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(54) Benævnelse: **Fremgangsmåde til katalytisk denitrifikation af forbrændingsgasser**

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Description

The present invention relates to a method for the catalytic denitrification of combustion fumes.

During the combustion of materials such as coal or fuel oil, for example, for the purpose of producing energy, or even during the incineration of waste, the fumes from these combustion processes contain an appreciable proportion of nitrogen oxides and cannot be discharged into the atmosphere without being processed.

During combustion other pollutants, in particular acid gases such as hydrochloric acid or sulphur dioxide, are emitted as well as dusts and solid particles. As a general rule, nitrogen oxides must be eliminated and there are several technologies available that are widely accepted in industry.

Firstly, action can be taken at the actual combustion level. In this case, so-called low-NOx burners can be used in the case of coal or fuel oil combustion, or the excess air or its staging can be modified such that the formation of nitrogen oxides from the nitrogen in the air is minimised in the very hot zones. It has also been proposed to enrich the combustion atmosphere with oxygen or to recycle carbon dioxide to obtain this effect. This approach is limited in its efficiency and, moreover, has proved rather difficult to implement within the framework of waste incineration. Moreover, this solution cannot be at all adequate to bring the nitrogen oxide content in the combustion fumes to below 150 mg/Nm^3 of nitrogen oxides.

A second approach consists of injecting a reagent, usually ammonia or urea, into a particular zone of combustion. The reagent then breaks down and the radicals generated react to prevent the formation of nitrogen oxides or to destroy those already formed. Once again this solution has limits and it is difficult to go beyond decomposition efficiency rates of more than 70% without making allowances for a discharge of ammonia exceeding about ten milligrams per Nm^3. Once again for the particular case of waste incineration it is not possible to obtain much more than 120 mg/Nm^3 of nitrogen oxides without having a significant discharge of ammonia. This solution, referred to as SNCR (selective non-catalytic reduction), is therefore no longer sufficient to meet the needs of modern units.

Traditionally, the technique pursued when nitrogen oxide contents of less than 80 mg/Nm^3 need to be obtained is to resort to a denitrification process referred to as SCR (selective catalytic reduction). The nitrogen oxides are reacted with an appropriate reagent on a catalyst maintained at a relatively high temperature. The denitrification reagent used is typically ammonia or also urea. While this technique has been well mastered, certain concerns and limitations lead to a progressive loss of activity of the catalyst, such as the existence of poisons such as alkaline oxides, phosphorus, arsenic that can attach to the active sites of the catalyst, and such as the existence of compounds such as sulphates and ammonium hydrogen sulphates, which can be deposited and block the pores of the catalyst. This necessitates either simply replacing the catalyst or undertaking its regeneration. Such a regeneration can be of a thermal nature by raising the temperature of the catalyst by means of burners, or can also result from a washing operation. In both cases the catalytic unit is taken off line, which results in a non-availability of the installation.

It has been proposed, particularly in EP 1 576 999, to perform a complete compartmentalisation of the catalyst and to regenerate compartment by compartment, which allows the installation to be kept online overall during regeneration. However, this solution is costly because of the compartmentalisation, the number of registers and the complexity of the circuits of the resulting fumes.

In practice, the SCR catalysts are frequently used in the form of catalysts with honeycomb structures, ducts or plates that provide a high opening ratio for the fumes. Such a structure gives a low load loss and also gives the best tolerance for solid particles and dusts, which is, however, achieved to the detriment of the volume of catalyst used. To circumvent this limitation, a catalyst in the form of granules is sometimes used, but such a granulate form then becomes highly susceptible to fouling and blockage, as the dusts accumulate between the granules. Finally, the catalyst is sometimes incorporated as active principle directly within a filtering agent, e.g. in rigid or semi-rigid layers, or also within a semi-flexible medium: in this case as the particles are held on the outside, they do not block the catalytic device, but this approach does not allow the catalyst to be regenerated online once it is deactivated. Moreover, the cost of such a catalytic filtering agent is high.

For its part, DE-A-196 12 240 discloses a denitrification process, in which the fumes to be treated are denitrified by feeding them into a dust collector after being mixed with a

denitrification catalyst in powdered form and with ammonia or urea, which are introduced directly into the fumes as addition of fresh materials. In addition, the catalyst is recycled by successively recuperating a fraction of the solids collected by the dust collector, reactivating this fraction in an appropriate unit supplied with hot air, and on exiting this unit returning it to the fumes to be treated upstream of the dust collector. Although such a process appears promising, DE-A-196 12 240 is imprecise if not silent with regard to certain parameters that are indispensable for its implementation. Moreover, the case of introducing fresh urea into the fumes to be treated is difficult, if not impossible to implement in view of the high temperatures required for the use of urea without processing particularly hot fumes, which is not very common or unprofitable.

The object of the present invention is to propose a viable improved catalytic denitrification method that combines efficiency, low cost and the possibility of regeneration online.

To this end, the invention relates to a method for the catalytic denitrification of combustion fumes as defined in claim 1.

Thus, the invention is based on the simple, economic and efficient use of an SCR denitrification catalyst in divided form, the catalytic activity of which is permanently maintained by continuous regeneration by means of an appropriate reactivation reactor and urea, the decomposition of which is achieved rapidly and efficiently in the aforementioned reactor, into which the urea is introduced directly in solid form, if need be.

Additional advantageous features of the method according to the invention are outlined in the dependent claims.

The invention will be better understood on reading the following description given solely by way of example and with reference to the drawings:

Figure 1 is a schematic view of an installation implementing the method according to the invention; and

Figure 2 is a diagram showing details of a possible embodiment of a part of the installation of Figure1.

In Figure 1 combustion fumes to be denitrified 1 issue from a gas-solid separator 101 located upstream on the course of these fumes and are passed into a dust collector 201. The technology of the gas-solid separator 101 and the dust collector 201 is known per se: each of them is formed by a bag filter, for example. In practice, the gas-solid separator 101 is not necessarily located directly upstream of the dust collector 201, but it is important to understand that on entering the dust collector 201 the fumes to be denitrified 1 must no longer contain too large a quantity of dust or solids, otherwise the catalyst, which will be described in detail below, would be contaminated with these dusts and solids. Typically, it is desirable that the content of dust in the fumes to be denitrified 1 does not exceed 5 mg/Nm^3, wherein this value is only an indication and does not restrict the present invention.

In order to denitrify the fumes 1 these are brought into contact with a denitrification reagent and a denitrification catalyst at the same time, noting that such a denitrification reagent and such a catalyst are known per se, as explained in the introduction of the present document.

Hence, the active material of such a catalyst is generally formed from metal oxide, salts or metals and for operational reasons this active principle is often deposited or dispersed on a support. As an example, this active material is vanadium oxide, iron oxides, manganese oxides or copper-based compounds, to mention just a few compounds. The support is often formed from titanium oxide, an aluminium oxide, a zeolite, possibly with added additives used for their formulation. Thus, current examples of catalysts are based on vanadium oxide or tungsten oxide on a substrate such as titanium oxide (anatase).

On this basis, one of the important features of the invention is that such a denitrification catalyst is used in divided form, preferably in powdered form, and in this divided, preferably powdered, form is mixed with the fumes to be denitrified 1. "In divided form" is understood to mean that the catalyst is presented in a form that is sufficiently fine to enable it to be carried by the fumes to be treated 1. As shown in Figure 1, this catalyst in divided form is supplied by a recycling flux 6, which will be explained in detail below, and by an addition of fresh catalyst 7, and these are both mixed with the fumes to be denitrified 1 upstream of the dust collector 201.

With respect to the denitrification reagent, it is introduced into the fumes to be denitrified 1 upstream of the dust collector 201 by a flux 8', which, as illustrated in Figure 1 and explained in detail below, is combined with the aforementioned flux 6.

In the presence of the reagent supplied by the flux 8' and in contact with the catalyst supplied by fluxes 6 and 7, the fumes 1 are denitrified, i.e. their content of nitrogen oxides, in particular NO and NO_2, is reduced, this being the case both in the conduit carrying the fumes mixed with the reagent and the catalyst and in the dust collector 201. It is thus understood that the dust collector 201 constitutes a catalytic denitrification reactor.

For information purposes, and therefore not restrictive of the invention, the concentration of catalyst in divided form is most frequently in the range of between 0.2 and 5 g/Nm^3, but other concentrations can be used, the only limitation being that the quantity of catalyst effectively used in particular in the dust collector 201 is sufficient to ensure the desired denitrification.

The dust collector 201 receives and collects the divided catalyst in its hoppers, for example, if this is a bag filter, which is a technology that is particularly well suited to this function.

On exiting the dust collector 201 the denitrified fumes 2 are evacuated while the collected solids that are rich in catalyst are extracted by a flux 3. According to one of the features of the invention a portion 4 of this flux of collected solids 3 is extracted and evacuated, wherein this portion 4 constitutes a purging of the system. The principal remaining portion 5 of the flux of collected solids 3, which constitutes at least 95%, preferably more than 98%, of the latter, is directed towards a reactivation reactor 301 for the purposes of regeneration.

The technology of the reactivation reactor 301 is known per se: it is formed, for example, by a double-screw contactor, a bubbling bed or a fluidised bed.

In addition to the fraction 5 of the flux of collected solids 3, the reactivation reactor 301 receives a regeneration flux 51 formed from hot gases, which have a temperature of at least 220°C, preferably in the range of between 250 and 350°C.

As shown in Figure 1, the flux of solids 6 and a gas flux 52 are extracted from the reactivation reactor 301 and are reintroduced into the fumes to be denitrified 1 upstream of the dust collector 201. In practice, fluxes 6 and 52 can be at least partially combined: thus, all or part of the flux of solids 6 can be carried by the gas flux 52 up to the conduit that carries the fumes 1. If the gas flux 52 is extracted from the reactivation reactor 301 separately from the flux of solids 6, this gas flux 52 is not necessarily introduced into the conduit carrying the fumes 1 at the same location as the flux of solids 6. As a variant (not shown) this flux 52 can, for example, be introduced upstream of the gas-solid separator 101.

As mentioned above, the reactivation reactor 301 allows the thermal regeneration of the recycled catalyst in the fraction 5 of the flux of collected solids 3, wherein the flux of hot gases 51 is such that the temperature of the exiting fluxes 6 and 52 is brought to approximately 220°C or more, otherwise the regeneration of the recycled catalyst is ineffective or inadequate. Hence, in the reactivation reactor 301 compounds such as ammonium hydrogen sulphate and certain volatile metal salts are desorbed from the recycled catalyst through the action of the heat. As the catalyst is continuously recirculated by means of fluxes 3, 5 and 6 and the reactivation reactor 301, this catalyst permanently has a satisfactory state of activity in contrast to the prior art, in which a static catalyst is used that is typically subject to deactivation in the order of 5% per year.

Moreover, the reactivation reactor 301 provides another advantage that would not be accessible to the prior art, in which a static catalyst is used. In fact, with the invention the movement of the divided form of the catalyst causes an attrition effect that detaches solid deposits that could form on the surface of the catalyst and would reduce its activity purely by the mechanical effect of blocking the catalyst.

According to a feature of the invention urea is used in order to introduce the denitrification reagent of the flux 8'into the fumes to be treated 1. When urea is used in this way, ammonia is generated both by thermal decomposition of the urea, then on contact between the urea or its decomposition by-products and the divided catalyst. The use of urea has several advantages in terms of safety and can be preferred over ammonia or ammonia solutions. However, the decomposition of the urea requires a temperature of at least 220-230°C for it to be accomplished in a sufficiently short time, typically less than a few seconds. The invention also provides that the urea 8 is introduced into the reactivation reactor 301, which, because it

operates at a higher temperature than that of the fumes to be treated 1 and that of the dust collector 201, ensures rapid decomposition of this urea 8. The solid and/or gaseous by-products resulting from the decomposition of the urea 8 in the reactivation reactor 301 and forming the abovementioned flux 81, on exiting this reactor, are then respectively mixed with the solid flux 6 and/or the gas flux 52 described above with respect to Figure 1. These by-products 8' are incorporated into the fumes to be denitrified 1 together with fluxes 6 and 52 and thus act as reagents in the denitrification reaction of the fumes 1, which takes place in the conduit that carries these fumes and in the dust collector 201 at the same time. This introduction of urea 8 into the reactor 301 is of greater interest when the temperature at which the dust collector 201 operates is less than 220-230°C.

Advantageously, urea 8 can be introduced into the reactivation reactor 301 in solid form. The continuous agitation that takes place in this reactor assists the decomposition of the urea and also prevents problems of deposits or structures that can be formed when a urea solution is pulverised in a conduit.

As indicated above, the flux of hot gases 51 must have a temperature of at least 220°C, preferably in the range of between 250° and 350°C. This flux of hot gases can be formed by dry water vapour, otherwise referred to as superheated steam, or hot air or even clean fumes, in particular extracted downstream of the dust collector 201. As a general rule, such clean fumes or even readily available low-pressure water vapour are not naturally at an appropriate temperature. Taking into account that the reactivation reactor 301 operates at approximately atmospheric pressure, even high-pressure vapour after pressure reduction and the inevitable associated thermal losses is not available at an appropriate temperature. This is why, as illustrated in Figure 2, an optional arrangement of the invention useful for these cases provides that a heater 401 is included upstream of the reactivation reactor 301 on the course of the flux of hot gases 51, and this flux of hot gases 51 is thus formed from a gaseous flux 50 made up of dry water vapour, air or clean fumes, for example, wherein the temperature of this gaseous flux 50 is increased to the required level of at least 220°C, preferably between 250° and 350°C, by the heater 401. The technology of this heater 401 is known per se and it is in the form of an electric battery, for example.

In extension of the preceding statements it will be noted that where the flux of hot gases 51 has a low flow rate in relation to that of the fumes 1, the energy consumption associated with

the use of the heater 401 remains low from the viewpoint of the advantages offered. Since the flux of hot gases 51 is determined so that the reactivation reactor 301 operates at a temperature of at least 220°C, there is some freedom with respect to the combination of flow rate/temperature of this flux of hot gases 51. For example, considering a flux of 100 000 Nm^3/h of fumes to be treated 1 with a catalyst recycling rate of 100 kg/h, a flux 51 of 250 kg/h of vapour or air heated to 300°C is sufficient to assure a temperature of more than 250°C for fluxes 6 and 52 exiting from the reactivation reactor 301. To form such a flux 51 of air heated to 300°C, the flux 50 of 250 kg/h of air is reheated with about 20 kW.

Whatever its implementation, the method according to the invention thus offers a simple economical and effective method of using an SCR denitrification catalyst in divided form and of permanently maintaining its activity by continuous regeneration. The use of the catalyst in divided form allows lower volumes of catalyst to be used insofar as the average journey of the molecules between the fumes and the catalyst is much more reduced than in a classic honeycomb- or plate-type catalyst. Moreover, as the catalyst is in divided form, the concentration of active catalytic material can be higher than for a classic supported catalyst, and this allows use at lower temperatures. Hence, while the SCR catalysts usually operate at temperatures in the range of between 220° and 300°C and sometimes more, the use of a more active catalyst in divided form allows the dust collector 201 to be utilised for the purposes of denitrification at lower temperatures typically in the range of between 140° and 200°C (it being understood that nothing opposes this dust collector 201 operating at a higher temperature) without, moreover, compromising the use of urea, since this is introduced into the reactivation reactor 301, which operates at a temperature that is sufficiently high to decompose the urea 8.

In addition, as explained above, the action of the flux of hot gases 51 allows a permanent regeneration of the catalyst in divided form. The addition 7 and the purging 7 allow the used catalyst to be replaced and evacuated and thus corresponds to what would in functional terms be a replacement of layers of non-divided catalyst, which requires a line stoppage in a configuration of the prior art. Another advantage of the invention is that in the case of a major poisoning of the used catalyst, this can be rapidly replaced in full, which is not the case when structured catalysts are used.

Furthermore, taking into account the above explanations, it is understood that the invention brings other advantages:

- the invention allows an assembly of simple and compact equipment to be used, wherein the need to pulverise a solution of urea or ammonia homogeneously disappears, and therefore a single reactor, i.e. the reactor 301, is used for reactivation of the catalyst and for decomposition of the urea;
- urea of industrial quality can be used, since the problem of structures in the conduit carrying the fumes is eliminated completely, and this is a significant economic advantage; and
- in contrast to the existing solutions that propose using urea in solution, the solution formation and pulverisation are avoided because of the invention; urea in solid form, typically in crystals, can even be used for the flux 8.

Various arrangements and variants of the method according to the invention are additionally conceivable. For example, optionally and not shown in the figures, a sulphur dioxide and hydrochloric acid analyser can be provided upstream of the dust collector 201.

Patentkrav

1. Fremgangsmåde til katalytisk denitrifikation af forbrændingsgasser, hvor:
- gasser, som skal behandles (1), og hvorfra der er udskilt støv, denitrificeres ved at blande dem med et denitrifikationsreagensmiddel (8') og med en denitrifikationskatalysator i delt form (6, 7) og derefter indføre dem i en støvudskiller (201),
- urea (8), en strøm af varme gasser (51), som har en temperatur på mindst 220°C, og en fraktion (5) af strømmen af faste stoffer (3), der opsamles af støvudskilleren (201), og som udgør mindst 95% deraf, indføres i en reaktiveringsreaktor (301), og
- biprodukter (8'), som stammer fra nedbrydningen af urea (8) i reaktiveringsreaktoren (301), og som danner denitrifikationsreagensmidlet (8'), genanvendes sammen med en strøm af faste stoffer (6), som kommer fra reaktiveringsreaktoren (301), mens de blandes med de gasser, som skal behandles (1), opstrøms for støvudskilleren (201).

2. Fremgangsmåde ifølge krav 1, hvor urea (8), som indføres i reaktiveringsreaktoren (301) er i fast form.

3. Fremgangsmåde ifølge et af kravene 1 eller 2, hvor temperaturen af strømmen af varme gasser (51) ligger mellem 250 og 350°C.

4. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor reaktiveringsreaktoren (301) fungerer ved en højere temperatur end temperaturen af de gasser, som skal behandles (1), og temperaturen af støvudskilleren (201).

5. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor strømmen af varme gasser (51) består af tør vanddamp.

6. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 4, hvor strømmen af varme gasser (51) består af luft.

7. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 4, hvor strømmen af varme gasser (51) består af røggasser, som udtrækkes opstrøms for

støvudskilleren (201).

8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor strømmen af varme gasser (51), inden den indføres i reaktiveringsreaktoren (301), kommer op på en temperatur på mindst 220°C ved hjælp af en varmeindretning (401).

9. Fremgangsmåde ifølge krav 8, hvor varmeindretningen (401) er et elektrisk batteri.

10. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor temperaturen af strømmen af faste stoffer (6), som stammer fra reaktiveringsreaktoren (301), mindst er 220°C.

11. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor hele eller en del af strømmen af faste stoffer (6), som kommer fra reaktiveringsreaktoren (301), føres tilbage til de gasser, som skal behandles (1), hvor de bæres af en gasstrøm (52), som kommer ud fra reaktiveringsreaktoren, hvor strømmen af faste stoffer (6) og gasstrømmen (52) blandes med de henholdsvis faste og gasholdige biprodukter (8'), som stammer fra nedbrydningen af urea (8) i reaktiveringsreaktoren (301).

12. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor støvudskilleren (201) er et posefilter.

13. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor reaktiveringsreaktoren (301) består af en dobbeltskruekontakt.

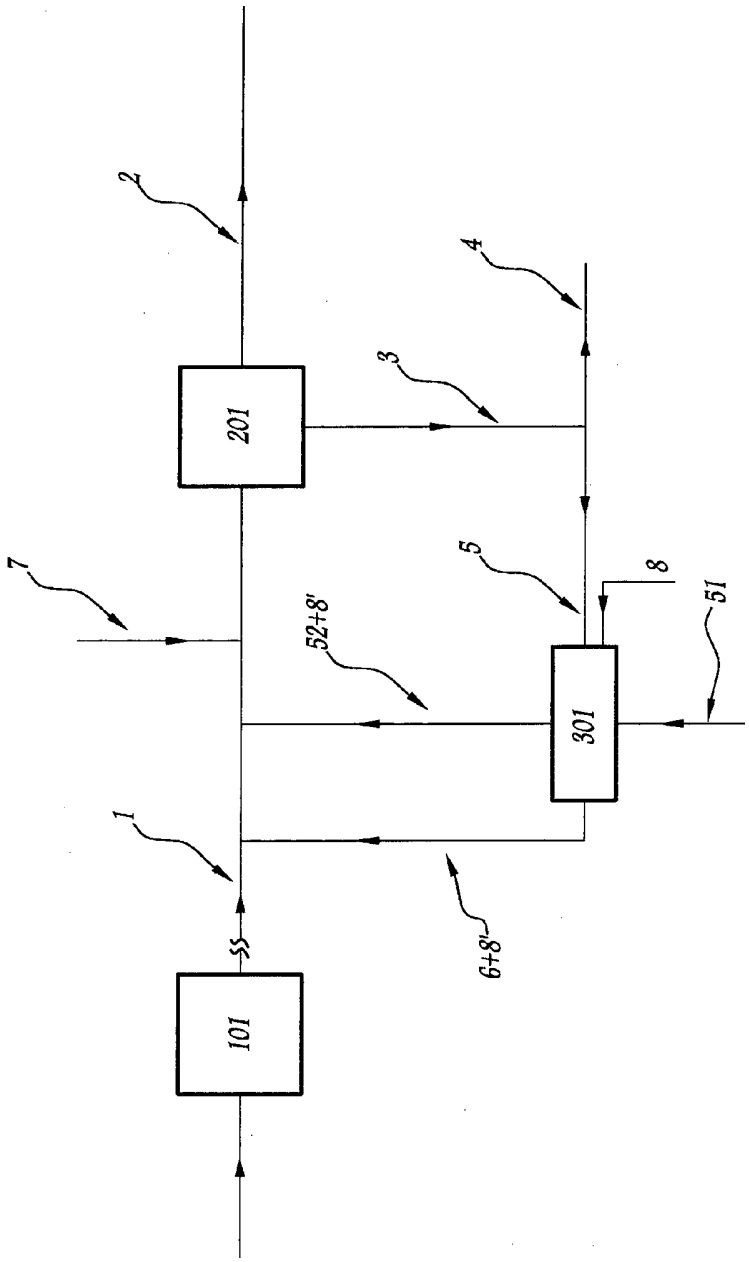

Fig. 1

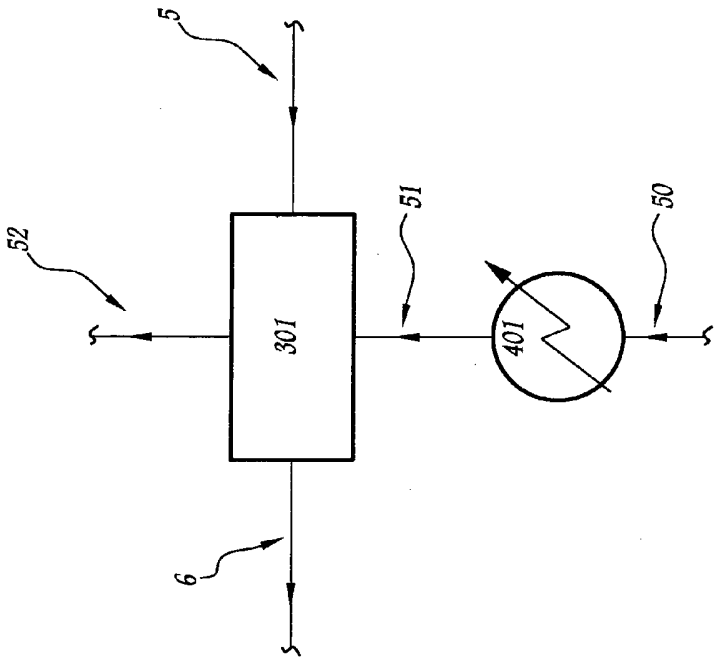

Fig.2