(19)

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

(11) N° de publication : **93012**

(12) **BREVET D'INVENTION** **B1**

(21) N° de dépôt: 93012

(51) Int. Cl.:
B01D 53/86, C01B 17/78

(22) Date de dépôt: 04/04/2016

(30) Priorité:

(43) Date de mise à disposition du public: 08/11/2017

(47) Date de délivrance: 08/11/2017

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(54) **SULFUR DIOXIDE REMOVAL FROM WASTE GAS.**

(57) Abstract: The present invention concerns a process wherein a gas, containing SO2 and O2 is brought in contact with a mixture of from 95% vol. to 50% vol. of activated carbon catalyst and from 5% vol. to 50% vol. of an inert filler material; wherein the SO2 is converted to H2SO4 on the activated carbon catalyst and is then washed from the activated carbon catalyst to obtain a solution. (Fig. 1)
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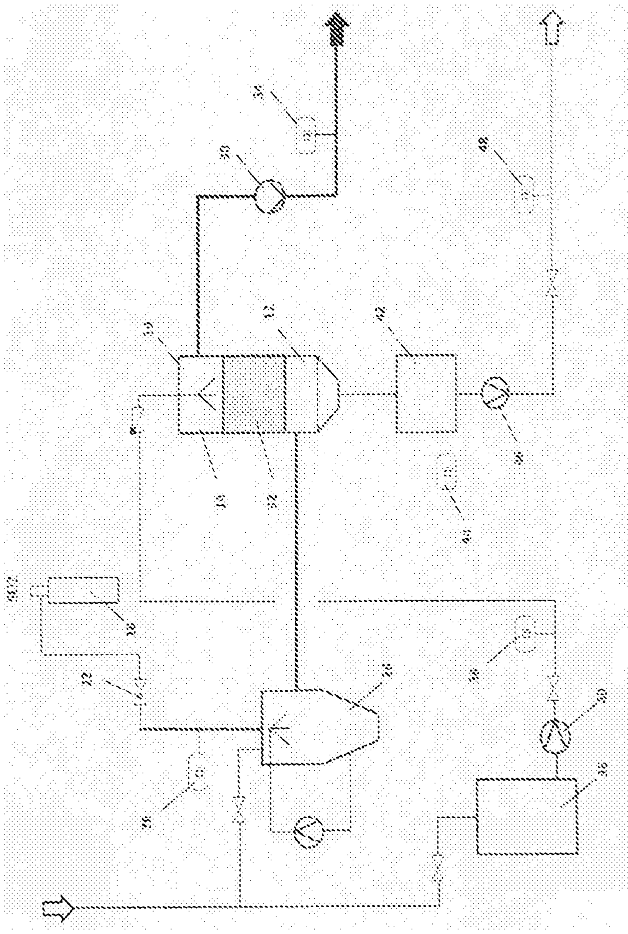


Fig. 1

SULFUR DIOXIDE REMOVAL FROM WASTE GAS

Technical field

[0001] The present invention generally relates to sulfur dioxide removal from waste gas.

Background Art

[0002] A known method for sulfur dioxide removal from waste gas is the Sulfacid® process. This process has been especially developed to meet the dual objectives of SO_2 removal from waste gases generated by chemical and metallurgical processes and transformation into industrial grade sulfuric acid. It lends itself particularly well to applications where sulfuric acid can be directly used, for example titanium dioxide production or similar sulfuric acid based processes. Additionally, the fixed activated carbon bed is able to remove heavy metals (such as Hg and Cd) from the waste gas.

[0003] Typical waste gas inlet parameters:

SO_2 content	up to 1 vol.%
Hg content	150 µg/Nm³ dry
O_2 content	min. 7 vol.%
Temperature	50 - 80°C
Dust content	< 30 mg/m³ STP (all data refers to dry gas)

[0004] Typical clean gas outlet parameters:

SO_2 content	≤ 50 mg/Nm³ dry
Hg content	25 µg/Nm³ dry

[0005] The raw gas flows through an activated carbon catalyst fixed bed inside a reactor. The SO_2 is converted to sulfuric acid by wet catalysis in the presence of oxygen and water. A water-saturated clean gas is discharged to atmosphere via a stack. The sulfuric acid collected in the pores and on the surface of the catalyst is intermittently washed out by spraying water over the catalyst. Clear industrial grade sulfuric acid of 10 to 50 wt.% strength is collected in a buffer tank. The conversion of sulfur dioxide to sulfuric acid on the catalyst works according to the following reaction equation:

[0006] $SO_2 + ½ O_2 + n H_2O \Rightarrow H_2SO_4 \cdot (n-1) H_2O$ + heat

[0007] The first Sulfacid® plant was started-up in 1968; now a few hundred plants are in operation worldwide.

[0008] It has been found however that the process is less efficient for a higher SO_2 concentration in the flue gas. It has been found that using more catalyst does not lead to higher removal of SO_2.

Technical problem

[0009] It is an object of the present invention to enhance the performance of the SO_2 removal from waste gases generated by chemical and metallurgical processes and the transformation into industrial grade sulfuric acid.

[0010] This object is achieved by a process as claimed in claim 1.

General Description of the Invention

[0011] To achieve this object, the present invention proposes a process wherein a gas containing SO_2 and O_2 is brought into contact with a mixture of from 95% vol. to 50% vol. of activated carbon catalyst and from 5% vol. to 50% vol. of an inert filler material; wherein the SO_2 is converted to H_2SO_4 on the activated carbon catalyst and is then washed from the activated carbon catalyst to obtain a H_2SO_4 solution.

[0012] In a preferred embodiment the mixture is soaked by water or an acid or alkaline aqueous solution.

[0013] Alternatively the mixture is dry.

[0014] The gas used in the present process is a waste gas generated by chemical and metallurgical processes.

[0015] Surprisingly, the fact that the activated carbon catalyst is mixed with a filler material allows obtaining a more complete removal of SO_2 from the gas.

[0016] The activated carbon catalyst is preferably extruded and has a grain size of 0.80 - 130 mm. The activated carbon catalyst is preferably granulated and has a grain size: 0.30 to 4.75mm.

[0017] In an embodiment the activated carbon catalyst is preferably a mixture of granulated and extruded catalyst.

[0018] The carbon catalyst may be produced from brown and bituminous coals, fruit pits, coconut shells, lignite, peat, wood, sawdust / sawchip, petroleum coke, bone and paper mill waste (lignin), synthetic polymers like PVC, rayon, viscose, polyacrylonitrile or phenols.

[0019] The carbon catalyst may be activated by :

a physical treatment : heat, steam, oxygen, CO_2, air

a chemical treatment : impregnation with acid, strong base or salts (e.g. sulfuric, chlorhydric or phosphoric acid, potassium or sodium hydroxide, calcium or zinc chloride)

a combination of both a physical and a chemical treatment.

[0020] The activated carbon catalyst may have a specific surface area (BET): 400 to 1800 m^2/g and an acid or alkaline pH.

[0021] In an embodiment, the filler material is between 10% vol. and 30% vol. of the mixture of activated carbon catalyst and a filler material.

[0022] Preferably at least 5% vol 6% vol, 7% vol, 8% vol, 9% vol, 10% vol, 11% vol, 12% vol, 13% vol, 14% vol, 15% vol, 16% vol, 17% vol, 18% vol, 19% vol, 20% vol, 21% vol, 22% vol, 23% vol, 24% vol, 25% vol, 26% vol, 27% vol, 28% vol, 29% vol, or at least 30% vol of filler are used in the mixture of activated carbon catalyst and a filler material.

[0023] Preferably at most 50% vol 49% vol, 48% vol, 47% vol, 46% vol, 45% vol, 44% vol, 43% vol, 42% vol, 41% vol, 40% vol, 39% vol, 38% vol, 37% vol, 36% vol, 35% vol, 34% vol, 33% vol, 32% vol, 31% vol, or at most 30% vol. of filler are used in the mixture of activated carbon catalyst and a filler material.

[0024] In an embodiment, the filler material may comprise an active catalyst material (e.g. V, Fe, Zn, Si, Al_2O_3, ...).

[0025] The filler is preferably chosen from fillers made of ceramic material, made of metal, fillers made of plastic mineral or mixtures thereof.

[0026] In particular, fillers made of ceramic material, having a free volume of 50-79% may be used:

i. Novalox® Saddle : 12.7-76.2 mm
ii. Berl saddle : 4-50 mm
iii. Cylindrical ring : 5-200 mm
iv. Pall® ring : 25-100 mm
v. Transitional grid lining
vi. Cylindrical ring with 1 bar or 1 cross : 80-200 mm
vii. Grid block : 215*145*90 mm

[0027] In particular, fillers made of metal, having a free volume of 95-98% may be used:

i. Cylindrical ring . 15-50 mm
ii. Pall® ring : 15-90 mm
iii. VSP® : 25-50 mm
iv. Top-Pak® : 15 mm
v. Novalox®-M : 15-70 mm
vi. Twin-Pak® : 10-15 mm
vii. Interpak® : 10-20 mm

[0028] In particular, fillers made of plastic, having a free volume of 87-97% may be used:

i. Novalox® saddle : 12.7 – 50.8 mm
ii. Pall® ring : 15-90 mm
iii. VSP® : 25-90 mm
iv. Igel® : 40 mm
v. Netball® : 45-90 mm

[0029] In an embodiment, the mixture of activated carbon catalyst and a filler material contains no other solid ingredients than the activated carbon catalyst and the filler material. The total of these two ingredients makes thus 100%vol. of the mixture.

[0030] The SO_2 removal is operated either as a so-called wet process or as a so-called dry process.

[0031] The wet process involves continuous rinsing/washing of the catalyst bed as described in DE 2 235 123.

[0032] In the dry process, the activated carbon catalyst is exposed to SO_2 until the conversion rate of SO_2 decreases, After this loading cycle, the supply of SO_2 is switched off and the catalyst is subjected to rinsing/washing with water or an aqueous solution and the H_2SO_4 is washed out. The catalyst is then dried and can be reused after this regeneration-cycle. Such methods are described in US 3,486,852 or US 4,122,150.

[0033] The present process can be used in an analogous way, either as a so-called wet process with a continuous rinsing/washing of the catalyst mixture or as a so-called dry process with a batch wise operation of a phase of loading the catalyst mixture with SO_2 and a phase of washing/rinsing/drying of the catalyst mixture. In the "dry process", the catalyst mixture is usually rinsed during 2 hours with a total of about 100 litres of water per m3 of mixture, i.e. about 50 $l/hour/m^3$ of mixture.During the wet process, the mixture of activated carbon catalyst and a filler material is preferably washed with water or an aqueous solution in an amount between 5 $l/hour/m^3$ of mixture and 100 $l/hour/m^3$ of mixture.

[0034] The mixture of activated carbon catalyst and a filler material is preferably washed by intermittent spraying with water or an aqueous solution in counterflow to the gas.

[0035] The process is operated preferably at a pressure from 0.9 to 1.1 atm and more preferably at atmospheric pressure.

[0036] In the process as described the gas containing SO_2 and O_2 can be a waste gas generated by chemical and metallurgical processes. Its SO_2 content is typically between 300 ppm and 200,000 ppm.

[0037] The gas being brought into contact with the mixture of activated carbon catalyst and a filler material is usually at a temperature between 10°C and 150°C.

[0038] The O_2 content of the gas is as a rule between 2 and 21% vol.

[0039] The H_2SO_4 content of the H_2SO_4 solution obtained is preferably between 5 and 50% vol. depending on the volume of water or aqueous solution used to rinse the mixture of activated carbon catalyst and a filler material.

[0040] Any heavy metals (such as Hg and Cd) are also removed from the gas during the process.

[0041] Any organic compounds are also removed from the gas in case of a dry process application.

Brief Description of the Drawings

[0042] 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 2 of the SO_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 3 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 4 of the SO_2 content of the waste gases at the inlet and outlet of the reactor.

FIG. 6 is a graph showing the values measured during Test 5 and 6 of the SO_2 loading capacity of an active carbon catalyst and of a mixture of an active carbon catalyst and a filler.

FIG. 7 is a graph showing the values measured during Test 5 and 6 of the drying time of an active carbon catalyst and of a mixture of an active carbon catalyst and a filler.

FIG. 8 is a graph showing the removal efficiency of an active carbon catalyst alone and different ways of mixing an active carbon catalyst with filler in relation to Test 10a, b, c and d,.

FIG. 9 is a graph showing the removal efficiency of an active carbon catalyst mixed with different quantities of a first filler material in relation to Test 11,

FIG. 10 is a graph showing the removal efficiency of an active carbon catalyst mixed with different quantities of a second filler material in relation to Test 12,

FIG. 11 is a graph showing the removal efficiency of an active carbon catalyst mixed with 1/4 of different sized filler materials in relation to Test 13,

FIG. 12 is a graph showing the removal efficiency of different types of active carbon catalyst mixed with 1/3 of filler materials in relation to Test 14,

Description of Preferred Embodiments

[0043] 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.

[0044] For the purpose of these tests, instead of waste gas a test gas is used to simulate the waste gases. The test gas consists of ambient air which is used as is, at a temperature between 10-12°C and to which SO_2 is subsequently added from a pressurized cylinder 18 via corresponding valve 22. A first measuring device 26 analyses the composition (SO_2 content, O_2 content), the temperature, the flow volume and the flow rate of the test gas.

[0045] The test gas is then cooled to saturation temperature in a quench 28 by evaporation of water. The test gas is drawn via the quench 28 into the reactor 10 by a fan 30. A coalescer, a droplet separator or a mist collector at the outlet of the quench 28 collects any droplets that might be contained in the test gas as it exits from the quench.

[0046] The test gas flows through the reactor 10 and through the activated carbon catalyst or the filling material or a combination of an activated carbon catalyst and filling material 32 arranged inside the test reactor 10. The test gas flows from the bottom to the top of the reactor 10 and is then examined once it is 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, O_2

content), the temperature, the flow volume and the flow rate, and is then released into the atmosphere.

[0047] 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 or the filling material or a combination of activated carbon and filling material 32 in counterflow to the test gas.

[0048] 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.

[0049] The water required for the quench 28 comes directly from the water supply and is circulated within the quench.

[0050] The SO_2 is catalytically converted into SO3 on the activated carbon catalyst, and is then converted into sulfuric acid if water is added.

[0051] The filling material is randomly mixed with the activated carbon catalyst and the mixture is located above the sieve i.e. a metallic mesh sieve with mesh inferior to the particle size of the mixture of catalyst and filler (e.g. > 2 mm.

[0052] The sulfuric acid formed is rinsed off from 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.

[0053] The presence of filling material surprisingly improves the conversion efficiency during SO_2 catalytic reaction and/or during spraying with water due to liquid/gas interaction. The presence of the filling material seems to enhance the liquid and gas flows as well as their repartition through the catalyst bed that allows a more uniform liquid and gas coverage of each catalyst grain and thus a higher SO_3 to H_2SO_4 conversion. Indeed the regeneration of the activated carbon during dry process is quicker and more efficient leading to a shorter regeneration-cycle time.

[0054] It has been found that there is a

Good fluid distribution

Low pressure drop in the reactor

Less temperature gradient

[0055] These main parameters may explain the better performance of the system.

[0056] The filler material may optionally be impregnated as stated before.

[0057] In the test reactor described above, spraying with water was carried out 1-4 times/hour using an amount of water of 12.5-125 l/hour/m^3 of mixture. The water is collected in a container 42 in the lower part 12 of the test reactor 10 together with the aqueous sulfuric acid solution produced during the process. The acid content is determined by means of a measuring device 44. The sulfuric acid solution is then pumped off by a pump 46 and the flow volume is ascertained using a further measuring device 48.

[0058] In the system described above, the sulfur dioxide of the waste gases is catalytically converted via SO_3 on wet catalyst particles to form sulfuric acid. 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.
- Gas temperature between 10 and 12° C.
- O_2 content approximately 20% by volume.
- Water saturation and eventually cooling of the waste gases by quenching.

[0059] Tested catalysts were provided by NORIT Nederland B.V. of Postbus 105 NL-3800 AC Amersfoot under the names Norit_RST-3. This catalyst is an extruded wood/charcoal based activated carbon catalyst with a particle size of about 3mm. The following general properties are guaranteed by the manufacturer: butane adsorption 24g/%; inner surface (BET) 880m^2/g; bulk density 370-420kg/m^3; ash content 4.7% by weight; pH alkaline; moisture (packed) 5% by weight.

[0060] In the tests, flue gas analyzers of a German company named Testo were used. The devices were calibrated by the manufacturer. In addition, the analysis data of these flue gas analyzers was confirmed by wet-chemical measurements carried out in parallel. The results of all measurements fell within the admissible deviation tolerances.

[0061] The progression of the SO_2 conversion by H_2SO_4 on the catalyst surface corresponds to the following total formula:

[0062] $SO_2+\frac{1}{2}O_2+nH_2O$ (catalytically)$\rightarrow H_2SO_4+(n-1)H_2O$

[0063] Without wanting to be committed to a particular theory, it is assumed that:

- O_2 and SO_2 migrate toward the active centers of the catalyst where they are converted into SO_3.
- SO_3 migrates out from the active centers 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 sulfuric acid in accordance with the reaction equation above.

[0064] The filling material mixed with activated carbon catalyst enables an optimal liquid and gas interaction with catalyst active sites.

[0065] Softened or demineralized water is used to wash out the catalyst.

[0066] The specific level of SO_2 saturation achieved in the pores of the catalyst in respect of the sulfuric acid formation occurs in the reactor once sufficient SO_2 has been converted into SO_3 and starts to form sulfuric acid.

[0067] Such a condition is reached after approximately 20 to 100 operating hours depending on the approach adopted (amount of SO_2/SO_3 fed and corresponding water spraying rate). The percentage by weight of acid produced is independent of the duration – i.e. the time of contact between the gas and the catalyst. The SO_2 to H_2SO_4 conversion is dependent on the SO_2 to SO_3 conversion efficiency and on the amount of water or aqueous solution used. For this reason, this process can produce solutions with different percentages by weight of sulfuric acids (H_2SO4).

[0068] Test 1: (Comparative Test) The tests were carried out under the following conditions:

Raw gas volume flow	min.	200	m^3/h
	max.	300	m^3/h
SO_2 content (inlet)	min.	2000	ppm
	max.	3000	ppm
Gas temperature	min.	10°	C.
	max.	12°	C.
Relative Humidity of the gas		100	%
O_2 content		>20%	by volume

[0069] The reactor is made of inert glass fiber reinforced plastics material, has a volume of approximately 2 m^3 and is filled with 1.2 m^3 of an activated carbon catalyst of the Norit_RST-3 type.

[0070] 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 2,000 and 3,000 ppm of SO_2 were added. Overall, the reactor was charged with approximately 88 kg of SO_2 (approximately 73 kg of SO_2/m^3 of catalyst bed). In accordance with this test, the addition of water at 15 l/hour was divided into 2 portions/hour (10.2 $l/hour/m^3$ of catalyst bed). The SO_2 content of the waste gases was measured 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 FIG. 2. The first measurements shown in this case were taken after saturation of the catalyst, i.e. 50 hours after start-up of the reactor. The SO_2 outlet concentration fluctuated repeatedly between 600 ppm and 900 ppm, with a SO_2 removal efficiency of 66%. The test was carried out continuously over approximately 9 hours.

[0071] Test 2 : The tests were carried out under the following conditions:

Raw gas volume flow	min.	200	m^3/h
	max.	300	m^3/h
SO_2 content (inlet)	min.	2000	ppm
	max.	3000	ppm
Waste gas temperature	min.	10°	C.

	max.	12°	C.
% of relative humidity		100	%
O_2 content		>20%	by volume

[0072] The reactor is made of inert glass fiber reinforced plastics material, has a volume of approximately 2 m^3 and is filled with 1.2 m^3 of an activated carbon catalyst of the Norit_RST-3 type modified by CPPE by mixing with 0.27 m3 of a ceramic filling material (Novalox ® saddle Acidur-Special-Stoneware supplied by Vereinigte Füllkörper-Fabriken).

[0073] Contrary to the test 1, the reactor was charged immediately when running with the addition of SO2 from gas cylinders, and in this instance between 2,000 and 3,000 ppm of SO_2 were added. In accordance with this test, the addition of water at 15 l/hour was divided into 2 portions/hour (10.2 l/hour/m^3 of catalyst bed). The SO_2 content of the waste gases was measured 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 FIG. 3. The first measurements shown in this case were taken directly after start-up of the reactor. The SO_2 outlet concentration fluctuated repeatedly between 15 ppm and 95 ppm with a SO_2 removal efficiency of 96%. The test was carried out continuously over approximately 7 hours.

[0074] Test 3 : The tests were carried out under the following conditions:

Raw gas volume flow	min.	200	m^3/h
	max.	300	m^3/h
SO_2 content (inlet)	min.	2000	ppm
	max.	3000	ppm
Waste gas temperature	min.	10°	C.
	max.	12°	C.
% of relative humidity		100	%
O_2 content	>20%	by volume	

[0075] The reactor is made of inert glass fiber reinforced plastics material, has a volume of approximately 2 m^3 and is filled with 1.2 m^3 of an activated carbon catalyst of the Norit_RST-3 type modified by CPPE by mixing with 0.27 m^3 of a ceramic filling material (Novalox ® saddle Acidur-Special-Stoneware supplied by Vereinigte Füllkörper-Fabriken).

[0076] Like the test 2, the reactor was charged immediately when running with the addition of SO_2 from gas cylinders, and in this instance between 2,000 and 3,000 ppm of SO_2 were added. In accordance with this test, the addition of water at 71 l/hour was divided into 2 portions/hour (48.3 l/hour/m^3 of catalyst bed). The SO_2 content of the waste gases was measured 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 FIG. 4. The first measurements shown in this case were taken directly after start-up of the reactor. The SO_2 outlet concentration fluctuated repeatedly between 9 ppm and 43 ppm, with a SO_2 removal efficiency of 98%. The test was carried out continuously over approximately 4 hours.

[0077] Test 4 : The tests were carried out under the following conditions:

Raw gas volume flow	min.	200	m^3/h
	max.	300	m^3/h
SO_2 content (inlet)	min.	2000	ppm
	max.	3000	ppm
Waste gas temperature	min.	10°	C.
	max.	12°	C.
% of relative humidity		100	%
O_2 content	>20%	by volume	

[0078] The reactor is made of inert glass fiber reinforced plastics material, has a volume of approximately 2 m^3 and is filled with 1.2 m^3 of an activated carbon catalyst of the Norit_RST-3 type modified by CPPE by mixing with 0.27 m^3 of a plastic filling material (Pall®-V-ring supplied by Vereinigte Füllkörper-Fabriken).

[0079] Like the test 2, the reactor was charged immediately when running with the addition of SO_2 from gas cylinders, and in this instance between 2,000 and 3,000 ppm of SO_2 were added. In accordance with this test, the addition of water at 15 l/hour was divided into 2 portions/hour (10.2 l/hour/m^3 of catalyst bed). The SO_2 content of the waste gases was measured at the inlet and at the outlet of the reactor, as illustrated in FIG. 1. The measurements were taken every hours and are shown in graphs in FIG. 5. The first measurements shown in this case were taken directly after start-up of the reactor. The SO_2 concentration fluctuated repeatedly between 90 ppm and 160 ppm, with a SO_2 removal efficiency of 95%. The test was carried out continuously over approximately 30 hours.

[0080] Test 5 : The tests were carried out under the following conditions:

Raw gas volume flow	min.	200	m^3/h
	max.	300	m^3/h
SO_2 content (inlet)	min.	18000	ppm
	max.	22000	ppm
Waste gas temperature	min.	10°	C.
	max.	12°	C.
% of relative humidity		<10	%
O_2 content	>18%	by volume	

[0081] The reactor is made of inert glass fiber reinforced plastics material, has a volume of approximately 2 m^3 and is filled with 1.2 m^3 of an activated carbon catalyst of the Norit_RST-3 type.

[0082] The quench was switched off during this test and dried activated carbon is used.

[0083] Like the test 2, the reactor was charged immediately when running with the addition of SO_2 from gas cylinders, and in this instance between 18,000 and

22,000 ppm of SO_2 were added without addition of water during the SO_2-loading phase. The SO_2 content of the waste gases was measured at the inlet and at the outlet of the reactor, as illustrated in FIG. 1. The measurements were taken each minute. The SO_2 concentration fluctuated repeatedly between 18000 ppm and 22000 ppm, with a SO_2 removal efficiency of more than 99%. The test was carried out over approximately 106 minutes until SO_2 outlet was higher than 100 ppm. The SO_2-loading efficiency was 23 kg of SO_2 per cubic meter of activated carbon. After this SO_2-loading step, the activated carbon was washed continuously for two hours through addition of water at 50 l/hour. In a next step, ambient air, heated at 80 °C, is pulled through the catalytic bed and the activated carbon is dried after a time period of 74 hours.

[0084] Test 6 : The tests were carried out under the following conditions:

Raw gas volume flow	min.	200	m^3/h
	max.	300	m^3/h
SO_2 content (inlet)	min.	18000	ppm
	max.	22000	ppm
Waste gas temperature	min.	10°	C.
	max.	12°	C.
% of relative humidity		<10	%
O_2 content	>18%	by volume	

[0085] The reactor is made of inert glass fiber reinforced plastics material, has a volume of approximately 2 m^3 and is filled with 1.2 m^3 of an activated carbon catalyst of the Norit_RST-3 type modified by CPPE by mixing with 0.27 m^3 of a ceramic filling material (Novalox ® saddle Acidur-Special-Stoneware supplied by Vereinigte Füllkörper-Fabriken).

[0086] The quench was switched off during this test and dried activated carbon is used.

[0087] Like the test 2, the reactor was charged immediately when running with the addition of SO_2 from gas cylinders, and in this instance between 18,000 and 22,000 ppm of SO_2 were added without addition of water during the SO_2-loading phase. The SO_2 content of the waste gases was measured at the inlet and at the outlet of the reactor, as illustrated in FIG. 1. The measurements were taken each minute. The SO_2 concentration fluctuated repeatedly between 18000 ppm and 22000 ppm, with a SO_2 removal efficiency of more than 99%. The test was carried out over approximately 117 minutes until SO_2 outlet was higher than 100 ppm. . The SO_2-loading efficiency was 26 kg of SO_2 per cubic meter of activated carbon. After this SO_2-loading step, the activated carbon was washed continuously for two hours through addition of water at 50 l/hour. In a next step, ambient air, heated at 80 °C, is pulled through the catalytic bed and the activated carbon is dried after a time period of 63 hours.

[0088] All the above tests have been carried out with 1.2 m^3 of catalyst (activated carbon). In the tests carried out with addition of filler (whatever its shape): 0.27 m^3 of filler were added to the initial 1.2m^3 of catalyst.

[0089] Vol% of the filler = 0.27/(0.27+1.2)*100 = 18.36% vol.

[0090] A positive effect of the filler can be measured between 5%vol filler and 50% filler, the remaining being activated carbon catalyst.

[0091] The surprising effect is that the removal of SO_2 is more efficient when the catalyst is mixed with fillers than the catalyst alone since more SO_2 is converted with the same amount of catalyst as shown in Fig. 8.

[0092] In addition in case of dry process conditions, the SO_2-loading capacity of activated carbon is higher and the regeneration cycle is shorter in case the activated carbon is mixed with fillers as shown in Fig. 6 and in Fig.7.

[0093] In the tests conducted it was found that ceramic filler material having a saddle shape seem to be the most efficient. Saddle shape means in the context of the present invention: shaped in the form of a horse's saddle, a shape that is bent down at the sides so as to give the upper part a rounded form, respectively an object having the form of an anticlinal fold.

[0094] Test 7 – Figure 8

[0095] In these tests different types of mixing were tested and compared to each other in a reactor as depicted on Fig. 1.

[0096] The conditions were as follows: Test 7a

Gas flow: 200-300 m3/h

Gas temperature: starting from 10°C

Gas flow inlet: 2000-3000 ppm

Activated carbon catalyst: 1.2 m^3 of extruded activated carbon catalyst with particle size 2-4 mm

Filler material: 0.27 m^3 of 38mm wide ceramic saddle filling material

CPPE mixing method; random mixture: most efficient with 90-98% SO_2 removal efficiency as shown on Fig. 8 – left hand side

[0097] Comparative Example Test 7b – Figure 8

[0098] The conditions were as follows:

Gas flow: 200-300 m^3/h

Gas temperature: starting from 10°C

Gas flow inlet: 2000-3000 ppm

Single activated carbon catalyst bed: 55-65% SO_2 removal efficiency as shown on Fig. 8 – second from the left.

[0099] Comparative Example Test 7c – Figure 8

[00100] The conditions were as follows:

Gas flow: 200-300 m^3/h

Gas temperature: starting from 10°C

Gas flow inlet: 2000-3000 ppm

Activated carbon catalyst: 1.2 m^3 of extruded activated carbon catalyst with particle size 2-4 mm

Filler material: 0.27 m^3 of 38mm wide ceramic saddle filling material

Two activated carbon catalyst beds (0.5 m^3 and 0.7 m^3 respectively) separated by a layer of 0.27 m^3 of filling material : less efficient with 50-65% SO_2 removal efficiency as shown on Fig. 8 – third from the left.

[00101] Comparative Example Test 7d – Figure 8

[00102] The conditions were as follows:

Gas flow: 200-300 m^3/h

Gas temperature: starting from 10°C

Gas flow inlet: 2000-3000 ppm

Activated carbon catalyst: 1.2 m^3 of extruded activated carbon catalyst with particle size 2-4 mm

Filler material: 0.27 m^3 of 38mm wide ceramic saddle filling material

Multi layers design: activated carbon catalyst/filler material layers (0.3 m^3 and 0.054 m^3 respectively): less efficient with 70-80% SO_2 removal efficiency as shown on Fig. 8 – right hand side

[00103] Test 8 – Figure 9

[00104] The conditions were as follows:

Gas flow: 200-300 m3/h

Gas temperature: starting from 10°C

Gas flow inlet: 2000-3000 ppm

Activated carbon catalyst: extruded activated carbon with particle size 2-4 mm

Filler material: 38mm wide ceramic saddle filling material

CPPE mixing method; random mixture with different ratio in volume (Filler material/extruded activated carbon catalyst):

1/20: 5 vol% filler material and 95 vol% activated carbon catalyst

1/10: 9 vol% filler material and 91 vol% activated carbon catalyst

1/5: 17 vol% filler material and 83 vol% activated carbon catalyst

1/4: 20 vol% filler material and 80 vol% activated carbon catalyst

1/3: 25 vol% filler material and 75 vol% activated carbon catalyst

1/2: 33 vol% filler material and 67 vol% activated carbon catalyst

1/1: 50 vol% filler material and 50 vol% activated carbon catalyst

This test shows the highest efficiency with 94-99% SO_2 removal when operating with 20 vol% filler material and 80 vol% activated carbon catalyst (ratio 1/4) as shown on Fig. 9.

[00105] Comparative test 9 – Figure 10

[00106] The conditions were as follows:

Gas flow: 200-300 m3/h

Gas temperature: starting from 10°C

Gas flow inlet: 2000-3000 ppm

Activated carbon catalyst: extruded activated carbon with particle size 2-4 mm

Filler material: 50mm wide plastic pall ring filling material

CPPE mixing method; random mixture with different ratio in volume (Filler material/extruded activated carbon catalyst):

1/20: 5 vol% filler material and 95 vol% activated carbon catalyst

1/10: 9 vol% filler material and 91 vol% activated carbon catalyst

1/5: 17 vol% filler material and 83 vol% activated carbon catalyst

1/4: 20 vol% filler material and 80 vol% activated carbon catalyst

1/3: 25 vol% filler material and 75 vol% activated carbon catalyst

1/2: 33 vol% filler material and 67 vol% activated carbon catalyst

1/1: 50 vol% filler material and 50 vol% activated carbon catalyst

Less efficient with 77-82% SO_2 removal efficiency when operating with 20 vol% filler material and 80 vol% activated carbon (ratio 1/4) as shown on Fig. 10.

[00107] Test 9 – Figure 11

[00108] The conditions were as follows:

Gas flow: 200-300 m3/h

Gas temperature: starting from 10°C

Gas flow inlet: 2000-3000 ppm

Activated carbon catalyst: extruded activated carbon catalyst with particle size 2-4 mm

Filler material: ceramic saddle filling material with different size from 12.7 to 76.2 mm

CPPE mixing method; random mixture with 20 vol% filler material and 80 vol% activated carbon catalyst (ratio 1/4)

Higher efficiency with 94-99% SO_2 removal efficiency when operating with 38mm ceramic saddle filling material (normalized size 4) as shown on Fig. 11

[00109] Test 10 – Figure 12

[00110] The conditions were as follows:

Gas flow: 200-300 m3/h

Gas temperature: starting from 10°C

Gas flow inlet: 2000-3000 ppm

Activated carbon catalyst: powder, bead, extruded or granulated activated carbon catalyst

Filler material: 38mm wide ceramic saddle filling material

CPPE mixing method; random mixture with 20 vol% filler material and 80 vol% activated carbon catalyst (ratio 1/4)

Higher efficiency with 94-99% SO_2 removal efficiency when operating with extruded activated carbon catalyst as shown on Fig. 12.

[00111] Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.

[00112] All the features disclosed in this specification (including any accompanying claims, abstract, and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar.

N° 93012

93012

P-INTFIB-008/LU

REVENDICATIONS

1. Procédé dans lequel un gaz, contenant du SO_2 et du O_2, est mis en contact avec un mélange de 95 % en volume à 50 % en volume d'un catalyseur à base de charbon activé et de 5 % en volume à 50 % en volume d'une matière de charge inerte, dans lequel le SO_2 est transformé en H_2SO_4 sur le catalyseur à base de charbon activé et est ensuite éliminé par lavage du catalyseur à base de charbon activé pour obtenir une solution de H_2SO_4.

2. Procédé selon la revendication 1, dans lequel la matière de charge représente entre 10 % en volume et 30 % en volume du mélange du catalyseur à base de charbon activé et d'une matière de charge.

3. Procédé selon la revendication 1 ou 2, dans lequel le mélange ne contient pas d'autres ingrédients solides en dehors du catalyseur à base de charbon activé et de la matière de charge.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le catalyseur à base de charbon activé est choisi parmi des catalyseurs imprégnés (tels que Fe, S, OH, ...) ou de charbon activé disponibles auprès de fournisseurs tels que Jacobi, Cabot Norit, Chemviron, Desotec, Carbotech et ATEC.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la matière de charge est choisie parmi des matières de charge en une matière céramique, en métal, des matières de charge en une matière plastique, ou leurs mélanges.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel la matière de charge possède une configuration choisie parmi une configuration en forme de selle, une configuration de forme annulaire, une configuration de forme sphérique, une configuration de forme torique, configuration de forme prismatique ou une configuration de forme irrégulière.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange est disposé dans un lit fixe.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange est lavé avec de l'eau ou avec une solution aqueuse en une quantité entre 5 l/heure/m^3 de catalyseur et 100 l/heure/m^3 de mélange.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange est lavé via une pulvérisation intermittente avec de l'eau ou avec une solution aqueuse à contre-courant par rapport au gaz.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le procédé est mis en oeuvre sous une pression de 0,9 à 1,1 atm., de préférence sous pression atmosphérique.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le gaz saturé en eau contenant du SO_2 et du O_2 est un gaz résiduaire généré par des processus chimiques et métallurgiques.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel la teneur du gaz en SO_2 se situe entre 300 ppm et 200.000 ppm.

13. Procédé selon l'une quelconque des revendications précédentes, dans lequel le gaz qui est mis en contact avec le mélange possède une température entre 10 et 150 °C.

14. Procédé selon l'une quelconque des revendications précédentes, dans lequel la teneur du gaz en O_2 se situe entre 2 et 21 % en volume.

15. Procédé selon l'une quelconque des revendications précédentes, dans lequel la teneur en H_2SO_4 de la solution de H_2SO_4 se situe entre 5 et 50 % en volume.

16. Procédé selon l'une quelconque des revendications précédentes, dans lequel les métaux lourds (tels que Hg et Cd) sont éliminés du gaz.

17. Procédé selon l'une quelconque des revendications précédentes, dans lequel les contaminants organiques sont éliminés du gaz.

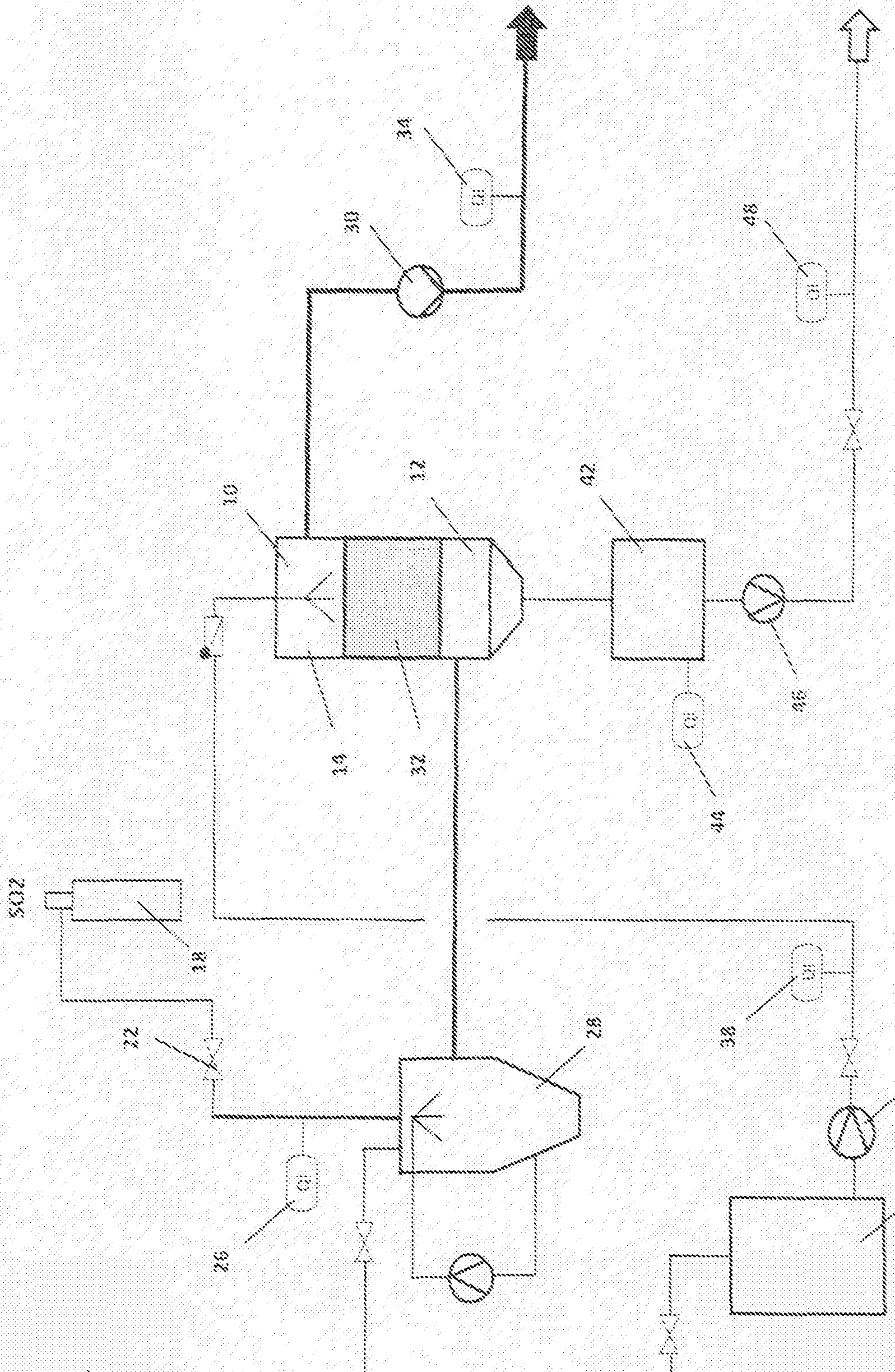


Fig. 1

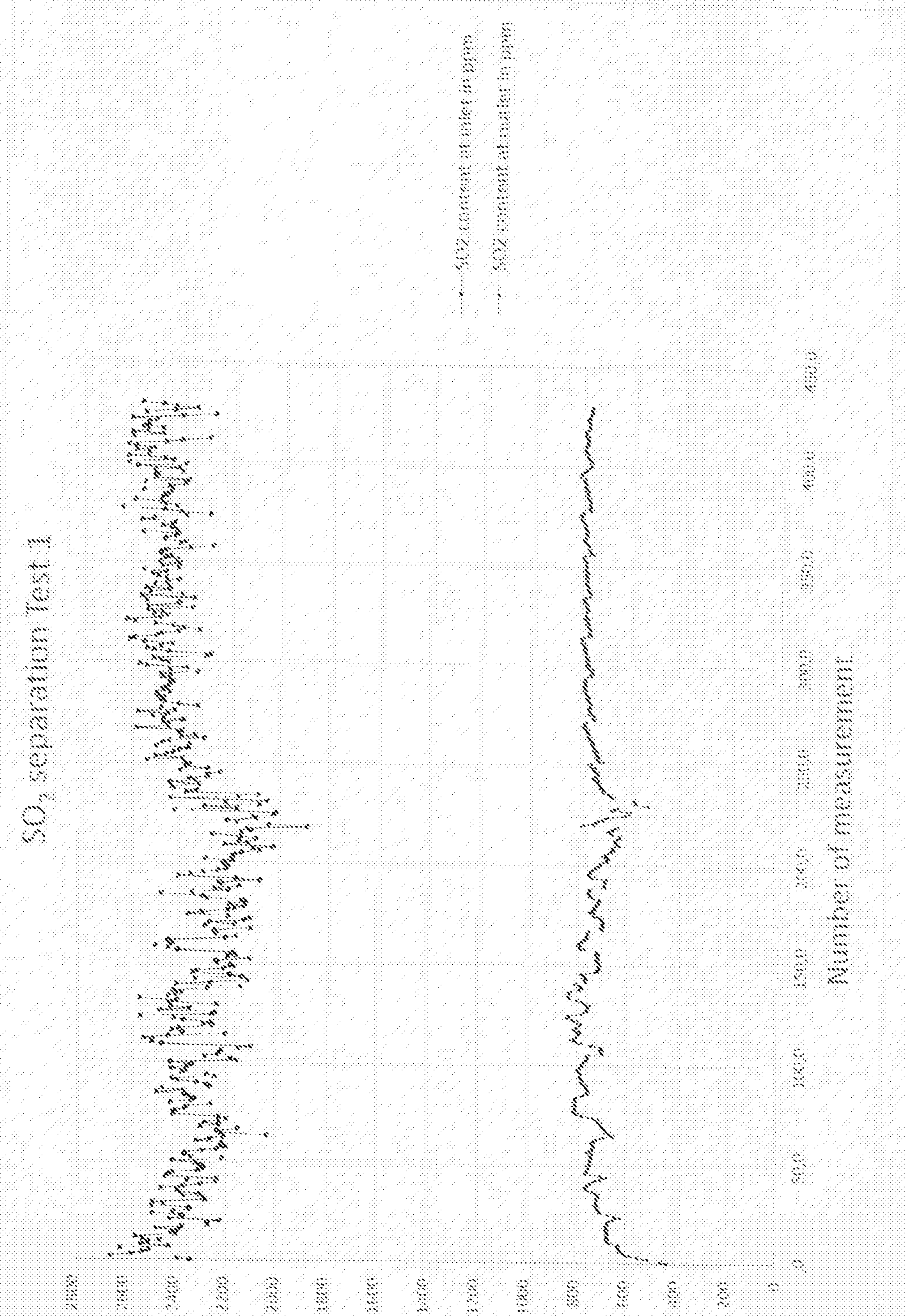

SO_2 separation Test 1
SO_2 concentration in ppm
Number of measurement

Fig. 2

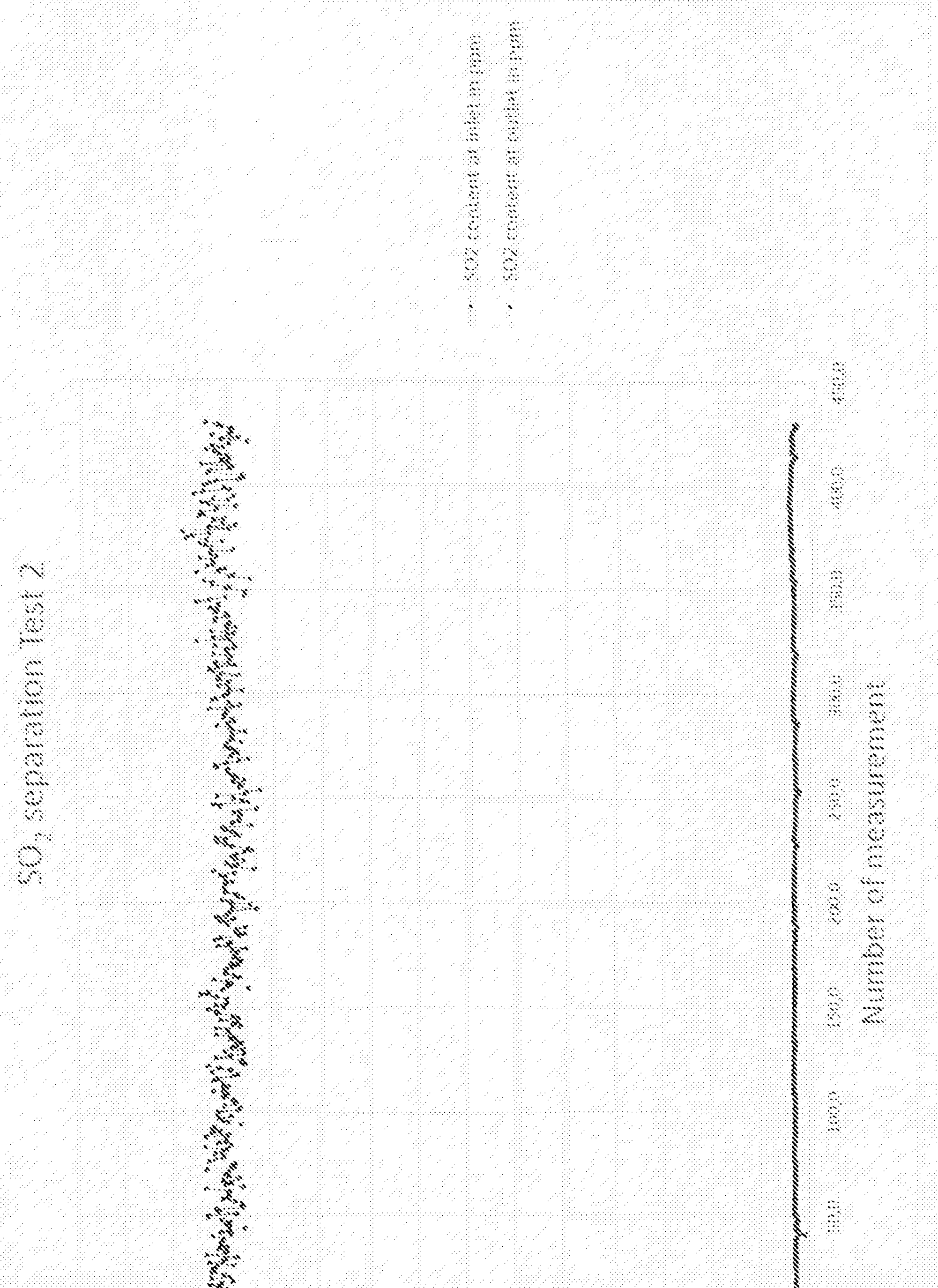

SO$_2$ separation Test 2
SO$_2$ concentration in ppm
Number of measurement
SO2 content at inlet in ppm
SO2 content at outlet in ppm

Fig. 3

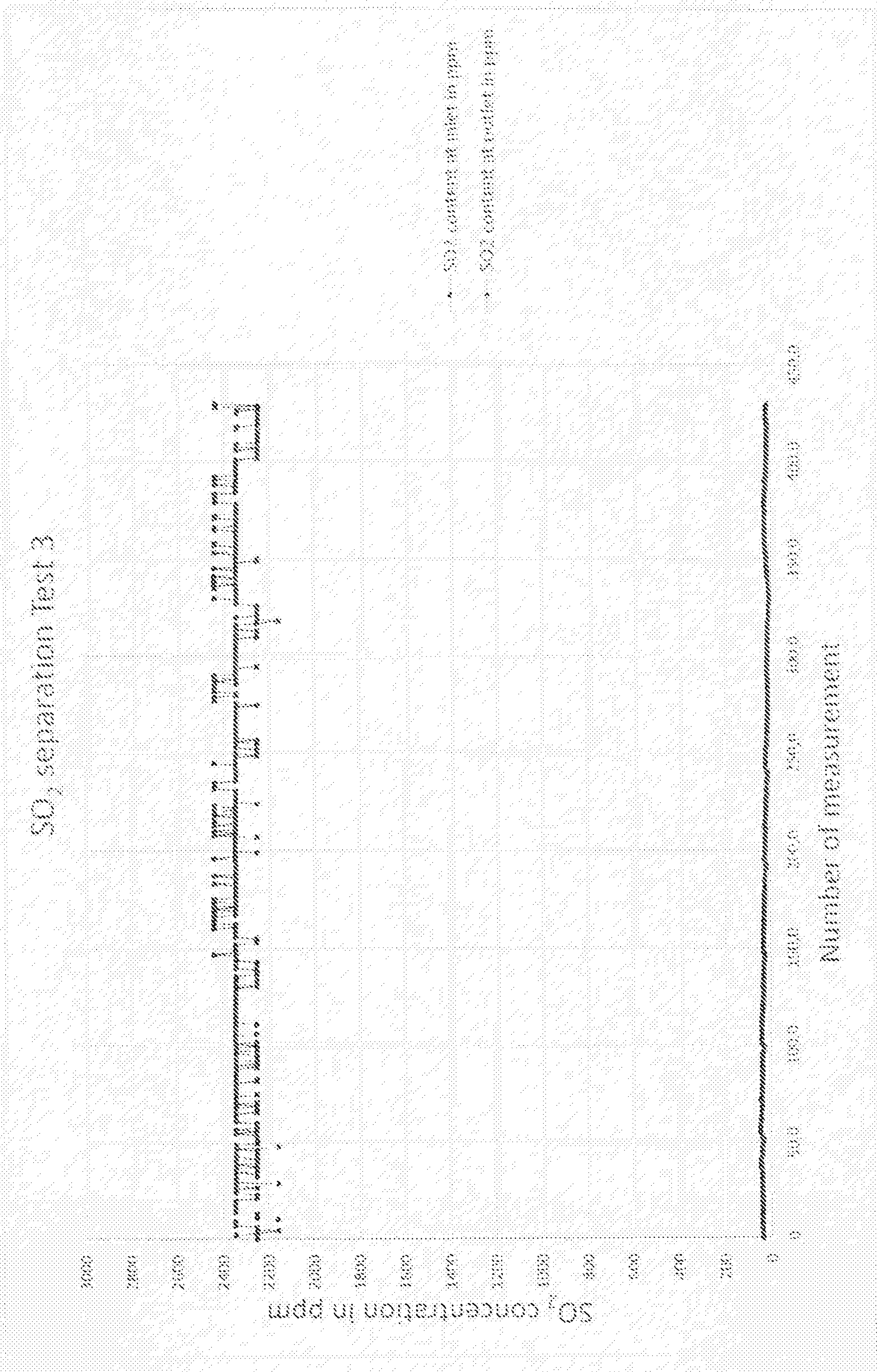

SO_2 separation Test 3
SO2 content at inlet in ppm
SO2 content at outlet in ppm
Number of measurement
SO_2 concentration in ppm

Fig. 4

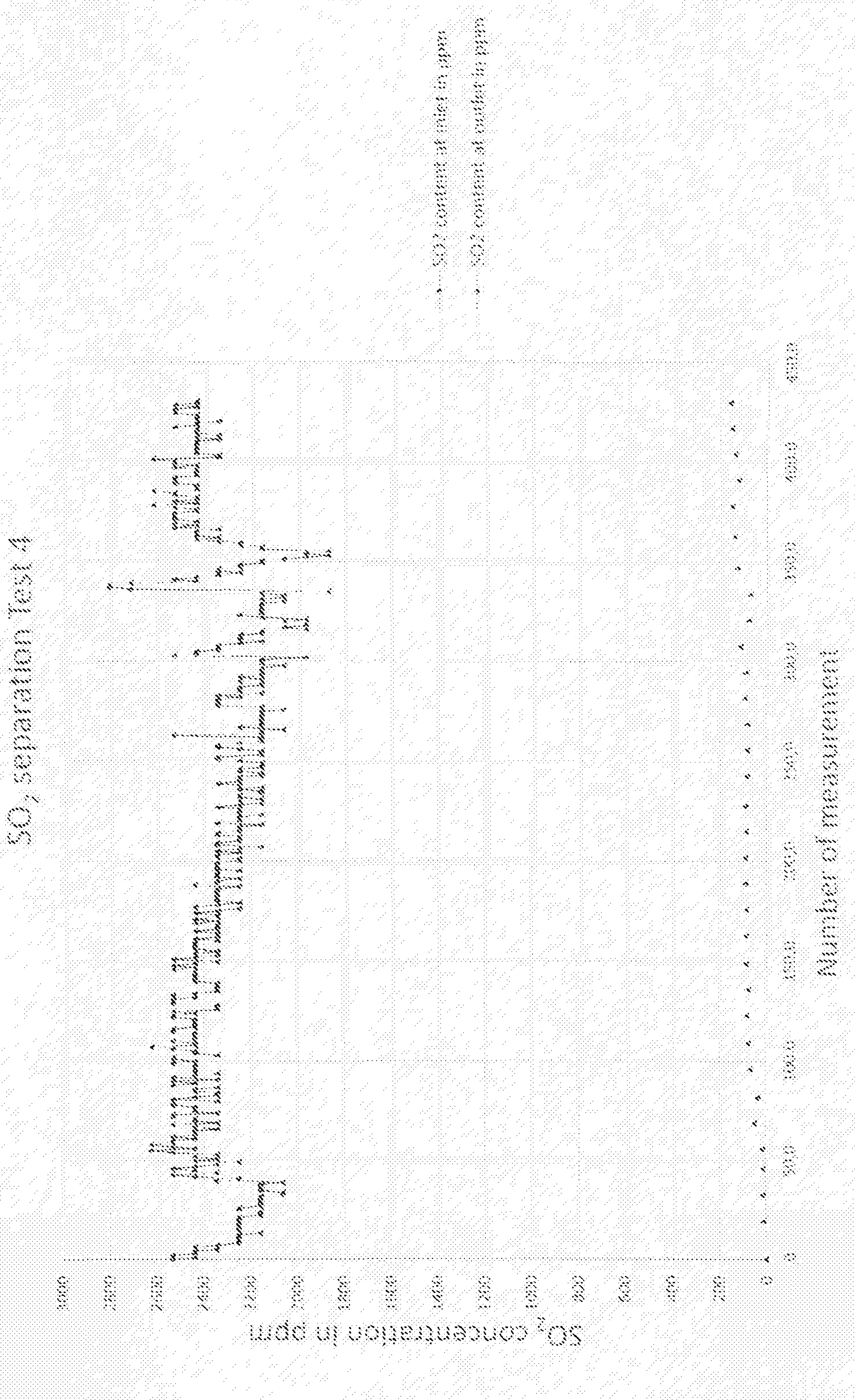

SO_2 separation Test 4
SO_2 concentration in ppm
Number of measurement
SO2 content at inlet in ppm
SO2 content at outlet in ppm

Fig. 5

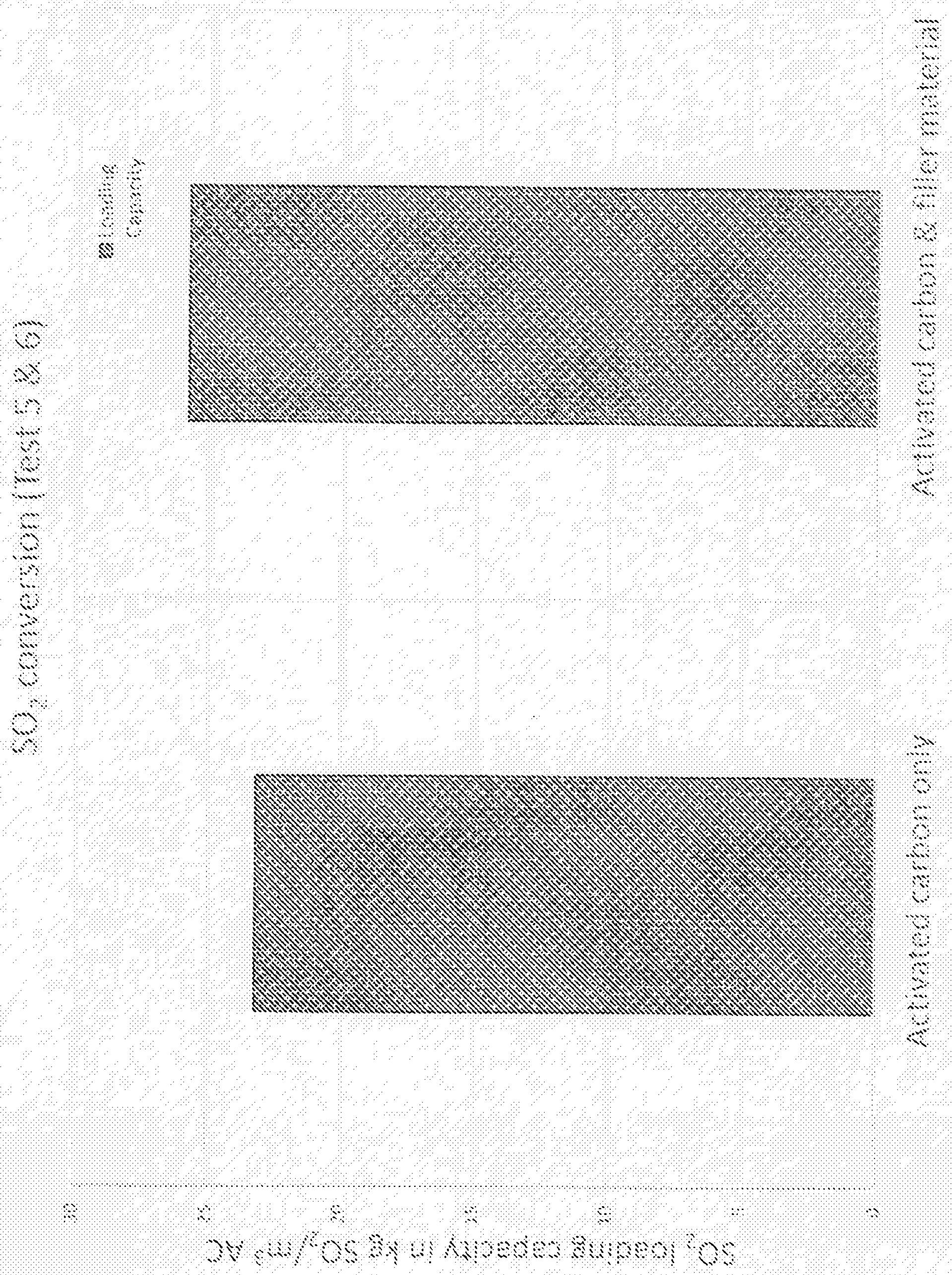

SO$_2$ conversion (Test 5 & 6)
Loading Capacity
Activated carbon only
Activated carbon & filler material
SO$_2$ loading capacity in kg SO$_2$/m^3 AC

Fig. 6


SO_2 conversion (Test 5 & 6)
Drying Cycle
Activated carbon only
Activated carbon & filler material
Drying Cycle in hours

Fig. 7

Fig. 8: Activated carbon and filler material mixture
Bed design vs SO_2 removal performance

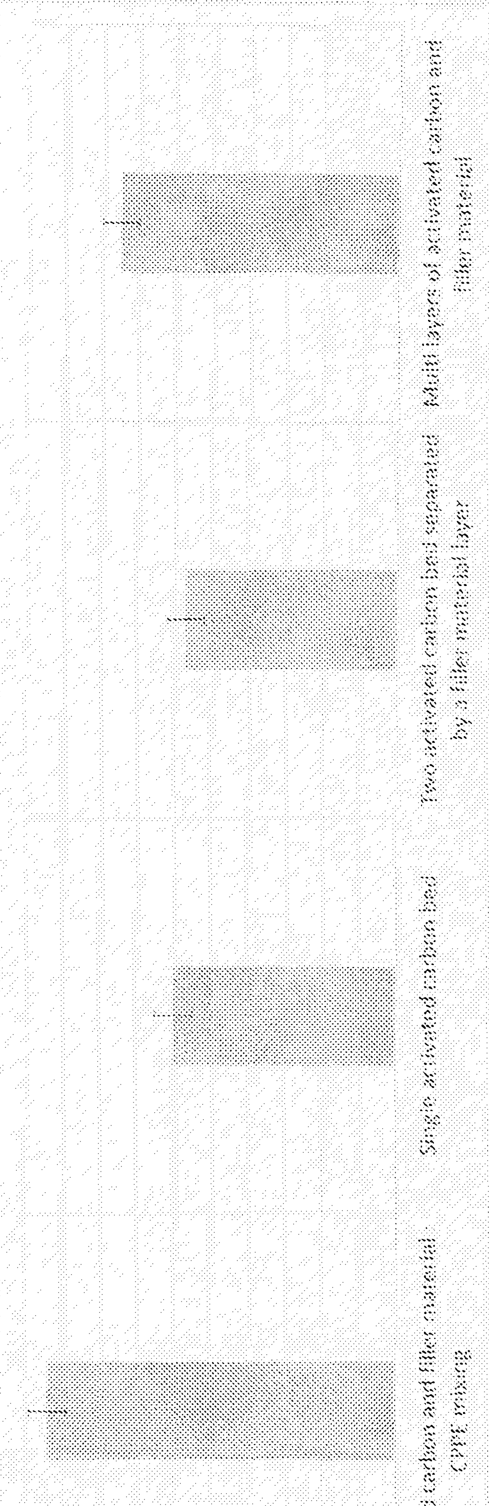


Fig. 9 : Effect of filler material (ceramic saddle)/activated carbon volumic ratio

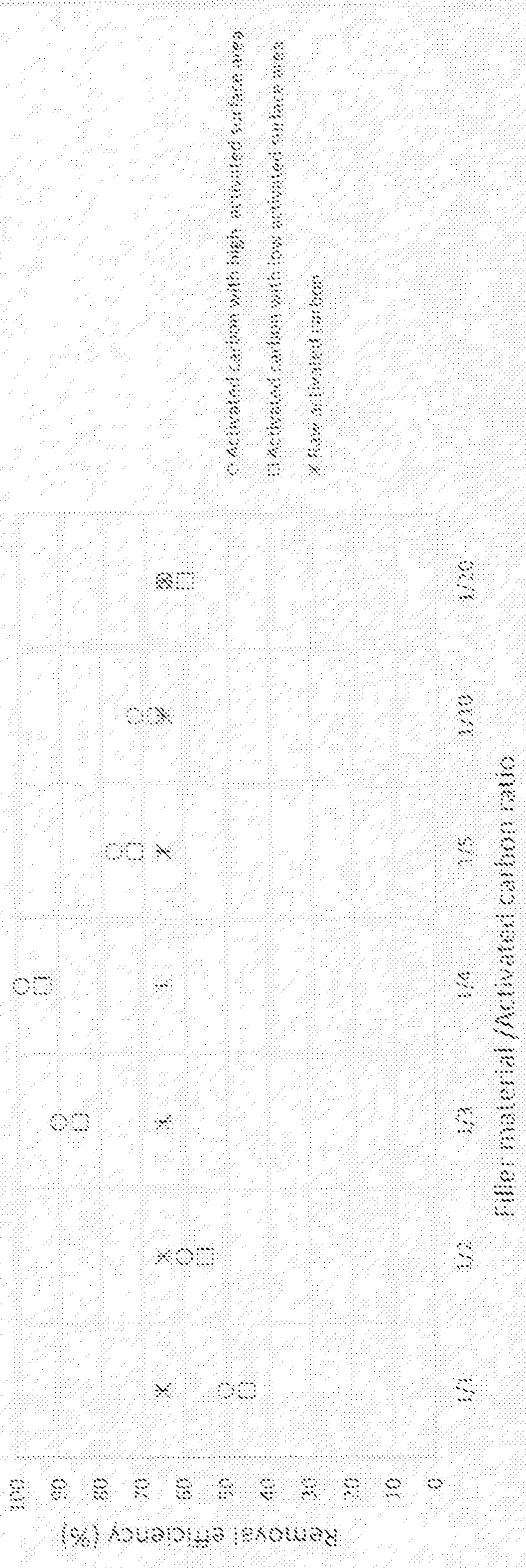
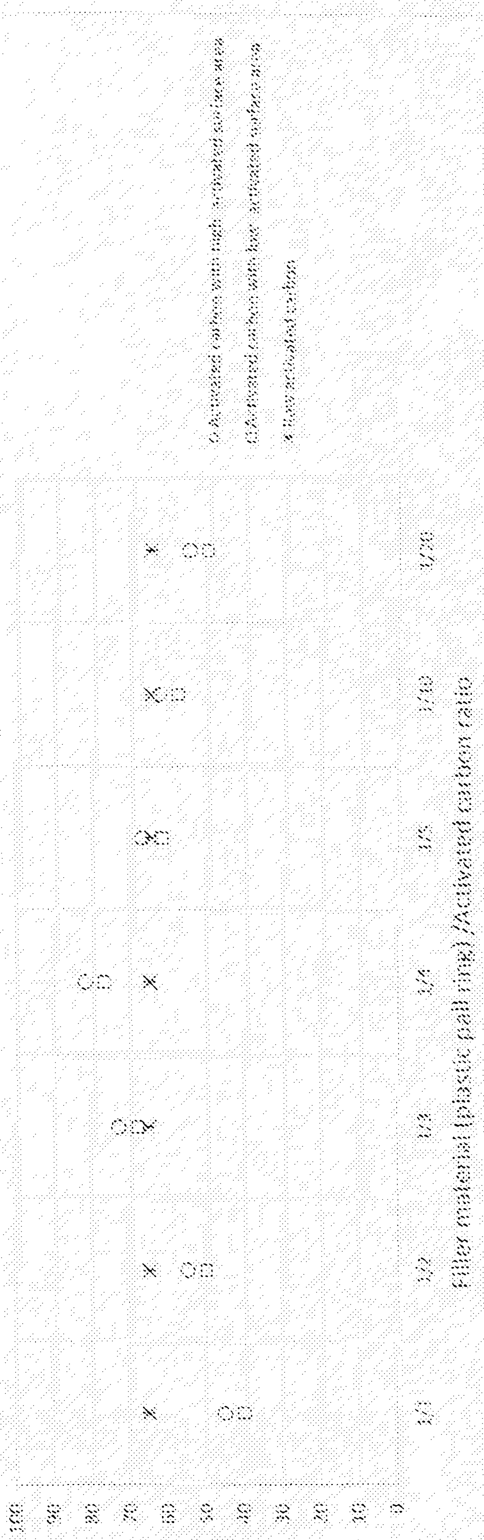


Fig. 10: Effect of filler material (plastic pall ring)/activated carbon ratio



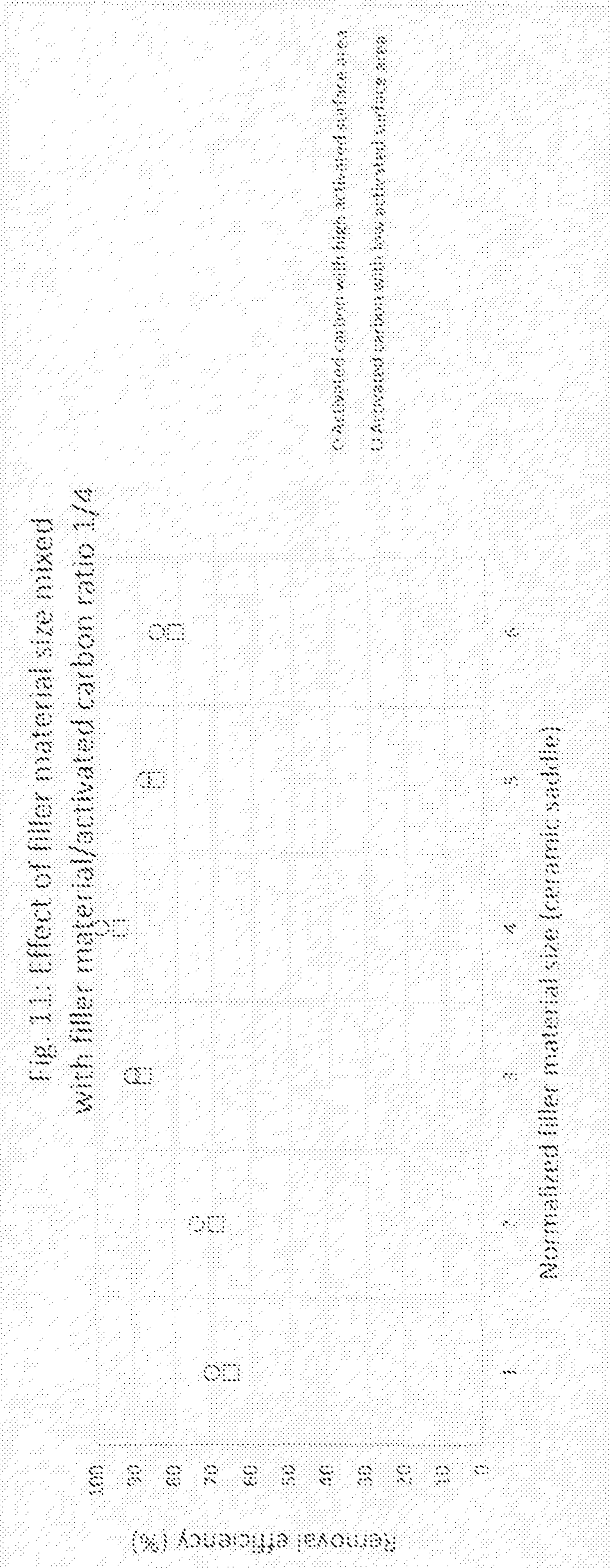


Fig. 11: Effect of filler material size mixed with filler material/activated carbon ratio 1/4

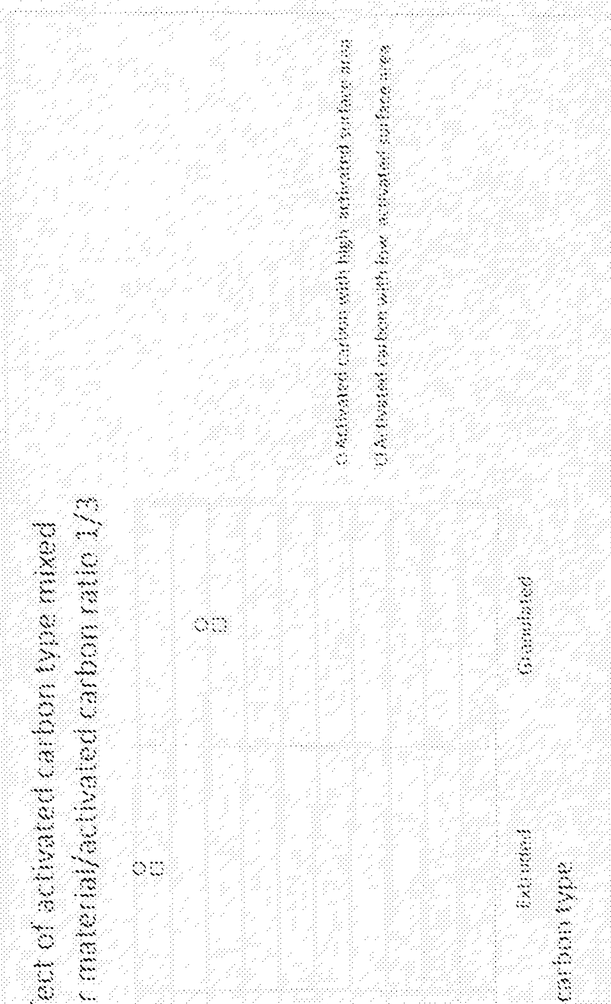


Fig. 12: Effect of activated carbon type mixed with filler material/activated carbon ratio 1/3

Abstract

The present invention concerns a process wherein a gas, containing SO_2 and O_2 is brought in contact with a mixture of from 95% vol. to 50% vol. of activated carbon catalyst and from 5% vol. to 50% vol. of an inert filler material; wherein the SO_2 is converted to H_2SO_4 on the activated carbon catalyst and is then washed from the activated carbon catalyst to obtain a H_2SO_4 solution.

(Fig. 1)

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DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie
et du Commerce extérieur

SEARCH REPORT

in accordance with Article 35.1 a)
of the Luxembourg law on patents
dated 20 July 1992

National Application Number

LO 1317
LU 93012

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 302 224 A2 (ZLEHIT TS LAB ELEKTROCHIMICHES [BG]) 8 February 1989 (1989-02-08) * column 3, lines 15-20; figure 1; example 1 *	1-15	INV. B01D53/86 C01B17/78
X	EP 2 260 940 A1 (CHIYODA CORP [JP]) 15 December 2010 (2010-12-15) * paragraph [0060]; claims 1,13,17-19; examples 9,13 *	1,2,4,7, 9-14,16, 17	
X	JP H11 236207 A (CHIYODA CHEM ENG CONSTRUCT CO) 31 August 1999 (1999-08-31) * paragraph [0004]; example 1 * * abstract *	1,2,7, 10-14, 16,17	
X	JP 3 562551 B2 (CHIYODA CHEM ENG CONSTRUCT CO) 8 September 2004 (2004-09-08) * example 1 *	1,2,7, 10-14, 16,17	

TECHNICAL FIELDS SEARCHED (IPC)

B01D
C01B

The present search report has been drawn up for all claims

	Date of completion of the search	Examiner
	12 December 2016	Gruber, Marco

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

ANNEX TO THE SEARCH REPORT ON LUXEMBOURG PATENT APPLICATION NO.

LO 1317
LU 93012

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-12-2016

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0302224	A2	08-02-1989	BG	47242	A1	15-06-1990
			CN	1032772	A	10-05-1989
			DE	3874044	D1	01-10-1992
			EP	0302224	A2	08-02-1989
			JP	H01100004	A	18-04-1989
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			CA	2718703	A1	24-09-2009
			CN	101977685	A	16-02-2011
			EP	2260940	A1	15-12-2010
			JP	5553966	B2	23-07-2014
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			MY	153950	A	15-04-2015
			US	2011020205	A1	27-01-2011
			WO	2009116183	A1	24-09-2009
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			JP	H11236207	A	31-08-1999
JP 3562551	B2	08-09-2004	JP	3562551	B2	08-09-2004
			JP	H10314588	A	02-12-1998

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie
et du Commerce extérieur

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
LO1317	04.04.2016		LU93012

International Patent Classification (IPC)
INV. B01D53/86 C01B17/78

Applicant
CPPE Carbon Process & Plant Engineering S.A.

This report contains indications relating to the following items:

- ☒ Box No. I — Basis of the opinion
- ☐ Box No. II — Priority
- ☐ Box No. III — Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV — Lack of unity of invention
- ☒ Box No. V — Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI — Certain documents cited
- ☐ Box No. VII — Certain defects in the application
- ☐ Box No. VIII — Certain observations on the application

Examiner
Gruber, Marco

Form LU237A (Cover Sheet) (January 2007)

Application No.
LU93012

WRITTEN OPINION

Box No. I Basis of the opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	6
	No:	Claims	1-5, 7-17
Inventive step	Yes:	Claims	
	No:	Claims	1-17
Industrial applicability	Yes:	Claims	1-17
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following documents:

D1 EP 0 302 224 A2 (ZLEHIT TS LAB ELEKTROCHIMICHES [BG]) 8 February 1989 (1989-02-08)

D2 EP 2 260 940 A1 (CHIYODA CORP [JP]) 15 December 2010 (2010-12-15)

D3 JP H11 236207 A (CHIYODA CHEM ENG CONSTRUCT CO) 31 August 1999 (1999-08-31)

D4 JP 3 562551 B2 (CHIYODA CHEM ENG CONSTRUCT CO) 8 September 2004 (2004-09-08)

2 The present application does not meet the criteria of patentability, because the subject-matter of claims 1 to 5, and 7 to 15 is not new.

2.1 D1 discloses (ref. abstract and Fig. 1) a process for producing H_2SO_4 by contacting (ref. col. 3, l. 15 to 20) a gas containing SO_2 and O_2 (4) with a mixture of an activated carbon catalyst (1) and a filler in form of a hydrophobic polymeric agent in a respective ratio of 25:1 to 1:4 (ref. abstract and claim 1). After contact with the catalyst (1), the SO_2 converted into H_2SO_4 is washed from the catalyst (1) and obtained as H_2SO_4 solution (9).

D1 is considered novelty destroying for the subject matter of claims 1 to 5, and 7 to 15 (ref. example 1).

2.2 Document D2 discloses (ref. abstract and claim 1) a carbon-based catalyst for flue gas desulfurization that is brought into contact with a flue gas containing at least SO_2 gas, oxygen and water vapor so that the SO_2 gas can react with the oxygen and the water vapor to form sulfuric acid which is to be recovered.

On a surface of the carbon-based catalyst, iodine, bromine or a compound thereof is added, ion exchanged or supported and a water-repellent treatment is applied to the carbon-base catalyst. According to §[0060], the water repellent material can be a resin such as fluororesins such as polytetrafluoroethylene and the like, polypropylene resins, polyethylene resins, polystyrene resins or the like, of which contact angle with water is 90° or more. The water repellent material can be considered an "inert filler material". As regards the quantity, example 1 discloses that activated carbon and polytetrafluoroethylene are mixed in a ratio of 90 to 10 parts by weight by solid concentration.

D2 is considered novelty destroying for the subject matter of claims 1,2,4,7,9 (ref. claims 17 to 19 in D2),10,11,12 (ref. ex. 13), 13 (ref. ex. 9),14 (ref. ex. 13),16 and 17.

2.3 Document D3 also discloses a carbon-based catalyst for flue gas desulfurization that is brought into contact with a flue gas containing at least SO_2 gas, oxygen and water vapor so that the SO_2 gas can react with the oxygen and the water vapor to form sulfuric acid which is to be recovered (ref. abstract and §[0004]). Active carbon particles are impregnated with polytetrafluoroethylene (PTFE) for reasons of water repellency, resulting in a PTFE content of 10%wt, ref. ex. 1.

D3 is considered novelty destroying for the subject matter of claims 1,2,7,10 to 14,16,17.

2.4 Document D4 is very similar in content to document D3 (ref. example 1). It is also considered novelty destroying for the subject matter of claims 1,2,7,10 to 14,16,17.

3 It is, at present, not clear to which extent the subject matter of claim 6 causes unexpected or surprising effects with respect to what is disclosed in the above mentioned prior art. Therefore, no inventive activity can be acknowledged for the time being.