

METHOD FOR THE CATALYTIC REMOVAL OF CARBON DIOXIDE AND NO_x FROM WASTE GASES

Technical field

[0001] The present invention relates generally to a method for the catalytic removal of carbon dioxide and NO_x from waste gases.

Prior art

[0002] Discussions on climate change have clearly demonstrated to mankind that the resources available to us are limited and that the harmful substances produced by human activities have a major impact on the environment and lead to long-term climate change. After sulfur emissions took centre stage in the 1970s, carbon dioxide emissions have now become the key topic. Intensive research has been being carried out for some years now to find ways in which the production of this gas can be avoided where possible or else ways in which this gas can be removed from the atmosphere. With regard to the latter option various methods have been proposed for binding the carbon dioxide from the atmosphere to solids or liquids and then storing it. Such methods are known, for example, from WO2005108297A, KR2005028624 A and WO2004098740 A. It has also been attempted to reduce the carbon dioxide electrochemically, in which case the electric energy can be obtained from solar energy in an environmentally friendly manner, as described in JP4063115 A.

[0003] However, these methods have the drawback that they either merely relocate the problem or else are very energy intensive.

Object of the invention

[0004] An object of the present invention is to provide a method which in particular removes NO_x and carbon dioxide from waste gases.

General description of the invention

[0005] This object is achieved in accordance with the invention by a method for the catalytic removal of carbon dioxide and NO_x from waste gases in a

reactor charged with activated carbon catalyst. This method is characterised by the following steps:

- a) saturating the catalyst with water
- b) saturating or partially saturating the waste gases with water,
- c) introducing the waste gases into the reactor,
- d) catalytically converting NO_x into $\text{NO}_2^-/\text{NO}_3^-$ and, in parallel with this, catalytically converting CO_2 into carbon and O_2 on the same catalyst,
- e) washing out the activated carbon catalyst with water and discharging the carbon as a solid and $\text{NO}_2^-/\text{NO}_3^-$ dissolved in water.

[0006] One advantage of the method is that NO_x and CO_2 are separated from the gas phase in the form of NO_3^- and C and are present once the method is complete as a liquid (NO_3^- dissolved in water) or as a solid and can be used further.

[0007] The method makes it possible to treat waste gases from industrial plants, in particular combustion waste gases, which contain carbon dioxide and NO_x (e.g. from burning natural gas) and to remove both harmful substances at the same time and in parallel, i.e. in a single method, either completely or in part from the waste gases.

[0008] The catalyst should advantageously be saturated or partially saturated with NO_x before it is first used.

[0009] The expression "saturation or partial saturation of the catalyst with NO_x " is understood in the context of the present invention to mean that the waste gases which subsequently reach the activated carbon catalyst have sufficient exothermic conversion energy, which results from the conversion of NO_x into NO_3^- subsequently to commence CO_2 conversion. This corresponds, as emerged from our tests, to an order of magnitude of 0.1-0.3 kg of NO_x/m^3 of activated carbon catalyst.

[0010] The expression "saturation of the catalyst with water" is understood in the context of the present invention to mean that the catalyst is exposed to water or water vapour until water runs out of the reactor. This corresponds, as

emerged from the tests described here-below, to an order of magnitude of 250 to 550 kg of water/m³ of activated carbon catalyst.

[0011] In contrast to the method CN 101 564 640, here the method is performed with a "wet" catalyst. The catalyst is wet before the start of the reaction and is sprayed with water before and while the method is being performed and the resultant solids are washed off while the method is performed, i.e. without the method having to be broken off. In CN 101 564 640, on the other hand, the catalyst is operated "dry" and only after cleaning no longer functions effectively (step 5 of the method) is the method interrupted and the catalyst is sprayed with water in order to wash off the products adhering thereto, whereby a dilute, liquid acid with residues is obtained (step 6 of the method). Air heated to 100 °C to 120 °C is added to the reactor in step 7 of the method CN 101 564 640 in order to dry the catalyst before the reactor is brought back into operation. The gases to be treated in the method of CN 101 564 640 do also contain water vapour but only in a very low concentration (2-12 % by volume).

[0012] A significant difference between the methods accordingly consists in the fact that the method in CN 101 564 640 has to be regularly interrupted to recycle the catalyst and the catalyst has to be dried after recycling by spraying with water. These method conditions obviously do not allow CO₂ to be converted into carbon in solid form, since after the catalyst has been washed off a dilute, liquid acid solution is obtained, which is purified on a membrane filter. Were carbon present as a solid in this solution, it would have been conspicuous, since the solution would have been black and the solid would have been obviously retained on the membrane filter.

[0013] In the method at least 30 % by volume of the CO₂ contained in the waste gases is converted, preferably at least 50 % by volume, particularly preferably at least 70 % by volume and in particular at least 90 % by volume. Furthermore, at least 20 % by volume of the NO_x content may be converted, preferably at least 50 % by volume, particularly preferably at least 70 % by volume and in particular at least 90 % by volume may be degraded.

[0014] The term "NO_x" is understood in the context of the present invention to mean nitrogen oxides or nitrous gases as collective terms for the gaseous oxides of nitrogen. They are conventionally abbreviated to NO_x, since the many oxidation states of nitrogen result in a plurality of nitrogen-oxygen compounds.

[0015] The expression "saturation/partial saturation of the waste gases with water" is understood in the context of the present invention to mean that waste gases are saturated/partially saturated with water by means for example of a quencher/washer. The waste gases are accordingly preferably saturated with water vapour to their dew point. The waste gases should, however, exhibit a relative humidity of at least 50 %, preferably 60 %, particularly preferably 80 %.

[0016] According to a preferred configuration of the invention, the waste gases are passed prior to step b) into a prereactor containing a second catalyst and then saturated or partially saturated with water in step b).

[0017] According to a further preferred configuration of the invention, the waste gases are passed after step b) into a prereactor containing a second catalyst and then introduced into the reactor in step c).

[0018] The second catalyst in the prereactor is preferably used in the dry state, i.e. no water is fed to it and care is taken to ensure that no condensed water forms during the reaction. In cases where the waste gases are only introduced into the prereactor downstream of the quencher, care must be taken to ensure that the temperature of the gases does not fall below their dew point during their residence time in the prereactor.

[0019] The expression "washing out the catalyst with water" is understood in the context of the present invention to mean feeding water into the upper part of the reactor, the water then flowing through the reactor countercurrently to the gases. Alternatively, the water may also be added cocurrently to the gases.

[0020] After the reaction the carbon is discharged from the reactor as a solid by washing out the catalyst. It may be present both as C and as C compounds. The expression C compounds is understood in context of the present invention to mean C(NO) complexes and other compounds between C, N and O. The term "carbon" is accordingly understood in the context of the present invention

to mean both carbon (C) and C compounds such as C(NO) complexes and other compounds between C, N and O.

[0021] Waste gases are preferably treated which contain between 100 and 1500 ppm of NO_x and between 0.3 and 15 % by volume of CO₂. Of course it is also possible to treat waste gases in which the ratio of the two harmful substances lies outside this range. In such a case it may happen, however, that the harmful substance which lies above the aforementioned limit is not completely removed from the waste gases, but is removed only in part.

[0022] According to a preferred embodiment of the invention, however, C_xH_y may also be removed from the waste gases, as additional harmful substances, at the same time as the CO₂ and NO_x, if C_xH_y is contained in the waste gases.

[0023] The term "C_xH_y" is understood in the context of the present invention to mean compounds which consist only of carbon and hydrogen, such as for example straight-chain or branched alkanes, cycloalkanes, straight-chain or branched alkenes, straight-chain or branched alkynes and aromatics.

[0024] The content of C_xH_y in the gases to be treated is preferably between 0 and 700 ppm of C_xH_y.

[0025] Below the above-stated limits there is marginal or no influence on the NO_x – CO₂ reaction. In the case where the additional harmful substances are above the above-stated limit, they are not removed completely from the waste gases, but rather only in part.

[0026] The inlet temperatures of the waste gases in the reactor preferably lie between ambient temperature and 150 °C. Higher temperatures could permanently damage the catalyst.

[0027] The oxygen content of the waste gases is not actually critical, but it should ideally be at least 5 % by volume, preferably at least 8 % by volume, particularly preferably at least 10 % by volume, and in particular at least 12 % by volume.

[0028] The waste gases may be saturated quite easily with water by quenching or with a washer or a similar method.

[0029] The waste gases should naturally contain as little solids, dust and the like as possible in order to prevent poisoning and/or clogging of the catalyst. This dedusting of the waste gases is carried out by conventional filtering before the waste gases are then fed into the quencher or the washer.

[0030] The purifying factor of CO_2 is influenced by washing-out of the activated carbon bed. For example, in tests carried out with identical waste gas inlet parameters, CO_2 separation of roughly 50 % is established in the case of washing out of the catalyst with water. In contrast, washing out the catalyst with a base, e.g. 5-30 % NaOH solution, may result in CO_2 separation of over 90 %.

[0031] The term "base" is understood in the context of the present invention to mean an aqueous solution of $\text{M}^{n+}(\text{OH}^-)_n$, wherein M is selected from the groups consisting of alkali metals and alkaline earth metals and wherein n is 1, 2 or 3. An aqueous NaOH solution is preferably used.

[0032] The concentration of the base is ideally of an order of magnitude of 5-30 % by weight in water. The introduction of very fine water droplets with or without $\text{M}^{n+}(\text{OH}^-)_n$ into the flue gas results in a lowering of the temperature and inter alia an increase in the water content with optionally a corresponding $\text{M}^{n+}(\text{OH}^-)_n$ content up to a relative humidity of a maximum of 100 % in the flue gas.

[0033] Washing out of the activated carbon bed may also be positively influenced by mixing ionic, non-ionic, amphoteric or anionic surfactants into the water or the base which is used to wash off the catalyst.

[0034] The term "surfactants" is understood in the context of the present invention to mean substances which reduce the surface tension of a liquid or the interfacial tension between two phases and allow or assist in the formation of dispersions or act as solubilisers.

Brief description of the figures

[0035] Further details and advantages of the invention can be taken from the following detailed description of a possible embodiment of the invention on the basis of accompanying Figures 1-10. In the drawings:

[0036] Fig. 1 is a schematic view of the first test arrangement;

[0037] Fig. 2 is a graph showing the values measured in the first test arrangement of the CO_2 , NO_x and O_2 contents of the waste gases at the inlet or outlet of the reactor, the catalyst having been washed out with NaOH ;

[0038] Fig. 3 is a graph showing the values measured in the first test arrangement of the CO_2 , NO_x , C_xH_y and O_2 contents of the waste gases at the inlet or outlet of the reactor, the catalyst having been washed out with NaOH ;

[0039] Fig. 4 is a graph showing the values measured in the first test arrangement of the CO_2 , NO_x and O_2 contents of the waste gases at the inlet or outlet of the reactor, the catalyst having been washed out with water;

[0040] Fig. 5 is a graph showing the values measured in the first test arrangement of the CO_2 , NO_x , C_xH_y and O_2 contents of the waste gases at the inlet or outlet of the reactor, the catalyst having been washed out with water;

[0041] Fig. 5a is a graph showing the mean values of several experiments measured in the first test arrangement of the CO_2 and NO_x contents of the waste gases at the inlet or outlet of the reactor, the catalyst having been washed out with NaOH ;

[0042] Fig. 6 is a schematic view of the second test arrangement;

[0043] Fig. 7 is a graph showing the values measured in the second test arrangement of the CO_2 , NO_x and O_2 contents of the waste gases at the inlet of the prereactor or the outlet of the reactor, the catalyst in the second reactor having been washed out with NaOH ;

[0044] Fig. 8 is a graph showing the values measured in the second test arrangement of the CO_2 , NO_x , C_xH_y and O_2 contents of the waste gases at the inlet of the prereactor or the outlet of the reactor, the catalyst in the second reactor having been washed out with NaOH ;

[0045] Fig. 9 is a graph showing the values measured in the second test arrangement of the CO_2 , NO_x and O_2 as well as C_xH_y contents of the waste gases at the inlet of the prereactor or the outlet of the reactor, the catalyst in the second reactor having been washed out with water;

[0046] Fig. 10 is a graph showing the values measured in the second test arrangement of the CO_2 , NO_x , C_xH_y and O_2 contents of the waste gases at the inlet of the prereactor or the outlet of the reactor, the catalyst in the second reactor having been washed out with water.

[0047] Fig. 11 is a graph showing the values measured in the second test arrangement of the CO_2 and NO_x contents of the waste gases at the inlet of the prereactor or the outlet of the prereactor.

Description of an embodiment of the invention

[0048] Test arrangement 1

[0049] The test arrangement 1 shown in Figure 1 in order to illustrate the invention comprises a test reactor 110, to the lower part 112 of which a test gas is supplied and into the upper part 114 of which water or a base is sprayed.

[0050] The test waste gas originates from natural gas combustion. The waste gas is dedusted with the assistance of an electrostatic dust filter (not shown) and passes via a fan 116 at approx. 300°C into a venturi quencher 118. The holding tank 122, incorporated into the mist collector 120, of the venturi quencher 118 was filled with water or a 15 % NaOH solution. The waste gases are cooled and saturated to saturation temperature in the venturi quencher 118.

[0051] A first measuring device 124 analyses the composition (NO_x content, CO_2 content, as well as O_2 content and in some tests C_xH_y content), the temperature, the flow volume and the flow rate of the test waste gas.

[0052] The test gas then enters the reactor 110.

[0053] The reactor 110 was charged with an activated carbon catalyst 130.

[0054] The test gas flows through the reactor 110 and the catalyst 130 arranged therein from bottom to top and is examined once discharged from the test reactor 110 in a second measuring device 132 for the same parameters as in the first measuring device 124, i.e. composition (NO_x content, CO_2 content, O_2 content and in some tests C_xH_y content), the temperature, the flow volume and the flow rate, and is then released into the atmosphere through a stack 134.

[0055] On the activated carbon catalyst 130, which is not additionally impregnated with metals, the NO_x , CO_2 and optionally C_xH_y is converted catalytically with ongoing addition of a base or water (washing off of the activated carbon bed).

[0056] The water or base required in the reactor 110 is fed from a storage container 136 by means of a pump 138 via a measuring device 140, where the flow rate is measured, into the upper part 114 of the reactor 110, where the water/base flows through the activated carbon catalyst 130 countercurrently to the test gas.

[0057] The water required for the quencher 118 comes directly from the water supply 142 and is circulated. If the quencher 118 is operated with a base, the base is delivered from the storage container 144 by means of a pump 146 into the holding tank 122 of the mist collector 120 of the quencher 118. The water located in the holding tank 122 of the mist collector 120 or the base is delivered by means of a pump 148 to the spray head 150 of the quencher 118.

[0058] The reactor 110 comprises a packing material 152, which is located under the activated carbon catalyst 130. This packing material 152 serves to distribute the gas and should consist of an inert material such as for example Al_2O_3 . This packing material ensures that the gases are distributed over the entire catalyst.

[0059] The NO_3^- and carbon or carbon compounds formed on the catalyst 130 by the reactions are rinsed off the catalyst 130 by spraying with water or a base, as a function of the volume of the activated carbon catalyst 130 and the NO_x and CO_2 concentrations and additionally, if present, C_xH_y concentrations, countercurrently to the gas.

[0060] In the case of the pilot system, the activated carbon catalyst 130 is continuously rinsed with a water/base quantity of 5-20 l/min. The quantity of water/base which is used up depends on the concentrations of harmful substances. If insufficient is washed off, given the concentrations of harmful substances arising, the pores of the activated carbon catalyst 130 may clog and the entire reactions may come to a standstill.

[0061] The process water is collected in a container 154 in the lower part 112 of the reactor 110 optionally together with the base and the carbon or carbon compounds produced during the process and suspended in said process water, and the pH is determined by means of a measuring device 156. The liquid is then pumped off by a pump 158 and the flow volume is ascertained using a further measuring device 160.

[0062] In the system described the NO_x of the waste gases is catalytically converted on moist activated carbon catalyst particles to form NO_3^- , and carbon dioxide is cleaved at the same time or in parallel to form carbon and oxygen or, if it is present, C_xH_y is converted into carbon and H_2 . However, some of the carbon may also be present as carbon compounds.

[0063] The tests were carried out under the following conditions: raw gas volume flow: 150 m^3/h min. up to max. 250 m^3/h ,

- NO_x content of the flue gases between 100 ppm and 1000 ppm
- CO_2 content of the flue gases between 0 % by volume and 6 % by volume
- Gas temperature on entry into reactor between 15 and 80 °C.
- O_2 content of flue gases between 10-18 % by volume
- Water saturation and cooling of waste gases in the reactor by quenching with water or 5-30 % NaOH solution
- Waste gas temperature (outlet): min. 30 °C to max. 45 °C
- Dew-point temperature, saturated.
- Tested activated carbon catalysts were provided by NORIT Nederland B.V. of Postbus 105 NL-3800 AC Amersfoort under the names Norit_PK1-3, Norit_PK_2-4 and Norit_PK_3-5.

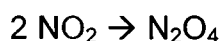
[0064] These activated carbon catalysts are an activated carbon granulate with a particle size of 1-3 mm, 2-4 mm or 3-5 mm, which were produced by steam activation. The following general properties are guaranteed by the manufacturer: iodine number 800; methylene blue adsorption 11 g/100 g; inner surface area (BET) 875 m^2/g ; bulk density 260 kg/m^3 ; density after back-wash

230 kg/m³; uniformity factor 1.3 – ash content 7 % by weight; pH alkaline; moisture (packed) 2 % by weight.

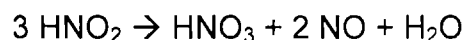
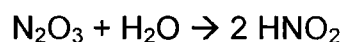
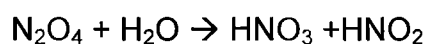
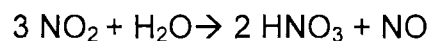
[0065] In the tests flue gas analysis devices of the Testo brand were used. The devices are of a recent generation (year of manufacture 2009) and were checked and calibrated by the manufacturer before the tests were carried out.

[0066] NO_x conversion on the catalyst surface proceeds in formal terms, in accordance with current knowledge, according to the following empirical formulae:

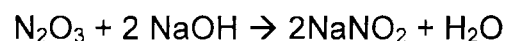
Oxidation



Production of nitric acid through addition of water



Neutralisation by a base



[0067] If present: the C_xH_y reaction proceeds after C and H₂ on the catalyst surface. The C may here also be temporarily absorbed onto the activated carbon and/or C compounds and/or other compounds.

[0068] Without wanting to be committed to a particular theory, it is assumed that:

- NO_x and O₂ migrate to the active centres of the catalyst. NO_x is here partially oxidised to NO₂ as well as N₂O₃ and N₂O₄.

- NO_2 then migrates out from the active centres of the catalyst and reacts with NaOH, if present, on the aqueous shell around the catalyst core to yield NO_2^- , NO_3^- and H_2O .
- The CO_2 molecule is also transported into the pores of the catalyst core, where it is separated by the addition of energies of formation or adsorbed on C compounds. The NaOH solution, if present, which is located in the aqueous shell around the core adsorbs the C portion of CO_2 and O_2 through high surface tensions (specific surface area). 'Carbon compounds' are likewise produced
- The C part located on a carbon compound is present within the water or with the base as a suspension.
- The formed C and/or the formed carbon compounds are discharged in a suspension with water or the base from the catalyst by washing with water or base. The formed C and/or the formed carbon compounds precipitate after a short period of time.

[0069] Softened or demineralised water, with or without the addition of base (e.g. NaOH), was used to wash the catalyst.

[0070] It is assumed, without wanting to be committed to a particular theory, that the CO_2 is adsorbed using the exothermic energy which is produced by the oxidation/neutralisation of NO_x to form NO_3^- and/or NO_2^- .

[0071] In the tests performed, the reactor is made of glass fibre reinforced plastics material, has a volume of approximately 2 m^3 and is filled with 2 m^3 of an activated carbon catalyst of the Norit_PK_2-4 type.

[0072] In a first phase the test system was run at a throughput of approx. $220 \text{ m}^3/\text{h}$ with the addition of between 500 and 800 ppm of NO_x . Overall, the reactor was charged with approximately 8 kg of NO_x (approximately 4 of NO_x/m^3 of activated carbon catalyst (Fig. 2).

[0073] According to this test, the waste gases were cooled from approx. 300°C to approx. 60°C in a quencher, which was charged with a 15 % NaOH base solution. In this instance, the waste gas was saturated, i.e. the waste gas

had a relative humidity of roughly 100 %. According to the tests (see Figs. 2 and 3) the ongoing addition of washing water consisting of a 5-30 % NaOH solution onto the activated carbon catalyst proceeded at up to 10 l/min. The NO_x and CO₂ contents of the waste gases were measured in each case at the inlet and at the outlet of the reactor, as illustrated in Fig. 1. The measurements were taken every 60 seconds and were shown in graphs in Figures 2 and 3. The measurements shown in Figure 2 proceeded after saturation of the catalyst with NO_x. The CO₂ concentration was between 4.8 % by volume and 5.6 % by volume. In the tests (see Fig. 3) it was established that after approx. 5 minutes purification of CO₂ was proceeding, the purifying values of CO₂ then rising continuously up to 99.5 %, irrespective of the increase or decrease in CO₂ values in the waste gas. The test was carried out continuously over approximately 60 minutes. Over this entire period the treated waste gases displayed a reduction of NO_x of approx. 30-40 %, as can be seen from Fig. 2. In the tests as illustrated in Fig. 3, C_xH_y was also contained in the waste gas and was 100 % separated.

[0074] In these tests (cf. Fig. 5a) it was found that the reduction of the CO₂ concentration, i.e. the breakdown of CO₂ in the reactor, is in a linear relation of the formula $y = -0.0314x + 10.113$ whereby the coefficient of determination R² is 0.9442 to the reduction of the NO_x concentration i.e. the breakdown of NO_x in the reactor, both values being expressed in % volume.

[0075] In these tests an increase in the O₂ content between input measurements and output measures was identified. The increase in O₂ content is largely parallel to the reduction in the CO₂ content.

[0076] The washing water discharged from the reactor was entirely deep black in colour in all the tests.

[0077] Both neutralising salts and carbon/carbon compounds could be detected in the washing water. Investigations by an independent laboratory have established that the carbon/carbon compounds are a different carbon from that in the activated carbon catalyst. Test with radioactively marked CO₂ test

gas showed that the carbon contained in the wash water originates from the CO₂ and does not come from the catalyst.

[0078] The neutralising salts and the carbon/carbon compounds settled out after a short period of time.

[0079] For the series of tests illustrated in Figures 4 and 5 water was used, instead of NaOH, to saturate the waste gases and to wash out the catalyst. Here too it has been established that NO_x and CO₂ (Fig. 4) or NO_x, CO₂ and C_xH_y (Fig. 5) were removed from the waste gases. It has also been established that CO₂ conversion was not as efficient in the instances where water was used instead of base. In these tests too an increase in the O₂ content between input measurements and output measures was identified.

[0080] The four test results shown in the graphs prove that both NO_x and CO₂ or C_xH_y were degraded. The tests have likewise shown that the O₂ content increases.

[0081] The tests (see Fig. 3) which were carried out in the context of this invention have demonstrated that a certain degree of saturation of the activated carbon catalyst with NO_x must be present before CO₂ separation starts.

[0082] Test series 2

[0083] The second test arrangement shown in Figure 6 in order to illustrate the invention differs from the first test arrangement in that the test gas is firstly charged into a prereactor 126 by the quencher 118, said prereactor being charged with a catalyst 128 and then passed into the reactor 110.

[0084] This catalyst 128 of the prereactor 126 is an activated carbon catalyst from NORIT Nederland B.V. of Postbus 105 NL-3800 AC Amersfoort, made available under the name Norit_RST-3. This activated carbon catalyst is an extruded activated carbon granulate with a particle size of 3 mm. The following general properties are guaranteed by the manufacturer: butane adsorption at p/p₀=0.1: 24 g/100 g; inner surface area (BET) 1200 m²/g; bulk density 400 kg/m³; hardness (ball-pan hardness): 98, moisture (packed) 5 % by weight, decomposition time max.: 15 min, min.: 8 min.

[0085] The main difference between the two test arrangements consists, as stated, in the fact that in the second test arrangement a prereactor 126 is used. This prereactor 126 is exposed to the waste gases from the quencher 118 without the addition of water or base. The catalyst 128 in the prereactor 126 accordingly operates in principle "dry" while the catalyst in the first reactor 110 operates "wet". The catalyst 128 in the prereactor 126 remains "dry"; since the temperature of the waste gases varies only insignificantly in this prereactor, there is also no or only insignificant condensation of the water vapour contained in the waste gases.

[0086] However, it is also possible and perhaps simpler to cool the test gas down (with a heat exchanger for example) and then to convey it into the prereactor 126. The gas is then conveyed into the quencher 118 and then from there into the reactor 110.

[0087] The results shown in Figures 7 and 8 originate from tests in which only water was used in the quencher and in each case a 5 % NaOH solution was used in the reactor.

[0088] The results shown in Figures 9 and 10 originate from tests in which in each case only water was used in the quencher and in the reactor.

[0089] In the tests from Figures 7 and 9 no C_xH_y was contained in the waste gases. In Figures 8 and 10 waste gases were used which contained between 10 and 300 ppm of C_xH_y .

[0090] As is apparent from Figures 7-10, NO_x underwent up to 100 % degradation. Only in the tests shown in Figure 10 did a few ppm of NO_x remain in the waste gases. In all the other tests the NO_x in the treated waste gases was equal to 0.

[0091] The tests from Figure 8 show that CO_2 and C_xH_y were also fully degraded. It is apparent from Figure 7 that CO_2 falls continuously after a few minutes and tends towards zero towards the end of the test.

[0092] The results of Figures 9 and 10 show that, when only water is used, the degradation of NO_x and of C_xH_y is virtually complete, whereas the degradation of CO_2 proceeds to just 20-30 %.

[0093] The results of Figure 11 show that, in the prereactor 126 that operates under dry conditions, NO_x is completely converted whereas CO_2 is not converted at all. This prereactor corresponds to the reactor of CN 101 564 640 and it was found that on the activated carbon catalyst in the prereactor operated under dry conditions no CO_2 was broken down. It is therefore obvious that in the method as disclosed in CN 101 564 640 no CO_2 is broken down either. A break down of CO_2 happens, as was shown in the tests, only on a "wet" catalyst, i.e. on a catalyst which has been soaked in water or in a watery solution.

[0094] The reaction which takes place on a "wet" catalyst is hence a reaction which differs from the reaction which takes place on the catalyst of CN 101 564 640 since that catalyst operates under different conditions.

[0095] The comparison between the tests with one reactor and the tests with two reactors shows that degradation of the harmful substances is virtually complete when using two reactors and when using a base to wash off the activated carbon catalyst in the second reactor. In the other configurations the contents of harmful substances may be markedly reduced.

[0096] From tests in a sewage sludge incinerator with typical flue gas values of approx. 10-12 percent CO_2 , approx. 8 to 10 percent O_2 and approx. 50 to 200 ppm NO_x , it was possible to confirm the following characteristics for conversion of NO_x and with parallel conversion of CO_2 .

[0097] For the above-stated flue gas composition it was established that at less than roughly 50 ppm NO_x , CO_2 separation drops and above this value CO_2 separation rises. At the same time, it was confirmed that at these concentrations roughly 100 percent of the NO_x input is converted and NO_x output is thus virtually zero. At much higher values NO_x is no longer fully converted and the reactor output NO_x concentration increases. This top

threshold value from which NO_x was no longer fully converted (being required for CO_2 separation) was approx. 75 ppm in the above-stated test.

[0098] At extremely high NO_x concentrations proportional to the input concentration of CO_2 , CO_2 separation comes to a complete standstill or is severely reduced.

[0099] At such NO_x concentration values it has been demonstrated that it is advisable to subject the waste gases to pretreatment in a reactor with a dry activated carbon.

[00100] The above-stated tests were confirmed by an international independent laboratory. A carbon balance confirmed the conversion of CO_2 into C and O_2 .

Key to drawings:

110	Reactor	136	Storage container
112	Lower part	138	Pump
114	Upper part	140	Measuring device
116	Fan	142	Water supply
118	Quencher	144	Storage container
120	Mist collector	146	Pump
122	Holding tank	148	Pump
124	Measuring device	150	Spray head
126	Prereactor	152	Packing material
128	Prereactor catalyst	154	Container
130	Reactor catalyst	156	Measuring device
132	Measuring device	158	Pump
134	Stack	160	Measuring device

Claims

1. A method for the catalytic removal of carbon dioxide and NO_x from waste gases in a reactor charged with activated carbon catalyst, said method being characterised by the following steps:
 - a. saturating the catalyst with water
 - b. saturating or partially saturating the waste gases with water,
 - c. introducing the waste gases into the reactor,
 - d. catalytically converting NO_x into $\text{NO}_2^-/\text{NO}_3^-$ and, in parallel with this, catalytically converting CO_2 into carbon and O_2 on the same catalyst,
 - e. washing out the activated carbon catalyst with water and discharging the carbon as a solid and $\text{NO}_2^-/\text{NO}_3^-$ dissolved in water.
2. A method according to claim 1, characterised in that saturation or partial saturation of the activated carbon catalyst with NO_x by 0.1 to 0.3 kg NO_x/m^3 of activated carbon catalyst proceeds before the waste gases are conveyed into the reactor.
3. A method according to any one of the preceding claims, characterised in that C_xH_y is removed from the waste gases at the same time as the CO_2 and NO_x .
4. A method according to any one of claims 1-3, characterised in that the activated carbon catalyst is an activated carbon granulate with a particle size of 1-3 mm, 2-4 mm or 3-5 mm produced by steam activation and having the following general properties: iodine number 800; methylene blue adsorption 11 g/100 g; inner surface area (BET) 875 m^2/g ; bulk density 260 kg/m^3 ; density after back-wash 230 kg/m^3 ; uniformity factor 1.3 – ash content 7 % by weight; pH alkaline; moisture (packed) 2 % by weight.
5. A method according to any one of the preceding claims, characterised in that the waste gases are passed prior to step b) into a prereactor containing a second catalyst and then saturated or partially saturated with water in step b).

6. A method according to claim 7, characterised in that the second catalyst is an extruded activated carbon granulate with a particle size of 3 mm with the following general properties: butane absorption at $p/p_0=0.1$: 24 g/100 g; inner surface area (BET) 1200 m²/g; bulk density 400 kg/m³; hardness (ball-pan hardness): 98, moisture (packed) 5 % by weight, decomposition time max.: 15 min, min.: 8 min.
7. A method according to any one of claims 1-6, characterised in that the waste gases are passed after step b) into a prereactor containing a second catalyst and then introduced into the reactor in step c).
8. A method according to claim 5, 6 or 7, characterised in that the second catalyst is used in the dry state in the prereactor.
9. A method according to any one of the preceding claims, characterised in that there are added to the water in steps a), b) and/or e):
 - a base $M^{n+}(OH^-)_n$, M being selected from the groups consisting of alkali metals and alkaline earth metals and n being 1, 2 or 3 and/or,
 - an ionic, anionic, amphoteric or nonionic surfactant or mixtures thereof.
10. A method according to any one of the preceding claims, characterised in that the waste gases contain between 100 and 1500 ppm of NO_x and between 0.3 and 15 % by volume of CO₂.
11. A method according to any one of claims 3 to 10, characterised in that the waste gases contain between 0 and 700 ppm of C_xH_y.
12. A method according to any one of the preceding claims, characterised in that the inlet temperature of the waste gases in the reactor lies between ambient temperature and 150 °C.
13. A method according to any one of the preceding claims, characterised in that the oxygen content of the waste gases is at least 5 % by volume, preferably at least 8 % by volume, particularly preferably at least 10 % by volume, and in particular at least 12 % by volume.
14. A method according to any one of the preceding claims, characterised in that O₂ is discharged during the method.