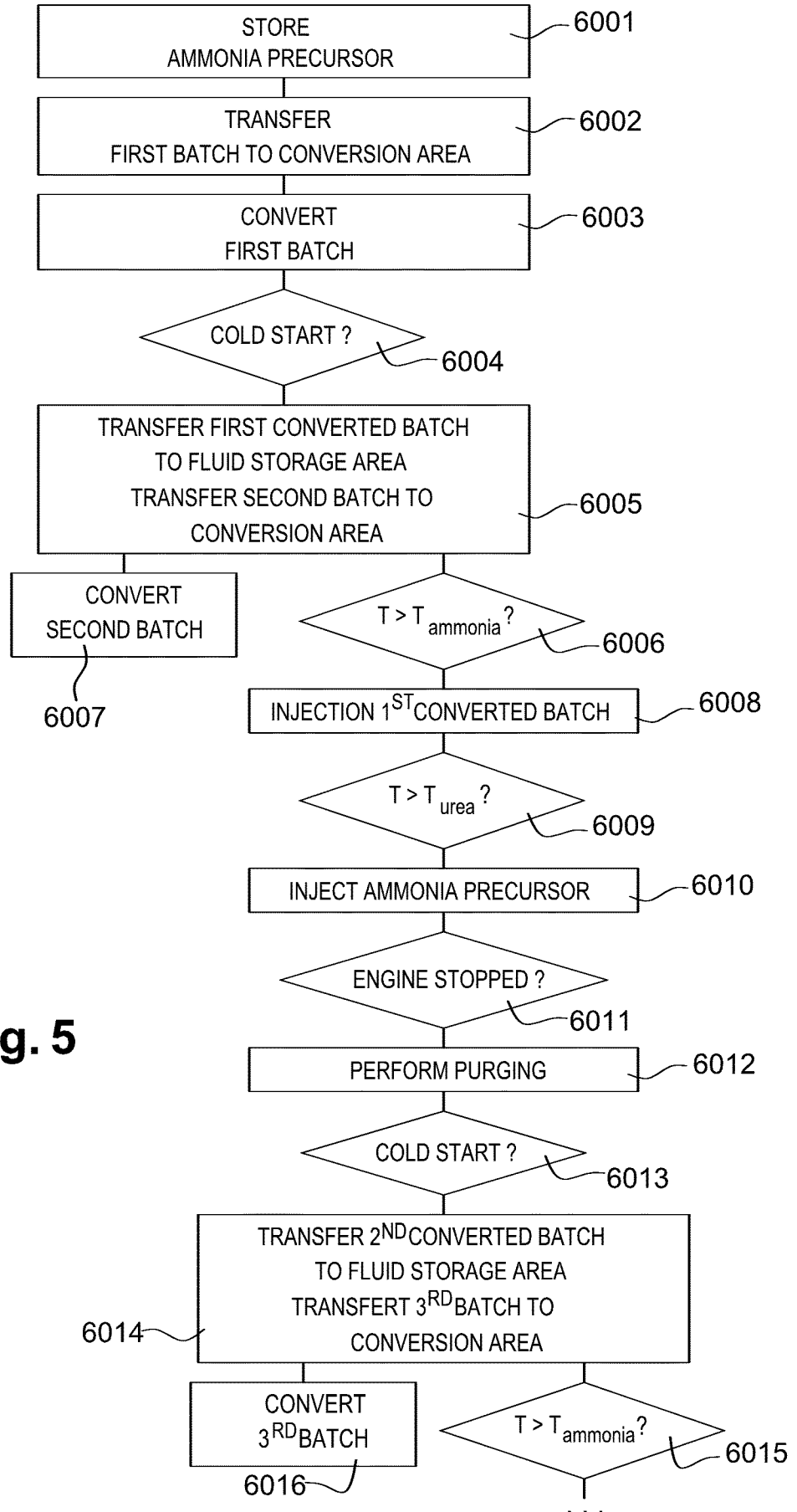


Fig. 5

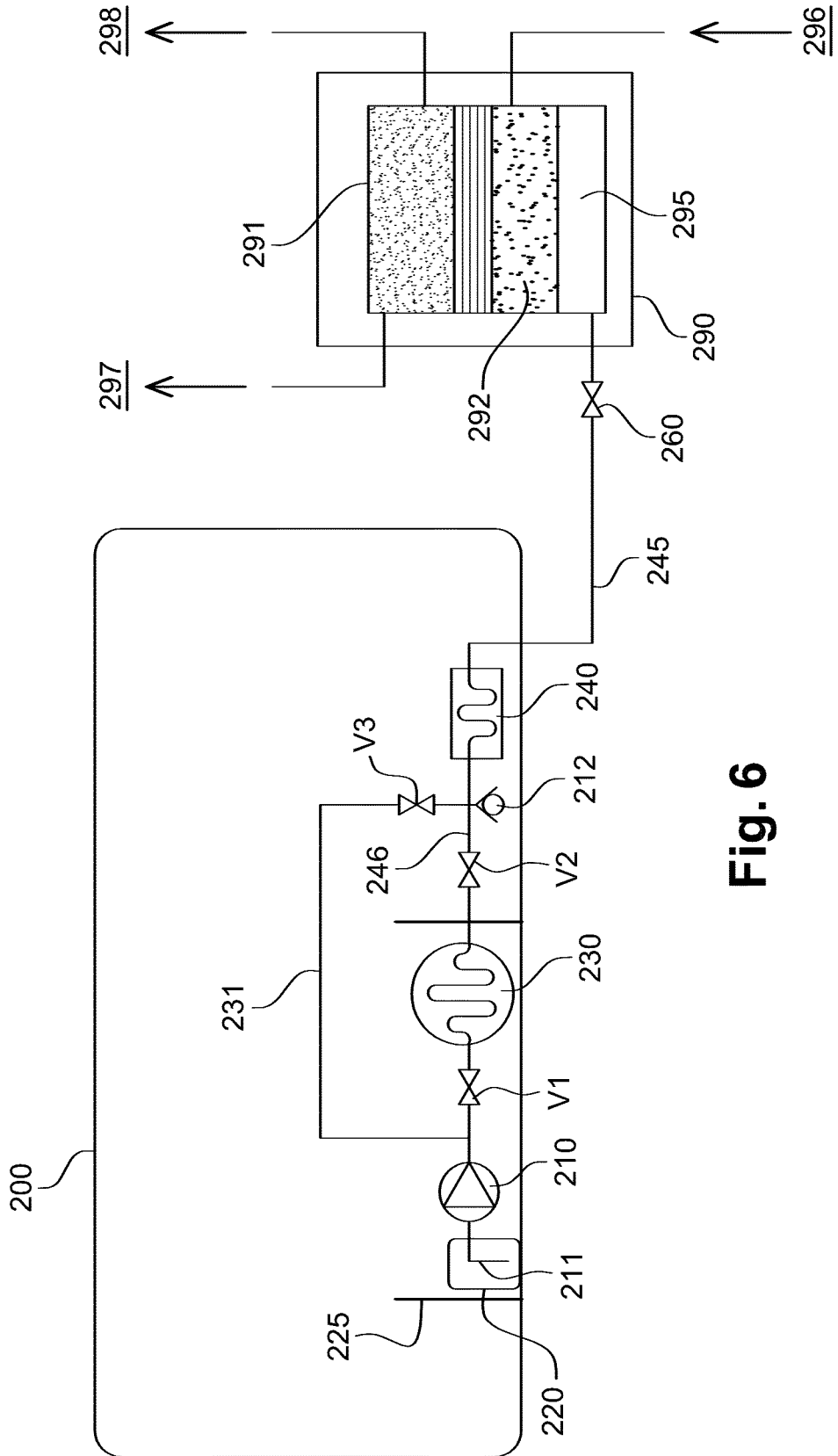


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/074263

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/032811 A1 (INERGY AUTOMOTIVE SYSTEMS RES [BE]; DOUGNIER FRANÇOIS [BE]; MADOUX DOM) 12 March 2015 (2015-03-12)	1-6,9-14
A	abstract; claims 1,2,4,5,12; figures 1-6 page 1, line 24 - page 4, line 35 page 7, lines 1-26 page 8, lines 29-34 page 9, lines 9-35 page 10, lines 13-18 page 12, lines 1-10 page 13, line 17 - page 14, line 17 ----- -/--	7,8,15

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search  17 November 2017	Date of mailing of the international search report  28/11/2017
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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  Steinberger, Yvonne
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/074263

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	abstract; claims 1-6; figures 2,3,4,5A-5F,6,7 paragraphs [0005], [0024] - [0028], [0040], [0045], [0029] - [0032], [0039], [0061] paragraphs [0015], [0024], [0063] - [0071] -----	8,15
X	EP 2 927 452 A1 (INERGY AUTOMOTIVE SYSTEMS RES [BE]) 7 October 2015 (2015-10-07)	1,3,5,6, 9-12,14
A	abstract; claims 1,8,13; figure 1 paragraphs [0011], [0028] - [0031], [0033], [0040], [0041], [0047] - [0049] -----	2,4,7,8, 13,15
A	EP 2 926 886 A1 (INERGY AUTOMOTIVE SYSTEMS RES [BE]) 7 October 2015 (2015-10-07)	1-15
	abstract; figure 1 paragraphs [0005] - [0031] -----	
A	WO 2008/020207 A1 (IMI VISION LTD [GB]; MILLS DAVID [GB]; BHIMANI ALAN [GB]; HEYES KEITH) 21 February 2008 (2008-02-21)	1-15
	abstract; figure 7 page 2, line 26 - page 7, line 17 -----	

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Information on patent family members

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