(19) DANMARK

(10) DK/EP 2726412 T5

Patent- og Varemærkestyrelsen

(12) Rettet oversættelse af europæisk patentskrift

(51) Int.Cl.: *C 01 C 1/08 (2006.01)* *B 01 D 53/56 (2006.01)* *B 01 D 53/90 (2006.01)*
B 01 D 53/92 (2006.01) *B 01 D 53/94 (2006.01)* *B 01 J 8/04 (2006.01)*
C 01 C 1/04 (2006.01) *F 01 N 3/20 (2006.01)*

(45) Oversættelsen bekendtgjort den: **2019-01-14**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2018-09-12**

(86) Europæisk ansøgning nr.: **12732830.0**

(86) Europæisk indleveringsdag: **2012-06-29**

(87) Den europæiske ansøgnings publiceringsdag: **2014-05-07**

(86) International ansøgning nr.: **EP2012062752**

(87) Internationalt publikationsnr.: **WO2013004630**

(30) Prioritet: **2011-07-01 DE 102011106237**
2011-07-01 DE 102011106233
2011-07-01 DE 102011106243

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

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(54) Benævnelse: **FREMGANGSMÅDE TIL FREMSTILLING AF AMMONIAK FRA EN AMMONIAKUDGANGSSUBSTANS FOR AT REDUCERE NITROGENOXIDER I UDSTØDNINGSGASSER**

(56) Fremdragne publikationer:
EP-A1- 0 487 886
EP-A1- 1 052 009
EP-A2- 1 647 324
WO-A1-2008/077588
DE-A1- 4 203 807
DE-A1- 4 230 056

Method for generating ammonia from an ammonia precursor substance in order to reduce nitrogen oxides in exhaust gases

Description

The present invention relates to a method for generating ammonia from an ammonia precursor substance and to the use thereof in exhaust gas aftertreatment systems for reducing nitrogen oxides in exhaust gases.

The exhaust gases of internal combustion engines often contain substances, the release of which into the environment is undesirable. Therefore, many countries set limits which must be adhered to on the release of these pollutants, such as in the exhaust gas from industrial facilities or automobiles. These pollutants include nitrogen oxides (NOx) such as, in particular, nitrogen monoxide (NO) or nitrogen dioxide (NO2), as well as a range of other pollutants.

The release of these nitrogen oxides from the exhaust gases of combustion engines can be reduced in various ways. Emphasis should be placed in this context on reduction by way of additional exhaust gas aftertreatment measures, in particular those based on selective catalytic reduction (SCR). What these methods have in common is that a reducing agent which acts selectively on the nitrogen oxides is added to the exhaust gas, the nitrogen oxides thus being converted in the presence of a corresponding catalyst (SCR catalyst). The nitrogen oxides are in this case converted into substances which are less harmful to the environment, for example nitrogen and water.

One reducing agent for nitrogen oxides which is already used nowadays is urea (H2N-CO-NH2), which is added to the exhaust gas in the form of an aqueous urea solution. In this context, the urea in the exhaust gas stream may break down into ammonia (NH3), for example as a result of the action of heat (thermolysis) and/or a reaction with water (hydrolysis). The ammonia which is thus formed is the actual reducing agent for nitrogen oxides.

The development of exhaust gas aftertreatment systems for automobiles has been going on for some time and has been the subject-matter of numerous publications.

For example, European patent EP 487 886 B1 thus discloses a method for selective catalytic NOX reduction in oxygen-containing exhaust gases of diesel engines, in which urea and the thermolysis products thereof are used as reducing agents. In addition, a device for generating ammonia in the form of a tubular evaporator is disclosed, and comprises a spraying device, an evaporator comprising an evaporator tube, and a hydrolysis catalyst.

Further, European patent EP 1 052 009 B1 discloses a method and a device for carrying out the method for thermal hydrolysis and metering of urea or urea solutions in a reactor with the aid of a partial exhaust gas stream. In the method, a partial exhaust gas stream is removed from an exhaust line upstream of the SCR catalyst and passed through the reactor, in which case the partial stream, which is loaded with ammonia following hydrolysis in the reactor, is likewise further passed back into the exhaust line upstream of the SCR catalyst.

In addition, European patent EP 1 338 562 B1 discloses a device and method making use of the catalytic reduction of nitrogen oxides by ammonia. The ammonia is in this case obtained from urea in solid form under flash thermolysis conditions as well as from isocyanic acid through hydrolysis, then supplied to the exhaust gas stream of a vehicle.

In addition, European patent application EP 1 348 840 A1 discloses an exhaust gas purification system in the form of an assembly, which can be transported as a whole unit, in the form of a 20-foot container. The system is operated in such a way that a urea or ammonia solution is injected directly into the exhaust gas stream by means of an injection device. The nitrogen oxides contained in the exhaust gas are reduced in an SCR catalyst.

Furthermore, German patent application DE 10 2006 023 147 A1 discloses an ammonia generating device which is part of an exhaust gas aftertreatment system.

In addition, international applications WO 2008/077 587 A1 and WO 2008/077 588 A1 disclose a method for the selective catalytic reduction of nitrogen oxides in exhaust gases of vehicles by means of aqueous solutions of guanidine salts. This method uses a reactor which generates ammonia from the aqueous guanidine salt solutions.

DE 42 03 807 A1 describes a device used for catalytic NOx reduction. Proposed therein is a device for the catalytic reduction of NOx in exhaust gas containing oxygen by means of urea, said device containing a hydrolysis catalyst consisting of thin flow channels which, by means of deflectors and apertures or slits, permit partial streams which are oriented in a direction nearly perpendicular to the main flow.

EP 0 487 886 A1 describes a method and an apparatus for the selective catalytic reduction of NOX in exhaust gases containing oxygen. In order to operate an SCR catalyst for reducing nitrogen oxides, it is proposed that a urea solution from a container be finely sprayed on a heated evaporator/catalyst and aftertreatment performed as necessary by means of a downstream hydrolysis catalyst.

WO 2008/07T588 A1 describes a method for the selective catalytic reduction of nitrogen oxides in the exhaust gases of vehicles. In this case, solutions of guanidine salts with an ammonia forming potential of between 40 and 850 gm/kg, optionally in combination with urea and/or ammonia and/or ammonium salts, are catalytically decomposed in the presence of catalytically active, non-oxidation-active coatings of oxides selected from the group comprising titanium dioxide, aluminium oxide, silicon dioxide, or mixtures thereof, as well as hydrothermally stable zeolites that are fully or partially metal-exchanged.

Even though ammonia gas generators have been known for some time, the technology has not thus far been implemented in a vehicle or any other application. Thus far, the concept of directly injecting an ammonia precursor substance into the exhaust gas stream of an internal combustion engine has been pursued, this ammonia precursor substance being broken down into the actual reducing agent in the exhaust gas stream

by means of suitable measures. However, as a result of incomplete decomposition or secondary reactions of decomposition products in the exhaust gas system, depositions are always observed which damage the catalysts and the filters that are also present in the exhaust gas system.

Therefore, the object of the present invention is to provide a method for generating ammonia which overcomes said drawbacks of the prior art. A further object of the present invention is to provide a method which can be carried out by means of simple equipment-related measures, provides a high conversion rate of ammonia precursor substances into ammonia gas, and makes long-term use without maintenance possible. These objects will be achieved by a method according to claim 1 of the present invention.

According to a first execution, the subject-matter of the present invention is a method for continuously generating ammonia from a solution of an ammonia precursor substance by means of an ammonia gas generator, which method comprises a catalytic unit, which comprises a catalyst for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber upstream from the catalyst in the flow direction, the catalyst being of a catalyst volume VKat and the mixing chamber being of a mixing chamber volume VMisch, in which method the solution of the ammonia precursor substance is introduced into the mixing chamber in such a way that the end face loading of the catalyst measures 3.0 to 15 gm/(h*cm2). More particularly, the solution of the ammonia precursor substance is injected into the mixing chamber by means of a nozzle.

It should be emphasized in this context that the ammonia gas generator used in the method according to the present invention is a separate unit used for generating ammonia from ammonia precursor substances. A unit of this kind may, for example, be used for reducing nitrogen oxides in industrial exhaust gases or for the exhaust gas aftertreatment of exhaust gases from combustion engines such as diesel engines. This ammonia gas generator may operate independently or even be operated using lateral exhaust gas streams, although nitrogen oxides are in any event not reduced by means of ammonia until a subsequent method step. In the event that an ammonia gas generator according to the invention is used as a separate component in an exhaust gas aftertreatment system of a combustion engine, for example a diesel engine, the nitrogen oxides in the exhaust gas stream can as a consequence be reduced without introducing further catalysts used for breaking down ammonia precursor substances or other components into the exhaust gas stream itself. The ammonia produced using the ammonia gas generator according to the invention can consequently be introduced into the exhaust gas stream as required. Any potential decrease in the service life of the SCR catalyst due to impurities in the form of depositions, for example of ammonia precursor substances or decomposition products of ammonia precursor substances, is likewise prevented.

Thus, according to the invention, ammonia is in particular generated from an ammonia precursor substance in an ammonia gas generator that is a separate unit. This ammonia, and not the ammonia precursor substance, is then introduced into an exhaust gas stream, for example in order to bring about reduction of nitrogen oxides therein. The ammonia formed in the method according to the invention is preferably fed into exhaust gas at a location downstream of a combustion engine, and in particular at a location downstream of an oxidation catalyst. Furthermore, the ammonia produced according to the invention is in particular supplied to an exhaust gas stream upstream of an SCR catalyst.

An ammonia gas generator according to the present invention in particular comprises a catalytic unit, which in turn comprises a catalyst for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber upstream from the catalyst in the flow direction, the catalyst being of a catalyst volume VKat and the mixing chamber being of a mixing chamber volume VMisch, as well as an injection device for introducing the solution of the ammonia precursor substance into the mixing chamber and an outlet for the ammonia gas formed. In particular, an ammonia gas generator furthermore comprises an inlet for a carrier gas, which particularly preferably generates a carrier gas that is tangential with respect to the stream injected into the mixing chamber

In the context of the present invention, it is essential to the invention that the end face loading of the catalyst falls in the range from 3.0 gm/(h*cm2) to 15 gm/(h*cm2). It has specifically been found to be vital to the failure-free and thus deposition-free operation of an ammonia gas generator that only a certain quantity of solution is permitted to be finely distributed on a given catalyst end face within a specific period of time (respecting mass flow and metering quantity). The impact and initial contact with the frontmost part of the catalyst (catalyst end face) is vital to the complete decomposition of the ammonia precursor. The end face loading is in this case independent of the type of ammonia precursor substance used, or of the solution thereof.

It has furthermore been found that the ratio of metering quantity to catalyst end face must be in the range from 3.0 to 15 gm/(h*cm2) so as to prevent excessively rapid cooling on the catalyst end face and halt an excessively low conversion to ammonia. In this context, the end face loading is defined as the result of dividing the metering mass flow of ammonia precursor solution which reaches the catalyst end face within one hour by the catalyst end area wetted by the spray cone.

Particularly preferable is a method in which the end face loading measures at least 3.0 gm/(h*cm2) and quite particularly preferably at least 4.0 gm/(h*cm2). Simultaneously or independently thereof, the end face loading can in particular measure at most 14.0 gm/(h*cm2), more particularly at most 12.0 gm/(h*cm2), more particularly at most 10.0 gm/(h*cm2), more particularly at most 9.0 gm/(h*cm2), and quite particularly preferably at most 8.0 gm/(h*cm2).

It has been found that, were an excessively large mass flow of ammonia precursor solution to meet the hot end face, then excessively high local cooling would occur owing to the heating and evaporation of the liquid, as a result of which complete conversion would no longer take place. Measurements have shown that, in the case of an excessively high metering quantity at the catalyst end face and thus excessively large end face loading, cooling of the wetted end face by far greater than 100 K occurs, thus failing to reach the temperature level for complete decomposition on the catalyst end face, which results in spontaneous further reactions forming undesired by-products. If the selected catalyst end face is too large and the end face loading is thus too low, then the ammonia gas generator becomes inefficient due to an excessively large catalyst being operated.

It has in further comprehensive testing been found that a corresponding amount of energy with respect to the quantity of ammonia precursor solution is also advantageous in addition to a defined quantity of ammonia precursor solution per catalyst end face. In this context, it has surprisingly emerged that the total amount of energy for the complete and residue-free conversion of the ammonia precursor solution into ammonia is essentially independent of the ammonia precursor solution used. Only the metered mass flow of the solution of the ammonia precursor substance correlates with a certain energy flow in the form of an enthalpy flow (essentially a heat flow). It has been found that a specified amount of energy must be available for the endothermic process of complete conversion of the ammonia precursor solution into ammonia. It has also emerged in this context that the temperature level at which this decomposition takes place does not need to be taken into account. It has been found that the temperature level required essentially depends on the use of hydrolysis catalysts which can reduce the decomposition temperatures required without altering the total amount of energy required in this case for decomposition.

It has been found in testing that the heat flow supplied can be taken from a hot gas stream, for example hot exhaust gas from a combustion engine as transport gas, as well as introduced into the ammonia gas generator by way of additional active heating (electrical, heat exchanger, heating tube or other heat exchangers using heat conduction or radiation).

Therefore, the subject-matter of the present invention is also a method for continuously generating ammonia from a solution of an ammonia precursor substance by means of an ammonia gas generator comprising a catalyst unit, which comprises a catalyst for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber upstream from the catalyst in the flow direction, the catalyst being of a catalyst volume VKat and the mixing chamber being of a mixing chamber volume VMisch, in which method the solution of the ammonia precursor substance and a carrier gas are introduced into the mixing chamber, the carrier gas and optionally an additional energy source in total having a specific enthalpy flow of HTG/mPrecursor from 8,000 - 50,000 kJ/kg (enthalpy flow with respect to the mass flow of the solution introduced).

Particularly preferable is a method in which the specific enthalpy flow measures at least 10,000 kJ/kg, more particularly at least 12,000 kJ/kg, and quite particularly preferably at least 15,000 kJ/kg. Simultaneously or independently thereof, it can be provided that the specific enthalpy flow is at most 45,000 kJ/kg, more particularly at most 40,000 kJ/kg, and quite particularly preferably at most 35,000 kJ/kg.
In this context, the specific enthalpy flow is defined as the result of dividing the enthalpy flow which is conducted into the ammonia gas generator by the metering mass flow of ammonia precursor solution which is supplied to the catalyst per unit of time. In this case, the necessary energy is mainly introduced into the generator in the form of heat. In case of an excessively large metering mass flow at a given enthalpy flow, the specific enthalpy flow according to the invention is not reached since insufficient energy is supplied for the endothermic reaction. The result is insufficient conversion of the ammonia precursor and depositions or formation thereby of undesired by-products that make continuous generator operation impossible. It has likewise been found that an excessively large specific enthalpy flow leads to an unnecessary load on the ammonia gas generator and thus to inefficient operation and to a high load on the components used.

According to a refinement of the invention, the subject-matter of the present invention is also a method in which the solution of the ammonia precursor substance and a carrier gas is introduced into the mixing chamber, wherein the carrier gas and optionally an additional energy source in total have a specific enthalpy flow of HTG/mPrecursor from 8,000 - 50,000 kJ/kg (enthalpy flow with respect to the mass flow of the solution introduced), and in which method the solution of the ammonia precursor substance is introduced into the mixing chamber such that the end face loading of the catalyst measures from 0.2 to 15 gm/(h*cm2).

Ideally, in terms of achieving a conversion of the ammonia precursor substance into ammonia greater than 95%, a number of additional conditions according to the invention must be met during metering. To achieve particularly favourable results, it is necessary to inject the ammonia precursor substance into the mixing chamber in such a way that, for a given catalyst end face, the spray cone diameter upon incidence on the catalyst end face is at most 98%, preferably at most 95%, and more particularly at most 93% of the catalyst diameter. By contrast, the spray cone diameter must measure at least 80%, preferably at least 83%, and more particularly at least 85% of the catalyst end face diameter in order to avoid an excessively high concentration for a given area and excessive loading of the end face with precursor substance thereby. Excessive loading of the catalyst end face causes insufficient contact with the catalyst and to excessive cooling due to evaporation of the liquid, and thus likewise to incomplete conversion as well as to undesired secondary reactions associated with depositions. Ideally, there emerge thereby combinations of end face load and/or specific enthalpy flow along with further parameters which will be dictated by the injection device. Worthy of mention in this context is the type of injection device in particular to be used as well as the distance of the opening of the injection device from the given catalyst end face and the ratio of the spray cone diameter to the catalyst end face.

In the context of the present invention, an injection device is intended to mean any device which sprays, atomizes, or otherwise forms into drops a solution, preferably an aqueous solution, of an ammonia precursor substance, the solution of the ammonia precursor substance being in the form of drops which in particular have a d32 droplet diameter of less than 25 µm. In the context of the present invention, the d32 droplet diameter relates to the Sauter mean diameter as per the German DIN 66 141 industrial standard.

Therefore, according to a preferential embodiment of the present invention, it is provided that the injection device itself comprises a nozzle or a plurality of nozzles which generate droplets having a d32 droplet diameter of less than 25 µm. According to the present invention, it is furthermore preferably provided that the nozzle in this case generates droplets having a d32 droplet diameter of less than 20 µm and quite particularly preferably less than 15 µm. Simultaneously or independently thereof, it is furthermore preferable for the nozzle to generate droplets having a d32 droplet diameter of greater than 0.1 µm and in particular greater than 1 µm. An ammonia formation level (AG) of > 95% (see above) can also be achieved when nozzles of this kind are used. A particularly uniform distribution of the solution on the catalyst end face can also be achieved. In this context and hereinafter, the ammonia formation level (AG) is defined as the molar quantity of NH3 generated in the method with respect to the molar quantity of ammonia precursor

substance theoretically generated given complete hydrolysis. According to the present invention, an ammonia formation level of > 95% is considered to be complete conversion.

According to a particularly preferable variation, it may in particular be provided that the injection device itself comprises a nozzle which is known in the present invention as a two-substance nozzle. In this context, a two-substance nozzle is understood to be a nozzle which uses a pressurized gas, commonly air, as a propellant for breaking up the surface in the liquid phase and for droplet formation thereby. This pressurized gas is also referred to as atomization air. This manner of nozzle makes particularly fine distribution of the ammonia precursor substance possible, along with a d32 droplet diameter of less than 25 µm, in particular less than 20 µm.

In this context, the propellant, in particular the atomization air, is preferably introduced through the same nozzle opening into the mixing chamber together with the solution of the ammonia precursor substance.

Independently or simultaneously, the injection device may also comprise at least two nozzles, which can in particular be switched jointly or separately, in order to introduce the ammonia precursor substance into the mixing chamber.

Alternatively, however, it may also be provided that the injection device comprises what is known as a flash evaporator.

The spray cone according to the present invention is the cone of the solution being sprayed which can be generated using a nozzle or a plurality of nozzles having a defined spray angle α, the spray cone diameter being the diameter which is obtained when the droplets are incident on the catalyst end face. This is set by a liquid pressure of 0.1 to 10 bar on the solution being sprayed at 25°C and, optionally, by an operating range of 0.5 to 10 bar for the atomization air (for two-substance nozzles). When using an optional carrier gas according to the invention, the spray cone diameter is set by a liquid pressure of 0.1 to 10 bar on the solution being sprayed at 25°C and, optionally, an operating range of 0.5 to 10 bar for the atomization air (for two-substance nozzles) when using carrier gas.

According to a refinement of the present invention, in order to achieve a spray cone diameter of at most 98% of the catalyst diameter, it can also be provided that the injection device itself comprises a nozzle, in particular a two-substance nozzle which has a theoretical spray angle α from 10° to 90°. Simultaneously or independently thereof, it can

in particular be provided that the distance from the nozzle opening to the catalyst end face is from 15 to 2,000 mm.

Particularly preferable is a nozzle, in particular a two-substance nozzle, which has a theoretical spray angle α of at least 10°, in particular at least 20°, more particularly at least 25°, particularly preferably at least 30°, particularly preferably at least 35°, particularly preferably at least 40° and quite particularly preferably at least 45°. Simultaneously or independently thereof, further preferable are nozzles which have a theoretical spray angle α of at most 90°, in particular at most 80°, more particularly at most 75°, more particularly at most 70°, particularly preferably at most 60°, particularly preferably at most 55° and quite particularly preferably at most 50°. As stated previously, a uniform distribution of the solution being sprayed can be achieved without depositions occurring on the walls of the catalyst end face by the selective use of a nozzle having a defined spray angle α.

According to the present invention, the theoretical spray angle α (also referred to hereinafter as the spray angle α) is intended to mean a spray angle which is set at the outlet of the nozzle opening or nozzle openings with an operating pressure of 0.1 to 10 bar on the solution being sprayed at 25°C and, optionally, with an operating range from 0.5 to 10 bar for the atomization air (for two-substance nozzles), and that no carrier gas or any other influence on the sprayed solution is present.

In order that the inner wall of the catalyst unit is not wetted with the solution of the ammonia precursor substance, it may be provided as a further measure according to a refinement of the invention that the ammonia gas generator comprises a further inlet for a carrier gas which generates a tangential carrier gas stream with respect to the solution being injected into the mixing chamber. Alternatively, it may also be provided that at least one inlet for a carrier gas is provided around the nozzle and is formed in such a way that the carrier gas forms a casing around the solution being introduced into the mixing chamber. In this way, the sprayed solution is enclosed in a casing of carrier gas such that no wetting of the inner wall will be observed.

Therefore, a further embodiment of the invention relates to an ammonia gas generator which comprises at least one inlet for a carrier gas. The inlet is preferably located in the mixing chamber and is in particular separate or separated from the nozzle opening through which the solution of the ammonia precursor substance is introduced. As a result, the carrier gas can be introduced independently of the ammonia precursor substance solution. The inlet preferably generates a tangential or parallel carrier gas stream with

respect to the solution being injected into the mixing chamber. Regarding a parallel carrier gas stream, one or multiple inlet openings for a carrier gas are preferably arranged in the same wall in which the injection device used for introducing the solution of the ammonia precursor substance is located.

It has surprisingly been found that, as a result of a tangential or parallel carrier gas stream, depositions on the walls of the catalyst unit in the region of the mixing chamber can be further inhibited, and it can be provided that the carrier gas and the solution of the ammonia precursor substance are constantly thoroughly mixed. Wetting of the wall of the catalyst unit in the region of the mixing chamber can thus be almost completely inhibited. As a result of the tangential carrier gas stream, an eddy mist current comprising the droplets is generated which is guided axially in the direction of the hydrolysis catalyst onto the hydrolysis catalyst end face. This eddy mist current enables very good conversion into ammonia on the catalyst. The carrier gas is fed in a tangential direction into the head region of the generator at the level of the spraying device of the ammonia precursor solution and into the catalyst unit or into the mixing chamber. In this context, the gas stream is introduced as shallowly as possible against the wall of the mixing chamber in such a way that a downwardly directed eddy current is established in the catalyst unit in the direction of the catalyst end face.

A similar effect is produced if a nozzle is used which comprises a first number of nozzle openings for introducing the solution of the ammonia precursor substance into the catalyst unit; these nozzle openings are surrounded, ring-like, by a second number of nozzle openings for introducing a carrier gas or atomization air into the catalyst unit.

In the context of the present invention, it is furthermore provided that the distance of the nozzle opening from the end face of the catalyst may measure in particular 15 to 1500 mm, particularly preferably 15 to 1000 mm, and quite particularly preferably 15 to 800 mm. Independently or simultaneously, however, it may also be provided that the distance of the nozzle opening from the end face of the catalyst is at least 30 mm, particularly preferably at least 50 mm, particularly preferably at least 60 mm, particularly preferably at least 100 mm and quite particularly preferably at least 300 mm and, furthermore independently or simultaneously, at most 1500 mm, in particular at most 1000 mm, more particularly at most 800 mm, more particularly at most 500 mm, more particularly at most 400 mm, particularly preferably at most 200 mm and quite particularly preferably at most 150 mm.
According to a refinement of the present invention, it is also provided that the ratio of the volume of the mixing chamber V_{Misch} to the volume of the catalyst V_{Kat} is a ratio from

1.5:1 to 5:1. It has surprisingly been found that the sprayed ammonia precursor substance can in particular be completely broken down into ammonia (conversion rate of > 95%) if the solution droplets are already partially evaporated prior to incidence on the catalyst end face. This may be ensured by way of volume of the mixing chamber being greater than the volume of the catalyst. Due to the droplets being partially evaporated, the solution is already supplied with enough energy to prevent excessive cooling on the catalyst end face due to excessively large drops, thus acting to prevent poor decomposition or by-product formation. A corresponding mixing chamber volume VMisch furthermore ensures that the sprayed ammonia precursor substance incident on the catalyst is homogeneously distributed in the transport gas stream as an aerosol over the cross-section of the catalyst, thus preventing spots having an excessive concentration which could in turn result in poorer conversion. In this context, it is quite preferably provided that the ratio of the volume of the mixing chamber VMisch to the volume of the catalyst VKat is from 2.5:1 to 5:1, particularly preferably from 3: 1 to 5:1, and quite particularly preferably from 3.5:1 to 5:1.

The volume of the catalyst VKat preferably measures from 50 mL to 1,000 L. The volume of the mixing chamber V preferably measures at least 10 mL, more preferably at least 50 mL, more preferably at least 100 mL, more preferably at least 200 mL, more preferably at least 1,000 mL, more preferably at least 2,000 mL, and more preferably at least 5,000 mL. Simultaneously or independently thereof, the volume of the mixing chamber VMisch preferably measures at most 2.5 L, more preferably at most 10 L, more preferably at most 80 L, more preferably at most 500 L, more preferably at most 1,200 L, and more preferably at most 2,000 L.

Furthermore, a catalyst unit according to the present invention is intended to mean a unit which comprises a housing for receiving a catalyst, a mixing chamber positioned upstream of the catalyst in the flow direction, and at least one catalyst for decomposing and/or hydrolysing ammonia precursor substances into ammonia, the catalyst having a catalyst volume VKat and the mixing chamber having a mixing chamber volume VMisch. Optionally, the catalyst unit may additionally comprise an outlet chamber, which is positioned downstream of the catalyst in the flow direction and used as an outlet for the ammonia gas formed.

In the context of the present invention, any catalyst which makes it possible to release ammonia from the ammonia precursor substance under catalytic conditions may be used as the catalyst for decomposing and/or hydrolysing ammonia precursor substances. A preferred catalyst hydrolyses the ammonia precursor substance to form ammonia and

other harmless substances like nitrogen, carbon dioxide and water. This preferably then relates to a hydrolysis catalyst. For example, if a guanidine salt solution is used, in particular a guanidinium formate solution, a urea solution, or mixtures thereof, the catalytic decomposition into ammonia may take place in the presence of catalytically active, non-oxidation-active coatings of oxides selected from the group comprising titanium dioxide, aluminium oxide, silicon dioxide, as well as mixtures thereof, and/or hydrothermically stable zeolites which are fully or partially metal-exchanged, in particular iron zeolites of the ZSM 5 or BEA type. Potential metals in this context are in particular the subgroup elements, preferably iron or copper. Metal oxides such as titanium oxide, aluminium oxide, and silicon dioxide are preferably applied to metal carrier materials, for example heating line alloys (in particular chromium aluminium steels).

Particularly preferable catalysts are hydrolysis catalysts which in particular comprise catalytically active coatings of titanium dioxide, aluminium oxide and silicon dioxide, as well as mixtures thereof.

Alternatively, catalytic decomposition of ammonia precursor substance solutions, in particular the guanidinium formate solutions or the remaining components to form ammonia and carbon dioxide, may also be provided, in which case it is possible to use catalytically active coatings of oxides selected from the group comprising titanium dioxide, aluminium oxide, and silicon oxide, as well as mixtures thereof, and/or hydrothermally stable zeolites which are fully or partly metal-exchanged and impregnated with gold and/or palladium as oxidation-active components. The corresponding catalysts comprising palladium and/or gold as active components preferably have a precious metal content from 0.001 to 2 wt%, in particular from 0.01 to 1 wt%. Using oxidation catalysts of this kind, it is possible to prevent the undesired formation of carbon monoxide as a by-product when the guanidine salt is decomposed during the generation of ammonia.

Preferably, a catalytic coating comprising palladium and/or gold as active components, having a precious metal content from 0.001 to 2 wt%, in particular 0.01 to 1 wt%, is used for the catalytic decomposition of the guanidinium formate as well as, optionally, the further components.

Therefore, the subject matter of the present invention is also a method using a catalyst, in particular a hydrolysis catalyst comprising a catalytically active coating which is impregnated with gold and/or palladium, in particular having a gold and/or palladium content from 0.001 to 2 wt% (with respect to the catalytic coating). Further preferably, this catalyst comprises a catalytically active coating of oxides selected from the group comprising titanium dioxide, aluminium oxide, and silicon dioxide, as well as mixtures thereof, and/or hydrothermally stable zeolites, which is impregnated with gold and/or palladium, the content of gold and/or palladium more preferably being 0.001 to 2 wt% (with respect to the catalytic coating).

In the context of the present invention, it is possible to use a hydrolysis catalyst, the flow direction of which consists of at least two portions, the first portion containing non-oxidation-active coatings and the second portion containing oxidation-active coatings. Preferably, 5 to 90 vol% of this catalyst consists of non-oxidation-active coatings, and 10 to 95 vol% consists of oxidation-active coatings. In particular, 15 to 80 vol% of this catalyst consists of non-oxidation-active coatings, and 20 to 85 vol% consists of oxidation-active coatings. Alternatively, the hydrolysis may also be carried out in the presence of two catalysts arranged in series, the first catalyst containing non-oxidation-active coatings, and the second catalyst containing oxidation-active coatings. Further preferably, the first hydrolysis catalyst may also be a heated catalyst, and the second hydrolysis catalyst may be an unheated catalyst.

It may be furthermore provided that a hydrolysis catalyst consisting of at least two portions be used, with the first portion of the hydrolysis catalyst, being arranged in the flow direction in the form of a heated catalyst and the second portion thereof being arranged in the flow direction in the form of an unheated catalyst. Preferably, 5 to 50 vol% of the catalyst consists of the first portion, and 50 to 95 vol% consists of the second portion.

According to a particularly preferable execution of the present invention, it is provided that the ammonia gas generator comprises a catalyst unit having a hydrolysis catalyst which is at least divided in two, particularly preferably at least divided into three, the first part (in the flow direction) of which is in the form of a heated catalyst, which preferably comprises a direct electrical resistance heater and/or a jacket heater, and the second part of which is in the form of an unheated catalyst, which is most preferably followed downstream by an unheated catalyst having a mixer structure as the third part.

Particularly preferable is an ammonia gas generator which comprises a catalyst unit, and the ratio of the diameter DKAT of the catalyst therein to the length L of this catalyst is from 1:1 to 1:5, in particular from 1:2 to 1:4 and most preferably 1:3. The catalyst diameter DKAT preferably measures 20 to 2000 mm, more particularly 30 to 1000 mm, and even more preferably 30 to 100 mm. However, it may also be provided that the diameter DKat measures 30 to 80 mm, 80 to 450 mm, or 450 to 1,000 mm.

In this context, it is further preferable for the catalyst to be of a length L from 30 mm to 2000 mm, particularly preferably from 70 mm to 1000 mm, and quite particularly preferably from 70 mm to 700 mm.

It has been found that, in order for catalytic conversion of the ammonia precursor substance to be complete, it is preferable to use catalysts having a catalyst cell count of at least 60 cpsi (cpsi: cells per square inch) and having the aforementioned catalyst volumes. In this context, the increasing counterpressure (loss of pressure by way of the catalyst) limits the catalyst cell count to at most 800 cpsi for application in an ammonia gas generator. Particularly preferable are catalysts, hydrolysis catalysts in particular,

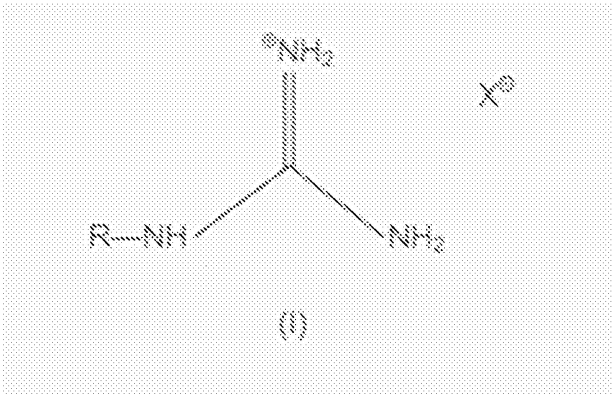
which have a catalyst cell count from 100 to 600 cpsi per inch2 of end face, of 100 to 500 cpsi per inch2 of end face and most preferably from 100 to 400 cpsi per inch2 of the end face of the catalyst.

As regards the configuration of the catalyst unit, it has been found in tests that a cylindrical design is particularly suitable. The optional tangential carrier gas stream can take full effect thereby. By contrast, other constructions are less suitable given that an excessively strong turbulence can be observed thereby. Therefore, the subject-matter of the present invention is also an ammonia gas generator which comprises a catalyst unit designed in the shape of a cylinder.

Moreover, it has proven to be particularly preferable for the ammonia gas generator to comprise a catalyst unit which itself comprises a thermal insulation layer, more particularly a thermal insulation layer made of microporous insulating material.

According to the present invention, the term ammonia precursor substances is intended to mean chemical substances which can be placed in solution and which can split off or otherwise release ammonia by means of physical and/or chemical processes. According to the present invention, urea derivatives, guanidine, biguanidine, as well as salts of these

compounds along with salts of ammonia can in particular be used as ammonia precursor compounds. According to the present invention, urea and guanidine or salts thereof can in particular be used. Salts which are formed from guanidines and organic or inorganic acids may in particular be used. Considered to be particularly preferable in this context are guanidine salts of the general formula (I),



where,

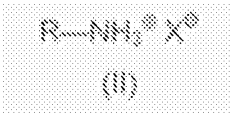
R = H, NH2 or C1-C12 alkyl

$X^{\ominus}$ = acetate, carbonate, cyanate, formate, hydroxide, methylate, or oxalate.

Guanidinium formate is particularly preferable.

In the context of the present invention, these guanidine salts may be used in the form of an individual substance or a mixture of two or more different guanidine salts. According to a preferential embodiment, the guanidine salts used according to the invention are combined with urea and/or ammonia and/or ammonium salts. Alternatively, however, in accordance with a further embodiment of the present invention aqueous urea solutions may also be used. The mixing ratios of guanidine salt with urea and ammonia or ammonium salts can be varied within a wide range. However, it has been found to be particularly advantageous if the mixture of guanidinium salt and urea has a guanidine salt content from 5 to 60 wt% and a urea content from 5 to 40 wt%, in particular from 5 to 35 wt%. Further, mixtures of guanidinium salts and ammonia or ammonium salts having a guanidine salt content from 5 to 60 wt% and an ammonia or ammonium salt content from 5 to 40 wt% should be considered to be preferred. Alternatively, however, a urea solution, in particular an aqueous urea solution, may be used.

Proven ammonium salts in this context are compounds of the general formula (II),



(II)

where

R = H, NH2 or C1-C12 alkyl

$X^{\ominus}$ = acetate, carbonate, cyanate, formate, hydroxide, methylate, or oxalate.

The ammonia precursor substances used according to the invention, in particular guanidine salts as well as the further optional components, consist of urea or ammonium salts and are used in the form of a solution, with water and/or a C1-C4 alcohol preferably being used as the solvent. In this context, the aqueous and/or alcoholic solutions preferably have a solids content from 5 to 85 wt%, in particular from 30 to 80 wt%.

It has surprisingly been found in this context that, according to the present invention, it is particularly expedient to use aqueous guanidinium formate solution in a concentration from 20 to 60 wt% as well as aqueous urea solution in a concentration from 25 to 40 wt% in addition to aqueous mixtures of guanidinium formate and urea solutions, in which case the mixture containing guanidinium formate and urea has a concentration from 5 to 60 wt% guanidinium formate and 5 to 40 wt% urea.

In this context, the aqueous solution of the ammonia precursor substances, in particular the guanidine salts, the mixtures of guanidine salts, or the guanidine salts in combination with urea in water, preferably have an ammonia formation potential from 0.2 to 0.5 kg ammonia per litre of solution, in particular from 0.25 to 0.35 kg ammonia per litre of solution.

It has also surprisingly been found that, as a result of a tangential carrier gas stream (also called a transport gas stream), depositions on the walls of the catalyst unit in the region of the mixing chamber can be further inhibited, and it can be provided that the carrier gas (also called a transport gas) and the solution of the ammonia precursor substance are constantly and thoroughly mixed. If a tangential carrier gas stream of this kind is not used, then spraying the solutions into the mixing chamber can cause the walls of the catalyst unit in the region of the mixing chamber to be wetted and lead to undesired secondary reactions such as polymerisation of the ammonia precursor substance. These secondary reactions lead to undesired depositions in the region of the mixing chamber, as a result of which thorough mixing of the carrier gas and the solution, which is extremely important for the functioning of the generator, is no longer sustainably possible. Owing to the lack of

thorough mixing of the carrier gas with the solution, additional depositions are also observed in and on the catalyst itself. As a result of the tangential carrier gas stream, an eddy mist current comprising the droplets
is generated which is guided axially in the direction of the hydrolysis catalyst onto the hydrolysis catalyst end face. This eddy mist current enables very good conversion into ammonia on the catalyst.

The carrier gas is fed in a tangential direction into the head region of the generator at the level of the spraying device of the ammonia precursor solution and into the catalyst unit or into the mixing chamber. In this context, the gas stream is introduced as shallowly as possible against the wall of the mixing chamber in such a way that a downwardly directed eddy current is established in the catalyst unit in the direction of the catalyst end face.

Therefore, according to a further aspect, the subject-matter of the present invention is also a method for continuously generating ammonia from a solution of an ammonia precursor substance by means of an ammonia gas generator, in particular by means of an ammonia gas generator described herein which comprises a catalyst unit, which itself comprises a catalyst for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber upstream from the catalyst in the flow direction, the catalyst being of a catalyst volume VKat and the mixing chamber being of a mixing chamber volume VMisch, in which method the solution of the ammonia precursor substance is introduced into the mixing chamber separately from a carrier gas, and the carrier gas is furthermore preferably introduced tangentially into the solution of the ammonia precursor substance. In particular, the solution of an ammonia precursor substance is injected into the mixing chamber by means of a nozzle.

Particularly preferable is a method in which i) the solution of the ammonia precursor substance is introduced into the mixing chamber such that the end face loading of the catalyst measures 3.0 to 15 gm/(h*cm2) and/or ii) the solution of the ammonia precursor substance and a carrier gas are introduced into the mixing chamber, the carrier gas and optionally an additional energy source in total have a specific enthalpy flow of HTG/mPrecursor from 8,000 - 50,000 kJ/kg (enthalpy flow with respect to the mass flow of solution introduced) and/or iii) the solution of the ammonia precursor substance is introduced into the mixing chamber separately from a carrier gas, and the carrier gas is furthermore preferably introduced tangentially into the solution of the ammonia precursor substance.

As a result of introducing the solution of the ammonia precursor substance and the carrier gas separately, selective metering of the required amount of energy or heat flow can be implemented for the fault-free and continuous operation of the generator. It has been found that, by virtue of a sufficient amount of energy at an appropriate temperature level, the method is able to be implemented without the formation of undesired by-products. Complete decomposition of the usable ammonia precursor solutions into ammonia requires, at a given quantity or mass flow of solution, a corresponding amount or mass flow of energy in the form of heat at a temperature level necessary for complete decomposition. The temperature level is determined in this case by the hydrolysis catalyst used. The vast majority of energy introduced into the process preferably comes from the carrier gas stream

According to the invention, an ammonia gas generator will in particular operate technically and efficiently if the heat lost from the carrier gas provides the energy introduced for decomposing the ammonia precursor solution. In this case, the quantity of carrier gas does not automatically correlate with the quantity of the liquid solution metered since the usable amount of energy from the carrier gas varies according to temperature. A carrier gas stream at a somewhat lower temperature level, thus a somewhat smaller temperature difference between the input and output of the ammonia gas generator can, for example, be equalised by a higher carrier gas mass flow and thus a higher heat flow input into the generator.

The carrier gas, and the tangential carrier gas stream in particular, is preferably introduced into the mixing chamber at a temperature of up to 550°C, preferably at a temperature from 250 to 550°C, more preferably at a temperature from 250 to 400°C, and most preferably at a temperature from 300 to 350°C.

It has in this case been found that the carrier gas used can be, for example, a partial stream of an exhaust gas or a carrier gas differing therefrom, for example a partial stream of engine charge air preconditioned to an appropriate temperature level by a heat exchanger. If a partial stream of an exhaust gas is used, it has been found to be particularly advantageous for the partial stream to contain less than 5% of the total exhaust gas. However, according to a refinement, it may also be provided that a partial stream which contains at least 0.1% of the total exhaust gas, more preferably less than 4%, and most preferably less than 2% of the total exhaust gas is used as a transport gas.

According to the invention, any gas can in principle be used as a carrier gas stream. Since the carrier gas stream should preferably be at a temperature from 250°C to 550°C, a gas which has already been heated, for example charge air or part of the exhaust gas stream,

is preferably used for good energy efficiency. However, it is also possible to heat any desired carrier gas to the desired temperature.

According to a further preferable execution, it can in particular also be provided that the solution is sprayed into the mixing chamber from the reservoir container by means of a pump and a nozzle at a theoretical spray angle α from 10 to 40°.

According to a further preferential execution of the method, it has been found that the method can be made to be particularly efficient if the solution of the ammonia precursor substance is injected at a pressure of at least 0.5 bar and the atomisation air is injected at a pressure from 0.5 to 2 bar.

It has been found to be particularly advantageous if the solution of the ammonia precursor substance is particularly finely distributed over the catalyst end face. Therefore, the subject-matter of the invention is also a method for generating ammonia in which the solution of the ammonia precursor substance is applied to the end face of the catalyst in the form of droplets having a d32 droplet diameter of less than 25 µm. According to the present invention, it is furthermore preferably provided that the nozzle in this case generates droplets having a d32 droplet diameter of less than 20 µm and quite particularly preferably less than 15 µm. Simultaneously or independently thereof, it is furthermore preferable for the nozzle to generate droplets having a d32 droplet diameter of greater than 0.1 µm and in particular greater than 1 µm. An ammonia formation level (AG) of > 95% (see above) can also be achieved when nozzles of this kind are used. A particularly uniform distribution of the solution on the catalyst end face can also be achieved.

It has furthermore been found that is preferable for the solution of the ammonia precursor substance to be sprayed into the mixing chamber in a direction perpendicular to the catalyst end face. Simultaneously or independently thereof, the volume ratio of carrier gas to atomisation air can in this case be 7:1 to 10:1.

Further parameters preferably adhered to during operation of the ammonia gas generator according to the invention are as follows.

- The metering mass flow of the solution of the ammonia precursor substance per hour is preferably from 50 gm/hr to 280 gm/hr, in particular from 100 gm/hr to 200 gm/hr.
- The mass flow of carrier gas is preferably 1 to 10 kg/hr, in particular 3 to 7 kg/hr.
- The mass flow of atomisation air is preferably 0.14 to 1.43 kg/hr, in particular 0.5 to 1 kg/hr.
- The additional amount of heating energy is preferably from 0 to 150 W, in particular from 50 to 100 W.
- The catalyst end face temperature is preferably set at 280 to 500°C, in particular at 300 to 400°C.
- The catalyst outlet temperature is preferably set at 250 to 450°C, in particular at 280 to 380°C.
- The catalyst space velocity is preferably 5,000 to 30,000 1/hr, in particular 10,000 to 20,000 1/hr.
- The metering pressure of the liquid of the ammonia precursor substance is preferably 1 to 8 bar, in particular 1.5 to 3 bar.

By virtue of their compact design, the ammonia gas generators disclosed herein are particularly suitable for use in industrial facilities, in combustion engines such as diesel engines and petrol engines, as well as in gas engines. Therefore, the use of the described method for reducing nitrogen oxides in exhaust gas from industrial facilities, from combustion engines such as diesel engines and petrol engines, and from gas engines is also within the scope of the present invention.

The invention furthermore comprises the following embodiments in isolation, in combination with the previously disclosed features, as well as in any combination thereof:

- A method for continuously generating ammonia from a solution of an ammonia precursor substance by means of an ammonia gas generator (100) comprising a catalyst unit (70), which comprises a catalyst (60) for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber (51) upstream of the catalyst (60) in the flow direction, the catalyst (60) being of a catalyst volume VKat and the mixing chamber (51) being of a mixing chamber volume VMisch, characterised in that the solution of the ammonia precursor

substance is introduced into the mixing chamber together with a carrier gas, the carrier gas and optionally an additional energy source in total having a specific enthalpy flow of HTG/mPrecursor from 8,000 - 50,000 kJ/kg (enthalpy flow with respect to the mass flow of solution introduced).

- A method for continuously generating ammonia from a solution of an ammonia precursor substance by means of an ammonia gas generator (100) comprising a catalyst unit (70), which comprises a catalyst (60) for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber (51) upstream of the catalyst (60) in the flow direction, the catalyst (60) being of a catalyst volume VKat and the mixing chamber (51) being of a mixing chamber volume VMisch, characterised in that the solution of the solution of the ammonia precursor substance is applied to the end face (61) of the catalyst (60) in the form of droplets having a d32 droplet diameter of less than 20 µm.

- A method for continuously generating ammonia from a solution of an ammonia precursor substance by means of an ammonia gas generator (100) comprising a catalyst unit (70), which comprises a catalyst (60) for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber (51) upstream of the catalyst (60) in the flow direction, the catalyst (60) being of a catalyst volume VKat and the mixing chamber (51) being of a mixing chamber volume VMisch, characterised in that, separately from the solution of the ammonia precursor substance, a carrier gas is also introduced into the mixing chamber (5), a partial stream of an exhaust gas that contains 0.1 to 5% of the total exhaust gas being used as the carrier gas.

- A method for continuously generating ammonia from a solution of an ammonia precursor substance by means of an ammonia gas generator (100) comprising a catalyst unit (70), which comprises a catalyst (60) for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber (51) upstream of the catalyst (60) in the flow direction, the catalyst (60) being of a catalyst volume VKat and the mixing chamber (51) being of a mixing chamber volume VMisch, characterised in that, separately from the solution of the ammonia precursor substance, a carrier gas is additionally introduced parallel to the solution of the ammonia precursor substance injected into the mixing chamber.

- A method for continuously generating ammonia from a solution of an ammonia precursor substance by means of an ammonia gas generator (100) comprising a catalyst unit (70), which comprises a catalyst (60) for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber (51) upstream of the catalyst (60) in the flow direction, the catalyst (60) being of a catalyst volume VKat and the mixing chamber (51) being of a mixing chamber volume VMisch, characterised in that the solution of the ammonia precursor substance is introduced into the mixing chamber in such a way that the spray cone diameter upon incidence on the catalyst end face is at least 80% and at most 98% of the catalyst diameter.

- A method for continuously generating ammonia from a solution of an ammonia precursor substance by means of an ammonia gas generator (100) comprising a catalyst unit (70), which comprises a catalyst (60) for decomposing and/or hydrolysing ammonia precursor substances into ammonia and a mixing chamber (51) upstream of the catalyst (60) in the flow direction, the catalyst (60) being of a catalyst volume VKat and the mixing chamber (51) being of a mixing chamber volume VMisch, characterised in that a catalyst (60), in particular a hydrolysis catalyst, is used which has a catalytic coating impregnated with gold and/or palladium.

The present invention is described hereinafter in greater detail in reference to drawings and associated examples. Shown are:

Figure 1: a schematic axial cross-sectional view of a first ammonia gas generator
Figure 2: a schematic design of an exhaust system in a vehicle
Figure 3: a radial cross-section of the mixing chamber (plan view) in the region of the tangential carrier gas stream supply
Figure 4: diagram 1 of the conversion of the ammonia precursor solution into ammonia depending on the end face loading
Figure 5: diagram 2 of the conversion of the ammonia precursor solution into ammonia depending on the specific enthalpy stream.

Fig. 1 shows a first ammonia gas generator (100) according to the present invention. The generator (100) is in the form of a cylinder and comprises an injection device (40), a catalyst unit (70), and an outlet (80) for the ammonia gas formed. The catalyst unit (70) consists of a multi-part hydrolysis catalyst (60), a mixing chamber (51), and an outlet chamber (55). In an operating condition, the ammonia precursor solution (B) is sprayed out of a reservoir container (20) via a metering pump (30) together with an atomisation air stream (A) via a two-substance nozzle (41) having a nozzle opening (42) into the mixing chamber (51) of the ammonia gas generator (100) at a defined spray angle, and distributed into fine droplets. Additionally, a hot transport gas stream (C) is introduced into the mixing chamber (51) tangentially via the inlet (56), causing an eddy mist flow comprising the droplets to be generated, which is passed axially in the direction of the hydrolysis catalyst (60) onto the hydrolysis catalyst end face (61). The catalyst (60) is designed in such a way that the first segment (62) is in the form of an electrically heatable metal support comprising a hydrolysis coating. This is followed by an unheated metal carrier catalyst (63), likewise comprising a hydrolysis coating and an unheated catalyst (64) comprising a hydrolysis coating configured as a mixer structure for better radial distribution. The generated ammonia gas (D) exits the generator (100) together with the hot carrier gas stream via the outlet chamber (55) comprising the outlet (80) and the valve (81). The generator may additionally be heated by a jacket heater (52) around the housing (54) of the catalyst unit. Apart from the head region in which the injection device (40) is located, the ammonia gas generator (100) is enclosed in a thermal insulation (53) of microporous insulating material.

Fig. 2 shows a schematic of material flow for exhaust gas aftertreatment in a combustion engine (10). In this context, the exhaust gas from the combustion engine (10) is guided through a charging unit (11), and incoming air (E) for the internal combustion engine is compressed in a counterflow. The exhaust gas (F) is guided over an oxidation catalyst (12) so as to achieve a higher NO2 concentration in relation to NO. The ammonia-containing gas stream (D) from the ammonia gas generator (100) can be supplied and mixed in upstream as well as downstream of a particle filter (13). In this context, an additional gas mixer (14) in the form of a static mixer or, for example, a Venturi mixer may be used. The NOx is reduced at the SCR catalyst (15) by means of the NH3 reducing agent in an SCR catalyst (SCR: selective catalytic reduction). In this context, the ammonia gas generator may be operated using separate carrier gas or else using a partial exhaust gas stream.

Figure 3 is a detailed view of the mixing chamber (51) in the region of the tangential carrier gas stream supply. The housing (54) of the catalyst unit is enclosed in thermal insulation (53) made of microporous insulating material in the region of the mixing chamber (51). The tangential supply of the carrier gas (C) is provided in the head region of the ammonia gas generator or in the head region of the mixing chamber (51) at the level of the nozzle opening (42) of the nozzle (41). In this context, the inlet (56) for the carrier gas stream (C) is designed in such a way that the gas stream is introduced as shallowly as possible against the wall (54) of the mixing chamber, in such a way that a downwardly directed eddy current is established in the catalyst unit in the direction of the catalyst end face.

Exemplary embodiment 1:

The design corresponds in principle to the ammonia gas generator shown in Figure 1. The ammonia gas generator is configured for a metering quantity of 10 -100 gm/hr NH3 and designed as a cylindrical pipe reactor. A two-substance nozzle made by Schlick (model 970, 0.3 mm), having a variable air cap and coated with amorphous Si, is arranged centrally in the head region. The ammonia precursor substance is metered in at room temperature through this nozzle and atomised in a full cone. The spray angle α measures 30°. In this context, the liquid is entrained by means of a pressurised air stream (0.5 - 2 bar) of approximately 0.8 kg/hr, passed through the nozzle, and atomised. The Sauter mean diameter of the resulting droplets below the nozzle is < 25 µm. Uniform radial distribution of the solution of the ammonia precursor substance occurs across the reactor cross-section in the hot transport gas stream upstream of the hydrolysis catalyst in a mixing chamber without the reactor wall being touched in the process, thus avoiding depositions. In the mixing chamber drops are already evaporating in such a way that, upon incidence on the catalyst end face, the drop diameter is reduced by up to 20%. As a result of the droplets still present, cooling of approximately 120 - 150°C occurs at the catalyst end face. As a result, the reactor is configured in such a way that the amount of heat supplied with the hot transport gas stream, the integrated heatable hydrolysis catalyst, and further supplies of energy introduce sufficient energy that for the quantity of solution metered in there is no cooling

to below approximately 300°C. The metering quantity of 50 - 280 gm/hr is controlled in this case by means of a Bosch PWM valve. The pressure for conveying the liquid is generated from a pressurised air line in a reservoir container via overpressure, thus requiring no additional conveyor pump.

A hot transport gas stream of approximately 1 - 5 kg/hr is likewise introduced tangentially into the head region of the ammonia gas generator in such a way that it is placed in a mist stream around the reactor wall and is passed through the mixing chamber in a spiral shape. By means of this gas stream axial transport through the reactor is achieved at a defined retention time (reciprocal value of the space velocity) and, in addition, sprayed droplets are prevented from coming into contact with the reactor wall. The diameter of the mixing chamber in the head region of the reactor measures 70 mm. The length of the mixing chamber measures 110 mm. The mixing chamber is additionally heated from the outside via an electric resistance heating casing (max. heating time of 1 min.) — Hewit model, 0.8 - 1 kW, 150-200 mm. The temperature is regulated in combination with temperature sensors (type K) arranged in and downstream of the catalyst and on the catalyst end face. All of the outer surfaces of the reactor are enclosed by Microtherm Super G insulation. The Microtherm Super G filling is embedded in this case between glass fibre meshing which is wound around the reactor. In order to improve heat dissipation, only the head region in which the solution is injected is uninsulated. The surfaces in the mixing chamber are coated with catalytically active TiO2 wash coats (anatase structure).

A heatable metal carrier catalyst of 55 mm diameter and 400 cpsi (Emitec Emicat, maximum power 1.5 kW, volume approximately 170 mL) is flange-mounted downstream of the mixing chamber. Said catalyst is designed as a hydrolysis catalyst and is likewise coated with catalytically active TiO2 (anatase, wash coat approximately 100 gm/L, made by Interkat/Südchemie), and is regulated in such a way that the temperature at the catalyst end face is between 300 and 400°C. In this context, only enough energy is supplied to compensate the cooling resulting from the evaporation of the droplets. In order to achieve a space velocity of up to at least 7,000 1/hr, a further hydrolysis catalyst of 400 cpsi is connected downstream, resulting in a total catalyst volume of approximately 330 mL.

The ammonia generated at the hot hydrolysis catalyst flows freely in the foot region via the outlet chamber, then centrally through an outlet opening and out of the reactor end piece. In this context, the outlet region is preferably shaped conically in order to prevent eddy formation at edges and thus depositions of possible residues. In order to prevent ammonium carbonate depositions, the gas mixture from the ammonia gas generator is preferably supplied to the engine exhaust gas stream upstream of the SCR catalyst at a temperature of > 80°C and distributed homogeneously into this exhaust gas stream by way of a static mixer.

1.4301 (V2A, Din X 5 CrNi 18-10) or alternatively 1.4401 (V4A, DIN X 2 CrNiMo 17-12-2), 1.4767, or other Fe Cr Al alloys typical of exhaust gas catalysts are used as the material for all of the metal components.

In the following, the influence of the end face loading and the specific enthalpy flow on the continuous generation of the ammonia is set out, the ammonia gas generator from example 1 having been used.

These generators were operated with a 60% guanidinium formate solution and with a 32.5% aqueous urea solution as well as with mixtures of the two. In this context, the results for these ammonia precursor solutions are approximately identical (± 1%).

Table 1: Processes depending on the end face loading

	V1*	V2	V3	V4*	V5*
Distance from nozzle opening to catalyst end face [mm]	100	100	100	100	100
Spray cone diameter [mm]	54	54	54	54	54
Metering mass flow of ammonia precursor substance solution per hour [gm/hr]	50	160	280	4	400
Catalyst end face loading per hour [gm/(h*cm2)]	2.1	7.0	12.0	0.17	17.5
specific enthalpy flow	8000	12000	16000	16000	16000
ammonia formation level [%]	≥95%	≥95%	≥95%	≥95%	<90%
Depositions on catalyst end face	none	none	none	none	yes
Depositions on mixing chamber wall	none	none	none	none	none

*V1, V4, and V5 are comparative examples

By setting the catalyst end face loading to at least 0.17 gm/(h*cm2) (see V4), a process can be provided in which depositions are also not formed over a time period of > 100 hrs. Even if the end face loading is 2.1 gm/(h*cm2) or 7.0 gm/(h*cm2) or 12.0 gm/(h*cm2) over a time period of > 100 hrs, no depositions are observed, a continuous process being ensured thereby. If the end face loading is set to a value of 17.5 gm/(h*cm2) (see V5), depositions on the catalyst end face are observed. A continuous process is thus no longer possible.

The formation of ammonia which depends on the end face loading is reproduced in Figure 4.

Table 2: Processes depending on the specific enthalpy flow

	V1	V2	V3	V4	V5
Distance from nozzle opening to catalyst end face [mm]	100	100	100	100	100
Spray cone diameter [mm]	54	54	54	54	54
Metering mass flow of ammonia precursor substance solution per hour [gm/hr]	160	160	160	160	160
Catalyst end face loading per hour [gm/(h*cm2)]	7.0	7.0	7.0	7.0	7.0
specific enthalpy flow	8,000	12,000	16,000	2,000	20,000
ammonia formation level [%]	≥95%	≥95%	≥95%	<90%	≥95%
Depositions on catalyst end face	none	none	none	yes	none
Depositions on mixing chamber wall	none	none	none	yes	none

By setting the specific enthalpy to at least 8,000 kJ/kg (see V1, V2, V3, and V5), a process can be provided in which depositions are also not formed over a time period of > 100 hrs, it being possible to provide a continuous process thereby. If the specific enthalpy is set to 2,000 kJ/kg (see V4), depositions on the mixing chamber wall and the catalyst end face are observed. The formation of ammonia which depends on the specific enthalpy flow is reproduced in Figure 5.

The operating parameters which should be adhered to during operation of the ammonia gas generator are specified in the following.

Table 3: Overview of further operating parameters

Description	Formula	Unit	Range		
			from	average	to
Carrier gas mass flow	mAbg	[kg/hr]	1	5	10
Atomisation air mass flow	mnozzle	[kr/hr]	0.14	0.71	1.43
Heating energy	EHeat	[J/s]=[W]	0	70	150
Catalyst end face temperature	Tin	[°C]	280	350	500
Catalyst outlet temperature	Tout	[°C]	250	320	450
Catalyst space velocity	RG	[1/hr]	5,000	15,000	30,000
Fluid metering pressure	pRed	[bar]	1	2	8

Exemplary embodiment 2:

The reactor in exemplary embodiment 2 is designed in such a way that the reactor is additionally heated in part as a result of counter flow heat exchange by the supplied hot carrier gas stream. In this context, the carrier gas stream is initially passed below the reactor head, via a double casing, counter to the flow direction in the inside of the double casing, to the reactor wall, and flows around said wall on the way to the reactor head. At the reactor head, the primary flow from the reactor double casing enters the reactor interior from the reactor double casing via a plurality of holes or alternatively via an annular gap in the region of the nozzle at the reactor head. In addition, an electrical resistance heater may be located in the double casing.

Exemplary embodiment 3:

The reactor in exemplary embodiment 3 is configured in such a way that the reactor is heated from the outside by heat exchange with hot components of a combustion engine or of a separate burner for exhaust gas heating or by hot gas flows, rather than by means of an electrical resistance heater. In this context, the heat can also be transported to the reactor via a heating tube over some distance.

Exemplary embodiment 4:

The reactor in exemplary embodiment 4 is configured in such a way that heat is supplied directly in the interior of the reactor by means of an electrically heatable Emikat catalyst made by Emitec, instead of the reactor being heated from the outside. Alternatively, heat can be generated in the reactor by means of glow plugs (Champion model, 60 W, 11 V).

Exemplary embodiment 5:

By preheating the liquid solution of the ammonia precursor substance—using an injector having critical superheating (flash evaporator).

Patentkrav

1. Fremgangsmåde til kontinuerlig fremstilling af ammoniak fra en opløsning af en ammoniakudgangssubstans ved hjælp af en ammoniakgasgenerator (100) omfattende en katalysatorenhed (70), som omfatter en katalysator (60) til at nedbryde og/eller hydrolysere ammoniakudgangssubstanser i ammoniak og et blandingskammer (51) anbragt opstrøms af katalysatoren (60) i strømningsretningen, hvor katalysatoren (60) har en katalysatorvolumen V_{kat} og blandingskammeret (51) har en blandingskammervolumen $V_{blanding}$,
kendetegnet ved, at
opløsningen af ammoniakudgangssubstans indføres i blandingskammeret på sådan en måde at endefladebelastningen på katalysatoren er 3,0 til 15 g/(h*cm^2).

2. Fremgangsmåde ifølge krav 1,
kendetegnet ved, at
en bærergas endvidere indføres i blandingskammeret (51), separat fra opløsningen af ammoniakudgangssubstans.

3. Fremgangsmåde ifølge krav 1 eller 2,
kendetegnet ved, at
opløsningen af ammoniakudgangssubstans indføres i blandingskammeret (51) separat fra en bærergas, og bærergassen indføres tangentielt i forhold til opløsningen af ammoniakudgangssubstans.

4. Fremgangsmåde ifølge krav 2 eller 3,
kendetegnet ved, at
en delstrøm af en udstødningsgas anvendes som bærergassen, hvilken indeholder mindre end 5 % af den samlede udstødningsgas.

5. Fremgangsmåde ifølge mindst et af de foregående krav,
kendetegnet ved, at
opløsningen af ammoniakudgangssubstans sprøjtes i blandingskammeret fra

opbevaringsbeholderen (20) ved hjælp af en dyse (41) ved en sprøjtevinkel α på 10 til 40°.

6. Fremgangsmåde ifølge mindst et af de foregående krav,
kendetegnet ved, at
opløsningen injiceres ved et tryk på mindst 0,5 bar og forstøvningsluft injiceres ved et tryk på fra 0,5 til 2 bar.

7. Fremgangsmåde ifølge mindst et af de foregående krav,
kendetegnet ved, at
opløsningen påføres til endefladen (61) af katalysatoren (60) i formen af dråber med en dråbediameter D_{32} på mindre end 20 µm.

8. Fremgangsmåde ifølge mindst et af de foregående krav,
kendetegnet ved, at
forholdet af bærergas til forstøvningsluft er fra 7:1 til 10:1.

9. Fremgangsmåde ifølge mindst et af de foregående krav,
kendetegnet ved, at
opløsningen sprøjtes i blandingskammeret (51) vinkelret i forhold til katalysatorendefladen (61).

10. Fremgangsmåde ifølge mindst et af de foregående krav,
kendetegnet ved, at
opløsningen indføres sammen med en bærergas i blandingskammeret (70), bærergassen og eventuelt en yderligere energikilde med en samlet specifik enthalpistrøm H_{TG} / $m_{Precursor}$ på 8.000 - 50.000 kJ/kg (enthalpistrøm baseret på massestrøm tilført til opløsningen).

11. Anvendelse af en fremgangsmåde ifølge mindst et af de foregående krav til at reducere nitrogenoxider i udstødningsgasser fra industrianlæg, forbrændingsmotorer, gasmotorer, dieselmotorer eller benzinmotorer.

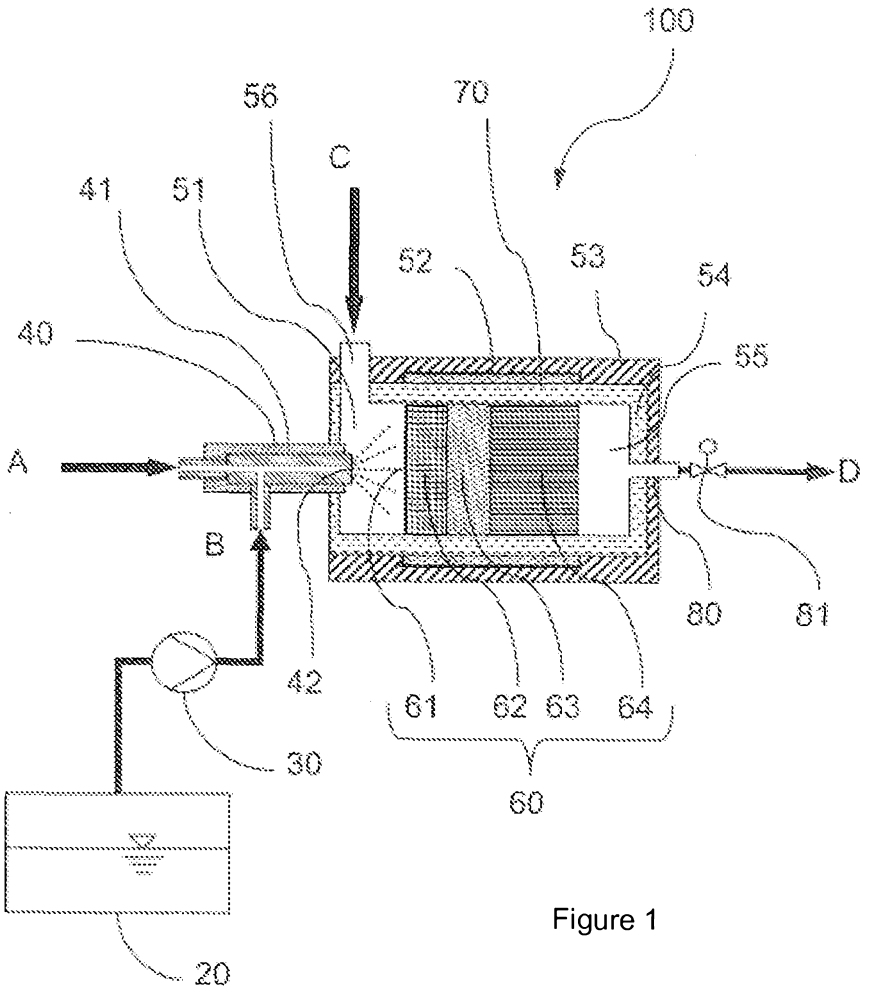


Figure 1

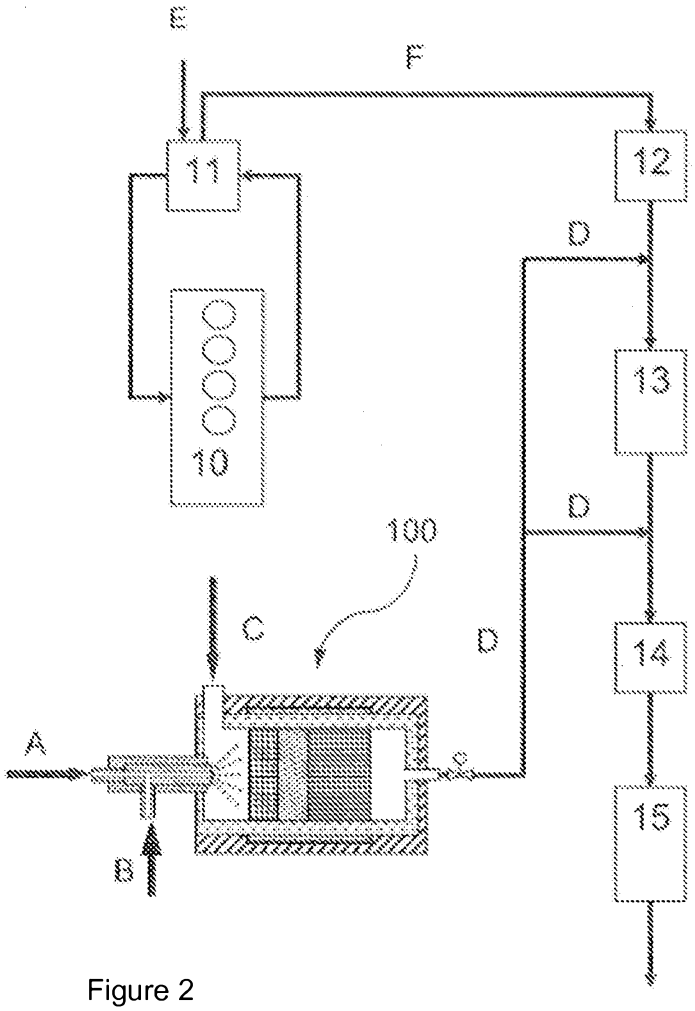


Figure 2

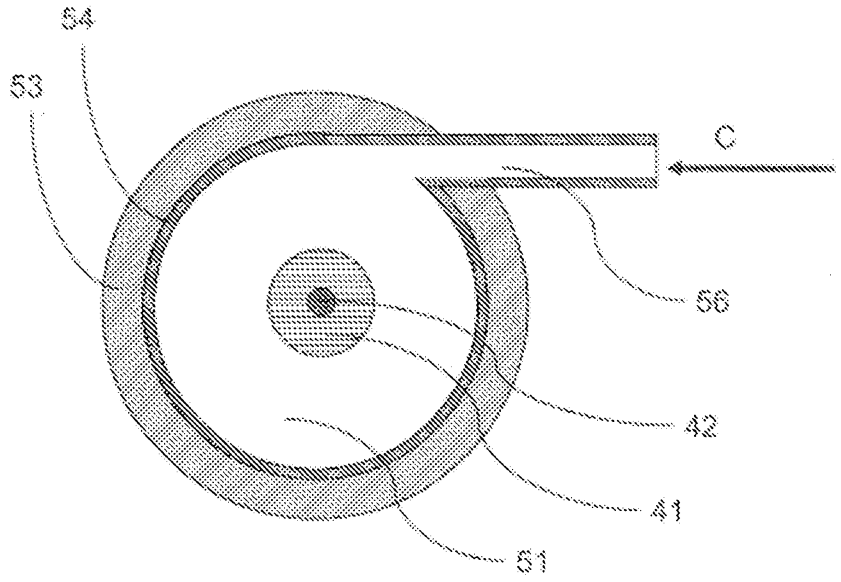


Figure 3

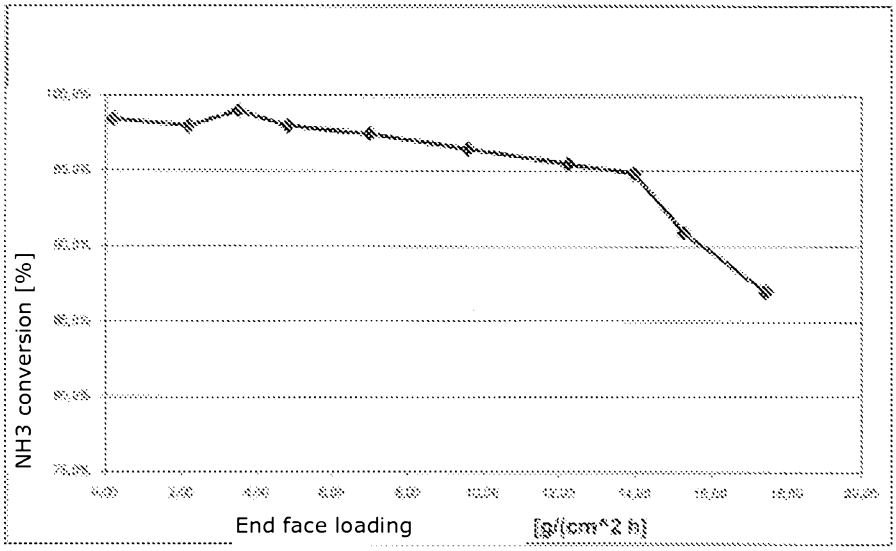


Figure 4

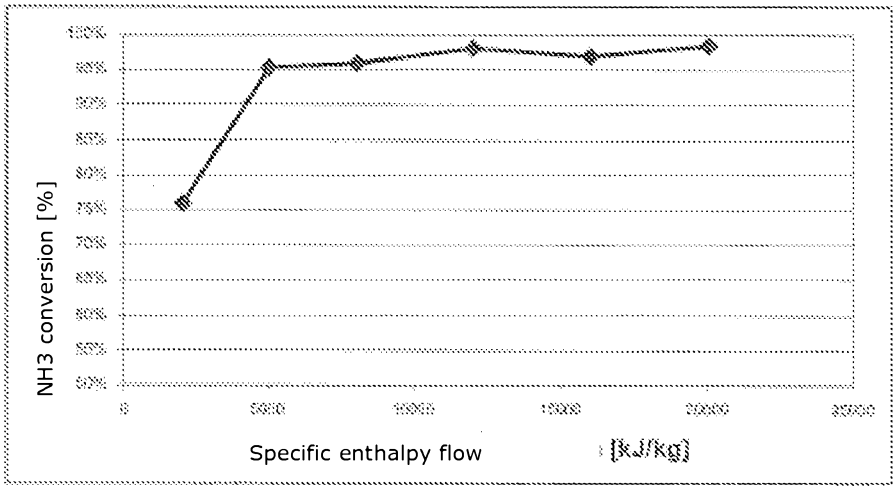


Figure 5