

Reduction of NO2 emissions in process gases

TECHNICAL FIELD

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The invention relates to a process for reduction of NO2 emissions from a process gas denitrification and desulfurization plant, to provide a cleaned process gas for a carbon capture process or emission to the atmosphere as a non-opaque gas.

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BACKGROUND

Due to climate change concerns, there is an increasing interest in capturing CO2 in process gases from processes involving oxidation of carbonaceous feed stocks, e.g., cement production, power plants firing biomass or fossil fuels, metal production, carbon black production and refinery operations such as fluid catalytic cracking (FCC). The CO2 concentration in these process gases will typically be in the concentration range 5-30 vol% and thus a process plant to capture the CO2 and concentrate the CO2 into an almost pure CO2 stream is required to be able to use the CO2 for sequestration, enhanced oil recovery or utilization for food/beverages or production of chemicals. The most mature technologies for CO2 capture are the so-called regenerative amine-based or hot potassium carbonate (HPC) processes. Common for these two processes is that the (acidic) CO2 gas is absorbed into an alkaline solution in an absorption process, typically an irrigated packed bed absorption tower. The CO2 loaded absorption liquid leaving the absorption process is then transferred to a

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distillation/stripping process in which the CO₂ is released as an almost pure CO₂ stream and the CO₂-depleted absorption solution is recovered and returned to the CO₂ absorption process. The CO₂ desorption typically take place
5 in a stripping column, where heat is supplied in a reboiler in the bottom of the column and the overhead from the column is cooled and partly condensed; the condensate, which is primarily water, is returned and only the pure CO₂ leaves the column. The heat supplied is typically low-
10 pressure steam but can be any stream with high energy density and temperatures low enough to protect the absorption liquid from thermal degradation. This could be heat transfer oil, process gas or hot air.

The absorption solution is not CO₂ specific, which means
15 that other acidic compounds such as SO₂ and NO₂ also are absorbed into the solution. These two compounds will react almost irreversibly with the absorption solution and form so-called heat-stable salts, which will degrade the absorption solution, resulting in lower CO₂ capture
20 efficiency and/or increased energy consumption in the distillation/stripping process.

To maintain high efficiency of the CO₂ capture process, it will then be necessary to either take out a fraction of the degraded absorption solution and replace it with fresh
25 absorption solution or carry out a chemical regeneration of the absorbent solution. Both solutions will increase the operating cost of the carbon capture process and provide a waste stream, which need to be taken care of.

It is therefore desirable to minimize the concentration of
30 SO₂ and NO₂ in the process gas before it enters the carbon capture plant.

The most common means for removal of SO₂ from process gases is by absorbing and reacting the (acidic) SO₂ with an alkaline reactant, such as aqueous solutions of e.g. NaOH, NH₃, Mg(OH)₂ and CaCO₃. These processes typically take
5 place in the 40-60 °C range. These processes have been used for decades and are characterized by being effective and relatively cheap and simple. The drawbacks of these processes are that a chemical needs to be supplied and a (waste-) product needs to be removed, requiring additional
10 logistics and storage facilities. Low local availability of chemicals or no use of the product can significantly increase the operating expenses of this solution. Another way to remove SO₂ from a process gas is to catalytically oxidize the SO₂ to SO₃ and, in combination
15 with water, condense sulfuric acid which can be sold as a valuable chemical. This process is often referred to as a wet gas sulfuric acid technology, abbreviated WSA. It requires that H₂O and O₂ is present in the process gas, which is very often the case. However, they could be added
20 as O₂ or air and liquid water or steam, should they not be present in sufficient amounts.

NO_x is commonly removed by the so-called selective catalytic reduction (SCR) process, in which NH₃ selectively
25 reacts with NO_x to form N₂ and H₂O. The process will have an inevitable small slip of NO, NO₂ and/or NH₃ and if oxidation of SO₂ is also included in the process this step will increase the NO₂ concentration as the step of SO₂ oxidation also oxidizes NO and NH₃. Due to the
30 deterioration of the amine capture solution by the NO₂, a step of NO₂ removal is desired.

KR20220075898 discloses a process in which CO and NO₂ are reacted upstream an SCR process. This process will not avoid the minor slip of NO₂ from the SCR process.

5 SUMMARY

A process is therefore provided for reduction of NO, NO₂ and optionally SO₂ concentrations in a process gas, said process comprising subjecting said process gas to:

- 10 a. an SCR step, catalytically converting NO and NO₂ in said process gas to N₂ and H₂O by reaction with a first NH₃ stream,
- b. a combined NO₂ reduction and CO oxidation step in the presence of a sulfur resistant dual-purpose catalyst, thereby catalytically reducing NO₂ to
- 15 NO in said process gas by reaction with CO and oxidizing CO to CO₂ by reaction with O₂,
- characterized in that the NO₂/NO_x molar ratio in the process gas, after passing through steps a and b, is lower
- 20 than 0.05, preferably lower than 0.02 and most preferably lower than 0.01.

Further details of the technology are presented in the following description, examples, and patent claims.

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LEGENDS

Figure 1 illustrates the overall process of the invention

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Figure 2 shows the efficiencies of the sulfur resistant dual-purpose catalyst from Example 2.

DETAILED DISCLOSURE

Conversion of SO₂ and NO_x (NO₂+NO) in process gases is well
5 known in the industry and there are numerous mature
technologies to accomplish such gas phase conversions, each
technology having inherent advantages and disadvantages.

The present invention presents a novel layout of the
10 combination of the SCR reaction and WSA process and
introduction of a new sulfur resistant dual-purpose
catalyst system to reduce NO₂ emissions down to sub-ppm
concentrations, while also eliminating CO emissions. The
new layout is very suitable for process gases containing
15 reducing species, such as CO, which is both used as a
reactant and later oxidized to CO₂. Such process gases
could e.g. be from a Fluid Catalytic Cracking process, a
Carbon black producing process, or a metallurgical process
such as a steel mill.

20 The present invention provides a process for reduction of
NO, NO₂ and optionally SO₂ concentrations in a process gas.

The process gas - prior to step (a) of the process -
25 typically comprises 10-5,000 ppmv CO and 1-1,000 ppmv
NO+NO₂, as some NO may be converted to problematic NO₂.

The process gas typically comprises up to 30%, preferably
5-20% CO₂.

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Suitably, the process gas - prior to step (a) - also comprises an excess of CO with respect to NO₂, i.e., the CO/NO₂ molar ratio is greater than 1.

5 The process gas also has one or more of the following:

- an O₂ concentration in the range 2-20 vol%,
- an H₂O concentration in the range 2-40 vol% and
- an SO₂ concentration in the range 100-10,000 ppmv.

10 The remainder of the process gas is suitably N₂, Ar and minor impurities.

The process gas containing SO₂, NO_x and a reducing species may be either heated or cooled to a temperature in the optimal 250-450 °C range. Before or after this temperature regulation, the process gas can have passed through a particulate filter (e.g., bag filter, ceramic candle filters or electrostatic precipitator) and/or an process gas blower to clean the gas from particulate matter (dust) and to provide the necessary gas pressure to pass the process gas through the process plant. Therefore, the process gas is suitably preconditioned by one or more preconditioning steps selected from:

- removal of particulate matter e.g., in a bag house filter, electrostatic precipitator or candle filter,
- adjustment of temperature by heating or cooling e.g. by means of heat exchangers, burners, heaters, and
- adjustment of pressure e.g., by means of a compressor or blower (e.g. to about atmospheric pressure).

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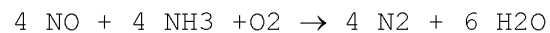
In the broadest aspect, the process comprises subjecting said process gas to:

a. an SCR step, followed by

b. a combined NO₂ reduction and CO oxidation step

The NO₂/NO_x molar ratio in the process gas, after passing through steps a and b, is lower than 0.05, preferably lower than 0.02 and most preferably lower than 0.01.

In the SCR step (a), NO and NO₂ in said process gas is catalytically converted to N₂ and H₂O by reaction with a first NH₃ stream. To reduce NO_x from process gases, the so-called catalytic SCR (Selective Catalytic Reduction) process is the most widely used process to reach very low NO_x concentrations. The process requires the addition of NH₃ in order for the catalytic reactions to take place:



An NH₃ source is added to the process gas such that the NH₃/NO_x ratio in the process gas becomes close to 1 in order to achieve high NO_x conversion to N₂ on the SCR catalyst. To obtain an even distribution of NH₃ and NO_x, a static mixing device is typically positioned between the NH₃ injection point and the SCR catalyst.

The NH₃ source can be liquid NH₃, an aqueous NH₃ solution, NH₃ vapor or urea and can be added to the process gas as a liquid via a number of spray nozzles or as a vapor, preferably together with an amount of carrier gas to ensure good mixing with the process gas.

The NH₃ used in step a is added to the process gas such that the obtained NH₃/(NO+NO₂) ratio is between 0.9 and 1.1.

The reaction typically takes place in the 250 – 450 °C temperature range, and at a pressure around 1 atm.

The so-called SNCR process is the non-catalytic version of the SCR and requires temperatures in the 700-1000 °C range. The process is not as effective as the catalytic version. In a low temperature application, ozone (O₃) can be added
5 to the process gas to oxidize the NO to NO₂/HNO₃, which can then be washed out in an absorption process.

On the SCR catalyst, most of the NO_x will react with the NH₃, producing a SCR process gas with decreased
10 concentrations of both NO_x and NH₃. Typically, the SCR catalyst is designed for more than 90% NO_x conversion, up to 98-99%.

If the NO_x conversion requirement is very high, it is often the (local) NH₃/NO_x ratio which is the determining factor
15 and therefore it may be necessary to use a second SCR catalyst and install a mixing device between the first and second SCR catalyst to ensure an even NH₃/NO_x ratio before the second catalyst. It may also be desired to add an additional amount of NH₃.

20 The SCR catalyst has been used for decades and many chemical formulations can be used for the purpose of this invention. The vanadium/titania/tungsten-based catalyst on a monolithic support is the most well-known type of SCR catalyst.

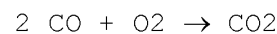
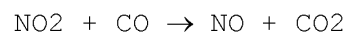
25 Downstream the SCR catalyst, the process gas will have a very low concentration of NO, NO₂ and unconverted NH₃. The SCR catalyst will not convert CO and thus the CO concentration is unchanged.

30 The combined NO₂ reduction and CO oxidation step (b) takes place in the presence of a sulfur resistant dual-purpose catalyst, thereby catalytically reducing NO₂ to NO in said

process gas by reaction with CO and oxidizing CO to CO₂ by reaction with O₂.

5 The CO and O₂ required in this step are typically present in the process gas itself, in the necessary concentrations. However, it is possible to add CO and/or O₂ from an external source, as required.

10 The present disclosure describes the use of a sulfur resistant dual-purpose catalyst system, which first uses CO to reduce the NO₂ to NO and then oxidizes the remaining CO to CO₂ according to the reactions:



15 The catalyst will reduce the problematic NO₂ to NO, which will not be absorbed into a downstream carbon capture plant and, thus, the lifetime of the carbon capture absorbent can be significantly increased. Furthermore, the catalyst oxidizes the toxic CO gas to the much less problematic CO₂,
20 which will be captured in a downstream carbon capture plant. The reaction rate of NO₂ with CO should be higher than the reaction of CO with O₂, otherwise the NO₂ reduction will not take place. Reaction rates for these reactions can be controlled by means of the catalyst
25 selection, reaction temperature or combinations thereof.

The dual-purpose catalyst system may comprise a platinum group metal, preferably palladium or platinum in combination with one or more oxides of a metal selected
30 from the group consisting of vanadium, chromium, tungsten, molybdenum, cerium, niobium, manganese, and copper on a support comprising one or more oxides of metals taken from

the group of aluminum, silicon and titanium. Similar effect may also be observed by gold as the active metal. The catalyst is preferably in monolithic form, but pellet-types can also be used.

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In a development of the process of the invention, SO₂ in the process gas may be removed. In this aspect, the process further comprises subjecting said process gas to:

- a1.** an SO₂ oxidation step, catalytically oxidizing SO₂ in
10 said process gas to SO₃ by reaction with O₂, between
 steps a and b (above),
- c.** a cooling and condensation step, in which sulfuric acid
 vapor is condensed and withdrawn from said process
 gas, after step b.,
- 15 wherein the NO₂/NO_x molar ratio in the process gas,
 after passing through steps a, a1, b and c is lower
 than 0.05, preferably lower than 0.02 and most
 preferably lower than 0.01.

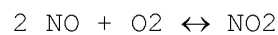
20 As an alternative, SO₂ may also be removed in a scrubber or
 similar following step (b).

The NO_x depleted process gas from step a. is - in this
aspect - directed to a SO₂ oxidation catalyst, which is a
25 well-known vanadium-based alkali-melt catalyst. On the
 catalyst, the main reaction is to oxidize the SO₂ to SO₃ by
 means of O₂ present in the process gas. The SO₂ oxidation
 catalyst reactor is typically designed for higher than 98%
 SO₂ conversion, the maximum conversion is limited by the
30 thermodynamical equilibrium between SO₂ and SO₃.

The SO₂ oxidation catalyst will also convert any NH₃ slip
from the SCR catalyst into either N₂ or NO_x. Depending on

the gas composition and catalyst temperature, typically 40-70 % of the NH₃ is converted to N₂, the remaining NH₃ becomes NO_x.

The SO₂ oxidation catalyst also equilibrates the reaction
5 between NO and NO₂:



The reaction is exothermal and thus more NO₂ is formed at lower temperature and with high O₂ concentration. The O₂ concentration is fixed from the process gas and the SO₂
10 conversion typically determines the operating temperature of the catalyst, i.e., there is not much which can be done to reduce the formation of NO₂. At 400 °C, around 30-50 % of the total NO_x concentration will exist as NO₂. In the 350-450 °C temperature range, the SO₂ oxidation catalyst
15 will not oxidize the CO.

After SO₂ oxidation (step a1), the NO₂ concentration is typically in the 2-20 ppm range, which will have a highly negative impact on the downstream carbon capture plant and may also cause a brown/red plume in the stack, should it be
20 directed to atmosphere. Also, the CO concentration is almost unchanged compared to the concentration in the process gas entering the plant.

For sulfuric acid producing desulfurization plants, the dual-purpose catalyst system will typically be positioned
25 just downstream the SO₂ oxidation catalyst for reduction of NO₂ to NO and oxidation of the remaining CO to CO₂.

The dual-purpose catalyst system may comprise a single dual-purpose catalyst arranged to perform both NO₂
30 reduction and CO oxidation, or comprise one or more catalyst beds, each one of which is arranged to perform NO₂

reduction and CO oxidation separately. One or more heat exchanger(s) may be arranged between the catalyst beds.

5 Downstream the dual-purpose catalyst system the SO₃ formed in the SO₂ oxidation catalyst reacts with H₂O present in the gas to form H₂SO₄ vapor. By process gas cooling e.g., in an acid resistant glass tube heat exchanger, the H₂SO₄ is condensed and withdrawn as a commercial grade sulfuric acid product. NO and NO₂ exhibit very low solubility in the
10 sulfuric acid and only up to a few % of the NO_x will be absorbed into the sulfuric acid product.

After passing through steps a and b, and optionally steps a, a₁, b and c, the process gas suitably has a NO₂
15 concentration below 2 ppmv, preferably lower than 1 ppmv.

In one aspect of the process of the invention, CO may be added to the process gas at any point upstream step b. As noted above, the process gas ideally comprises 10-5,000
20 ppmv CO.

In a further aspect of the process, at least one of the catalytic steps a, a₁ and b independently, and preferably all catalytic steps a, a₁ and b, take place in the
25 temperature range 250-450 °C. More specifically, at least catalytic step a₁ takes place in the temperature range 350-450 °C.

Suitably, at least one and preferably all of the catalytic
30 steps a, a₁ and b take place without active temperature control between the steps, such that heat exchangers between the catalytic steps can be avoided.

The cleaned process gas is then highly reduced in concentration of SO₂ and NO₂ and can thus be directed to a carbon capture plant or be emitted to the atmosphere.

5 Accordingly, following steps a and b, and optionally after steps a, a1, b and c - the process gas may be fed to a carbon capture plant, in which a CO₂-rich stream is separated from the process gas. The carbon capture plant is suitably based on absorption of CO₂ into an amine blend
10 (primary, secondary and/or tertiary amine), a hot (promoted or unpromoted) potassium carbonate solution or a combination thereof. To increase the carbon capture and energy efficiency of the hot potassium carbonate process, so-called promoters can be added to the carbonate solution.
15 Such promoters can be amines, amino acids and V-, B- and As-containing compounds. Optionally, the cleaned process gas can be directed to a final SO₂ polisher unit for even further reduction in SO₂.

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Figures

Figure 1 shows a layout of a process plant using the dual-purpose catalyst system to reduce NO₂ concentrations to sub-ppm concentrations.

25 A process gas (2), containing NO_x (NO+NO₂), SO_x (SO₂+SO₃), O₂, H₂O and CO, coming from an upstream process such as a carbon black process or a fluid catalytic cracker is directed to a process gas conditioning section (4). In the process gas conditioning section (4), particulate matter
30 can be removed by means of e.g., bag house filter, candle filter or electrostatic precipitator, the pressure can be increased by means of a blower/compressor and the

temperature can be adjusted by heaters/coolers/burners or other means to provide a conditioned process gas (6) ready for SCR reaction and NOX reduction.

5 An ammonia containing stream (5) is optionally split into a first ammonia containing stream (7) and a second ammonia containing stream (13). A major part of the ammonia is found in stream (7) and is added to the conditioned process gas (6) and mixed to provide a process gas (8) with an NH₃/NOX ratio close to 1. In (first) SCR reactor (10) most
10 of the NOX is reacted with NH₃ to form N₂ and H₂O. The NOX depleted process gas (12) leaves the SCR reactor and is optionally mixed with a minor amount of NH₃-containing stream (13) to form a process gas (14) ready for an optional second SCR reactor (16) where the remaining NOX
15 reduction takes place. The SCR off gas (18) contains low concentrations of NO, NO₂ and NH₃ and is optionally directed to the SO₂ oxidation reactor (20) in which SO₂ is oxidized to SO₃, NH₃ oxidized to N₂ and NOX and NO is partly oxidized to NO₂.

20 The converted process gas (18, 22) is passed to the dual-purpose catalyst reactor (24) in which NO₂ is reduced to NO by reaction with CO and CO is oxidized to CO₂ by reaction with O₂. The converted process gas, containing very low NO₂ concentration (26) is cooled to 220-290 °C in heat
25 exchanger (28) and the cooled converted process gas is directed to the sulfuric acid condenser (32) via line (30). By indirect heat exchange with a colder cooling stream (42), typically air, the cooled converted process gas is further cooled to around 70-100 °C and sulfuric acid is
30 condensed and leaves the corrosion resistant condenser (32) via bottom line (36). The practically sulfuric acid-, SO₂- and NO₂-free cooled process gas (34) may then be directed

to a carbon capture plant (38) in which CO₂ is captured and concentrated and leaves the plant as an almost pure CO₂ stream (40). The CO₂ depleted process gas (42) is then directed to the atmosphere via a stack.

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Another benefit of integrating WSA and carbon capture is that the heated cooling stream (44) leaving the sulfuric acid condenser (32) can be used for heating purposes, e.g., to meet the high energy requirements of the stripping section of the carbon capture plant, and/or as preheated combustion air in other processes and/or carrier gas for the NH₃ for the SCR process.

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The present technology has been described with respect to a number of embodiments and figures. The person skilled in the art may combine elements from these embodiments and figures as required, within the scope of the invention as defined in the appended claims. All documents referred to herein are incorporated by reference.

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Example 1

This example describes the evolution in NO_x concentration in the process gas as it passes through the process layout (as depicted in figure 1) and shows that the outlet NO₂ concentration is insensitive to the operation of the SCR system for NO_x reduction.

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The basis is a process gas with 350 ppm NO_x from an upstream process, such as a FCC unit or a carbon black production plant.

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The SCR is designed for 98 % NO_x conversion at a NH₃/NO_x ratio of 1.0. The actual NH₃/NO_x ratio will determine the actual NO_x conversion - increasing the NH₃ concentration

will increase NOX conversion but at the same time increase NH3 slip from the reactor. Decreasing the NH3 concentration will decrease the NOX conversion and result in a higher NOX slip from the reactor.

- 5 The SO2 oxidation catalyst is very efficient in converting NH3 but is not very selective towards N2. 100% NH3 conversion is achieved with an estimated selectivity towards N2 of 40%, i.e., the remaining 60% becomes NOX. The NO/NO2 ratio depend on the chemical equilibrium in the
- 10 SO2 oxidation catalyst - at the operating conditions the NO2/NOX ratio out of the catalyst is approximately 0.4. The sulfur resistant dual-purpose NO2 reduction catalyst is positioned downstream the SO2 oxidation catalyst and has as NO2 reduction efficiency of 99% when the CO to NO2 molar
- 15 ratio exceeds 1. All three catalyst systems operate in the same temperature range of 350-450 °C and it is desirable to operate the three catalysts at the same temperature, in that way eliminating the need for installing heat exchangers between
- 20 the catalysts. This simplifies the process layout, process control and reduce the cost of process equipment. The operational NH3/NOX ratio is not constant as it depends on the evolution in the NOX concentration in the process gas and the speed of analyzing the NOX concentration and
- 25 adjusting the NH3 flow. Therefore, both spatial and time-wise variations in the NH3/NOX ratio must be expected. The NO and NO2 concentrations in table 1 show that there is a minimum in NOX slip from the SCR when operating close to the design conversion efficiency - moving away from this
- 30 optimal operating point in both directions increase the NOX slip. With too low NH3/NOX ratios, unconverted NOX will leave the SCR, whereas at too high NH3/NOX ratios, the NOX

slip is very low but the NH₃ slip is high and the NH₃ will be partly converted to NO_x on the downstream SO₂ oxidation catalyst.

The sulfur resistant dual-purpose catalyst system
5 efficiently reduces the NO₂ concentrations, such that operation with NO₂ concentrations below 0.5 ppm is achieved over a wide range of operation of the SCR reactor.

Without the dual-purpose catalyst system, the NO₂ emission
outlet the SO₂ oxidation catalyst would be above 3-4 ppm,
10 even during optimal operation.

Using a layout with two SCR reactors in series, with
process gas mixing between the reactors, will allow for a
higher design SCR conversion, i.e., a lower emission at
optimal operation. However, underdosing or overdoing NH₃
15 will still result in an increase in NO_x emissions as seen
in Table 1 for NH₃/NO_x ratios of 0.9 and 1.10.

So-called Ammonia Slip Catalyst (ASC's) are able to convert
NH₃-slips from the SCR reactor into N₂ with a much better
selectivity than the SO₂ oxidation catalyst, i.e., 90%
20 instead of 40%. They will typically be positioned just
downstream the SCR reactor and ensure that the total NO_x
concentration to the SO₂ oxidation catalyst is reduced when
NH₃ is overdosed. However, it will not ensure NO₂
concentration below 2-3 ppm in the SO₂ oxidation catalyst
25 outlet gas in the present example.

ASC's can also have CO oxidation capabilities and thus
limit the use of a dual-purpose catalyst system downstream
the SO₂ oxidation catalyst as there will be less or no CO
to reduce the NO₂ to NO.

30 Similarly installing the dual-purpose catalyst system
between the SCR and SO₂ oxidation catalyst will reduce both

NO₂ and CO to the SO₂ oxidation catalyst, but NO will be reoxidized to NO₂ in the SO₂ oxidation catalyst.

Table 1:.

NH3/NOX ratio	0.90	0.95	0.98	1.00	1.02	1.05	1.10
SCR-conversion	90%	95%	98%	98%	98%	99%	99.5%
NOX slip from SCR	35 ppm	17 ppm	7 ppm	7 ppm	7 ppm	3 ppm	2 ppm
NH3 slip from SCR	0 ppm	0 ppm	0 ppm	7 ppm	14 ppm	21 ppm	37 ppm
Outlet SO2 oxidation catalyst							
NO slip	21 ppm	11 ppm	4 ppm	7 ppm	9 ppm	10 ppm	14 ppm
NO2 slip	14 ppm	7 ppm	3 ppm	4 ppm	6 ppm	6 ppm	10 ppm
NH3 slip	0 ppm	0 ppm	0 ppm	0 ppm	0 ppm	0 ppm	0 ppm
Outlet dual purpose catalyst							
NO slip	35 ppm	17 ppm	7 ppm	11 ppm	15 ppm	16 ppm	24 ppm
NO2 slip	0.2 ppm	0.1 ppm	< 0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm

Example 2

This example shows the efficiencies of the sulfur resistant dual-purpose catalyst, i.e. it's ability to first reduce NO₂ to NO by means of CO and then oxidize CO to CO₂ by means of O₂.

The data have been measured in a laboratory scale reactor using a simulated process gas, i.e., containing both NO, NO₂, O₂, CO and SO₂. SO₂ does not take part in the reactions but is a common poisoning agent for many catalyst systems.

The simulated process gas had the following composition:

3 vol% O₂

5 vol% H₂O

1000 ppm CO

50 ppm NOX (25 ppm NO / 25 ppm NO₂)

500 ppm SO₂

Balance N₂

Pressure was close to atmospheric.

Data from different operating temperatures show that the NO₂ to NO reduction by CO as reductant is almost complete in the 220-400 °C range, whereas the slower CO to CO₂ oxidation by O₂ requires a temperature above 350 °C to reach a similar conversion, cf. Figure 2.

This means that the dual-purpose catalyst has optimal performance around 350-450 °C, which is the normal operating temperature for the SO₂ oxidation catalyst. The dual-purpose catalyst system can thus beneficially be installed in direct connection with the SO₂ oxidation reactor.

The same high NO₂ reduction and CO conversion can also be obtained at the lower 250 °C, but it will require a larger

catalyst volume to reach the very high CO conversion. In the process layout shown in Figure 1, an alternative is to locate the sulfur resistant dual-purpose catalyst between the process gas cooler (28) and sulfuric acid condenser (32).

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Claims:

1. A process for reduction of NO, NO₂ and optionally SO₂ concentrations in a process gas (2), said process
5 comprising subjecting said process gas to:
- a. an SCR step (10), catalytically converting NO and NO₂ in said process gas to N₂ and H₂O by reaction with a first NH₃ stream (7),
 - b. a combined NO₂ reduction and CO oxidation step
10 (24) in the presence of a sulfur resistant dual-purpose catalyst system, thereby catalytically reducing NO₂ to NO in said process gas by reaction with CO and oxidizing CO to CO₂ by reaction with O₂,
 - 15 characterized in that the NO₂/NO_x molar ratio in the process gas, after passing through steps a and b, is lower than 0.05, preferably lower than 0.02 and most preferably lower than 0.01.
- 20 2. The process according to claim 1, said process further comprising subjecting said process gas to:
- a1. an SO₂ oxidation step (20), catalytically oxidizing SO₂ in said process gas to SO₃ by reaction with O₂, between steps a and b,
 - 25 c. a cooling and condensation step (32), in which sulfuric acid vapor is condensed and withdrawn from said process gas, after step b.,
 - wherein the NO₂/NO_x molar ratio in the process gas, after passing through steps a, a1, b and c is lower
30 than 0.05, preferably lower than 0.02 and most preferably lower than 0.01.

3. The process according to any one of the preceding claims, wherein the process gas - prior to step (a) - comprises 10-5,000 ppmv CO and 0-1,000 ppmv NO+NO₂.
- 5 4. The process according to any one of the preceding claims, wherein the process gas - prior to step (a) - has a CO:NO₂ molar ratio greater than 1:1.
- 10 5. The process according to any one of the preceding claims, wherein the process gas, after passing through steps a and b, steps a, a1, b and c or steps a, b, a1 and c, has a NO₂ concentration below 2 ppmv, preferably lower than 1 ppmv.
- 15 6. The process according to any one of the preceding claims, wherein the process gas is obtained from a Fluid Catalytic Cracking process, a Carbon black producing process, or a metallurgical process such as a steel mill.
- 20 7. The process according to any one of the preceding claims, wherein - prior to step (a) - the process gas fulfils at least one of the following:
 - 25 - an O₂ concentration in the range 2-20 vol%,
 - an H₂O concentration in the range 2-40 vol% and
 - an SO₂ concentration in the range 100-10,000 ppmv.
- 30 8. The process according to any one of the preceding claims, wherein CO is added to the process gas at any point upstream step b.

9. The process according to any one of the preceding claims, wherein at least one of the catalytic steps a, a1 and b independently, and preferably all catalytic steps a, a1 and b, take place in the temperature range 250-450 °C.
10. The process according to any one of the preceding claims, wherein at least catalytic step a1 takes place in the temperature range 350-450 °C.
11. The process according to any one of the preceding claims, wherein at least one and preferably all of the catalytic steps a, a1 and b take place without active temperature control between the steps.
12. The process according to any one of the preceding claims, wherein the NH₃ used in step a is added to the process gas such that the obtained NH₃/(NO+NO₂) ratio is between 0.9 and 1.1.
13. The process according to any one of the preceding claims, wherein - prior to step (a) - the process gas is preconditioned by one or more preconditioning steps (4) selected from:
- removal of particulate matter e.g., in a bag house filter, electrostatic precipitator or candle filter,
 - adjustment of temperature by heating or cooling e.g. by means of heat exchangers, burners, heaters, and
 - adjustment of pressure e.g., by means of a compressor or blower (e.g. to about atmospheric pressure).

14. The process according to any one of the preceding claims, wherein the sulfur resistant dual-purpose catalyst system in step b. is a sulfur resistant dual-purpose catalyst comprising a platinum group metal (e.g., Pt and/or Pd) in combination with one or more oxides of vanadium, chromium, tungsten, molybdenum, cerium, niobium, manganese and copper, on a support from the group of aluminum, silicon and titanium.
15. The process according to claim 14, wherein the sulfur resistant dual-purpose catalyst system used in step b is monolithic in structure.
16. The process according to any one of the preceding claims, wherein - in step b. - the reaction rate of NO₂ with CO is higher than the reaction of CO with O₂.
17. The process according to any one of the preceding claims, wherein - following steps a and b, steps a, a1, b and c or steps a, b, a1 and c - the process gas is fed to a carbon capture plant, in which a CO₂-rich stream (40) is separated from the process gas.
18. The process according to claim 17 wherein the carbon capture plant is based on absorption of CO₂ into an amine blend (primary, secondary and/or tertiary amine), a hot (promoted or unpromoted) potassium carbonate solution or a combination thereof.
19. The process according to any one of the preceding claims, wherein - in step c - sulfuric acid vapor is

condensed in an indirectly cooled corrosion resistant heat exchanger.