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(54) Title: SYSTEM AND METHOD FOR CATALYST REGENERATION

(57) Abstract: The various embodiments relate to a system and method for regenerating a direct oxidation catalyst that coverts H_2S to elemental S. One embodiment of the method comprises regenerating a direct oxidation catalyst by contacting the direct oxidation catalyst with steam.

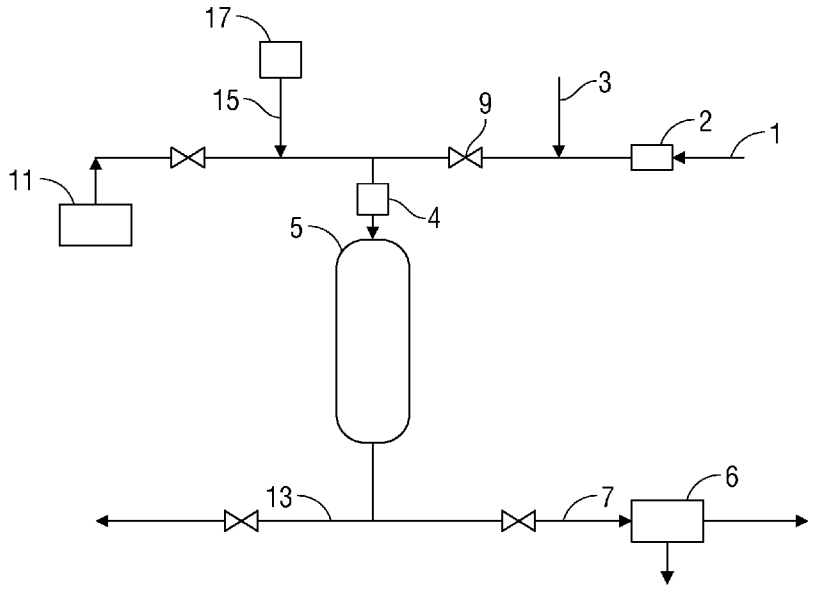


FIG. 1

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SYSTEM AND METHOD FOR CATALYST REGENERATION

BACKGROUND

[0001] This application claims the benefit of U.S. Provisional Application No. 61/894,293 filed on October 22, 2013, incorporated by reference herein in its entirety.

[0002] Embodiments disclosed herein generally relate to the field of catalysts for oxidation of hydrogen sulfide to sulfur and water.

[0003] Hydrogen sulfide (H_2S) is commonly found in natural gas wells and may also be produced in oil refining or other industrial processes. Because hydrogen sulfide increases corrosion and may be toxic in sufficient quantities, hydrogen sulfide content should be reduced to appropriate levels. An accepted method of reducing hydrogen sulfide content is the oxidation of hydrogen sulfide to sulfur and water. The sulfur product is considered benign in comparison to alternatives such as sulfur dioxide (SO_2), the product of burning hydrogen sulfide and a precursor to acid rain.

[0004] The Claus process is the state-of-the-art process for oxidizing hydrogen sulfide to convert it to sulfur and water. The Claus process is a two-step process. In the first step, a large quantity of the elemental sulfur is recovered in a furnace, and about one third of the remaining H_2S is oxidized to SO_2. In the second step, the remaining H_2S and the SO_2 are reacted in a Claus reactor to form sulfur according to the reaction:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

Unfortunately, the gas fed to the Claus process must have a relatively high concentration of H_2S gas to be efficiently incinerated in the furnace step. Also, the gas treated in a Claus process must have low amounts of hydrocarbons, which can interfere with the Claus reaction and generate other sulfur species, such as COS and CS_2. As a result, an H_2S-containing gas typically must be treated in an amine unit to first separate and concentrate the H_2S. Thus, the Claus process is generally economical only for large scale operations.

[0005] Direct oxidation catalysts that promote the oxidation of H_2S to sulfur and water in a single step are one alternative to the multistep Claus process. Direct oxidation is effective at lower concentrations of H_2S. So, H_2S separation in an amine unit is not necessary. Despite its advantages over the Claus process, direct oxidation is rarely used because the catalyst life is too short and attempts to regenerate the catalyst have failed.

[0006] Accordingly, there exists a need for a system and method for effectively regenerating the direct oxidation catalysts.

SUMMARY OF DISCLOSURE

[0007] In one aspect, the embodiments disclosed herein relate to a method for regenerating a direct oxidation catalyst. In one embodiment, the method may comprise contacting the direct oxidation catalyst with steam. In some embodiments, the direct oxidation catalyst may comprise at least one of titanium oxide, aluminum oxide, or mixtures thereof. The direct oxidation catalyst may further comprise a promoter metal oxide selected from a group consisting of oxides of Mn, Co, Cu, Nb, Mo, Tc, Ru, Rh, Hf, Ta, W, Au, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof. In some embodiments, direct oxidation catalyst to be regenerated was fouled by exposure to hydrocarbons and sulfur-containing compounds. In some embodiments, the steam may be high temperature steam having a temperature above 200 °C.

[0008] In another aspect, the embodiments disclosed herein relate to a process for treating a gas stream. In one embodiment, the process may include contacting a gas stream comprising hydrogen sulfide and at least one component with an oxygen-containing gas in the presence of a direct oxidation catalyst. The process may further include contacting the direct oxidation catalyst with steam to regenerate the direct oxidation catalyst.

[0009] In still another aspect, the embodiments disclosed herein relate to a system for treating a gas stream comprising hydrogen sulfide. In one embodiment, the system may include: at least one first direct oxidation reactor in fluid communication with the gas stream, the direct oxidation reactor comprising an oxygen source and a direct oxidation catalyst; and a steam source in fluid communication with the first direct oxidation reactor.

[0010] Other aspects and advantages of the disclosure will be apparent from the following description and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Fig. 1 is a schematic representation of a system in accordance with embodiments disclosed herein.

[0012] Fig. 2 is a schematic representation of a system in accordance with embodiments disclosed herein.

[0013] Fig. 3 is a schematic representation of a system in accordance with embodiments disclosed herein.

DETAILED DESCRIPTION

[0014] In one aspect, the embodiments disclosed herein relate to a method of regenerating a direct oxidation catalyst. A direct oxidation catalyst is a catalyst that promotes the direct oxidation of hydrogen sulfide (H_2S) with oxygen from air or enriched air to elemental sulfur (S) according to the following equation.

$$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + S$$

[0015] The direct oxidation catalyst promotes the selectivity of this reaction to elemental sulfur over the side reaction to sulfur dioxide (SO_2). In the absence of an effective direct oxidation catalyst, the reaction of H_2S with O_2 results in the formation of significant amounts of SO_2 and water.

[0016] In one embodiment, the direct oxidation catalyst comprises a metal oxide. In some embodiments the metal oxide is titanium oxide, aluminum oxide, or mixtures thereof. The direct oxidation catalyst may further comprise a second promoter metal oxide. These direct oxidation catalysts may be referred to as mixed metal oxide catalysts. In some embodiments, the promoter metal oxide may be selected from oxides of Mn, Co, Cu, Nb, Mo, Tc, Ru, Rh, Hf, Ta, W, Au, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof. In other embodiments, the promoter metal oxide may be selected from the group consisting of oxides of Nb, Mo, and Ce, and mixtures thereof. In one particular embodiment, the direct oxidation catalyst comprises titanium oxide

(TiO_2), niobium oxide (Nb_2O_5) and molybdenum oxide (MoO_3). Further description and embodiments of direct oxidation catalysts can be found in U.S. Patent No. 6,099,819, which is incorporated by reference as if fully set forth herein.

[0017] One drawback to using direct oxidation catalysts is that they typically foul when certain hydrocarbon compounds are present with the H_2S-containing gas being treated. These problematic hydrocarbons may include unsaturated hydrocarbons (such as ethylene) and high molecular weight hydrocarbons (>C4). The fouling occurs because deposits form on the catalyst leading to poor performance and/or deactivation of the catalyst. Even at extremely low levels, the hydrocarbon compounds can cause fouling. The problematic, deposit-forming hydrocarbons are found in most hydrocarbon sources. As a result, the fouling problem is so pervasive, that it has prevented direct oxidation catalysts from being adopted for H_2S treatment in the oil and gas industry to this point.

[0018] Because of the unique nature of the fouling deposits, attempts to prevent the fouling or regenerate a fouled direct oxidation catalyst have been surprisingly unsuccessful. Without being bound to a particular theory, it is believed that the deposits are particularly difficult to remove because they may be formed of carbonaceous materials that are essentially vulcanized by the sulfur in the H_2S-containing gas, crosslinking and stabilizing the deposits. As a result, direct oxidation catalysts have only been successfully used to treat extremely clean gases having only minimal hydrocarbon content, such as gases containing nearly 100% CO_2. Attempts to prevent fouling by removing from the gas the compounds that form the deposits have been unsuccessful because they are cost prohibitive and/or not efficient enough to remove of all the deposit-causing compounds. In the past, attempts to remove the deposits from the catalyst were similarly unsuccessful. For example, even the most aggressive technique known, essentially burning the deposit with air at high temperatures (>300 °C) is not effective at regenerating the fouled direct oxidation catalyst without destroying the catalyst. High temperature air regeneration causes temperatures to rise uncontrollably in the reactor to about 875 °C, which sinters the catalyst, massively reducing its surface area.

[0019] Referring to Fig. 1, embodiments of the system and method are shown. During the direct oxidation phase an H_2S-containing gas 1 and O_2-containing gas 3 are fed to a

direct oxidation reactor 5. The direct oxidation reactor 5 contains the direct oxidation catalyst. In various embodiments, the direct oxidation reactor 5 may be a packed-bed type reactor. The H_2S-containing gas 1 may include some hydrocarbon compounds, such as unsaturated and high molecular weight hydrocarbons. In some embodiments, the source of the H_2S-containing gas may be natural gas, a refining process, gases associated with oil production, or the byproduct of a chemical synthesis process, a landfill, or water treatment operations. In some instances, the source of O_2-containing gas may be air or any other oxygen-containing gas.

[0020] In the direct oxidation reactor 5, the H_2S and O_2 react in the presence of the direct oxidation catalyst, which promotes the selectivity of oxidizing the H_2S to elemental sulfur over the side reaction oxidizing H_2S to yield SO_2, total oxidation. The direct oxidation reaction is typically performed at temperatures elevated well above ambient temperature. In one embodiment, the temperature in the reactor 5 is controlled by heating H_2S-containing gas 1 in a heat exchanger 2. The O_2-containing gas 3 may be added to the heated H_2S-containing gas 1 and the combination is fed to a mixer 4, such as a static mixer. Additionally, the direct oxidation reactor itself may be heated and/or the O_2-containing gas may be heated. The temperature of the mixture of the H_2S-containing gas and the O_2-containing gas may be selected to optimize direct oxidation reaction's selectivity for producing S over SO_2 for the given conditions, e.g. the particular catalyst used and the levels of various constituents in the H_2S-containing gas. In addition, the temperature may be selected so that the temperature in the reactor is held high enough to avoid condensation of sulfur on the catalyst. In various embodiments, temperature in the reactor 5 may be heated to 100 °C - 400 °C.

[0021] Treated gas 7 exits the direct oxidation reactor 5. The treated gas 7 includes the sulfur product of the direct oxidation and the remaining constituents of the H_2S-containing gas, such as hydrocarbons and CO_2. The sulfur may be separated from the treated gas 7 in a condenser 6 by condensing the sulfur from treated gas 7.

[0022] While the direct oxidation reactor 5 is often referred to in the singular throughout the various embodiments, it should be understood that the term "reactor" may include multiple reactors operating in parallel or in series. The number of direct oxidation

reactors operating in parallel may be chosen to accommodate the volume of gas to be treated. The operation of multiple direct oxidation reactors in series, may be necessary to achieve the desired overall reduction is H_2S content. Optionally, sulfur may be condensed between the reactors or after the treated stream exits the last reactor in the series.

[0023] Over time, the direct oxidation catalyst fouls, becoming less effective at producing elemental sulfur. In some embodiments, fouling may be detected by monitoring the amounts of SO_2 generated in the direct oxidation reactor 5, which are present in the treated gas 7. The SO_2 levels in the treated gas 7 may be monitored by any number of SO_2 detectors known in the art.

[0024] The direct oxidation catalyst may be regenerated by contacting the catalyst with steam. In some embodiments, the catalyst to be regenerated is fouled by exposure to hydrocarbons, the H_2S-containing gas, condensed elemental sulfur and/or other sulfur-containing compounds. The hydrocarbons may be unsaturated hydrocarbons, high molecular weight hydrocarbons (>C4), or both. Steam regeneration may be performed at any point when it is considered useful or necessary. In various embodiments, steam regeneration is performed when a decrease in the catalyst's effectiveness is detected or after a pre-determined period of time. In one embodiment, the method comprises contacting the catalyst with high temperature steam at a temperature greater than 200 °C. In another embodiment, the method comprises contacting the catalyst with steam above 310 °C. In other embodiments, the steam is at 200 °C – 400 °C. In still other embodiments, the contact with steam occurs at 300 °C - 400 °C. Optionally, air or another oxygen source may be added to the steam used to regenerate the direct oxidation catalyst. In some embodiments, the amount of oxygen added to the steam may be less than 21% by volume.

[0025] In one embodiment, steam regeneration is performed by stopping the flow of H_2S-containing gas 1 to the direct oxidation reactor 5. This may be done using a control valve 9 or any other means, such as redirecting H_2S-containing gas 1 to another direct oxidation reactor. Steam is added to the direct oxidation reactor 5 from a steam source 11, such as a steam generator. The steam source may include a heat source thermally coupled to the

steam source. The amount of time necessary for the steam to regenerate the fouled direct oxidation catalyst will vary. In some cases, 4 hours of steam flow to the direct oxidation catalyst may be sufficient time to regenerate the catalyst. In other cases, as long as 15 days or more may be necessary. The waste 13 from the steam regeneration process exits the direct oxidation reactor 5. Optionally, the progress and completion of the regeneration process may be evaluated by monitoring the total sulfur content and/or the carbon content in the waste 13. When the total sulfur content or the carbon content in the waste 13 are within acceptable limits or no longer detectable, the steam regeneration of the catalyst may be deemed complete.

[0026] Optionally, after the steam regeneration is complete, the direct oxidation catalyst may be contacted with an inert gas 15, such as nitrogen, from an inert gas source 17. The inert gas may serve to cool the direct oxidation catalyst and/or to purge the direct oxidation reactor 5 of any remaining steam or hydrocarbon condensates.

[0027] Referring to Fig. 2, an embodiment is shown wherein multiple direct oxidation reactors are used to create a continuous process. In this so-called "swing bed" arrangement, at least one first direct oxidation reactor 21 and at least one second direct oxidation reactor 23 are configured so that H_2S-containing gas 25 may be routed to either reactor. Steam 27 may also be routed to either reactor 21 or 23. In this configuration, H_2S-containing gas 25 may be routed to a direct oxidation reactor for treatment while steam 27 is routed to another reactor to regenerate the direct oxidation catalyst.

[0028] Routing the H_2S-containing gas, steam, oxygen, and/or other streams to the various reactors, condensers, and other may be performed in any manner know in the art. In some embodiments, a piping system 28 comprising the necessary valves 29 may be used to route the various streams to the various reactors.

[0029] In some embodiments, the direct H_2S oxidation and catalyst regeneration process may be combined with a process for hydrolyzing carbonyl sulfide (COS). COS hydrolysis occurs in the presence of a catalyst according to following reaction:

$$COS + H_2O \rightarrow H_2S + CO_2$$

A number of catalysts are known to suitable for COS hydrolysis, including for example activated alumina. Because the products of COS hydrolysis include H_2S, treating the COS hydrolysis product in a direct oxidation reactor may be effective. In addition, when carbon monoxide (CO) is present in the feed gas to a direct oxidation reactor, COS may be formed in the direct oxidation reaction. Therefore in some embodiments, it may be useful to treat the effluent of the direct oxidation reactor with COS hydrolysis.

[0030] Referring to Fig. 3, various embodiments are shown of systems and methods comprising COS hydrolysis and H_2S direct oxidation having steam regeneration. In one embodiment, at least one COS hydrolysis reactor 30 may be positioned upstream from at least one direct oxidation reactor 32 to treat H_2S in the product 34 of the COS hydrolysis reactor. The direct oxidation reactor 32 is configured so that flow of the product 34 may be stopped and replaced by steam 38 to regenerate the direct oxidation catalyst. Optionally, one or more second direct oxidation reactors 36 may also be positioned downstream from the COS hydrolysis reactor 30 to enable continuous operation by alternating which direct oxidation reactor 32 or 36 is undergoing steam regeneration.

[0031] In another embodiment, a COS hydrolysis reactor 30 may be positioned downstream from a direct oxidation reactor 40 to hydrolyze any COS in the direct oxidation reactor's 40 product 42. The direct oxidation reactor 40 is configured to allow for steam regeneration of the direct oxidation catalyst. Optionally, a second direct oxidation reactor 44 may also be positioned upstream from the COS hydrolysis reactor to allow for alternating steam regeneration between the two or more direct oxidation reactors, i.e. swing bed operation.

[0032] In still another embodiment, direct oxidation reactors 32, 40 may be positioned both upstream and downstream of the COS hydrolysis reactor 30. The direct oxidation reactors are configured to allow for steam generation. This arrangement allows for the effective treatment of a gas stream 46 including CO, H_2S, and the deposit forming hydrocarbons.

[0033] The waste 13 from the steam regeneration process may be handled in a number of ways. In one embodiment, the waste of a direct oxidation reactor undergoing steam regeneration may be fed to another "swing reactor" that is currently performing direct

oxidation. In this embodiment, if there is any H_2S in the waste, it may be converted to S by direct oxidation. The outlet of the swing reactor may then be fed to a condenser to condense the steam to water. The water may then be injected into waste injection well or sent to a sour water stripper. In another embodiment, the waste from the steam regeneration process is sent to a condenser and not another direct oxidation reactor. The condensed water may be then be sent to a waste injection well or a sour water stripper.

EXAMPLES

[0034] Fouled direct oxidation catalyst was used as the test subject in these experiments. The test catalyst was comprised of titanium dioxide (TiO_2), niobium oxide (Nb_2O_5) and molybdenum oxide (MoO_3). The catalyst is available from SAINT-GOBAIN NORPRO of Stow, Ohio. The test catalyst was fouled by extended exposure to a gas stream containing both H_2S and hydrocarbons. While the exact amounts of the contents of this gas stream would, of course, vary over time, a representative composition in mole % includes 3.69% H_2, 65.89% N_2, 0.49% H_2S, 2.34% CO, 17.84% CO_2, 8.00% CH_4, 1.21% C_2H_6, 0.30% C_3H_8, 0.08% C4, 0.03% C5, and 0.14% C6+ (C6 hydrocarbons and greater). Prior to regeneration, the fouled test catalyst was observed in the field as being capable of converting only about 60% of H_2S to elemental sulfur at about 230 °C and 15 psig, down from its original >90%.

[0035] The fouled direct oxidation catalyst was regenerated with high temperature steam. A 100g sample of the fouled catalyst was regenerated with steam in a laboratory by slowly increasing the temperature of the catalyst to 330 °C. Water was then injected into the preheating zone of the laboratory reactor at rate of about 0.2 ml/min to generate the steam. The steam regeneration process was continued for 10 hours.

[0036] Direct oxidation was performed with the steam-regenerated catalyst at 156 °C and atmospheric pressure with a gas hourly space velocity of 1100/hour and a nearly constant O_2/H_2S ratio (0.71 -0.74). The steam-regenerated catalyst was observed as converting >90% of the H_2S to elemental sulfur. This conversion rate is comparable to that of fresh, un-fouled catalyst for the same conditions. Fresh direct oxidation catalyst having essentially the same composition was also observed to have >90% conversion at 159 °C.

[0037] While the disclosure has been described with respect to a limited number of embodiments, those skilled in the art, having the benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the disclosure as disclosed herein. Accordingly, the scope of the disclosure should be limited only by the attached claims. Also, while the embodiments included herein are often described with reference to a reactor or other elements in the singular for simplicity, this is not intended to limit the disclosure. A person of skill in the art would recognize that multiple reactors and other such elements could be utilized where the elements are referred to in the singular.

CLAIMS

1. A method of regenerating a direct oxidation catalyst, the method comprising:
contacting the direct oxidation catalyst with steam.

2. The method of claim 1 wherein the direct oxidation catalyst comprises at least one of titanium oxide, aluminum oxide, or mixtures thereof.

3. The method of claim 2 wherein the direct oxidation catalyst further comprises a promoter metal oxide selected from a group consisting of oxides of Mn, Co, Cu, Nb, Mo, Tc, Ru, Rh, Hf, Ta, W, Au, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof.

4. The method of claim 1 wherein the direct oxidation catalyst was fouled by exposure to hydrocarbons and sulfur-containing compounds.

5. The method of claim 1 wherein the direct oxidation catalyst is contacted with steam at a temperature greater than 200 °C.

6. The method of claim 1 wherein the direct oxidation catalyst is contacted with steam at a temperature greater than 310 °C.

7. The method of claim 1 wherein the direct oxidation catalyst is contacted with steam at a temperature between about 300 °C and about 400 °C.

8. The method of claim 1 further comprising adding oxygen to the steam.

9. The method of claim 1 further comprising flowing an inert gas across the catalyst after contacting the catalyst with steam.

10. A process for treating a gas stream, the process comprising:

contacting a gas stream comprising hydrogen sulfide and at least one hydrocarbon component with an oxygen-containing gas in the presence of a direct oxidation catalyst; and

contacting the direct oxidation catalyst with steam to regenerate the direct oxidation catalyst.

11. The process of claim 10 wherein in the step of contacting the direct oxidation catalyst with steam comprises:

contacting the direct oxidation catalyst with a mixture comprising steam and oxygen.

12. The process of claim 10 further comprising:

monitoring the amount of sulfur dioxide generated by contacting the gas stream with the direct oxidation catalyst; and

regenerating the direct oxidation catalyst when the amount of sulfur dioxide reaches a predetermined limit.

13. The process of claim 10 wherein the gas stream is contacted with the oxygen-containing gas in the presence of a direct oxidation catalyst in at least one first reactor.

14. The process of claim 13 wherein the method further comprises:

diverting the gas stream to at least one second reactor comprising the direct oxidation catalyst before regenerating the direct oxidation catalyst in the first reactor; and

contacting gas stream with the oxygen-containing gas and the direct oxidation catalyst in the second reactor.

15. The process of claim 13 further comprising converting carbonyl sulfide in the gas stream to hydrogen sulfide in at least one first carbonyl sulfide reactor.

16. The process of claim 15 further comprising contacting the gas stream with oxygen in the presence of the direct oxidation catalyst after the gas stream exits the carbonyl sulfide reactor.

17. A system for treating a gas stream comprising hydrogen sulfide (H_2S), the system comprising:

at least one first direct oxidation reactor in fluid communication with the gas stream, the first direct oxidation reactor comprising a direct oxidation catalyst; and

a steam source in fluid communication with the first direct oxidation reactor.

18. The system of claim 17 further comprising an inert gas source in fluid communication with the first direct oxidation reactor.

19. The system of claim 17 further comprising:

at least one second direct oxidation reactor in fluid communication with the gas stream; and

a piping system in fluid communication with the gas stream, the first direct oxidation reactor and the second direct oxidation reactor, wherein the piping system is capable of diverting the gas stream to the first direct oxidation reactors or the second direct oxidation reactor.

20. The system of claim 17 further comprising at least one carbonyl sulfide reactor in fluid communication with the first direct oxidation reactor.

21. The system of claim 20 wherein the carbonyl sulfide reactor receives the gas stream from the first direct oxidation reactor.

22. The system of claim 21 further comprising at least one subsequent direct oxidation reactor receiving the gas stream from the carbonyl sulfide reactor.

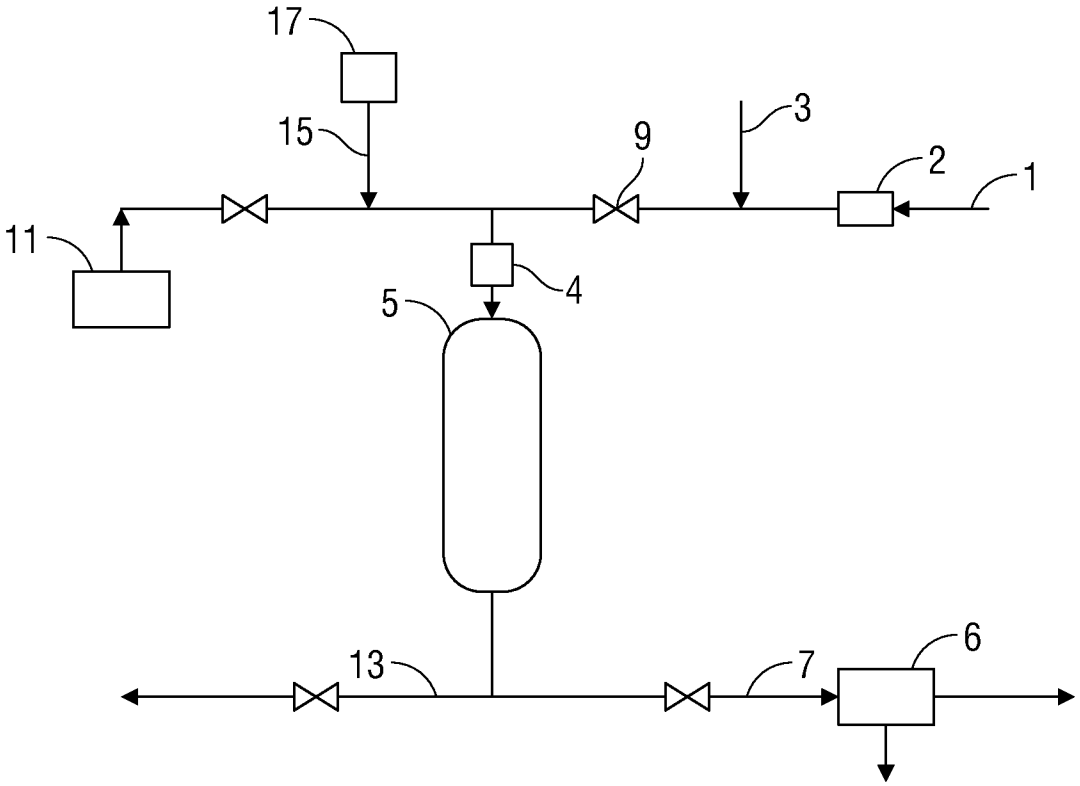


FIG. 1

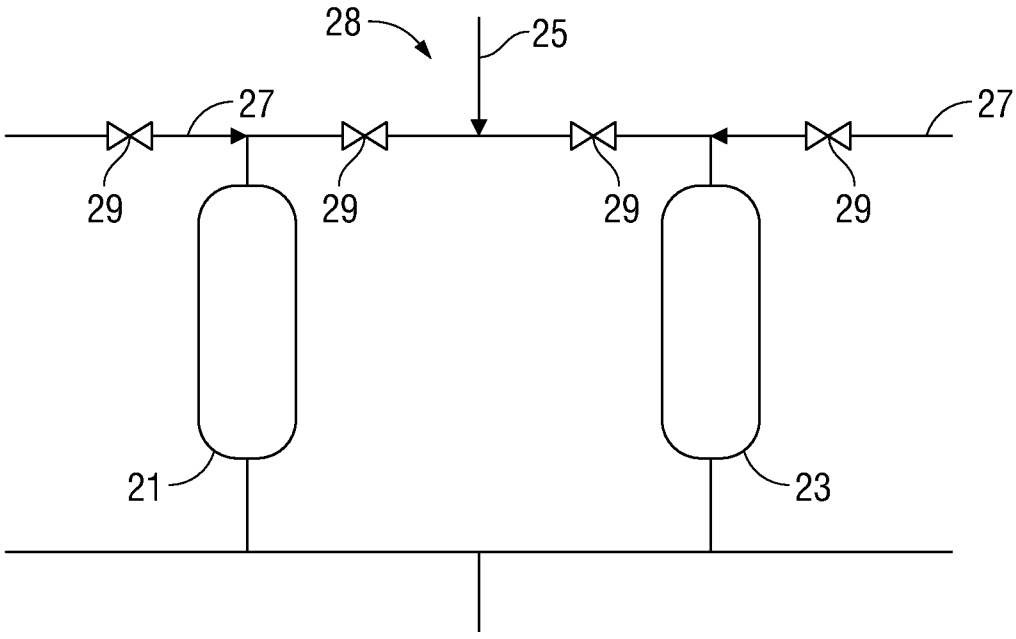


FIG. 2

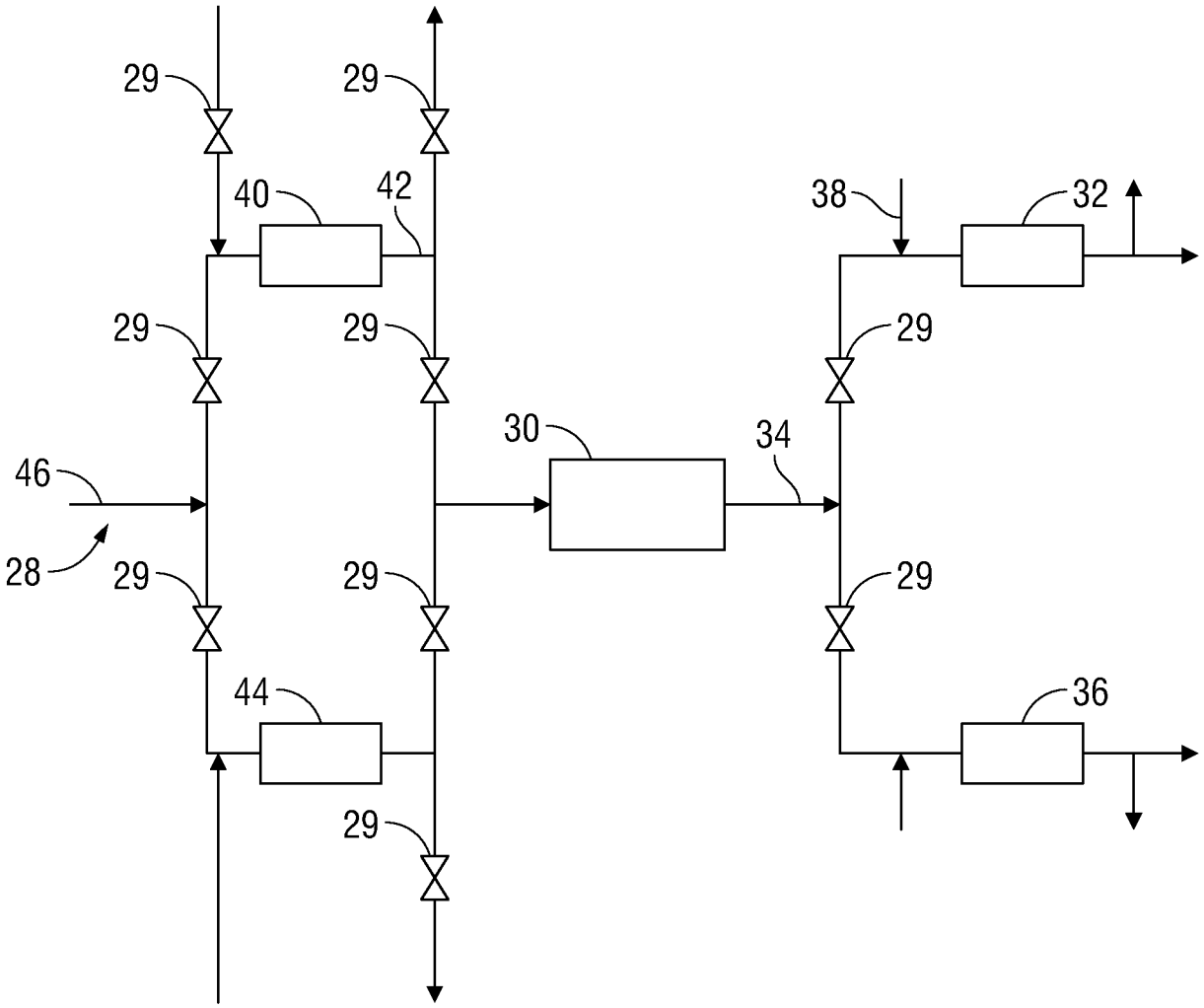


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/060903

A. CLASSIFICATION OF SUBJECT MATTER

B01J 38/06(2006.01)i, B01J 38/02(2006.01)i, C01B 17/02(2006.01)i

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)
B01J 38/06; C07C 51/16; B01J 38/12; B01D 53/48; B01J 23/50; B01J 23/96; B01J 38/04; B01J 20/20; B01J 23/94; B01J 38/02; C01B 17/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: regenerating, direct oxidation catalyst, steam, hydrogen sulfide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012-145310 A1 (M-I L.L.C.) 26 October 2012 See claims 1-22; and paragraphs [0006]-[0009].	1-22
X	US 5442108 A (KAWAJIRI, TATSUYA et al.) 15 August 1995 See abstract; column 2, lines 58-68, column 3, lines 13-39; and claim 17.	1,5-8
A		2-4,9-22
A	US 4795726 A (SCHAPER, HENNIE et al.) 03 January 1989 See abstract; and claim 1.	1-22
A	US 2008-0260611 A1 (ADERHOLD, JAMES L. et al.) 23 October 2008 See abstract; and claim 1.	1-22
A	US 4391735 A (BUSSE, PAUL J.) 05 July 1983 See abstract; and claims 1, 6.	1-22

☐ 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
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Date of the actual completion of the international search	Date of mailing of the international search report
13 January 2015 (13.01.2015)	**13 January 2015 (13.01.2015)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US2014/060903

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