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— *as to the identity of the inventor (Rule 4.17(i))*

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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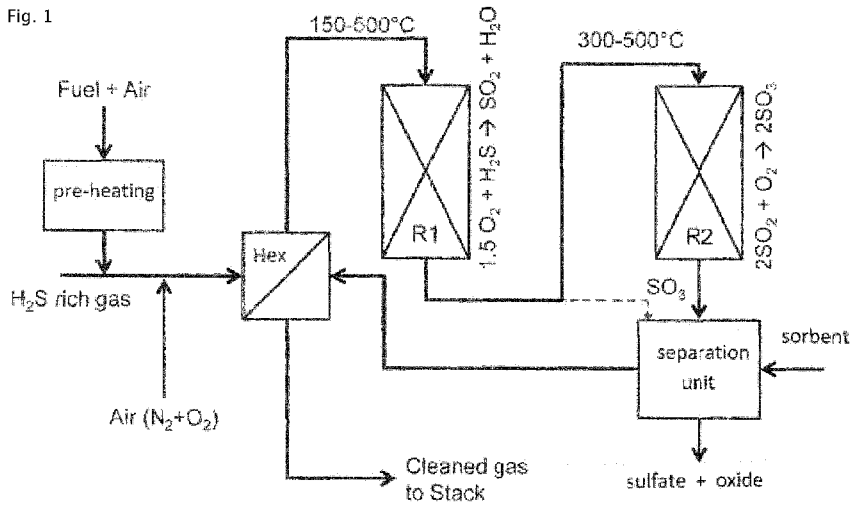
(54) Title: HYDROGEN SULFIDE ABATEMENT VIA REMOVAL OF SULFUR TRIOXIDE

Fig. 1



(57) Abstract: Sulfur trioxide is removed from a gas obtained by oxidizing hydrogen sulfide to sulfur trioxide in at least one catalyst-containing reactor. The method comprises feeding the effluent from the last reactor to a separation unit for sulfur trioxide removal, and it is characterized in that the effluent is mixed with a slurry or powder of a sorbent or a combination of sorbents, injected into the mixture through one or more injection points in the separation unit or upstream of it, to form a mixture of a sulfate and a hot clean gas, from which the sulfate is subsequently separated by any means selected among gas-solid separation unit operations, and wherein a mist filter in combination with the separation unit is used for removal of acid mist, while residual S03, which is not present as a mist, is removed in a quench scrubber.

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Hydrogen sulfide abatement via removal of sulfur trioxide

The present invention relates to the use of gas-solid separation unit operations for the removal of sulfur trioxide (SO_3) formed by catalytic oxidation of hydrogen sulfide (H_2S) with the purpose of removing H_2S from a gas. More specifically, this catalytic oxidation of H_2S first yields sulfur dioxide (SO_2) and then SO_3 through the use of known catalysts, and the subsequent recovery of SO_3 takes place in a separation unit, such as a filter or scrubbing unit, using a sorbent, which converts SO_3 to a sulfate to be separated in said unit.

The process of removing H_2S from a gas can be summarized schematically as follows: A potentially pre-heated H_2S-containing gas is mixed with air or oxygen, and then the mixture is fed to a first catalyst-containing reactor via a heat exchanger. In this first reactor, H_2S is oxidized to sulfur dioxide (SO_2). The effluent from the first reactor is passed to a second catalyst-containing reactor, where the SO_2 is oxidized to SO_3. Then the SO_3-containing effluent is fed to a separation unit, into which a sorbent slurry or powder is injected. The purpose of this is to remove SO_3 by converting it to a sulfate that can be separated from the gas.

The energy efficiency of the plant can be improved significantly by means of heat integration, i.e. the cold feed gas is heated to a suitable temperature by the hot effluent gas from the last reactor or the separation unit in a heat exchanger. Alternatively, the hot effluent gas can be used to produce steam.

The first oxidation reactor contains a monolith type catalyst, and the second oxidation reactor contains a supported liquid phase (SLP) catalyst, more specifically a VK catalyst.

The H_2S can also, on purpose, be oxidized directly to SO_3 in said first reactor by proper choice of oxidation catalyst and reaction conditions. In this case, the effluent from the first reactor is fed to the particle separation unit for removal of SO_3 in the form of a sulfate. As oxidation catalyst for this direct oxidation to SO_3, a noble metal catalyst, such as a Pt/Pd catalyst, is used.

With the exception of the case of sulfuric acid plants, SO_3 is generally undesired in process gas streams due to the risk of condensation of sulfuric acid and subsequent corrosion of the equipment operating below the acid dew point. Therefore, the SO_3 content in process gas streams is normally kept at a minimum. In the method of the present invention, H_2S is first oxidized to SO_2 and subsequently to SO_3 on purpose, because this approach offers the most cost efficient method for the removal of H_2S according to the present invention. Especially capital investment costs are reduced.

Usual routes to abatement of sulfur are solutions of absorbent type for low concentrations of H_2S, whereas higher concentrations of H_2S can be used for production of chemicals, e.g. elemental sulfur or sulfuric acid. For a variety of concentrations, combustion (understood as thermal non-catalytic oxidation) can also be used. The use of gas-solid

separation unit operations for the removal of SO_3 according to the present invention can be seen as an alternative measure to reduce the chemical consumption cost and reduce the water consumption with a minimal need for installed equipment, said measure especially being usable for H_2S levels between a few hundred ppm and a few percent.

The present invention utilizes catalytic oxidation of H_2S to SO_2 at temperatures between 150 and 500°C, preferably between 180 and 450°C and most preferably between 200 and 400°C. In comparison with combustion, which takes place at temperatures above 800°C, catalytic oxidation therefore offers the possibility of reducing the use of supplemental fuel in order to increase the temperature, thereby lowering the operating costs. Furthermore, the catalytic oxidation of H_2S can be performed at an oxygen concentration of below 2 vol%, measured at the outlet of the H_2S oxidation reactor, whereas combustion of H_2S typically requires an oxygen concentration of more than 3 vol% at the outlet of the furnace. This means that the process gas flow is reduced compared to combustion, thereby reducing both investment and operating costs.

The sulfate separated from the gas in the method according to the invention can easily be handled and sold, e.g. for the construction industry, or it can be landfilled. For certain applications, these are cost efficient options for the removal of H_2S compared to the production of elemental sulfur or sulfuric acid.

In the process of removing H_2S from a gas, a monolithic type catalyst is preferably used in the reactor converting

H_2S to SO_2. This catalyst is a corrugated fibrous monolith substrate coated with a supporting oxide. It is preferably coated with TiO_2 and subsequently impregnated with V_2O_5 and/or WO_3. The channel diameter of the corrugated monolith is between 1 and 8 mm, and the wall thickness of the corrugated monolith is between 0.1 and 0.8 mm.

The monolith type catalyst is preferably manufactured from a support material comprising one or more oxides of metals selected from aluminium, silicon and titanium, and the active catalytic components preferably comprise one or more oxides of a metal selected from vanadium, chromium, tungsten, molybdenum, cerium, niobium, manganese and copper. Said materials are effective in the catalytic oxidation of hydrogen sulfide at low temperatures.

The VK catalysts are specifically designed by the applicant to be used for converting SO_2 to SO_3 in any sulfuric acid plant. They are generally vanadium-based and may contain cesium as an additional catalyst promoter to enhance the action of the vanadium and activate the catalyst at a much lower temperature than conventional non-cesium catalysts. A major leap in activity has been obtained with VK catalysts containing a high fraction of vanadium in the active oxidation state V^{5+}.

Monoliths are increasingly being used, developed, and evaluated as catalyst supports in many new reactor applications such as chemical and refining processes, catalytic oxidation, ozone abatement etc. When the active catalyst has a monolithic structure, it displays a low pressure drop.

According to the invention, a number of gas-solid separation units and unit operations can be used for the removal of SO_3 formed by catalytic oxidation of H_2S. The separation units include metal filters, electrofilters, bag filters, ceramic filters, mist filters, cyclones and scrubbers, and unit operations for the gas-solid separation include use of low velocity filter, wet ESP (electrostatic precipitator) and other kinds of polishing technologies.

Wet and dry scrubbing processes are widely used to remove SO_2 from gas coming from combustion processes, such as in power plants. Typically, the SO_2 levels from power plants are in the range from 100 to 2000 ppm, with corresponding SO_3 levels from the combustion depending on the combustion temperature. The amount of SO_3 in the tail gas is within the range from 0.5% to 5% of the total SO_x (SO_2 + SO_3) amount, giving an SO_2 to SO_3 ratio in the range of 20 to 200.

The present invention utilizes catalytic oxidation of SO_2 to SO_3. Typically, more than 80%, preferably more than 90% and most preferably more than 95% of the SO_2 is converted to SO_3, resulting in an SO_2 to SO_3 ratio below 0.25, preferably below 0.11 and most preferably below 0.05. The high content of SO_3 makes the dry scrubbing process more efficient, resulting in lower scrubbing costs.

It would be possible to oxidize H_2S contained in a gas to SO_2 catalytically and subsequently remove this SO_2 using a wet or a dry scrubber.

It would likewise be possible to catalytically oxidize the SO_2 in a gas stream from a combustion process, such as a power plant, to SO_3 and subsequently remove this SO_3 using a dry scrubber.

A dry scrubber system is described in US 2013/0294992, which concerns an air quality control system useful for processing a gas stream, such as a flue gas stream emitted from a fossil fuel fired boiler, for at least partial removal of acidic and other polluting species, such as SO_2, SO_3, HCl, HF, fly ash particulates and/or other acidic polluting species, therefrom.

US 4.314.983 describes a process for converting H_2S to SO_2 with a solid catalyst comprising at least 5 wt% of bismuth. Essentially no SO_3 is formed in the catalytic process. In this patent it is stated that the bismuth content is necessary to stabilize the catalyst.

US 2014/020399 describes a method for generating current from an exhaust gas containing H_2S. The exhaust gas is combusted, possibly under addition of supplementary fuel, and the heat released is used for current generation. The SO_2 and the SO_3 in the gas after combustion of the H_2S are delivered for desulfurization.

US 2004/0109807 describes a method for removing SO_3 from flue gases, where a calcium hydroxide slurry is injected into the off-gases in the exhaust duct of an industrial plant, wherein sulfur-containing fuels are combusted. The calcium hydroxide slurry reacts with SO_3 produced as a result of the combustion process and forms a primary solid

calcium sulfate reaction product. The industrial plant includes a wet scrubbing system which utilizes wet slaking of calcium oxide for the removal of sulfur oxides from off-gases.

US 6,143,263 describes a method and a system for removing SO_3 and SO_2 from a flue gas produced by combusting of a fossil fuel. A calcium-based, sodium-based or magnesium-based dry sorbent is injected into the flue gas to react with and remove substantially all of the SO_3 from the flue gas, thereby producing a substantially SO_3-free flue gas containing both reacted dry sorbent and unreacted dry sorbent. The flue gas with reacted and unreacted dry sorbent is then fed to a wet scrubber to remove both the reacted and the unreacted dry sorbent, thereby making the unreacted dry sorbent available as a wet reagent for SO_2 removal.

In US 2005/0201914, a method for treating a flue gas stream to remove strong acid compounds, selected from HF, HCl, H_2SO_4 and SO_3, is described. The compounds are removed by injecting a sodium sorbent, selected from sodium sesquicarbonate, sodium carbonate-bicarbonate and various forms of 'trona' (trisodium hydrogen dicarbonate-dihydrate, a non-marine evaporite mineral also called sodium sesquicarbonate dihydrate; $Na_3(CO_3)(HCO_3) \cdot 2H_2O$) into the flue gas stream. Substantially all of the sodium sorbent is calcined in the presence of the flue gas stream to form a soda ash, and the concentration of the strong acid compounds in the flue gas is reduced by reaction with the soda ash to form a sodium-based by-product.

US 2010/0096594 describes a process for decontaminating syngas by contacting the syngas with one or more sorbents upstream of a catalytic candle filter containing a mixed cracking catalyst, wherein ammonia and tars are removed, leaving a purified syngas.

US 2009/0277325 discloses an emission treatment system, in which particles entrained in an emission stream can be removed using various separation devices, such as electrostatic precipitators, cyclone collectors and filter devices, e.g. candle filters.

Finally, WO 2004/037369 describes a system and a method for removing H_2S and SOx from a gas. The system comprises a sorbent slurry feeder and at least one reaction zone configured for introduction of a sorbent and the gas, and it also comprises fabric filter bags, wet scrubbing and electrostatic precipitator technologies. However, it does not comprise a mist filter in combination with the separation unit for removal of acid mist and also not a quench scrubber for the removal of residual SO_3, which is not present as a mist.

The treatment method for the removal of sulfur trioxide underlying the present invention differs from the prior art techniques in that a pre-heated gas containing H_2S is mixed with air, and the mixture is fed to a first catalyst-containing reactor via a heat exchanger. In this first reactor, H_2S is oxidized to sulfur dioxide (SO_2) according to the reaction

$$1.5\ O_2 + H_2S \rightarrow SO_2 + H_2O \qquad (1)$$

The catalyst in the first reactor is a monolith type catalyst as described earlier.

The catalyst can be manufactured from various ceramic materials used as a carrier, such as titanium oxide, and active catalytic components are usually either oxides of base metals (such as vanadium, molybdenum and tungsten), zeolites, or various precious metals. Catalysts of monolithic structure are known to provide favourable performance with respect to selectivity when the desired reaction is fast and the undesired reaction is slow. This is also the case in the present invention, where the conversion of H_2S to SO_2 is a fast reaction that benefits from the high surface area whereas the low load of active material per volume in a monolithic structure restricts the rate of oxidation of SO_2 to SO_3, thereby enabling full control of the catalytic reactions and subsequently reducing the risk of corrosion or fouling of the equipment.

Then the effluent from the first reactor is passed to a second catalyst-containing reactor, where the SO_2 is oxidized to SO_3 according to the reaction

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3 \qquad (2)$$

The catalyst used in this reaction is selected among the applicant's VK catalysts, which are so-called supported liquid phase (SLP) catalysts. With SLP catalysts, the oxidation of SO_2 takes place as a homogeneous reaction in a liquid film consisting of V_2O_5 dissolved in alkali-metal pyrosulfates on an inactive porous silica support made from

diatomaceous earth. This second catalytic step results in an SO_2 to SO_3 ratio which is much lower than what is seen in desulfurization processes utilizing sorbents for direct removal of SO_2. The introduction of this catalytic step is deemed to be particularly inventive because it makes the desulfurisation of the gas stream, here in the form of adsorbing SO_3, sulfate formation and separation, very cost effective compared to known wet scrubbing solutions for SO_2.

Finally a sorbent, preferably an alkaline sorbent, is added to the SO_3 containing gas and SO3 is absorbed as sulfate. Subsequently, the gas and solid is fed to a gas-solid separation unit, where the spent sorbent with sulfur is separated from the gas. The solid discharge of sulfate and partially spent sorbent can be mixed with water and reinjected in the system.

A preferred alkaline sorbent to be injected is calcium hydroxide ($Ca(OH)_2$), but instead of calcium hydroxide, calcium carbonate may be used. Other alkaline sorbents may be used as well. For example it is possible to use a magnesium-based sorbent, such as magnesium oxide or magnesium hydroxide, or a sodium-based sorbent, such as sodium carbonate.

Further it has turned out that certain sodium-based alkaline sorbents, such as sodium bicarbonate ($NaHCO_3$) and Trona (trisodium hydrogendicarbonate dihydrate, also known as sodium sesquicarbonate dihydrate; $Na_3(CO_3)(HCO_3)\cdot 2H_2O$), are more reactive with SO_2 than calcium-based sorbents in the temperature range from 135 to 500°C.

Thus, the present invention concerns a method for removing sulfur trioxide from a gas obtained by oxidizing hydrogen sulfide to sulfur trioxide in at least one catalyst-containing reactor, said method comprising feeding the effluent from the last reactor to a separation unit for sulfur trioxide removal,

wherein the effluent from the last reactor is mixed with a slurry or powder of a sorbent or a combination of sorbents, injected into the mixture through one or more injection points in the separation unit or upstream of it, to form a mixture of a sulfate, unused sorbent and a hot clean gas, from which the sulfate and unused sorbent is subsequently separated by any means selected among gas-solid separation unit operations,

and wherein a mist filter in combination with the separation unit is used for removal of acid mist, while residual SO_3, which is not present as a mist, is removed in a quench scrubber.

The sorbents are preferably alkaline sorbents.

The separation unit, which constitutes the crux of the present invention, can be selected from a range of devices based on gas-solid separation unit operations and suitable for the removal of absorbed SO_3 formed by catalytic oxidation of H_2S. As already mentioned, a number of gas-solid separation units and unit operations can be used for said removal of SO_3. These separation units include (without being limited thereto) various metal filters, electrofilters,

bag filters, ceramic filters, mist filters, cyclones and dry scrubbers. The preferred choices are bag filters, metal filters and ceramic filters because of build-up of filter cake, which enhances the scrubbing efficiency.

The filter unit may be a catalytic filter unit.

The unit operations for the gas-solid separation include use of polishing technologies such as low velocity filter, wet ESP (electrostatic precipitator) and other kinds of technologies. Use of these technologies in combination with a dry scrubber makes it possible to go from 10-30 ppm SO_3 at the outlet of the separation unit down to practically 0 ppm emissions.

More specifically, the sorbent can be injected into the ducting or an absorption unit, such as a fluidized bed or entrained flow reactor, placed between the last reactor, in which the catalytic oxidation of SO_2 to SO_3 takes place, and a separation unit, e.g. a bag filter or a ceramic filter, to lower the acid dew point by removing SO_3 from the gas, and enable cooling of the gas to a temperature that is suitable for bag filter operation. This temperature will typically be in the range from 150 to 500°C.

According to the invention it is possible to use one or more sorbent injection points. In case of more sorbent injection points, these can be either in the separation unit, upstream of it or a combination of both. For example, one injection point may be placed in the ducting between the last reactor and the separation unit and a second injection point may be placed in the housing of the separation unit.

Different modes of sorbent injection can be used. These include (without being limited thereto) dry injection, spray drying injection and in-duct injection.

In addition, a mist filter in combination with the separation unit is used for removal of any acid mist. Residual SO_3, which is not present as a mist, is removed in a quench scrubber, e.g. a venturi scrubber. A venturi scrubber is designed to effectively use the energy from an inlet gas stream to atomize the liquid being used to scrub the gas stream.

For gases with a high H_2S concentration, recovery of elementary sulfur is considered to be a cost effective method for desulfurization. For lean gases, oxidation to SO_2 and subsequent wet scrubbing of SO_2 or absorption of H_2S in a disposable sorbent is considered to be a cost effective method for desulfurization. The present invention is considered to be a cost effective method for desulfurization in a range between lean and strong H_2S gases, specifically in the range from 25 ppm to 50000 ppm H_2S, preferably from 100 ppm to 20000 ppm H_2S and most preferably from 200 ppm to 15000 ppm H_2S. An especially preferred interval is from 300 ppm to 10000 ppm H_2S. Especially the investment costs are considered to be lower than those of competitive technologies in these intervals.

The catalyst for oxidizing the H_2S to SO_2 is preferably impregnated with V_2O_5 and one or more oxides of a metal selected from chromium, tungsten, molybdenum, cerium, niobium, manganese and copper.

Preferably a part of the effluent from the first or the second reactor is recycled to the H_2S containing feed gas.

The overall method according to the invention can be carried out in a plant for oxidizing hydrogen sulfide to sulfur trioxide. Such plant, which is depicted on the appended figure, mainly consists of two oxidation reactors R1 and R2 for the above oxidation reactions (1) and (2), respectively, and a separation unit for the removal of absorbed sulfur trioxide from the process gas. The plant further comprises a unit for pre-heating the H_2S-containing gas, and a heat exchanger (Hex). In the heat exchanger, the gas is heated to a temperature of 150-500°C before entering the first reactor R1. Following the reaction (1) in R1 the effluent gas is either fed to the reactor R2 at a temperature of 300-500°C or fed directly to the separation unit (as shown by the dotted line in the figure). After the reaction (2) in R2 the resulting SO_3-containing gas is led to the separation unit, where a sorbent, preferably an alkaline sorbent, or a combination of two or more such sorbents is injected to remove SO_3.

The SO_3 ends up as sulfate in the filter cake, possibly together with an excess of oxide. The cleaned gas with a temperature around 150-500°C is passed through the heat exchanger for heating up the feed gas, and it leaves the heat exchanger as a cleaned gas with a temperature around 100°C.

In the above plant design, all oxidation catalysts can fit into the reactors, and the separation unit is replacing similar technologies where wet caustic scrubber systems are

used. A major advantage in this respect is that the caustic chemicals cost will be markedly reduced, and a hot clean gas is produced, which can be used in the heat exchanger of the plant as mentioned above.

Claims:

1. A method for removing sulfur trioxide from a gas obtained by oxidizing hydrogen sulfide to sulfur trioxide in at least one catalyst-containing reactor, said method comprising feeding the effluent from the last reactor to a separation unit for sulfur trioxide removal,

wherein the effluent from the last reactor is mixed with a slurry or powder of a sorbent or a combination of sorbents, injected into the mixture through one or more injection points in the separation unit or upstream of it, to form a mixture of a sulfate, unused sorbent and a hot clean gas, from which the sulfate and unused sorbent is subsequently separated by any means selected among gas-solid separation unit operations,

and wherein a mist filter in combination with the separation unit is used for removal of acid mist, while residual SO_3, which is not present as a mist, is removed in a quench scrubber.

2. Method according to claim 1, wherein the sorbents are alkaline sorbents.

3. Method according to claim 1 or 2, wherein the separation unit is selected from metal filters, electrofilters, bag filters and ceramic filters, preferably from bag filters, metal filters and ceramic filters.

4. Method according to claim 1 or 2, wherein the separation unit is a cyclone.

5. Method according to claim 1 or 2, wherein the separation unit is a catalytic filter unit.

6. Method according to claim 1, wherein the unit operations for the gas-solid separation are combined with the use of polishing technologies, such as low velocity filter or wet ESP (electrostatic precipitator) technologies.

7. Method according to claim 6, wherein the polishing technologies are used in combination with a dry scrubber.

8. Method according to any of the preceding claims, wherein the sorbent is injected into the ducting or an absorption unit, such as a fluidized bed or entrained flow reactor, placed between the last reactor, in which the catalytic oxidation of SO_2 to SO_3 takes place, and a bag filter to lower the acid dew point by removing SO_3 from the gas and enable cooling of the gas to a temperature that is suitable for bag filter operation.

9. Method according to claim 1, wherein multiple sorbent injection points are used, either in the separation unit, upstream of it or a combination of both.

10. Method according to claim 9, wherein one injection point is placed in the ducting between the last reactor and the separation unit and a second injection point is placed in the housing of the separation unit.

11. Method according to claim 1, wherein different modes of sorbent injection are used, including dry injection, spray drying injection and in-duct injection.

12. Method according to claim 1, wherein the quench scrubber is a venturi scrubber.

13. Method according to any of the preceding claims, wherein the SO_2 to SO_3 ratio of the effluent gas from the last reactor is below 0.25, preferably below 0.11 and most preferably below 0.05.

14. Method according to any of the preceding claims, wherein the temperature during the oxidation of H_2S is in the range between 150 and 500°C, preferably between 180 and 450°C and most preferably between 200 and 400°C.

15. Method according to any of the preceding claims, wherein the H_2S content in the gas before the first reactor is between 25 ppm and 50000 ppm, preferably between 100 ppm and 20000 ppm.

16. Method according to any of the preceding claims, wherein the H_2S content in the gas before the first reactor is between 200 ppm and 15000 ppm, preferably between 300 ppm and 10000 ppm.

17. Method according to any of the preceding claims, wherein the catalyst for oxidizing the H_2S to SO_2 is impregnated with V_2O_5 and one or more oxides of a metal selected from chromium, tungsten, molybdenum, cerium, niobium, manganese and copper.

18. Method according to any of the preceding claims, wherein a part of the effluent from the first or the second reactor is recycled to the H_2S containing feed gas.

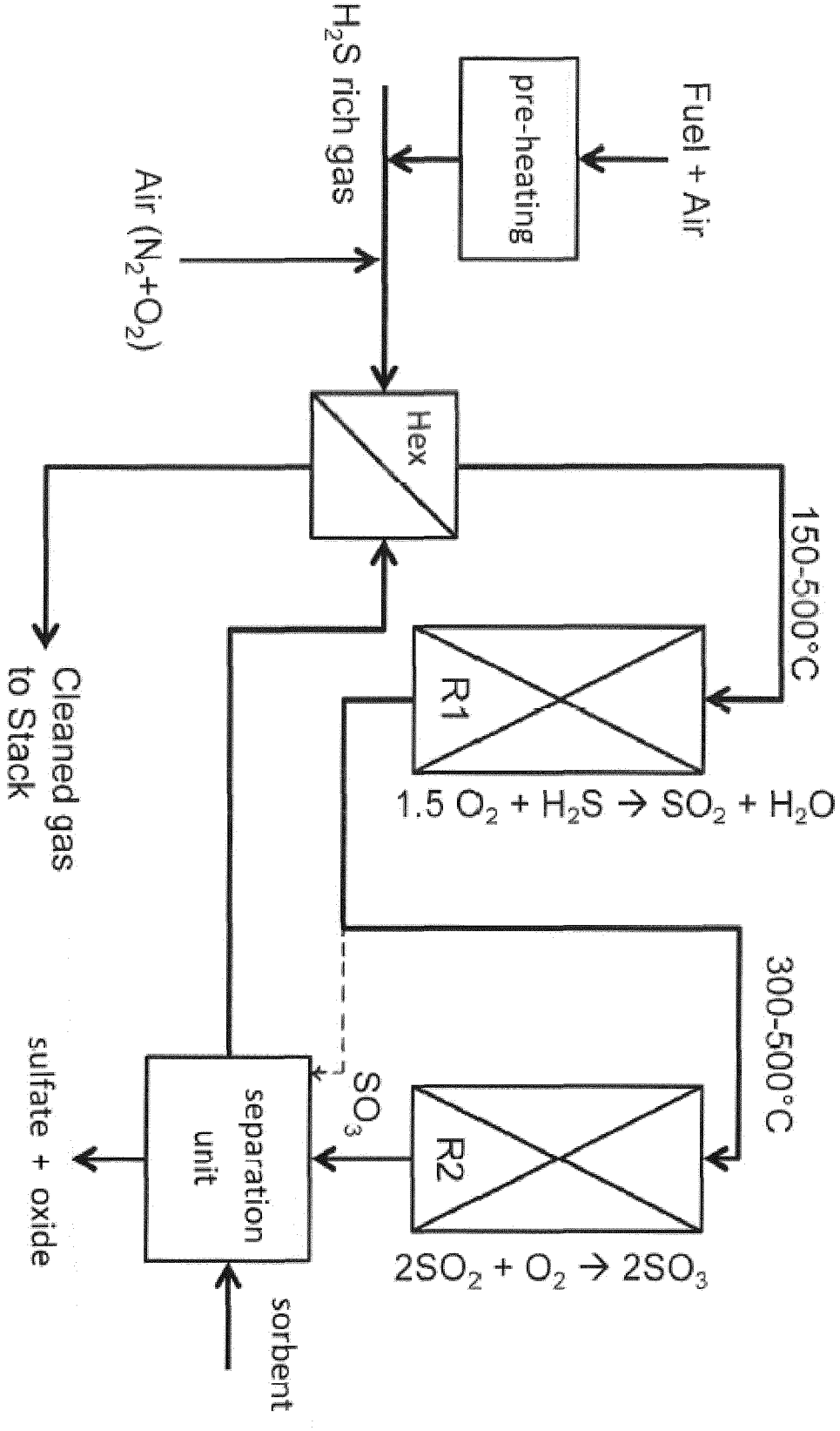
H2S rich gas
pre-heating
Fuel + Air
Air (N2+O2)
Hex
150-500°C
Cleaned gas to Stack
R1
1.5 O2 + H2S → SO2 + H2O
300-500°C
SO3
separation unit
sulfate + oxide
R2
2SO2 + O2 → 2SO3
sorbent

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/062830

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/52 B01J23/22 B01D53/75 B01D53/50 B01D53/86
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2007/031551 A1 (SOLVAY CHEMICALS INC [US]; MAZIUK JONH JR [US]) 22 March 2007 (2007-03-22) page 1, lines 1-3 page 1, line 24 - page 2, line 27 page 4, line 26 - page 6, line 36 figure 2	1-18
Y	US 6 776 974 B1 (BURMASTER BRIAN M [US] ET AL) 17 August 2004 (2004-08-17) column 5, line 61 - column 6, line 27 column 9, line 57 - column 10, line 23 column 15, lines 30,31	1-12

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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29 August 2016	08/09/2016

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 102 205 202 A (BEIJING FUNGHAN ENGINEERING CONSULTING CO LTD) 5 October 2011 (2011-10-05) paragraphs [0007] - [0011], [0015] - [0019], [0022], [0037], [0039], [0042] - [0047], [0055] - [0059], [0066] - [0071]	13-15
Y	FR 2 208 702 A1 (INST FRANCAIS DU PETROLE [FR]) 28 June 1974 (1974-06-28) page 1, line 1 - page 2, line 29	12-16,18
Y	EP 2 878 358 A1 (TOPSOE HALDOR AS [DK]) 3 June 2015 (2015-06-03) paragraphs [0001], [0002], [0006] table 1	12-18
A	US 2004/109807 A1 (D ALESANDRO RAYMOND J [US]) 10 June 2004 (2004-06-10) the whole document	1-18
A	US 2005/201914 A1 (RITZENTHALER DOUGLAS P [US]) 15 September 2005 (2005-09-15) the whole document	1-18

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/062830

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2007031551 A1	22-03-2007	BR PI0616030 A2	07-06-2011
		CA 2622064 A1	22-03-2007
		CA 2856974 A1	22-03-2007
		CN 101262930 A	10-09-2008
		EA 200800830 A1	29-08-2008
		EP 1937390 A1	02-07-2008
		JP 4932840 B2	16-05-2012
		JP 2009507631 A	26-02-2009
		US 2007081936 A1	12-04-2007
		WO 2007031551 A1	22-03-2007
US 6776974 B1	17-08-2004	NONE	
CN 102205202 A	05-10-2011	NONE	
FR 2208702 A1	28-06-1974	NONE	
EP 2878358 A1	03-06-2015	NONE	
US 2004109807 A1	10-06-2004	NONE	
US 2005201914 A1	15-09-2005	NONE	