



(51) International Patent Classification:

C01B 17/50 (2006.01) *B01D 53/48* (2006.01)
B01J 21/00 (2006.01)

(21) International Application Number:

PCT/EP2018/050623

(22) International Filing Date:

11 January 2018 (11.01.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

201710033153X 16 January 2017 (16.01.2017) CN

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(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- of inventorship (Rule 4.17(iv))

(54) Title: METHOD AND SYSTEM FOR CATALYTIC OXIDATION OF A LEAN H₂S STREAM

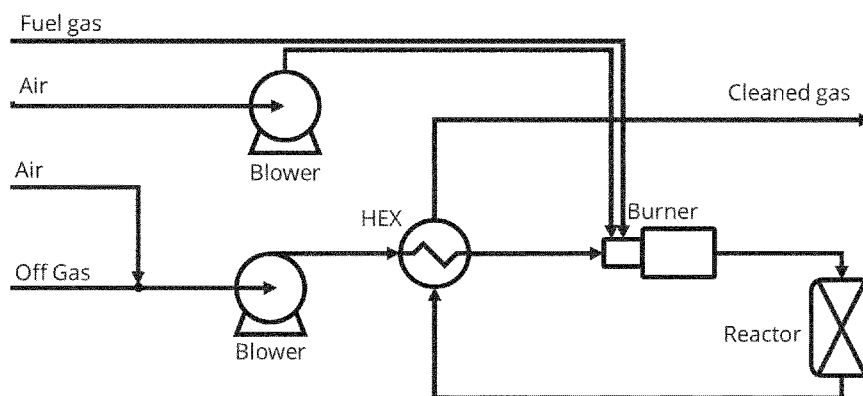


Fig. 1

(57) Abstract: The present invention relates to a method and a system for catalytic oxidation of a lean H₂S stream. More specifically, the invention concerns a novel way of removing sulfur dioxide (SO₂) formed by catalytic oxidation of hydrogen sulfide (H₂S) with the purpose of removing H₂S from a gas. This catalytic oxidation of H₂S yields sulfur dioxide (SO₂) through the use of known catalysts, so-called SMC catalysts.



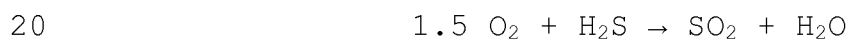
Published:

— *with international search report (Art. 21(3))*

Title: Method and system for catalytic oxidation of a lean H₂S stream

The present invention relates to a method and a system for catalytic oxidation of a lean H₂S stream. More specifically, the invention concerns a novel way of removing sulfur dioxide (SO₂) formed by catalytic oxidation of hydrogen sulfide (H₂S) with the purpose of removing H₂S from a gas. This catalytic oxidation of H₂S yields sulfur dioxide (SO₂) through the use of known catalysts, so-called SMC catalysts, which will be described in the following.

The process of removing H₂S from a gas can be summarized schematically as follows: An optionally pre-heated H₂S-containing gas is mixed with air or oxygen, and then the mixture is fed to a catalyst-containing reactor via a heat exchanger. In this reactor, H₂S is oxidized to sulfur dioxide (SO₂) according to the reaction



The idea underlying the present invention is to add syngas to a lean H₂S stream, which is to be treated by catalytic oxidation as described above, thereby obtaining SO₂. The treatment is carried out in an SMC (Sulfur Monolith Catalyst) unit.

Thus, the present invention relates to a method for the oxidation of hydrogen sulfide, carbonyl sulfide or carbon disulfide to sulfur dioxide, said method comprising the steps of:

- providing a feed gas lean in H₂S,
- adding air or O₂ to the feed gas,
- heating the feed gas to the desired inlet temperature,
- feeding the gas mixture to an oxidation reactor, which
- 5 contains a catalyst, and
- recovering a cleaned gas,

wherein syngas is added to the gas mixture prior to feeding the gas mixture to the oxidation reactor.

10

The catalyst is preferably a sulfur monolith catalyst.

Preferably the gas mixture is fed to the oxidation reactor via a heat exchanger.

15

Furthermore, the invention relates to a system, in which the method for the oxidation of hydrogen sulfide to sulfur dioxide is carried out. This system comprises a gas blower, a heat exchanger and an oxidation reactor, which contains a

20 catalyst, preferably a sulfur monolith catalyst.

The SMC technology is aimed at sulfur abatement in gases with low fuel value. The conventional way of treating such gases consists in using support fuel in combination with

25 thermal oxidation. Another way is to blend the gas of low fuel value with the feed gas to a Claus plant or a sulfuric acid plant which, however, often will lead to an increased demand for support fuel and a substantial increase of the size of such a unit.

30

The core of the SMC technology is the SMC catalyst, which selectively oxidizes H₂S and other sulfur compounds, such

as carbonyl sulfide (COS) and carbon disulfide (CS₂), to SO₂ and oxidizes higher hydrocarbons, hydrogen and CO to CO₂ and water. The SMC catalyst can operate at temperatures from 200°C, and the unique design of the catalyst enables
5 operation with a very low pressure drop, a low surplus of oxygen, low formation of SO₃ and without formation of NO_x. If required, the SO₂ formed can be removed in a caustic scrubber.

10 In the method of the present invention, the oxidation of H₂S proceeds at an inlet temperature to the catalyst between 200 and 450°C. Preferably, the inlet temperature to the catalyst is between 250 and 400°C, most preferably between 250 and 300°C.

15 Fig. 1 illustrates a typical design as used in the conventional way of gas treatment. In addition to the catalytic oxidation reactor, the design includes two gas blowers, a heat exchanger and a burner to raise the temperature of the
20 feed gas before entering the catalytic reactor.

Fig. 2 illustrates the design of an SMC unit to be used when carrying out the process of the invention. This design comprises only one gas blower, and use of a gas burner to
25 raise the temperature of the feed gas is not needed.

By adding syngas to a lean H₂S stream, which is to be treated by catalytic oxidation, the heating value of the gas will increase. Further, the amount of equipment needed
30 is minimized, which also holds true for the size of the individual pieces of equipment, especially the size of the

feed/effluent heat exchanger(s) constituting the most expensive part of the SMC unit. In addition, the OPEX (the operating expense) decreases because expensive feed gases or natural gas can be replaced by cheaper fuel gases, which also are oxidized at a lower air surplus. This decreases the air requirement and the duty of the blowers.

Basically the SMC technology is the catalytic oxidation of H₂S at temperatures between 200°C and 450°C. The oxidation reactions can increase the temperature across the reactor by 10 to 150°C depending on the gas composition. The feed gas is often delivered at ambient temperatures, and heating of the feed gas can be accomplished by a feed/effluent heat exchanger. However, if the gas is lean (low temperature increase), such heat exchangers will become uneconomically large due to a low driving force for the heat exchange process. The heat exchanger itself will often constitute a large fraction of the overall CAPEX (capital expenditure) of an SMC unit. Therefore, a fired heater using fuel gas or natural gas is sometimes used to raise the temperature. This adds to both the CAPEX and the OPEX, since a burner as well as a combustion air blower is needed along with continuous consumption of fuel gas or natural gas. Furthermore, NO_x (i.e. NO and/or NO₂) may be formed in the burner. As mentioned above, use of a burner is not needed in the process of the invention.

The method according to the invention, which is especially relevant for coal gasification units, includes adding a small fraction of syngas (containing H₂, CO and CO₂) to increase the temperature raise across the reactor, since both

CO and H₂ can be oxidized over the SMC catalyst. This approach has the benefits of decreasing the size of the heat exchangers without adding more equipment to the plant. In addition, the oxygen consumption as well as the air blower power consumption will be lower since the SMC unit operates at a lower air surplus compared with a burner, and formation of NO_x is avoided. Syngas is most often cheaper than fuel gas or natural gas, whereby the OPEX is reduced.

Methods as well as catalysts for oxidative conversion of H₂S to SO₂ are well-known in the art. Thus, EP 2 878 367 A1, belonging to the applicant, relates to materials consisting of V₂O₅ on a porous support, that are catalytically active in the oxidation of sulfur compounds, such as oxidation of H₂S to SO₂, at temperatures between 180 and 450°C.

US 4.314.983 describes a process for converting H₂S to SO₂ with a solid catalyst comprising at least 5 wt% of bismuth. Essentially no SO₃ is formed in the catalytic process. In this patent it is stated that the bismuth content of at least 5 wt% is necessary to stabilize the catalyst.

US 2014/0020399 describes a method for generating current from an exhaust gas containing H₂S. The exhaust gas is combusted, possibly under addition of supplementary fuel, and the heat released is used for current generation. The SO₂ and the SO₃ in the gas after combustion of the H₂S are delivered for desulfurization.

In RU 2.276.097 C, a process for selective catalytic oxidation of H₂S is disclosed. The catalyst is iron oxide supported by a porous oxide. A similar process, in which a

different catalyst is used, is disclosed in RU 2.533.140 C.

In none of these documents the possibility of adding syngas to the feed gas prior to entering the catalyst-containing oxidation reactor is mentioned.

Usual routes to abatement of sulfur are solutions of absorbent type for low concentrations of H₂S, whereas higher concentrations of H₂S can be used for production of chemicals, e.g. elemental sulfur or sulfuric acid.

The present invention utilizes catalytic oxidation of H₂S to SO₂ at temperatures between 200 and 450°C, preferably between 250 and 400°C and most preferably between 250 and 300°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 H₂S can be performed at an oxygen concentration of below 2 vol%, measured at the outlet of the H₂S oxidation reactor, whereas combustion of H₂S 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.

In the process of removing H₂S from a gas, an SMC catalyst, i.e. a monolithic type catalyst, is used in the reactor converting H₂S to SO₂. This catalyst is a corrugated fibrous monolith substrate coated with a supporting oxide. It is preferably coated with TiO₂ 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.

5 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
10 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.

15 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 as already mentioned.

20

The invention is illustrated further in the examples which follow.

Examples:

25

The addition of syngas is interesting in situations where the temperature increase over an SMC catalyst is less than 40°C , which corresponds to a concentration of H_2S below 2000-3000 ppm H_2S (dependent on the remaining constituents
30 and whether other combustible compounds, like CO or H_2 , are present). The lower heating value (LHV) should be less than roughly 22 kCal/h.

Two situations are investigated: One according to the prior art and one according to the invention, illustrated in Fig. 1 and Fig. 2, respectively.

5

Example 1

This example illustrates the prior art as shown in Fig. 1. In this prior art design, a burner is utilized to increase the temperature approach in the feed/effluent heat exchanger (HEX). The basis of the examples is the feed gas, which has the properties and the composition given in Table 1 below:

15

Table 1

Properties and composition of feed gas

properties	
Temperature [°C]	10
Pressure [mbar g]	150
Flow [Nm ³ /h]	100,000
composition	
N ₂ [mole%]	14
CO ₂ [mole%]	84.7
H ₂ O [mole%]	1
H ₂ S [ppm]	3000

20

In this example, the consumption of fuel gas amounts to 541 Nm³/h.

Example 2

This example illustrates the present invention as shown in Fig. 2. In this inventive design, it is not required to use a burner to increase the temperature approach in the heat exchanger (HEX).

Syngas is added to raise the temperature increase in the SMC reactor, hereby also improving the temperature approach in the feed/effluent heat exchanger.

The consumption of fuel gas and syngas, as well as an estimated OPEX based on a fuel gas price of 3 RMB/Nm³ and a syngas price of 0.5 RMB/Nm³ can be seen in Table 2 below. More syngas will be required since the heating value is lower. However, the syngas cost will be much lower compared to Example 1.

Table 2
Comparison of examples 1 and 2

	Gas consumption [Nm ³ /h]	Price [mRMB/yr]	Relative [%]
Example 1	541	13	100
Example 2	1380	5.5	44

Regarding the equipment, a blower is saved as well as a burner in the design according to the invention, as can be seen in Fig. 1 and Fig. 2.

Claims:

1. A method for the oxidation of hydrogen sulfide, carbonyl sulfide or carbon disulfide to sulfur dioxide, said
5 method comprising the steps of:

- providing a feed gas lean in H₂S,
- adding air or O₂ to the feed gas,
- heating the feed gas to the desired inlet temperature,
- 10 - feeding the gas mixture to an oxidation reactor, which contains an oxidation catalyst, and
- recovering a cleaned gas,

wherein syngas is added to the gas mixture prior to feeding
15 the gas mixture to the oxidation reactor.

2. Method according to claim 1, wherein the oxidation catalyst is a sulfur monolith catalyst.

20 3. Method according to claim 1 or 2, wherein the gas mixture is fed to the oxidation reactor via a heat exchanger.

4. Method according to any of the claims 1-3, wherein the oxidation of H₂S proceeds at an inlet temperature to the
25 catalyst between 200 and 450°C.

5. Method according to claim 4, wherein the inlet temperature to the catalyst is between 200 and 400°C, preferably between 250 and 300°C.

30

6. A system for carrying out the method according to any of the claims 1-5 for the oxidation of hydrogen sulfide to

sulfur dioxide, said system comprising a gas blower, a heat exchanger and an oxidation reactor, which contains a catalyst, preferably a sulfur monolith catalyst.

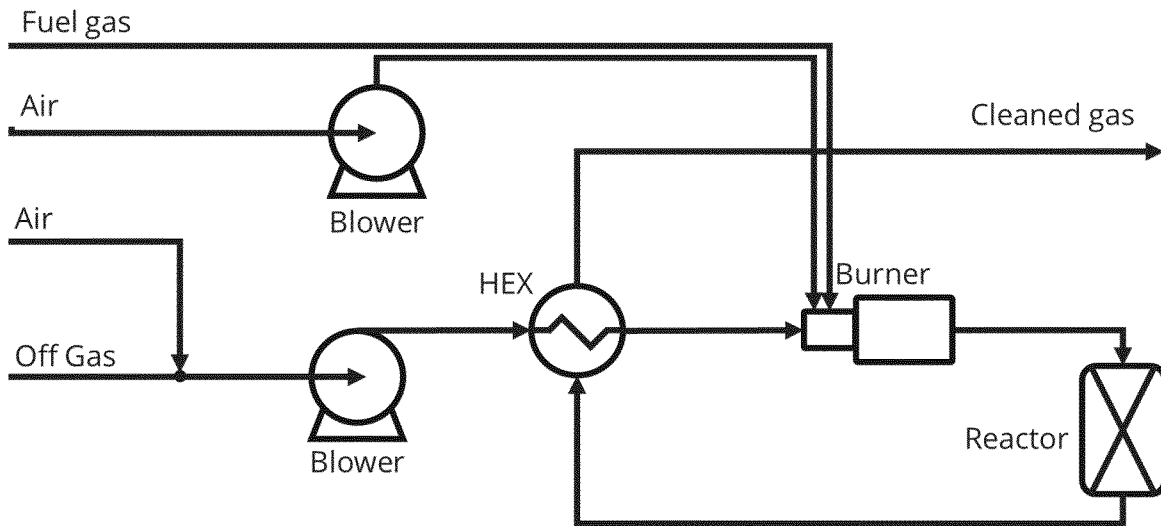


Fig. 1

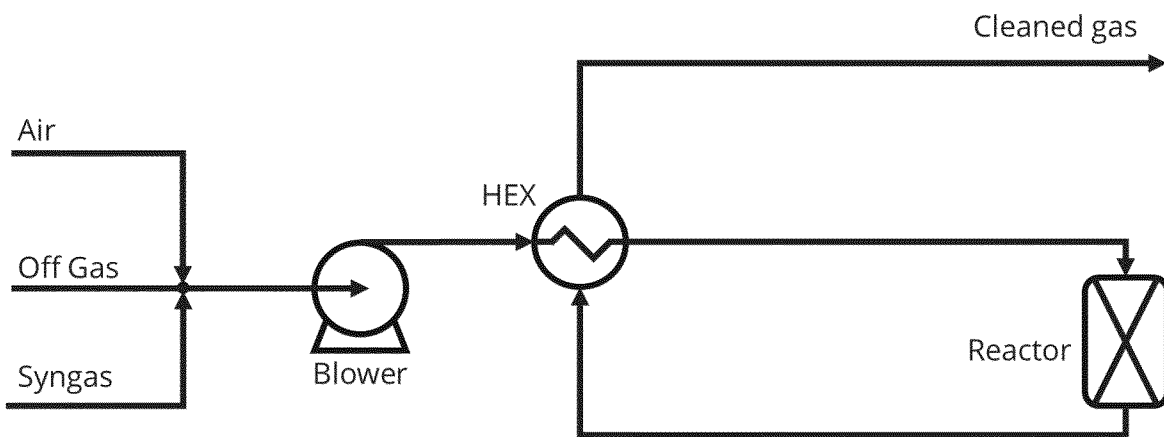


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/050623

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B17/50 B01J21/00 B01D53/48
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)
C01B B01J B01D

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 A	US 2002/134706 A1 (KELLER ALFRED E [US] ET AL) 26 September 2002 (2002-09-26) claims 1-3 paragraphs [0082] - [0089] figure 3	1-5 6
Y A	US 6 610 264 B1 (BUCHANAN JOHN SCOTT [US] ET AL) 26 August 2003 (2003-08-26) claims 1,2 column 4, line 66 - column 5, line 16 column 7, lines 15-27 figures 1,2	1-5 6
A	WO 2016/041822 A1 (HALDOR TOPSØE AS [DK]) 24 March 2016 (2016-03-24) claims 1,2 figure 1	1-6
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 9 March 2018	Date of mailing of the international search report 16/03/2018
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Gerwann, Jochen
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/050623

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2017/140662 A1 (HALDOR TOPSØE AS [DK]) 24 August 2017 (2017-08-24)	6
A,P	the whole document -----	1-5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/050623

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002134706	A1	26-09-2002	NONE
US 6610264	B1	26-08-2003	NONE
WO 2016041822	A1	24-03-2016	CA 2960919 A1 24-03-2016
		CN 106714938 A	24-05-2017
		EP 3194051 A1	26-07-2017
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		US 2017239618 A1	24-08-2017
		WO 2016041822 A1	24-03-2016
WO 2017140662	A1	24-08-2017	NONE