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(54) Title: AMMONIA GENERATOR CONVERTING LIQUID AMMONIA PRECURSOR SOLUTIONS TO GASEOUS AMMONIA FOR DENOX-APPLICATIONS USING SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES

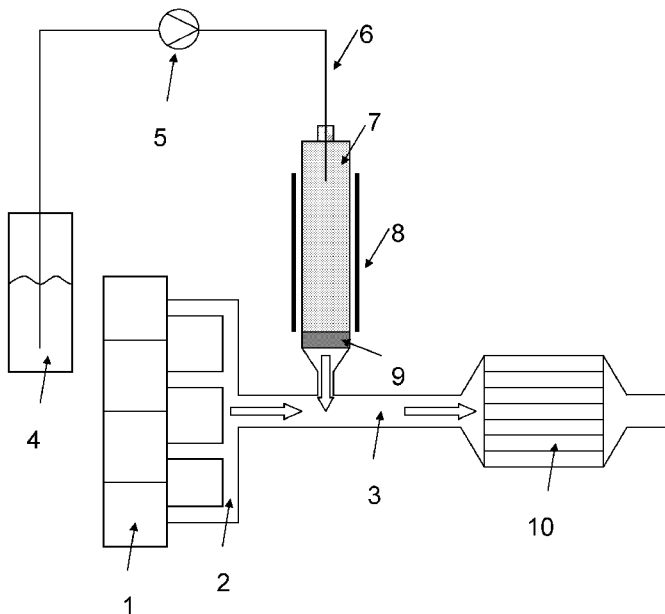


Fig. 1

(57) Abstract: The presented invention is an ammonia generator, constructed to convert liquid ammonia precursor solutions to gaseous ammonia. The precursor compound is decomposed in the liquid reducing agent solution at elevated pressures and temperatures. After conversion of most of the ammonia precursor compound to ammonia and other gases, the evolved gases are released to ambient pressure. Providing heat to the precursor compound solution without allowing it to boil enables good hydrolysis reaction conditions for the ammonia precursor compound. The high pressure in the ammonia generator keeps water mostly in its liquid state and in direct contact with the reactant ammonia precursor compound and the catalyst bed. The heat transfer is accelerated if water is still mostly liquid, as the heat consumed by the decomposition reactions is quickly replenished. Applying the presented principle according to claims 1 to 820 enables the design and production of a highly compact converter unit for continuous hydrolysis of ammonia precursor compounds to hot ammonia gas. The yielded ammonia gas can be introduced into the hot exhaust gas without causing cooling, thus enabling SCR of NOx at unprecedented low exhaust gas temperatures. In the ammonia generator described the formation of deposits due to incomplete precursor compound decomposition can be eliminated. Ammonia mixes much faster with the exhaust gas than the spray of a liquid

reducing agent giving the described generator a significant increase in reaction rate and yield for DeNOx compared to previous designs for the SCR process. It may even be possible to replace a spray nozzle in an existing SCR system by a compact converter.

WO 2012/104205 A1

Ammonia generator converting liquid ammonia precursor solutions to gaseous ammonia for DeNOx-applications using selective catalytic reduction of nitrogen oxides

5 The presented invention relates to a method and an apparatus comprising a separate ammonia generator to convert liquid ammonia precursor solutions into gaseous ammonia for NOx reduction (DeNOx) applications utilizing selective catalytic reduction of nitrogen oxides.

10 Emission guidelines for on-road, off-road and industrial applications yielding exhaust gases have become ever more stringent. Some of the undesired components in exhaust gases are the nitrogen oxides which are formed from nitrogen and excess
15 oxygen during the combustion process at high temperatures. As these compounds cannot be reduced down to the demanded concentrations by optimizing engine operation or the combustion process alone, a DeNOx system needs to be introduced. The most promising process, which has been already in commercial use for
20 several decades in power plants and a few years in mobile applications, is selective catalytic reduction (SCR).

In the SCR process, ammonia gas reacts with the nitrogen oxide (NOx) gases on the SCR-catalyst to yield harmless nitrogen and
25 water. In stationary applications, such as power plants, ammonia gas is injected into and mixed with the exhaust gas, which is not feasible for mobile applications due to safety issues of transporting ammonia gas. Therefore, an ammonia precursor compound solution, such as urea in water is injected into the hot exhaust
30 gas. The urea is then either decomposed on a special hydrolysis catalyst or on the SCR-catalyst itself to yield gaseous ammonia for the SCR reaction. Thus, the decomposition of the ammonia precursor compound yields the necessary ammonia, but also creates
35 no issues with legislation as only a harmless ammonia precursor compound solution is transported.

This invention describes the production of ammonia gas and its introduction into the exhaust gas of combustion engines. However,

it may also be used for any other application requiring a dynamic or constant flow of ammonia and/or hydrogen containing gas.

Obviously, this includes stationary applications of SCR or SNCR (selective non-catalytic reduction of NO_x) in e.g. power plants, incineration facilities or boilers, but also less apparent applications like the supply of a fuel cell with a CO-free hydrogen and ammonia containing gas flux for direct use or use after reforming also the contained ammonia to hydrogen.

10 In SCR systems utilizing liquid ammonia precursors it is hard to mix the ammonia precursor spray with the exhaust gases and simultaneously avoid deposit formation in the region between the spray nozzle and the catalyst. Incomplete mixing of the reducing agent with the exhaust gas will result in a poor DeNO_x performance, as some channels of the SCR catalyst will not be supplied with the required amount of reducing agent. On the other hand an excess of reducing agent in other channels will lead to an unwanted ammonia slip. The decomposition of the ammonia precursor compound or compound mixture and the evaporation of the solvent it is dissolved in will draw a significant amount of heat from the exhaust gas.

Today's major challenge is to have a good reaction of ammonia gas with NO_x gases at low temperatures on the SCR catalyst. The increasing need for a low temperature SCR process is also a result of the trend for using the hot exhaust gas as energy source for turbo-chargers, thereby lowering exhaust gas temperature by the conversion of heat to mechanical energy. Often the exhaust gas would cool down during the evaporation of solvent in the reducing agent solution, preventing the precursor from decomposing completely and reducing the yield and rate of the reaction between produced ammonia with NO_x. Thus, at low exhaust gas temperatures the dosing of ammonia precursor into the exhaust is often unsuitable in mobile applications.

If gaseous ammonia is dosed into the system rather than spraying an ammonia producing solution, the exhaust gas could have lower

temperatures than are used in the conventional SCR process and there would be enough heat to satisfy the conditions of the reaction on the SCR catalyst. Our invention is an ammonia generator which can be operated independently of the exhaust gas temperature to provide hot ammonia gas for direct injection into the exhaust gas.

Existing systems:

10 Most commercial systems and disclosed inventions for the decomposition of liquid NO_x reducing agents inherited a basic setup like in patent DE 40 38 054 A1 concerning the way the reducing agent is introduced. In the cited disclosure, the reducing agent solution is sprayed onto a devoted hydrolysis catalyst or the SCR catalyst itself for decomposition.

15 Consequently, the reducing agent solution is either situated in the gas phase or present as an aerosol, both being diluted with either exhaust gas and/or pressurized air while passing the decomposition catalyst. As a result, the ratio of reactants dosed per catalyst volume is much lower than the ratio which results when pumping the liquid reducing agent solution through a heated catalyst bed.

20 In patent DE 40 38 054 A1 two of the main claims are: the vaporization of the reducing agent to form droplets of less than 10 μm and the vaporization of the reducing agent within 1 s on an evaporator.

25 Later amendments like DE 42 03 807 A1 focused, for instance, on replacing the laminar flow of the hydrolysis catalyst, on which the reducing agent is sprayed, by a more turbulent flow within the channels to increase the conversion efficiency of urea to ammonia gas and carbon dioxide.

30 Recent patents like WO2008077587A1 have been dealing with alternative reducing agents in various solutions and separating the exhaust gas flow from the ammonia production from the decomposition of the precursor compounds. WO2008077587A1 and many other recent patents still contain a spraying apparatus involving either a gas to assist spraying and/or a gas into which the

ammonia storage compound is sprayed and a subsequent evaporation and decomposition system.

5 However, there are also some inventions concerning the conversion of the reducing agent solution without spraying:

FR 29 36 957 A1 and FR 29 36 958 A1 describe a device comprising a chamber for receiving aqueous urea. The chamber is filled with a porous material with a catalytic coating (100 cm² surface area per 10 1 cm³) on the pores to decompose aqueous urea to ammonia. The chamber contains a heating element inside which is heated to 40-200°C (FR 29 36 958 A1) or to 200-400°C (FR 29 36 957 A1). During heating in a first heating zone to 50°C or during heating up of the solution after insertion, urea is claimed to precipitate in 15 the chamber, but due to the filling with a porous material (pore size 1 - 100 µm) only small urea crystals can form. These urea crystals are claimed to decompose to ammonia during further heating. The device is operated at atmospheric pressure, or slightly elevated pressure to inject the produced gases into the 20 exhaust duct.

In contrast, the presented method will utilize catalytic coatings or catalyst with surface areas which are larger by at least two, preferably three orders of magnitude. The heating will always be intended to be from the outside of the reactor, and restricted to 25 a single zone. No porous material will be necessary to restrict the formation of urea crystals, and pressures used will be significantly larger than atmospheric pressure. In addition, the use will not be restricted to urea solution, and, therefore, also the production of hydrogen along with ammonia is possible.

30 US 58 27 490 A describes a method for the conversion of aqueous urea solution (concentration of less than 20% urea) to ammonia. The method is primarily intended for the treatment of NO_x in the exhaust gas stream of a boiler. While heating to a temperature of 35 350-650°F (177-343°C), the solution is pressurized to a pressure required to keep urea reaction products in the liquid phase, at least 300 psi (20.7 bar). The heated solution is contacted with a

catalyst for the conversion of urea to ammonium carbamate which is claimed to be practically equivalent to a conversion to ammonia. The catalyst is preferably composed of chromium or molybdenum as metal, metal oxide or compound, but possibly also of aluminum, cobalt, niobium, titanium or vanadium as metal, metal oxide or compound. Conversion of >90% of urea to ammonia is reported for a 5% urea aqueous solution at 260°C with 4.5 min reaction time. Conversion of a 2.4% urea aqueous solution at 300 psi (20.7 bar) and 350°F (177°C) with a reaction time of 3.5 min yielded 80% ammonia on a Cr catalyst, 72% on Mb and just 48% on Al, 40% on Ti or 0% without catalyst.

In contrast, the presented method will use urea solutions with concentrations from 30% (by mass) onward, and focus on combustion engine exhaust gas. The catalysts which were reported to be the most active ones will not be considered preferably. The operation without catalyst which was reported to be very bad (0% yield) will be a feasible option in the presented method for urea decomposition.

WO 98 42 623 A1 describes a method for the conversion of a solution of urea, but also biuret or ammonium carbamate to ammonia. The solution is pumped into a reactor which is heated. The heating is used to influence temperature and pressure in the reactor. While under pressure, ammonia and CO₂ are removed as gases from the reaction mixture, while the remaining solution is recycled. Ammonia and CO₂ are then mixed into the process gas stream of a furnace, incinerator or power plant. The decomposition is enhanced by preferably oxides, ammonium or alkali salt of vanadium or molybdenum, but also chromium, tin, bismuth or boron or by "active surface solids" like activated carbon, activated silica, activated alumina and ion-exchange resins in their acid and basic form. The temperature for operation is preferably 130-170°C, in general 110-200°C, the coupled pressure 20-120 psi (1.4-8.3 bar), in general 20-500 psi (1.4-34.5 bar).

In contrast, the presented method will not control pressure by the heating rate, but by mechanical means. Also, the solution will not be recycled, but completely inserted into the exhaust gas duct.

The conversion temperature for urea solution will be significantly higher than 170° and even 200°C. The mentioned catalysts will not be preferably utilized, with the exception of alumina as hydrolysis catalyst.

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US 63 61 754 B1 describes a system for the conversion of urea, urea hydrolysis products, urea dimers and polymers, urea adducts or urea condensation products to yield ammonia gas without the formation of urea decomposition products in solid or molten form.

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Conversion is performed at 50-600 psi (3.4-41.4 bar) and temperatures above 140°C, in order to be above the hydrolysis temperature of urea. A liquid catalyst may be added to the urea solution (e.g. phosphoric acid) or a solid catalyst may be present in the heating unit (e.g. aluminum oxides).

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In contrast, various other ammonia storage compounds will be utilized with the advantage of producing hydrogen in addition to ammonia to further increase the efficiency of NOx removal. No liquid catalysts will be considered, but some solid catalysts could be inserted in the reactor to accelerate the decomposition

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of the ammonia precursor compounds.

The objective of the present invention is to disclose a method and a compact apparatus for the efficient generation of ammonia from liquid ammonia precursors for the selective catalytic reduction of NOx in engine exhaust gas.

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This objective is achieved by the use of aqueous ammonia precursor solutions containing 30-80% by mass of urea, ammonium formate, guanidinium formate, methanamide or mixtures thereof, and their catalyzed hydrolysis by heating under pressure in presence of a hydrolysis catalyst in a reactor. The product gas mixture from the described ammonia generator is first produced as gas flow apart from the engine exhaust gas. Only upon release from the reactor the product gas is mixed into the main exhaust flux. The position of the mixing must be upstream of the SCR catalyst but could be as far upstream as the exhaust manifold on the engine before entering a turbo charger. In the extreme scenario of insertion at the

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exhaust manifold before turbocharger, the turbine would enable good mixing of the product gas with exhaust gas while the high pressure inserted gas may add to the performance of the turbine. Addition of the product gas at a further downstream position of the exhaust gas duct could be very advantageous in order to raise the temperature of the exhaust gas flow before entering the SCR catalyst, thereby increasing DeNOx activity.

The production of ammonia "apart from the engine exhaust gas" shall mean that the engine exhaust gas stream does not flow through the ammonia generator, but its walls or other parts of it may be in direct or indirect (using e.g. a heat pipe) contact with the engine exhaust gas flow in order to transfer heat from the exhaust gas to the ammonia reactor. The heat transfer from the exhaust gas to the ammonia reactor may satisfy the complete need for decomposition heat or a part thereof.

Applying the presented principle enables the design and production of a highly compact converter unit for continuous hydrolysis of ammonia precursor compounds to hot ammonia gas. The yielded ammonia gas can be introduced into the hot exhaust gas without causing cooling, thus enabling SCR of NOx at unprecedented low exhaust gas temperatures. In the described ammonia generator the formation of deposits due to incomplete precursor compound decomposition can be avoided. Hot ammonia gas mixes much faster and more homogeneously with the exhaust gas than the spray of a liquid reducing agent giving the described generator a significant increase in reaction rate and yield for DeNOx compared to previous designs for the SCR process. It may even be possible to replace a spray nozzle in an existing SCR system by a compact converter. The addition of the hot ammonia gas to the exhaust gas flow is performed by a valve to control the amount of dosed ammonia. The signal for the valve originates from a control unit which may determine the amount of necessary ammonia either solely from engine operation parameters like load and rpms, from NOx sensors before and/or after the SCR catalyst or a combination of these techniques.

In order to achieve a substantially complete hydrolysis of the ammonia precursor compound in the ammonia generator a choice with respect to the pressure and the temperature for the catalytic decomposition of the reducing agent solution is made in a way that hydrolysis of the ammonia precursor compound takes place preferably in the liquid phase inside the ammonia generator while contacting the catalyst.

10 Preferably, the decomposition of the ammonia precursor is performed at high pressure to yield ammonia which is released as ammonia gas along with carbon dioxide gas and water vapor upon pressure release. Typically, the suppression of the boiling of the reducing agent solution is achieved by applying high pressures of 15 5 to 100 bar, depending on the operation temperature.

In some applications it can be desirable that the complete conversion of the ammonia precursor compound to ammonia is replaced by an incomplete conversion of the precursor compound with the production of a precursor compound gas and therefore requiring less heat input, particularly in dependence of the reactant material which is used as ammonia precursor material.

In order to limit the wear of the catalyst used in the ammonia reactor, a catalytic bed is arranged inside the ammonia reactor with a sufficiently large void volume to provide for a constant flow of liquid through the void volume; said catalytic bed contains catalyst particles with of size from 0.01 mm to 10 mm, preferably 0.1 mm to 10 mm, more preferably 0.1 mm to 5 mm, most preferably 0.1 mm to 1 mm. Typically, the catalytic bed comprises either solid catalyst particles, catalyst coated on non-catalytic particles, catalyst coated on ceramic or metallic substrates or extruded catalysts. Catalyst materials may be chosen to be TiO₂, Al₂O₃, ZrO₂, zeolite, metal organic frameworks (MOF) or mixtures thereof, preferably TiO₂, Al₂O₃, ZrO₂, zeolite, most preferably TiO₂, Al₂O₃ and/or ZrO₂. The catalyst may possibly be stabilized by WO₃ or Si₂O₃. The catalyst could be doped with metals, metal oxides

or combinations thereof to facilitate the decomposition of ammonia precursor compounds other than urea. Metals or metal oxides for doping could be Au, Pt, Pd, Re, Ru, Ag, Rh as well as rare earth metals and/or transition metals, such as Cr, Ni, Cd, Cu, Mn, V, 5 Co, Fe, Zn, Nb, Ta, Os, Ir, Sn, or alloys/mixtures thereof, preferably Au, Pt, Pd, Ag, Cu, Nb, more preferably Au, Ag, Pt, Pd, most preferably Au. The catalyst has a specific surface area (determined by BET N₂-physisorption) of at least 50 m²/g. If coated, at least 50 g of catalyst are deposited per Liter of 10 support material. This implies a specific surface area of 2.5 m² per cm³ of supported catalyst at the minimum.

A further preferred embodiment of the present invention may contain a porous material, most preferred a metal frit, of 15 tailored length and pore size, a pressurizer (a valve which will open above a set pressure but close below the set pressure) or a controllable valve that is used at the outlet of the ammonia generator to create the necessary pressure. Instead of and/or in addition to a porous material a valve may be used at the outlet of 20 the ammonia generator to create the necessary pressure and/or improve the dynamics of the ammonia dosage into the exhaust gas system.

The respective apparatus claims refer to the claims 9 to 17 listed 25 below.

Preferred examples of the present invention are hereinafter described with reference to the attached drawings which depict in:

30 Figure 1 a schematic overview of a system for the hydrolysis of an ammonia precursor material;

Figure 2 a plot of the conversion rate and the contents of the involved compounds as a function of the reactor wall temperature; 35 and

Figure 3 a plot of the conversion rate with different catalyst as a function of the reactor temperature.

Figure 1 shows a first system for the hydrolysis of the ammonia precursor material. A stainless steel tube with 10 mm internal diameter was sealed at one end with a 0.1 μm diameter pore size stainless steel frit (9). A high pressure valve with small flow diameter could have been chosen instead. A volume of 7.9 ml (corresponding to a tube length of 100 mm) was filled with 300 μm D50 diameter $\gamma\text{-Al}_2\text{O}_3$ (7). A flow of 1 ml/min 32.5% urea (by mass) in de-ionized water (4) was pumped by a high pressure pump (5) into the packed bed via a capillary of 128 μm internal diameter (6). The tube was electro-thermally heated from the outside (8) to a temperature of 300°C (measured on the outside wall) and the solution inside the packed bed heated up. The expected boiling of water at this temperature was suppressed by the high pressure created by the frit at the exit (9) and the catalytic bed, so the liquid was heated up to a temperature sufficient for quantitative hydrolysis in the liquid phase. Using the hydrolysis catalyst packed bed which was wetted by hot water, the urea was completely decomposed to ammonia. If deposits of cyanuric acid, biuret, triuret, ammeline and/or other side products of the ammonia production via hydrolysis of the precursor were formed, they were hydrolytically decomposed under the previously described reaction conditions present in the ammonia generator.

In previous systems undesired side-products of the ammonia production from the precursor inhibit the SCR process, however the ammonia generator decomposes these side products and prevents the inhibition of the process. The decomposition of the side-products from the ammonia production from the precursor in the ammonia generator would also prevent the plugging of the packed bed by deposits. Furthermore, the nitrogen contained in potentially formed side-products would be released as ammonia, improving the yield of ammonia gas.

In the first series of experiments performed, the reaction products ammonia, carbon dioxide and water vapor were released as hot gases from the exit of the ammonia generator from the 1 ml/min input of 32.5% urea in water. The ammonia content was determined quantitatively by bubbling the gases through an acidic solution and titrating the resulting solution. Assuming 100% conversion of ammonia to ammonium in the acidic solution, the amount of gaseous ammonia produced by the generator was calculated backwards. Additionally, product gas was quenched in acidic and basic absorbing solutions and analyzed by HPLC for other compounds like urea, carbonate and side products. At $T \geq 250$ °C, no urea, HNCO or byproducts could be detected. At $T \leq 230$ °C, the conversion was incomplete and significant amounts of urea and biuret were detected (see Fig. 2). As the reactor temperature was measured at the outside of the reactor wall, the effective temperature of the catalyst bed needed for complete conversion could have been lower than 250 °C. Also, the used γ -Al₂O₃ catalyst was chosen due the suited particle size and the good mechanical stability of the particles. TiO₂ and ZrO₂ have been determined to provide better decomposition activity in the gas phase than γ -Al₂O₃, which could lower the temperature needed for complete conversion.

The obtained results therefore may suggest a complete conversion of urea to gaseous products, provided that the reactor is sufficiently heated. The gases water : ammonia : carbon dioxide were in a 6.83 : 2 : 1 ratio. The product gas mixture is then dosed into an exhaust gas stream (3) collected by the exhaust manifold (2) in a combustion engine (1). The NO_x produced by the combustion process will react with the dosed ammonia gas on the SCR-catalyst (10).

A second system for the hydrolysis of the ammonia precursor material has been designed and constructed similar to the first one. The second system was also operated for several hours. At the exit end of a stainless steel tube with 10 mm internal diameter and 15 cm length (= 11.8 ml) a pressurizer (a valve which will open above a set pressure but close below the set pressure) with a

set pressure of 50 bar was attached. The tube was heated from the outside, the temperature sensor for the feedback loop was connected on the outside wall of the reactor 5 cm before the exit. Experiments with a thermocouple placed inside the reactor showed the temperature on the outside wall was identical to the inside temperature. A flow of 5 ml/min of an ammonia precursor fluid, either 32.5% urea (by mass) in water or 40% methanamide (by mass) in water was pumped through the inlet of the tubular reactor. The reactor was filled with different catalyst materials: TiO₂ anatase particles with diameters of 425-710 μm or ZrO pellets with 3 mm diameter or Al₂O₃ particles of 0.8-1 mm or a TiO₂ anatase monolith (400 cpsi; stabilized with SiO₂) doped with 1.5% Au. Only methanamide was tested with the Au-doped TiO₂ anatase monolith catalyst. An extra experiment was performed with urea solution without catalyst filling.

Some of the results are shown in Fig. 3. At a temperature below 240°C, less than 80% of the contained ammonia was released from urea solution. The catalyst filling actually only had a small effect on the release of ammonia from urea solution, it could be compensated by a temperature elevation of max. 10K.

Up to 180°C methanamide was decomposed on the Au-doped TiO₂ to the same degree as urea was at 40K higher temperatures. During the decomposition of methanamide, ammonia, CO₂, H₂O and H₂ were measured in the gas phase. Methanamide can be hydrolyzed to ammonia and formic acid. Formic acid can decompose to yield CO₂ and H₂. The ammonia generator can therefore be used to produce a gas flow containing ammonia and hydrogen. Hydrogen has been shown to enhance the catalytic removal of NO_x.

Ammonium formate and guanidinium formate are expected to show a similar decomposition product gas mixture, as they can be decomposed to ammonia and formic acid, and formic acid could again be decomposed to yield H₂.

During the experiment, the pressure of 50 bar was not constantly sufficient to keep all components in the liquid phase. The vapor

pressure of water is far below 50 bar at the presented temperatures, but the produced CO₂ could not be kept completely in the liquid phase. However, the vast majority of CO₂ was still contained in the liquid phase, only a small fraction evaporated to form a gas phase. In case of methanamide, where hydrogen gas was formed, a gas phase evolved due to the limited solubility of hydrogen in water. As a consequence, the liquid and/or gas flow released at the pressurizer was fluctuating. The composition of the dosed gas flow changed only slightly, as the amount of products contained in the gas phase was only very small. An application could contain a second pressure containment after the pressurizer. The operating pressure of the second containment would be below the pressure of the reactor, in order to enable a complete evaporation of the liquid phase. The gases would therefore be uniformly mixed and could be dosed with constant gas flow.

Claims

1. A method for the selective catalytic reduction (SCR) of NO_x in engine exhaust gas by the use of liquid ammonia precursors like aqueous solutions containing 30-80% by mass of urea, ammonium formate, guanidinium formate, methanamide or mixtures thereof (1), characterized by the catalyzed hydrolysis of the ammonia precursor compound, being heated and pressed in a separate ammonia reactor apart from the engine exhaust gas stream and guiding the so-generated ammonia gas into the engine exhaust gas stream upstream of an SCR catalyst.
2. The method according to claim 1, characterized by the choice of pressure and temperature for the catalytic decomposition of the reducing agent solution in a way that hydrolysis of the ammonia precursor compound takes place preferably in the liquid phase.
3. The method according to claim 1, characterized by the decomposition of the ammonia precursor at high pressure to yield ammonia, which is released as ammonia gas along with carbon dioxide gas, water vapor and hydrogen gas (if applicable) upon pressure release.
4. The method according to claims 1 to 3, characterized by the suppression of the boiling of the liquid ammonia precursor by applying high pressures of 5 to 100 bar, depending on the operation temperature.
5. The method according to claim 3, wherein the complete conversion of the ammonia precursor to ammonia is replaced by incomplete conversion of the precursor with the production of a precursor gas and therefore requiring less heat input in the separate ammonia reactor.
6. The method according to claims 1 to 4, characterized by a high hydrolytic decomposition efficiency of the ammonia precursor in the presence of solvents, in particular liquid water, at

temperatures between 50 to 600°C, preferably between 150 to 350°C, by presence of a decomposition catalyst.

7. The method according to any of the preceding claims,
5 characterized by a catalytic bed (7) inside the ammonia generator with sufficiently large void volume to provide a constant flow of liquid through the void volume; said catalytic bed comprising catalyst particle of size from 0.01 mm to 10 mm, preferably 0.1 mm to 10 mm, more preferably 0.1 mm to 5 mm, most preferably 0.1 mm
10 to 1 mm.

8. The method according to any of the preceding claims, wherein the catalytic bed comprises either solid catalyst particles, catalyst coated on non-catalytic particles, catalyst coated on
15 ceramic or metallic substrates or extruded catalysts;
i) catalyst materials are TiO_2 , Al_2O_3 , ZrO_2 , zeolite, metal organic frameworks (MOF) or mixtures thereof, preferably TiO_2 , Al_2O_3 , ZrO_2 , zeolite, most preferably TiO_2 , Al_2O_3 and/or ZrO_2 ;
ii) the catalyst is further preferably stabilized by WO_3 or Si_2O_3 ;
20 iii) the catalyst is furthermore preferably doped with metals, metal oxides or combinations thereof to facilitate the decomposition of ammonia precursor compounds other than urea;
iv) metals or metal oxides for doping are Au, Pt, Pd, Re, Ru, Ag, Rh as well as rare earth metals and/or transition metals, such as
25 Cr, Ni, Cd, Cu, Mn, V, Co, Fe, Zn, Nb, Ta, Os, Ir, Sn, or alloys/mixtures thereof, preferably Au, Pt, Pd, Ag, Cu, Nb, more preferably Au, Ag, Pt, Pd, most preferably Au;
v) the catalyst has a specific surface area (determined by BET N_2 -physisorption) of at least 50 m^2/g , and preferably in the coated
30 version, at least 50 g of doped material are deposited per Liter of catalyst material which implies a specific surface area of 2.5 m^2 per cm^3 of supported catalyst at the minimum.

9. The method according to any of the preceding claims, wherein a
35 porous material, most preferred a metal frit, of tailored length and pore size or a valve that is used at the outlet of the ammonia generator to create the necessary pressure; instead of and/or in

addition to a porous material preferably a valve is used at the outlet of the ammonia generator to create the necessary pressure and/or improve the dynamics of the ammonia dosage into the exhaust gas system.

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10. An apparatus for the selective catalytic reduction (SCR) of NO_x in engine exhaust gas by the use of liquid ammonia precursors like aqueous solutions containing 30-80% by mass of urea, ammonium formate, guanidinium formate, methanamide or mixtures thereof (1),
10 wherein the catalyzed hydrolysis of the ammonia precursor is performed in liquid solution, being heated and pressed in a separate ammonia reactor apart from the engine exhaust gas stream and guiding the so-generated ammonia gas into the engine exhaust gas stream upstream of an SCR catalyst.

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11. The apparatus according to claim 10, characterized by the choice of pressure and temperature for the catalytic decomposition of a liquid ammonia precursor in a way that hydrolysis of the NH₃ precursor compound takes place preferably in the liquid phase.

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12. The apparatus according to claim 10, characterized by the decomposition of the ammonia precursor at high pressure to yield ammonia, which is released as ammonia gas along with carbon dioxide gas, water vapor and hydrogen gas (if applicable) upon
25 pressure release.

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13. The apparatus according to claims 10 to 12, characterized by the suppression of the boiling of the liquid ammonia precursor by applying high pressures of 5 to 100 bar, depending on the
30 operation temperature.

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14. The apparatus according to claim 12, wherein the complete conversion of the liquid ammonia precursor to ammonia is replaced by incomplete conversion of the precursor compound with the
35 production of a precursor compound gas and therefore requiring less heat input in the separate ammonia reactor.

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15. The apparatus according to claims 10 to 13, characterized by a high hydrolytic decomposition efficiency of the ammonia precursor in the presence of solvents, in particular liquid water, at temperatures between 50 to 600°C, preferably between 150 to 350°C, by presence of a decomposition catalyst.
16. The apparatus according to any of the preceding claims 10 to 15, characterized by a catalytic bed (7) inside the ammonia generator with sufficiently large void volume to provide for a constant flow of liquid through the void volume; said catalytic bed comprising catalyst particle of size from 0.01 mm to 10 mm, preferably 0.1 mm to 10 mm, more preferably 0.1 mm to 5 mm, most preferably 0.1 mm to 1 mm.
17. The apparatus according to any of the preceding claims 10 to 16, wherein the catalytic bed comprises either solid catalyst particles, catalyst coated on non-catalytic particles, catalyst coated on ceramic or metallic substrates or extruded catalysts;
- i) catalyst materials are TiO_2 , Al_2O_3 , ZrO_2 , zeolite, metal organic frameworks (MOF) or mixtures thereof, preferably TiO_2 , Al_2O_3 , ZrO_2 , zeolite, most preferably TiO_2 , Al_2O_3 and/or ZrO_2 ;
- ii) the catalyst is further preferably stabilized by WO_3 or Si_2O_3 ;
- iii) the catalyst is furthermore preferably doped with metals, metal oxides or combinations thereof to facilitate the decomposition of ammonia precursor compounds other than urea;
- iv) metals or metal oxides for doping are Au, Pt, Pd, Re, Ru, Ag, Rh as well as rare earth metals and/or transition metals, such as Cr, Ni, Cd, Cu, Mn, V, Co, Fe, Zn, Nb, Ta, Os, Ir, Sn, or alloys/mixtures thereof, preferably Au, Pt, Pd, Ag, Cu, Nb, more preferably Au, Ag, Pt, Pd, most preferably Au;
- v) the catalyst has a specific surface area (determined by BET N_2 -physisorption) of at least 50 m^2/g , and preferably in the coated version, at least 50 g of doped material are deposited per Liter of catalyst material which implies a specific surface area of 2.5 m^2 per cm^3 of supported catalyst at the minimum.

18. The apparatus according to any of the preceding claims 10 to 17, wherein a porous material, most preferred a metal frit, of tailored length and pore size or a valve that is used at the outlet of the ammonia generator to create the necessary pressure
5 wherein instead of and/or in addition to a porous material a valve is used at the outlet of the ammonia generator to create the necessary pressure and/or improve the dynamics of the ammonia dosage into the exhaust gas system.
- 10 19. The apparatus according to any of the preceding claims 10 to 18 wherein the liquid ammonia precursor is pre-heated by cooling water or lubrication oil from the engine to reduce the heat requirement of the catalyst bed, preferably provided that the catalyst is sufficiently active, the catalyst bed is heated
15 exclusively by cooling water and/or lubrication oil from the engine, rendering any other heat source like electrical heating or heat transfer from the exhaust gas unnecessary.
- 20 20. The apparatus according to any of the preceding claims 10 to 19 wherein the catalyst is coated on a metallic or semi-conducting substrate, which is electrically resistance heated.
- 25 21. The apparatus according to any of the preceding claims 10 to 20 wherein instead of one single tube containing the catalyst bed, two or several tubes containing catalyst beds are used in parallel to facilitate the heat transfer from a heat source to the catalyst bed(s).
- 30 22. The apparatus according to any of the preceding claims 10 to 21, wherein the catalyst bed is heated by microwave irradiation or other electromagnetic radiation.
- 35 23. The apparatus according to any of the preceding claims 10 to 22 wherein a second pressure containment after the pressurizer is comprised wherein the operating pressure of the second containment is below the pressure of the reactor in order to enable a complete evaporation of the liquid phase allowing the gases to be uniformly

mixed and dosed with constant gas flow.

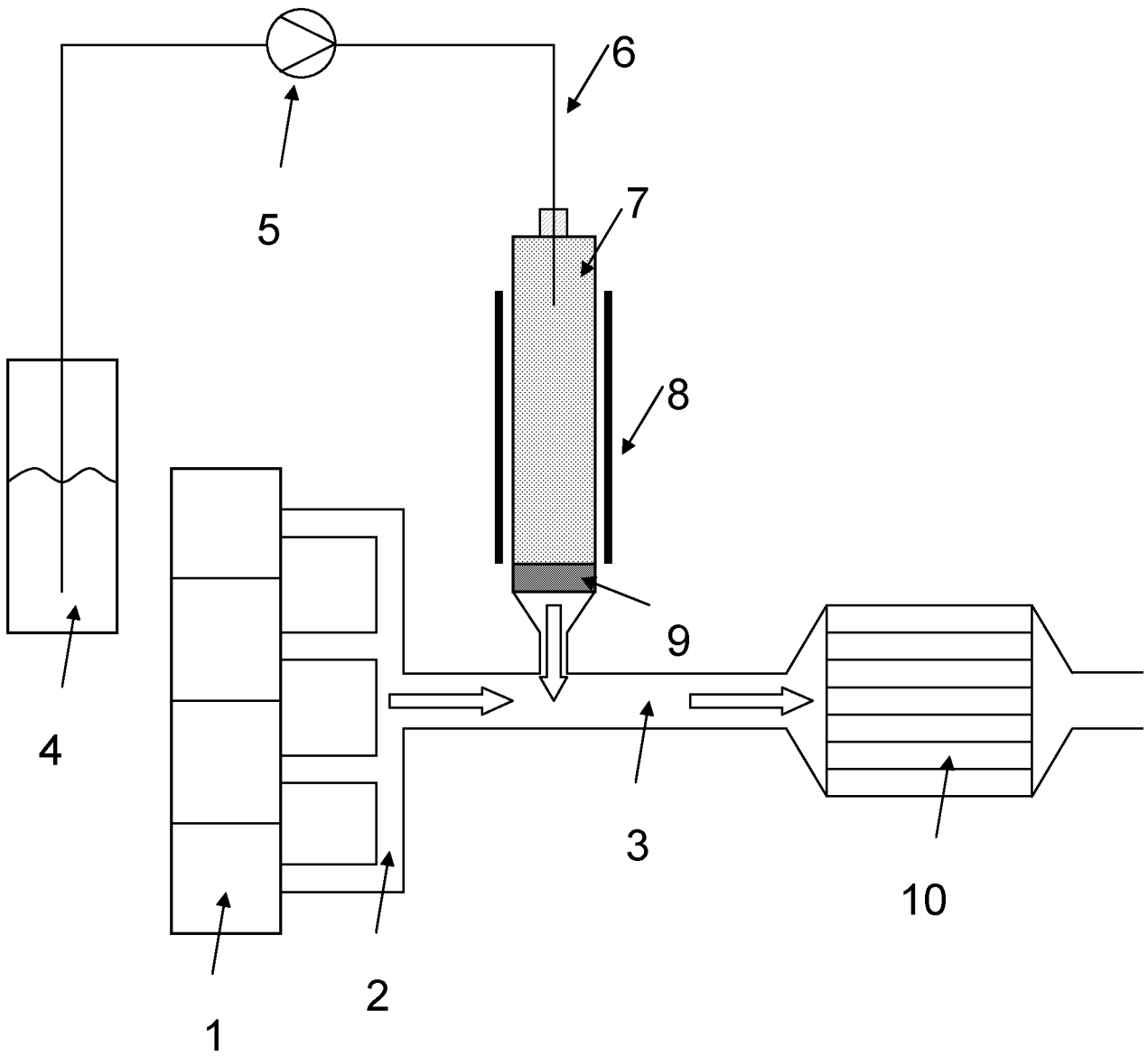


Fig. 1

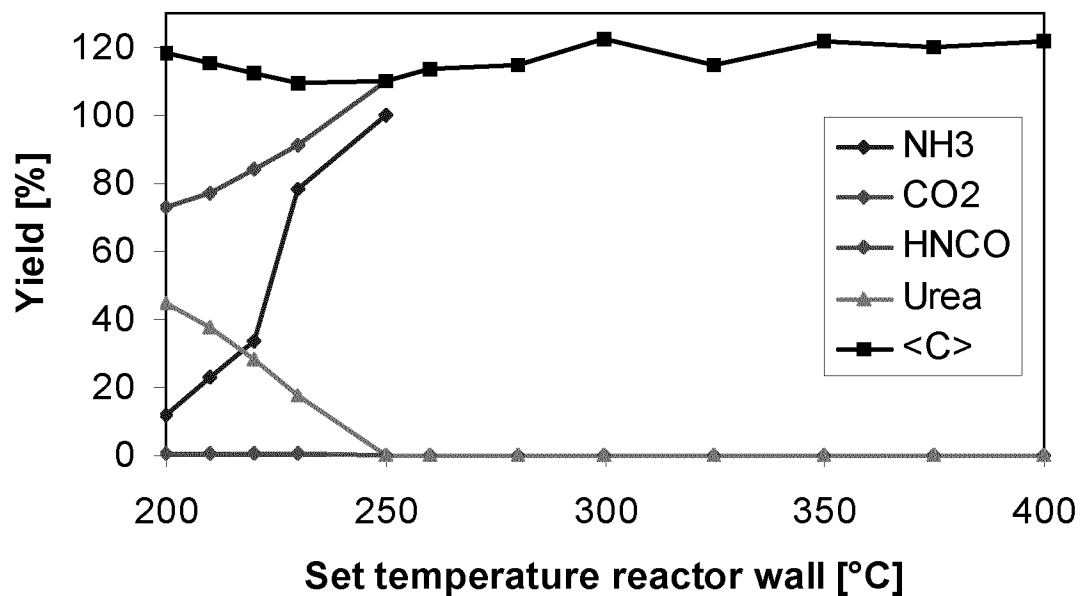


Fig. 2

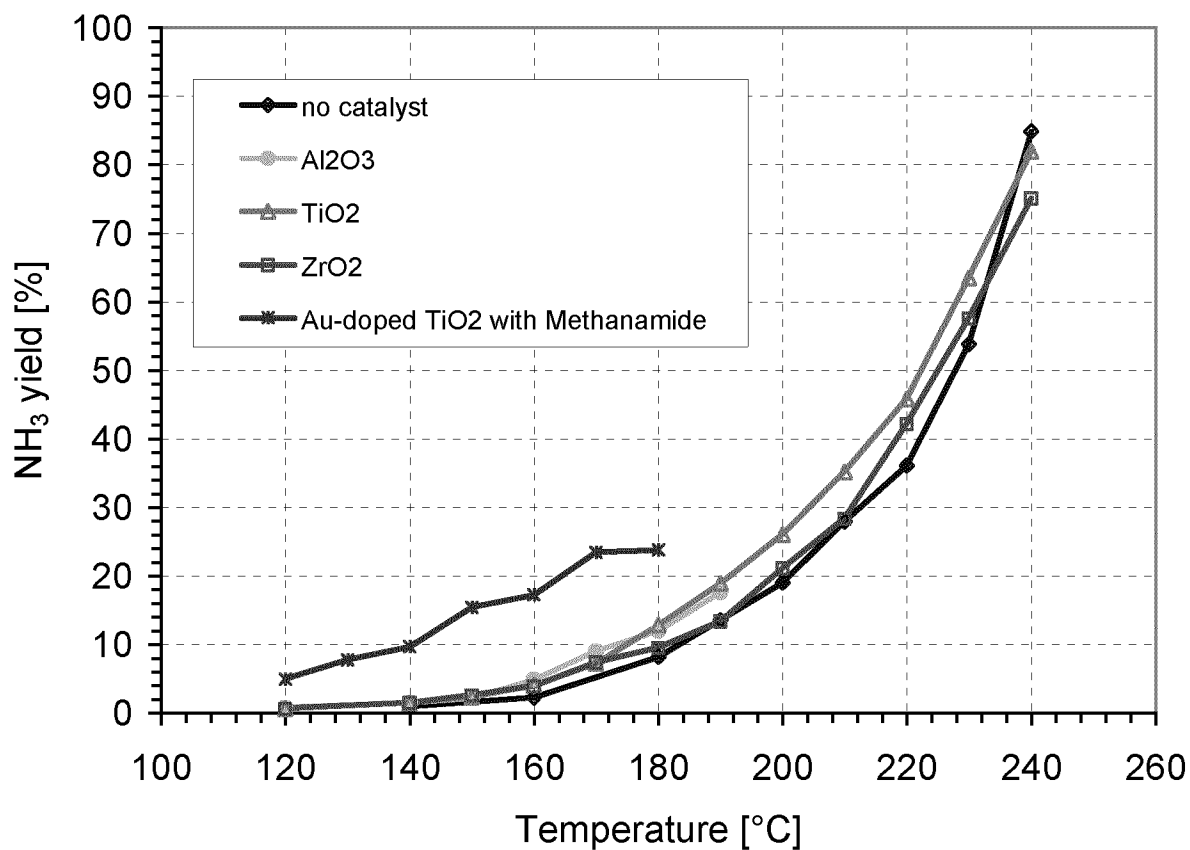


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2012/051296

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 10-23
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/051296

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/90 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)
B01D F01N C01C

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 practical, 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	JP 2004 202450 A (BABCOCK HITACHI KK) 22 July 2004 (2004-07-22) paragraphs [0005], [0006], [0009] - [0012], [0019] - [0025] figures 1-3 claims 1-6	1-9
X	JP 2006 223937 A (BABCOCK HITACHI KK) 31 August 2006 (2006-08-31) paragraphs [0002], [0008], [0017], [0029], [0032], [0040] figure 3 examples 2,6 claims 1-6	1-9
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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 document 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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 12 April 2012	Date of mailing of the international search report 20/04/2012
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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 Hackenberg, Stefan
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/051296

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 827 490 A (JONES DALE GORDON [US]) 27 October 1998 (1998-10-27) cited in the application column 1, line 13 - column 2, line 15 column 3, line 34 - column 4, line 26 column 5, line 9 - column 6, line 61 column 9, line 10 - line 17 figures 1,4 -----	1-6,8,9
X	WO 2007/099372 A1 (JOHNSON MATTHEY PLC [GB]; GIDNEY JEREMY TEMPLE [GB]; TWIGG MARTYN VINC) 7 September 2007 (2007-09-07) page 1, line 3 - line 6 page 7, lines 20-23 page 10, line 1 - page 11, line 12 figures 5,6 -----	1-7,9
X	DE 10 2006 047018 A1 (EMITEC EMISSIONSTECHNOLOGIE [DE]) 3 April 2008 (2008-04-03) paragraphs [0012], [0033] the whole document -----	1,3-7,9
A	US 5 240 688 A (VON HARPE THURE [DE] ET AL) 31 August 1993 (1993-08-31) the whole document -----	1-9
A	WO 93/22047 A1 (NALCO FUEL TECH [US]) 11 November 1993 (1993-11-11) page 4, lines 11-16 page 6, line 1 - page 13, line 2 page 15, lines 14-16 page 16, lines 12-15 -----	1-9
A	US 2005/207961 A1 (BROOKS BURTON [US] ET AL) 22 September 2005 (2005-09-22) paragraphs [0003], [0011], [0015] - [0020], [0037], [0043], [0102] - [0108] -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/051296

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2005207961 A1	22-09-2005	NONE	

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 10-23

The features in claim 10 relate to a method of using the apparatus rather than clearly defining the apparatus in terms of its technical features. The intended limitations are therefore not clear from this claim, contrary to the requirements of Article 6 PCT. As there are no clear technical features of an apparatus present, a meaningful search of this claim is not possible. It is noted that even if technical apparatus features could be derived from the claim, the scope for which protection is sought is still unclear. From the wording of claim 10 it is unclear whether the apparatus refers to the separate ammonia reactor (as hinted by the title of the application), the SCR catalyst or to the whole exhaust system including the separate ammonia reactor and the SCR catalyst. It is furthermore noted, that dependent claims 11-15, 19, 22 and 23 also relate to a method of using the apparatus rather than clearly defining the apparatus in terms of its technical features. Therefore, no apparatus features can be derived from these claims. The formulation of claim 18 is as such that the scope for which protection is sought is completely unclear. The only claims comprising technical features of an apparatus are claims 16, 17, 20 and 21. However, these claims are unclear as well. Claim 16 claims that the apparatus is characterized by a catalytic bed comprising catalyst particles of size from 0,01 mm to 10 mm. Claim 17 on the other hand claims that the catalyst bed comprises either solid catalyst particles, catalyst on non-catalytic particles, catalyst on ceramic or metallic substrates or extruded catalysts. Claim 20 furthermore claims that the catalyst is coated on a metallic or semi-conducting substrate. It is therefore unclear, what type of catalyst bed is intended. A bed of particles with a defined size range, or catalytically coated or extruded substrates. In view of the clarity issues mentioned above no meaningful search is possible for the apparatus of claims 10-23 and the search has therefore been restricted to the method of claims 1-9.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.