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

Technical field

[0001] The present invention relates generally to a method for the catalytic removal of carbon dioxide and sulphur dioxide 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 sulphur emissions took centre stage in the 1960s, 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, KR200502862 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 only 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 removes the 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 sulphur dioxide from waste gases in a reactor charged with an activated carbon catalyst, characterised by the following steps:

- saturating the activated carbon with SO_2,
- saturating or partially saturating the waste gases with water,
- introducing the exhaust gases into the reactor,
- catalytically converting the SO_2 into H_2SO_4 and, in parallel with this, catalytically converting CO_2 into C and O_2 on the same catalyst and/or adding C to sulphur compounds,
- washing out the catalyst and discharging the H_2SO_4 as a liquid and the C as a solid or/and bound to sulphur compounds.

[0006] One advantage of the method is that the reaction products H_2SO_4 and C are separated from the gas phase of the waste gases and are present once the method is complete as a liquid (H_2SO_4) and as a solid (C or C on sulphur compounds) and can be used further.

[0007] The method makes it possible to treat waste gases from industrial plants which contain carbon dioxide and SO_2 and to remove both harmful substances at the same time and in parallel, i.e. in a single method, either completely or to a considerable extent from the waste gases.

[0008] In the method at least 40 % of the CO_2 contained in the waste gases is converted, preferably at least 50 %, particularly preferably at least 60 % and in particular at least 82 %.

[0009] Sulphur-carbon compounds are understood in the context of the present invention to mean compounds which contain both sulphur and carbon, irrespective of the number, the oxidation state and the presence of other elements

[0010] The expression "saturation of the activated carbon with SO_2/SO_3" is to be understood in the context of the present invention to mean that the activated carbon catalyst has sufficient exothermic conversion energy, which is produced by the $SO_2/SO_3/H_2SO_4$ conversion, to commence CO_2 conversion subsequently. As emerged from our tests, this corresponds to approximately of 20-50 kg of SO_2/m^3 of catalyst.

[0011] The expression "saturation of the waste gases with water" is to be understood in the context of the present invention to mean an introduction of very fine water droplets into the flue gas, reducing the temperature and increasing the water content until a relative atmospheric humidity of a maximum of 100 % is produced in the flue gas. This saturation of the waste gases with water is preferably carried out in a quench cooler or injection cooler. The pH of this water may be neutral, alkaline or acidic. The pH of the water used to saturate the waste gases is preferably between 3 and 11 and particularly preferably between 5 and 9.

[0012] This method is somewhat similar to the "SULFACID" method, in which SO_2 is converted into H_2SO_4 on an activated carbon catalyst. However, in this method the carbon dioxide is not converted into carbon and oxygen or into sulphur-carbon compounds, since in this method the exothermic energy produced during the conversion of SO_2 via SO_3 to form H_2SO_4 is supplied almost completely to the aqueous covering in the catalyst bed.

[0013] From the tests which were carried out in conjunction with the research which led to this invention it was established that no separation of CO_2 was observed, either in the tests or in the industrial applications, in any of the possible conventional ways of carrying out SULFACID methods since in this case the exothermic energy which is produced during the conversion of SO_2 via SO_3 to form H_2SO_4 is supplied to the aqueous covering in the bed so as to produce the aforementioned H_2SO_4.

[0014] Waste gases in which the ratio of CO_2 to SO_2 is between 0.25 mol/mol and 0.58 mol/mol are preferentially treated. Of course it is also possible to treat waste gases in which the ratio of the two harmful substances lies outside this range. In this instance however the harmful substance which lies above the aforementioned limit is not completely removed from the waste gases, but is only removed in part.

[0015] The inlet temperatures of the waste gases preferably lie between the ambient temperature and 150 °C. Higher temperatures in continuous operation could permanently damage the catalyst.

[0016] The oxygen content of the waste gases is not actually critical, but should ideally be at least 5 % by volume. The O_2 content should preferably be more than 8 times greater than the SO_2 content

[0017] The waste gases may be saturated quite easily with water by quenching or a similar method. The waste gases should naturally contain as little solids, dust and the like as possible in order to prevent intoxication and 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.

[0018] The SO_2 purifying factor for the exhaust gases preferably lies between 0.4 and 0.6 with the aid of the catalyst. Between 40 % and 60 % of the SO_2 is thus converted via SO_3 into H_2SO_4; the rest of the SO_2/SO_3 reacts to form sulphur-carbon compounds and is discharged into the exhaust air in the form of SO_2/SO_3. Example: with 100 % separation of SO_2 in the CO_2 process this corresponds to a conversion of 40-60 % into H_2SO_4 and a 60-40 % conversion into sulphur-carbon compounds (with an overload of SO_2/SO_3 there is thus no longer a 40-60 % conversion into H_2SO_4, and the excess is discharged into the exhaust air in the form of SO_2/SO_3 – in this case the CO_2 separation is also reduced or halted). In the SULFACID process there is a 70-90 % conversion into H_2SO_4 with 100 % separation of SO_2 and an approximately 30-10 %

release of SO_2/SO_3 into the exhaust air. With an overload of SO_2/SO_3 in the SULFACID process the 70-90 % conversion into H_2SO_4 is not increased, but instead the excess again re-enters the exhaust gases in the form of SO_2/SO_3.

[0019] Therefore, in the method according to the invention, with large volume flows and/or high concentrations of $SO_2/SO_3/CO_2$, a plurality of reactors can be connected in parallel and/or in series in order to achieve required values.

Brief description of the figures

[0020] 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 the accompanying Fig. 1. In the drawings:

Fig. 1 is a schematic view of the arrangement;

Fig. 2 is a graph showing the values measured during Test 1 of the SO_2 content of the waste gases at the inlet and outlet of the reactor;

Fig. 3 is a graph showing the values measured during Test 1 of the CO_2 content of the waste gases at the inlet and outlet of the reactor;

Fig. 4 is a graph showing the values measured during Test 2 of the SO_2 content of the waste gases at the inlet and outlet of the reactor;

Fig. 5 is a graph showing the values measured during Test 2 of the CO_2 content of the waste gases at the inlet and outlet of the reactor;

Description of an embodiment of the invention

[0021] The test arrangement shown in Fig. 1 in order to illustrate the invention comprises a test reactor 10, to the lower part 12 of which a test gas is supplied and in the upper part 14 of which water is sprayed.

[0022] The test gas which was used to simulate the waste gases consists of ambient air which is heated in a heating device 16 to approximately 80 °C and to which SO_2 is subsequently added from a first pressurised cylinder 18 as well as CO_2 from a second pressurised cylinder 20 via corresponding valves 22, 24. A first measuring device 26 analyses the composition (SO_2 content, CO_2 content, O_2 content), the temperature, the flow volume and the flow rate of the test gas.

[0023] The test gas is then cooled to saturation temperature in a quencher 28 by evaporation of water. The test gas is drawn via the quencher 28 into the test reactor 10 by a waste gas fan 30. A mist collector at the outlet of the quencher 28 collects the spray.

[0024] The test gas flows through the test reactor 10 and the activated carbon catalyst 32 arranged therein from bottom to top and is then examined once discharged from the test reactor 10 in a second measuring device 34 for the same parameters as in the first measuring device 26, i.e. composition (SO_2 content, CO_2 content, O_2 content), the temperature, the flow volume and the flow rate, and is then released into the atmosphere.

[0025] The water required in the process is fed from a storage container 36 via a metering device 38, where the flow is measured, and a pump 40 into the upper part 14 of the test reactor 10, where the water flows through the activated carbon catalyst 32 in counterflow to the test gas. The water required for the quencher 28 comes directly from the water supply and is circulated within the cycle.

[0026] Alternatively however, the water required in the process can also be fed through the reactor in co-current flow with, i.e. in the same direction as, the test gas. The selection of a co-current or counterflow method depends for example on the local conditions.

[0027] The SO_2 is catalytically converted into SO_3 on the activated carbon catalyst, which is not additionally impregnated with metals, and is then converted into sulphuric acid if water is added. The packing materials are located beneath the molecular sieve and distribute the gas and may be doped. The sulphuric acid and the carbon and sulphur-carbon compounds formed are rinsed off by the activated carbon catalyst by intermittent spraying with water, as a function of the volume of the catalyst and of the SO_2/SO_3 concentration, in counterflow to the gas. In the pilot system, spraying was carried out 1-4 times/hour using an amount of water of 2-15 l/hour. The water is collected in a container 42 in the lower part 12 of the test reactor 10 together with the aqueous sulphuric acid solution produced during the process and the carbon and carbon-sulphur compounds suspended therein, and the acid content is determined by means of a measuring device 44. The sulphuric acid solution is then pumped off by a pump 46 and the flow volume is ascertained using a further measuring device 48.

[0028] In the system described the sulphur dioxide of the waste gases is catalytically converted via SO_3 on moist catalyst particles to form sulphuric acid, and carbon dioxide is cleaved at the same time or in parallel to form carbon and oxygen. However, some of the carbon is also absorbed in sulphur compounds.

[0029] The method was tested successfully under the following conditions:

- water saturation of the waste gases before entry into the reactor by quenching.
- SO_2 content of the flue gases between 300 ppm and 6000 ppm. In this instance it should be noted that in the ideal situation and with continuous operation only 174 to 3480 ppm of this SO_2 can be converted during the CO_2 conversion. The excess of SO_2 is in this case used for the H_2SO_4 acid formation or is released into the atmosphere in the form of SO_2/SO_3.
- CO_2 content of the flue gases between 0.1 % by volume (1000 ppm) and 15 % by volume (150 000 ppm).

- Gas temperature between 10 and 80 °C.
- O_2 content approximately 20 % by volume.
- Water saturation and cooling of the waste gases by quenching.
- Tested catalysts were provided by NORIT Nederland B.V. of Postbus 105 NL-3800 AC Amersfoot under the names Norit_PK1-3, Norit_PK_2-4 and Norit_PK_3-5.

[0030] These catalysts are an activated carbon granulate with a particle size between 1-3 mm, 2-4 mm or 3-5 mm and 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 (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.

[0031] In the tests flue gas analysis devices of the Testo brand were used. The devices are of the newest generation (year of manufacture 2009) and were calibrated by the manufacturer. In addition, the analysis data of these flue gas analysis devices was confirmed by wet-chemical measurements carried out in parallel. The results of all measurements fell within the admissible deviation tolerances.

[0032] The progression of the SO_2 conversion by H_2SO_4 on the catalyst surface corresponds to the following total formula:

$$SO_2 + ½\ O_2 + n\ H_2O\ \text{(catalytically)} \rightarrow H_2SO_4 + (n\text{-}1)\ H_2O$$

[0033] Without wanting to be committed to a particular theory, it is assumed that:

- O_2 and SO_2 migrate toward the active centres of the catalyst where they are converted into SO_3.
- SO_3 migrates out from the active centres of the catalyst and forms H_2SO_4 with the aqueous covering around the catalyst core.

- SO_2 reacts with oxygen and water to form sulphuric acid in accordance with the reaction equation above.
- The CO_2 molecule, which is of approximately the same size as a SO_2 molecule, is also transported into the pores of the catalyst core, where it is separated by the addition of energies of formation and is adsorbed on sulphur compounds. The concentrated sulphuric acid which forms in the aqueous cover around the core adsorbs the C portion of CO_2 and O_2 through high surface tensions (specific surface). 'Carbon-sulphur compounds' are thus produced.

  The following reactions take place, inter alia:

$$CO_2 + SO_2 + H_2O \rightarrow C + H_2SO_4 + \frac{1}{2} O_2$$

$$H_2SO_4 + CO_2 \rightarrow SCO_3 + H_2O + O_2$$

- the C portion located on a sulphur compound is provided inside the sulphuric acid as a suspension,
- the formed carbon compounds are discharged in a suspension with the sulphuric acid from the catalyst by washing with water, thus diluting the sulphuric acid. The carbon compounds formed precipitate after a short period of time.

[0034] Softened or demineralised water can be used to wash out the catalyst.

[0035] It is assumed, without wanting to be committed to a particular theory, that the CO_2 is adsorbed using the thermal energy which is produced by the oxidation of SO_2 to form SO_3 and/or during the formation of the sulphuric acid (SO_3- H_2SO_4). The exothermic energy which is released during the oxidation is ΔHR = -98.77 kJ/mol; for the sulphuric acid formation, this value is ΔHR = -123.23 kJ/mol; a total exothermic energy of ΔHR total = -231 kJ/mol is thus available. The energy of +394.4 kJ/mol which is required for the conversion of CO_2 can be drawn from an exothermic reaction from SO_2 into SO_3, or can be drawn from the two exothermic reactions of SO_2 to SO_3 to H_2SO_4. This means that an exothermic energy between -98.77 kJ/mol and -231 kJ/mol is available.

[0036] Ideally, i.e. with no energy losses, it is accordingly possible to convert, during oxidation, 0.25 mol CO_2 to SO_3 per mol SO_2. However, acid is also produced, so in the ideal situation 0.58 mol CO_2 are converted per mol SO_2, or 0.39 kg CO_2 are converted per kg SO_2 and 1.53 kg H_2SO_4 are produced simultaneously. However, it should be noted that other reactions (can) also take place, as well as for example the above-described formation of sulphur-carbon compounds.

[0037] The above-mentioned reactions of CO_2 separation can only take place once a specific level of saturation with SO_2 has been achieved in the pores of the catalyst in respect of the sulphuric acid formation. This equilibrium occurs in the reactor once sufficient SO_2 has been converted into SO_3 and starts to form sulphuric acid. Such a condition is reached after approximately 20 to 100 operating hours depending on the approach adopted (amount of SO_2/SO_3 fed). This condition is independent of the percentage by weight of acid formation. For this reason, this process can also be carried out with different percentages by weight (H_2SO4) of acids. Example: with 100 % separation of SO_2 in the CO_2 process, this corresponds to a conversion of 40-60 % of SO_2 into H_2SO_4 and 60-40 % of SO_2 into sulphur-carbon compounds.

Test 1

[0038] The tests were carried out under the following conditions:

Raw gas volume flow	min.	200	m^3/h
	max.	300	m^3/h
CO_2 content (inlet)	min.	0.20	% by volume
	max.	1.50	% by volume
SO_2 content (inlet)	min.	300	ppm
	max.	4,500	ppm
Waste gas temperature	min.	10	°C
	max.	12	°C
Dew-point temperature	saturated		

O2 content		>20	% by volume

[0039] The reactor is made of glass fibre reinforced plastics material, has a volume of approximately 2 m^3 and is filled with 1 m^3 of an activated carbon catalyst of the Norit_PK_2-4 type.

[0040] In a first phase the test system was run for approximately 50 hours with the addition of SO_2 from gas cylinders, and in this instance between 3,000 and 4,000 ppm of SO_2 were added. Overall, the reactor was charged with approximately 45 kg of SO_2 (approximately 45 kg of SO_2/m^3 of catalyst). In accordance with this test, the addition of water at 2 to 15 l/hour was divided into 1 to 4 portions/hour. In this instance, in contrast to the SULFACID process, no significant concentration of sulphuric acid was observed (4-6 % by weight). CO_2 was dedusted after approximately 40 hours (approximately 36 kg of SO_2/m^3 of catalyst). The SO_2 and CO_2 content of the waste gases was measured in each case at the inlet and at the outlet of the reactor, as illustrated in Fig. 1. The measurements were taken every 30 seconds and are shown in graphs in Figs 3 and 4. The first measurements shown in this case were taken after saturation of the catalyst, i.e. 40 hours after start-up of the reactor. The CO_2 concentration fluctuated repeatedly between 1.0 % by volume and 1.55 % by volume and it was established that the purifying values of CO_2 were on average less than 60 %. The test was carried out continuously over approximately 40 minutes. Over this entire period the treated waste gases no longer contained any SO_2, as can be seen from Fig. 3.

[0041] If the activated carbon catalyst is overloaded with SO_2, the CO_2 may be converted only in part or even not at all. The amount of water should also not be added during the process since otherwise the conversion of CO_2 will be reduced in favour of H_2SO_4 conversion or increased SO_2/SO_3 will be released into the waste air. It should be noted that in the case of a conventional SULFACID process, much greater amounts of water are added. For example, in a comparative SULFACID process, approximately 8-10 litres would be added

regularly every 15 minutes (32-40 l/hour/m^3 of catalyst). By contrast, in the CO_2 process a maximum of 15 litres (generally 8 litres) are added every hour at irregular intervals.

Test 2

Raw gas volume flow	min. max.	200 300	m^3/h m^3/h
CO_2 content	min. max.	0.30 1.00	% by volume % by volume
SO_2 content (inlet)	min. max.	300 500	ppm ppm
Waste gas temperature	min. max.	70 80	°C °C
Dew-point temperature	saturated		
O2 content		>20	% by volume

[0042] The reactor is made of glass fibre reinforced plastics material, has a volume of approximately 2 m^3 and is filled with 0.3 m^3 of a catalyst of the Norit_PK_2-4 type.

[0043] In a first phase the test system was run for approximately 50 hours with the addition of SO_2 from gas cylinders, and in this instance between 300 and 500 ppm of SO_2 were added owing to the low level of catalyst filling. Overall, the reactor was charged with approximately 15 kg of SO_2 (approximately 50 kg of SO_2/m^3 of catalyst). In accordance with this test, water was added anti-cyclically. Between 2 and 5 l/hour were added in 1 to 4 portions/hour, i.e. 6.6 to 16.6 l/hour/m^3 of catalyst. In this instance, in contrast to the Sulfacid process, no significant concentration of sulphuric acid was observed (1-2 % by weight). CO_2 was dedusted after approximately 40 hours (approximately 40 kg of SO_2/m^3 of catalyst). The SO_2 and CO_2 content of the waste gases was measured in each case at the inlet and at the outlet of the reactor, as illustrated in Fig. 1. The measurements were taken every 30 seconds and are shown in

graphs in Figs 4 and 5. The first measurements shown in this case were taken after saturation of the catalyst, i.e. 40 hours after start-up of the reactor. The CO_2 concentration fluctuated repeatedly between 0.8 % by volume and 0.3 % by volume and it was established that the purifying values of CO_2 were on average more than 85 %. The test was carried out continuously over approximately 2 hours. Over this entire period a nearly 100 % conversion of SO_2 was achieved simultaneously, as can be seen from Fig. 3.

[0044] The tests which were carried out in conjunction with the invention revealed that a specific level of saturation of the catalyst with SO_2 must be present in order to start the CO_2 separation (see tests). Until this level of saturation is reached, there is no CO_2 separation or else only partial CO_2 separation with a low separation yield, as in test 1. It is assumed that the amount of O_2 adsorbed in this instance has a positive effect on the conversion of SO_2/SO_3 into H_2SO_4, in such a way that less SO_2/SO_3 is also released from the reactor and, where necessary, greater amounts of SO_2/SO_3 can be separated. In contrast to the SULFACID process the exothermic energy is used to separate the CO_2 and is not released into the aqueous covering in the bed.

[0045] An important criterion for CO_2 separation is the SO_2 purifying factor of the catalyst. This is 0.7 and 0.9 under normal continuous operation for SO_2 conversion into H_2SO_4 (in SULFACID operation). This also results in an acid concentration of 10-15 % by weight. For CO_2 separation the SO_2 purifying factor of the catalyst is lower. The tests indicated that approximately 40-60 % of the SO_2 is converted into H_2SO_4. This also confirms that the acid concentration in these cases is between 1 and 6 % by weight.

Key to drawing of test reactor 10:

10	test reactor
12	lower part
14	upper part
16	heating device
18, 20	pressurised cylinder
22, 24	valve
26	first measuring device
28	quencher
30	waste gas fan
32	activated carbon catalyst
34	second measuring device
36	storage container
38	metering device
40	pump
42	container
44	measuring device
46	pump
48	measuring device

Claims

1. Method for the catalytic removal of sulphur dioxide and carbon dioxide from waste gases in a reactor charged with an activated carbon catalyst, characterised by the following steps:
    - saturating the activated carbon with SO_2,
    - saturating or partially saturating the waste gases with water,
    - introducing the exhaust gases into the reactor,
    - catalytically converting the SO_2 into H_2SO_4 and, in parallel with this, catalytically converting CO_2 into C and O_2 and into sulphur-carbon compounds on the same catalyst,
    - washing out the catalyst and discharging the H_2SO_4 as a liquid and the C as a solid or/and bound to sulphur compounds.

2. Method according to claim 1, characterised in that the ratio of SO_2 and CO_2 in the waste gases is between 0.25 and 0.58 mol/mol.

3. Method according to either claim 1 or claim 2, characterised in that the inlet temperature of the waste gases lies between the ambient temperature and 150 °C.

4. Method according to any one of claims 1 to 3, characterised in that the O_2 content of the waste gases is at least 5 % by volume.

5. The method according to any one of claims 1 to 4, characterised in that the O_2 content is more than 8 times greater than the SO_2 content.

6. Method according to any one of claims 1 to 5, characterised in that the waste gases are saturated with water by quenching.

7. Method according to any one of claims 1 to 6, characterised in that softened or demineralised water is used to wash out the catalyst.

8. Method according to any one of claims 1 to 7, characterised in that the catalyst is washed out in co-current flow with or in counterflow to the waste gases.

9. Method according to any one of claims 1 to 8, characterised in that the SO_2 purifying factor of the catalyst is between 0.4 and 0.6.

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

Abstract

The present invention relates to a method for the catalytic removal of sulphur dioxide and carbon dioxide from waste gases in a reactor charged with an activated carbon catalyst, characterised by the following steps:

- saturating the activated carbon with SO_2,
- saturating or partially saturating the waste gases with water,
- introducing the exhaust gases into the reactor,
- catalytically converting the SO_2 into H_2SO_4 and, in parallel with this, catalytically converting CO_2 into C and O_2 and into sulphur-carbon compounds on the same catalyst,
- washing out the catalyst and discharging the H_2SO_4 as a liquid and the C as a solid and/or bound to sulphur compounds.

(Fig. 1)