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(54) Title: CONFIGURATIONS AND METHODS FOR EFFLUENT GAS TREATMENT

(57) Abstract: Methods and configurations are drawn to a plant in which an effluent gas (102) comprising oxygen and sulfur dioxide is catalytically reacted with hydrogen sulfide (148) and hydrogen and/or carbon monoxide (114) to form a treated gas that is substantially oxygen free and in which sulfur dioxide is converted to hydrogen sulfide. In most preferred aspects, the hydrogen sulfide is provided to the process via a recycle loop (134B).



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## CONFIGURATIONS AND METHODS FOR EFFLUENT GAS TREATMENT

### Field of The Invention

The field of the invention is treatment of effluent gases, and especially removal of sulfur  
5 dioxide from oxygen-containing gases.

### Background of The Invention

Sulfur removal from waste gases has become increasingly important as regulations  
require refineries and other petrochemical facilities to reduce their output of sulfurous  
compounds below previously tolerated concentrations. Depending on the type of waste gas (*e.g.*,  
10 effluent gas from a Claus plant, fluid catalytic cracking (FCC) unit, or coking unit), various  
processes are known in the art to recover sulfur from waste gases.

For example, sulfur dioxide is removed in some of the known configurations using a  
caustic process in which gaseous sulfur compounds are converted into soluble sulfite/sulfate  
compounds, and typical examples of such configurations are described in U.S. Pat. Nos.  
15 3,719,742 to Terrana et al. and 3,790,660 to Earl et al. However, most of such configurations  
have a relatively high stripping steam requirement and are therefore economically less attractive.  
Other known caustic processes are described, for example, in U.S. Pat. No. 3,920,794 to La  
Mantia et al. Here, NaOH and Na<sub>2</sub>CO<sub>3</sub> scrubbing solutions remove SO<sub>2</sub> from gas streams. After  
the adsorption or scrubbing step, an oxidation step is performed to convert sulfites to sulfates by  
20 addition of catalytically effective metals (*e.g.*, Fe, Cu, Co, Mn, and/or Ni). While such oxidation  
is relatively simple and effective, salts need to be added, and a secondary oxidation step may be  
required if the level of sulfites in the scrubbing solution after adsorption of SO<sub>2</sub> is relatively high.

To overcome at least some of the problems associated with caustic solutions,  
alkanolamines (*e.g.*, aqueous solutions of triethanolamine) can be used to absorb SO<sub>2</sub> from a  
25 waste gas as described for example, in U.S. Pat. No. 3,904,735 to Atwood et al. However,  
several difficulties nevertheless remain. Among other things, many alkanolamines have a  
relatively low selectivity towards SO<sub>2</sub>, and tend to absorb significant quantities of CO<sub>2</sub>. Still  
further, at least some of the alkanolamines exhibit relatively high evaporative losses, and often  
promote oxidation of SO<sub>2</sub> to SO<sub>3</sub> where oxygen is present.

In still further known non-caustic processes, as described in U.S. Pat. No. 4,634,582 to Sliger et al., SO<sub>2</sub> is removed from a waste gas stream by absorption in a buffered aqueous thiosulfate and polythionate solution, followed by regeneration of the enriched solution with hydrogen sulfide to form sulfur. Hydrogen sulfide recovered from the regeneration step is then introduced to the absorption step to reduce bisulfite concentration in the enriched solution. While such desulfurization is conceptually relatively simple, maintenance of the buffered solution often limits the capacity of such systems in at least some instances.

Alternatively, as described in our co-pending International patent application (published as WO 03/045544), sulfur dioxide-containing waste gas is introduced into a reducing gas generator that is operated using natural gas, air, and hydrogen to supply sufficient reducing gas to the effluent gas. Typical operation conditions are selected such that the oxygen is substantially completely removed from the waste gas, operation temperatures will generally be between about 1000° and 1500°F. The so formed hydrotreated feed gas comprises hydrogen sulfide, which is removed using a contactor. Such configurations advantageously improve desulfurization under most conditions. However, high temperature operation and supplemental fuel gas are generally needed, which typically increases cost and complexity of the operation.

Although various configurations and methods are known to reduce sulfur concentrations in oxygen-containing effluent streams, all or almost all of them suffer from one or more disadvantages. Therefore, there is still a need to provide improved methods and configuration to reduce the sulfur content in such streams.

### **Summary of the Invention**

The present invention is directed to configurations and methods for sulfur dioxide removal from oxygen-containing waste gases in which oxygen is catalytically removed using hydrogen sulfide to form sulfur dioxide, and in which the sulfur dioxide is catalytically converted to hydrogen sulfide (*e.g.*, using hydrogen or carbon monoxide), which is then removed from the gas stream using solvent absorption.

In one aspect of the inventive subject matter, a plant includes a first catalytic reactor that receives an effluent gas comprising oxygen and sulfur dioxide, and a second gas comprising H<sub>2</sub>S. The first reactor further comprises a catalyst that catalyzes a reaction in which the oxygen reacts

with the hydrogen sulfide to form an oxygen-free gas comprising water and sulfur dioxide. A second catalytic reactor is fluidly coupled to the first reactor and receives the oxygen-free gas, wherein the second catalytic reactor further includes a hydrogenation catalyst that catalyzes a reaction in which the sulfur dioxide from the oxygen-free gas and hydrogen and/or carbon  
5 monoxide react to form a reduced oxygen-free gas comprising hydrogen sulfide.

In particularly contemplated plants, a separator receives the reduced oxygen-free gas to form a condensate and a hydrogen sulfide containing gas, and may further include an absorber that receives the hydrogen sulfide containing gas, wherein a lean solvent absorbs at least part of the hydrogen sulfide to form a treated gas. While not limiting to the inventive subject matter, it is  
10 generally preferred that the second gas comprises the hydrogen sulfide containing gas from the separator and/or the treated gas from the absorber.

In another aspect of the inventive subject matter, a plant for desulfurization of a waste gas that includes oxygen and sulfur dioxide includes a first reactor that receives the waste gas and in which hydrogen sulfide is recycled from either upstream or downstream of the absorber and added to the waste gas in an amount effective to catalytically deplete the waste gas from  
15 oxygen. A second reactor receives the oxygen-depleted waste gas and hydrogen is added to the oxygen-depleted waste gas to catalytically reduce the sulfur dioxide to hydrogen sulfide.

In preferred aspects of contemplated plants, a separator receives the reduced and oxygen-depleted waste gas from the second reactor to form a condensate and a hydrogen sulfide  
20 containing gas, and an absorber receives the hydrogen sulfide containing gas from the separator, wherein a lean solvent absorbs at least part of the hydrogen sulfide to form a treated gas. It is still further preferred that the hydrogen sulfide that is added to the waste gas is derived from at least one of the hydrogen sulfide containing gas from the separator and the treated gas from the absorber.

In a further aspect of the inventive subject matter, a method of desulfurizing an oxygen-containing waste gas includes a step in which a waste gas is provided that includes sulfur dioxide and oxygen. In another step, the waste gas is combined with hydrogen sulfide in an amount  
25 sufficient to deplete the waste gas from oxygen in a catalytic reaction in which the hydrogen sulfide is oxidized to sulfur dioxide to thereby form an oxygen-depleted gas, and in yet another  
30 step, the oxygen-depleted gas is reacted with hydrogen to reduce the sulfur dioxide to hydrogen

sulfide to thereby form a reduced oxygen-depleted gas. With respect to a separator and an absorber, the same considerations as provided above apply.

Various objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of preferred embodiments of the invention, along with the accompanying drawings in which like numerals represent like components.

### **Brief Description of The Drawings**

Figure 1 is an exemplary schematic configuration for removal of sulfur dioxide from oxygen-containing gases according to the inventive subject matter.

### 10 **Detailed Description**

The inventors have discovered that sulfur dioxide can be removed from oxygen-containing effluent gases in a highly efficient manner without the need of a high-temperature operation (*e.g.*, as used in direct firing). In especially preferred aspects, the temperatures for oxygen and sulfur removal are typically below 600 °F - 900 °F, and both oxygen and sulfur dioxide are removed in separate catalytic reactions using hydrogen sulfide and hydrogen, respectively.

In one particularly preferred aspect, as depicted in **Figure 1**, a plant includes a desulfuration unit 100 having a first catalytic reactor 110 that is fluidly coupled to a second catalytic reactor 120. The effluent of the second catalytic reactor 120 is separated in separator 130, which provides a gas stream to absorber 140.

Most typically, a waste gas 102 containing oxygen and sulfur dioxide at a temperature of, or preheated to a temperature of about 400 °F– 600 °F is mixed with the hydrogen sulfide-containing recycle stream 148 (which is heated by heater 160 to a temperature of about 400 °F– 600 °F) to form mixed stream 104 that is introduced into the first catalytic reactor 110. The first catalytic reactor 110 typically includes a catalyst that catalyzes a reaction in which the oxygen from the waste gas 102 is substantially completely (*i.e.*, at least 95%, more typically at least 98%) consumed to form sulfur dioxide and water, which leaves the first catalytic reactor 110 in oxygen-free product stream 112. It should be noted that some of the sulfur dioxide in the first

catalytic reactor will react with hydrogen sulfide in a Claus-type reaction to form elemental sulfur as the typical operating temperature in the first catalytic reactor is between about 400 °F–800 °F.

The so formed oxygen-free product stream 112 is then cooled via mixing with the recycle stream 148 and hydrogen, and/or carbon monoxide stream 114 such that the temperature of the combined stream 116 is in the range of about 400 °F– 600 °F. Consequently, as the second catalytic reactor 120 includes a catalyst that catalyzes reduction of sulfur dioxide to hydrogen sulfide, the sulfur dioxide (and at least part of the elemental sulfur) of the oxygen-free product stream 112 is converted to hydrogen sulfide in the second catalytic reactor 120. Typical effluent temperature of the second catalytic reactor is generally between 600 °F– 850 °F, which is preferably controlled by adjusting the amount of recycle stream 148 to the second catalytic reactor 120. Second product stream 122 leaves the second catalytic reactor 120, and heat is extracted from stream 122 in exchanger 150 (e.g., by converting boiler feed water into steam) before entering separator 130. Water condensate is removed from second catalytic reactor effluent 122 (which includes reduced oxygen-free gas comprising hydrogen sulfide) in the separator 130 as stream 132, and one portion of the so processed vapor stream 134 enters the absorber 140 as stream 134A, while another portion 134B is recycled to the first catalytic converter 110 as stream 148. Depending on the actual characteristics of the stream 102 and the specific sulfur removal requirement, stream 134B can be eliminated and replaced by stream 146 as the recycle stream to the first catalytic converter 110. In such cases, the entire stream 134 enters the absorber 140 without splitting. Recycle stream 148 is boosted by booster 170, and at least a portion of the recycle stream 148 is heated by exchanger 160 before mixing the (heated) recycle stream with the waste gas 102 and/or oxygen-free product stream 112.

The regenerator 140 is preferably a conventional absorber tower in which an amine solution absorbs the hydrogen sulfide from stream 134 or stream 134A to thereby generate a desulfurized stream 146, which is either vented into the atmosphere or recycled to the first catalytic converter 110 as stream 148. Under most operating conditions, the desulfurized stream 146 comprises less than 10-150 ppmv of hydrogen sulfide. Lean amine enters the absorber as stream 144 and rich amine solution exits the absorber as stream 142, which is regenerated using known processes.

With respect to the waste gas, it should be recognized that while regenerator gases from an S Zorb process (Sulfur removal process using a sulfur-containing sorbent that removes sulfur from a sulfur-containing molecule in a feed contacting the catalyst (see *e.g.*, Conoco Phillips' S Zorb process)) are typically preferred, numerous alternative gases are also deemed suitable for use herein and generally include all gases that comprise oxygen (preferably less than 10%) and sulfur dioxide (preferably less than 5%). Therefore, contemplated waste gases include FCC flue gases, or coker flue gases. In some of the preferred aspects, the waste gas may have a sulfur dioxide concentration of less than 2.0 %. For example, the sulfur dioxide concentration in suitable gas streams may be between 1.2 % and 2.0%, and even lower. Where the sulfur dioxide concentration of a feed gas is higher, it is generally preferred that the ratio of recycle gas to waste gas is adjusted such that the maximum sulfur dioxide concentration in the mixed stream 104 is less than 2 %, and more typically less than 1.5 %.

It should be particularly recognized, however, that the amount of recycle gas that is admixed to the waste gas is chosen such that the recycle gas will provide hydrogen sulfide in a quantity sufficient for the oxygen contained in the waste gas to be consumed by a reaction in the first reactor that produces (among other things) sulfur dioxide from oxygen and hydrogen sulfide. Therefore, the composition of the recycle gas may vary, and it should be appreciated that the hydrogen sulfide content of the recycle gas may be regulated by adjusting the ratio of stream 134B (rich in hydrogen sulfide) or stream 146 (lean in hydrogen sulfide). However, in alternative aspects, reducing agents (*e.g.*, hydrogen sulfide, hydrogen, etc.) may be provided by sources other than streams 134B and 146, and suitable hydrogen sulfide sources include Claus plant feed streams, or sour gas streams from amine regeneration.

Preferred first catalytic reactors include a catalyst that catalyzes a reaction in which oxygen from an oxygen-containing gas reacts with hydrogen sulfide (contained in that gas or added to that gas) to form an oxygen-free gas (*i.e.*, less than 1%, more typically less than 0.5 %, and most typically less than 0.1 %) comprising sulfur dioxide. Therefore, contemplated catalysts include all catalysts that promote oxidation of hydrogen sulfide, and especially include various alumina catalysts, titanium oxide catalysts and vanadium-antimony catalysts. It should further be appreciated that depending on the type of catalyst and oxygen content, the reaction temperature in the first catalytic reactor will generally be in the range of between about 400 °F to 800 °F. However, lower temperatures (*e.g.*, between 300 °F to 400 °F) or higher temperatures (*e.g.*,

between 800 °F to 950 °F) are also deemed suitable. Appropriate operating temperatures can be maintained by preheating the recycle gas and/or the waste gas (*e.g.*, to a temperature of between about 400 °F to 600 °F). Typically, some of the hydrogen sulfide in the first catalytic reactor will react with some of the sulfur dioxide in a Claus-type reaction to form water and elemental sulfur.

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With respect to the second catalytic reactor, it is contemplated that all known hydrogenation reactors may be employed for use in conjunction with the teachings presented herein. Furthermore, it is generally preferred that contemplated second catalytic reactors will include a hydrogenation catalyst that catalyzes a reaction in which sulfur dioxide and hydrogen, and/or carbon monoxide, react to form hydrogen sulfide and water. There are numerous hydrogenation catalysts known in the art and all of the known catalysts are considered suitable for use herein. However, especially preferred catalysts include cobalt molybdenum catalysts, ceria catalysts, or zirconia catalysts. Consequently, the sulfur dioxide from the oxygen-free gas provided by the first reactor will react in the second reactor with added hydrogen to form a reduced oxygen-free gas comprising H<sub>2</sub>S.

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Hydrogen is generally added to the effluent from the first catalytic reactor or directly to the second catalytic reactor in an amount sufficient to convert substantially all (*i.e.*, at least 95 %, more typically at least 99 %) of the sulfur dioxide into hydrogen sulfide. Therefore, the exact amount of hydrogen, and/or carbon monoxide, will vary, however, it should be recognized that a person of ordinary skill in the art will readily be able to determine the appropriate quantity. Hydrogen and/or carbon monoxide may be added in numerous manners and from various sources, and contemplated hydrogen streams may include purified hydrogen (*e.g.*, from a PSA), or streams enriched in hydrogen and/or carbon monoxide (*e.g.*, hydrogen-containing recycle streams).

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With respect to the temperature of the oxygen-depleted gas that enters the second catalytic reactor, it is generally preferred that the oxygen-depleted gas is cooled to a temperature range of between about 400 °F to 600 °F and the SO<sub>2</sub> concentration of less than 2%. Preferably, such cooling and/or dilution are accomplished via mixing the oxygen-depleted gas 112 from the first catalytic reactor with recycle gas 148 (which may or may not be preheated). In such configurations, it should be especially recognized that the cooling/diluting agent (*i.e.*, the recycle

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gas) is free from oxygen and may comprise hydrogen sulfide. However, cooling may also be done via heat sinks (*e.g.*, heat exchanger), and it should be recognized that lower temperatures (*e.g.*, between 300 °F to 400 °F) or even higher temperatures (*e.g.*, between 600 °F to 750 °F) are also contemplated.

- 5           The so produced effluent from the second catalytic reactor (the hydrogen sulfide-containing oxygen-free gas) is then cooled, preferably in a heat exchanger and condensate is removed after cooling in a separator before the cooled gas is desulfurized in an absorber using methods well known in the art. Typically, the absorber is an amine absorber that uses an amine-based solvent to extract the hydrogen sulfide from the effluent of the second catalytic reactor.
- 10       The so produced rich solvent is then processed using solvent regeneration processes well known in the art. Alternatively, a direct contact condenser could be used for cooling and condensate removal.

- Therefore, the inventors generally contemplate a plant comprising a first catalytic reactor that receives an effluent gas comprising oxygen and sulfur dioxide, and that further receives a
- 15       second gas comprising hydrogen sulfide, wherein the first reactor further includes a catalyst that catalyzes a reaction in which the oxygen reacts with the hydrogen sulfide to form an oxygen-free gas comprising water and sulfur dioxide. Such plants also include a second catalytic reactor that is fluidly coupled to the first reactor and receives the oxygen-free gas. Suitable second catalytic reactors comprise a hydrogenation catalyst that catalyzes a reaction in which the sulfur dioxide
- 20       from the oxygen-free gas and hydrogen, and/or carbon monoxide react to form a reduced oxygen-free gas comprising hydrogen sulfide. It should further be appreciated that the first and second reactors could be disposed in a single vessel comprising of two separate catalyst beds with sufficient space for gas mixing in between the two separate catalytic beds.

- Viewed from another perspective, it is therefore contemplated that a plant for
- 25       desulfuration of a waste gas that includes oxygen and sulfur dioxide will include a first reactor that receives the waste gas and in which hydrogen sulfide is added to the waste gas in an amount effective to catalytically deplete the waste gas from oxygen, and a second reactor that receives the oxygen-depleted waste gas and in which hydrogen and/or carbon monoxide is added to the oxygen-depleted waste gas to catalytically reduce the sulfur dioxide to hydrogen sulfide.

Consequently, a method of desulfurizing an oxygen-containing waste gas has one step in which a waste gas is provided that includes sulfur dioxide and oxygen. In another step, the waste gas is combined with hydrogen sulfide in an amount sufficient to deplete the waste gas from oxygen in a catalytic reaction in which the hydrogen sulfide is oxidized to sulfur dioxide to  
5 thereby form an oxygen-depleted gas. In yet another step, the oxygen-depleted gas is catalytically reacted with hydrogen to reduce the sulfur dioxide to hydrogen sulfide, to thereby form a reduced oxygen-depleted gas.

Thus, specific embodiments and applications for configurations and methods for improved effluent gas treatment have been disclosed. It should be apparent, however, to those  
10 skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the appended claims. Moreover, in interpreting both the specification and the claims, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be  
15 interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, components, or steps that are not expressly referenced.

## CLAIMS

What is claimed is:

1. A plant comprising:
  - a first catalytic reactor receiving (a) an effluent gas comprising oxygen and sulfur dioxide, and (b) a second gas comprising a reducing agent, the first reactor further comprising a catalyst that catalyzes a reaction in which the oxygen reacts with the reducing agent to form an oxygen-free gas comprising water and sulfur dioxide; and
  - a second catalytic reactor fluidly coupled to the first reactor and receiving the oxygen-free gas, the second catalytic reactor further comprising a hydrogenation catalyst that catalyzes a reaction in which the sulfur dioxide from the oxygen-free gas and at least one of hydrogen and carbon monoxide react to form a reduced oxygen-free gas comprising hydrogen sulfide.
2. The plant of claim 1 further comprising a separator that receives the reduced oxygen-free gas to form a condensate and a hydrogen sulfide containing gas.
3. The plant of claim 2 further comprising an absorber that receives the hydrogen sulfide containing gas, and in which a lean solvent absorbs at least part of the hydrogen sulfide to form a treated gas.
4. The plant of claim 3 wherein the second gas comprises at least one of the hydrogen sulfide containing gas from the separator and the treated gas from the absorber.
5. The plant of claim 1 wherein heat is extracted from the reduced oxygen-free gas before entering a separator or absorber.
6. The plant of claim 1 wherein at least one of the effluent gas and the second gas are heated to a temperature of between 400 °F to 600 °F before entering the first catalytic reactor.
7. The plant of claim 1 wherein the catalyst in the first catalytic reactor comprises alumina, titanium oxide, or a vanadium-antimony catalyst.
8. The plant of claim 1 wherein the catalyst in the second catalytic reactor comprises a cobalt molybdenum catalyst, a ceria catalyst, or a zirconia catalyst.

9. A plant for desulfurization of a waste gas that includes oxygen and sulfur dioxide, comprising:
  - a first reactor that receives the waste gas and in which a reducing agent is added to the waste gas in an amount effective to catalytically deplete the waste gas from oxygen; and
  - a second reactor that receives the oxygen-depleted waste gas and in which at least one of hydrogen and carbon monoxide are added to the oxygen-depleted waste gas to catalytically reduce the sulfur dioxide to hydrogen sulfide.
10. The plant of claim 9 further comprising a separator that receives the reduced and oxygen-depleted waste gas from the second reactor to form a condensate and a hydrogen sulfide containing gas.
11. The plant of claim 10 further comprising an absorber that receives the hydrogen sulfide containing gas from the separator, and in which a lean solvent absorbs at least part of the hydrogen sulfide to form a treated gas.
12. The plant of claim 11 wherein the hydrogen sulfide is added to the waste gas is derived from at least one of the hydrogen sulfide containing gas from the separator and the treated gas from the absorber.
13. A method of desulfurizing an oxygen-containing waste gas, comprising:
  - providing a waste gas that includes sulfur dioxide and oxygen;
  - combining the waste gas with hydrogen sulfide in an amount sufficient to deplete the waste gas from oxygen in a catalytic reaction in which the hydrogen sulfide is oxidized to sulfur dioxide to thereby form an oxygen-depleted gas; and
  - reacting the oxygen-depleted gas with at least one of hydrogen and carbon monoxide to reduce the sulfur dioxide to hydrogen sulfide to thereby form a reduced oxygen-depleted gas.

14. The method of claim 13 wherein the reduced oxygen-depleted gas is separated in a separator to form a condensate and a gas comprising the hydrogen sulfide, wherein at least a portion of the gas comprising the hydrogen sulfide is combined with the waste gas.
15. The method of claim 13 wherein the reduced oxygen-depleted gas is separated in a separator to form a condensate and a gas comprising the hydrogen sulfide, and wherein at least a portion of the gas comprising the hydrogen sulfide is fed into an absorber in which the hydrogen sulfide is absorbed by a solvent to thereby for a treated gas.
16. The method of claim 15 wherein a portion of the treated gas is combined with the waste gas.

**AMENDED CLAIMS**

**[received by the International Bureau on 01 November 2004(01.11.04);  
original claims 1-16 replaced by new amended claims 1-16, (3 pages)]**

What is claimed is:

1. A plant comprising:  
a first catalytic reactor receiving (a) an effluent gas comprising oxygen and sulfur dioxide, and (b) a second gas comprising a reducing agent, the first reactor further comprising a catalyst that catalyzes a reaction in which the oxygen reacts with the reducing agent to form an oxygen-free gas comprising water and sulfur dioxide; and  
a second catalytic reactor fluidly coupled to the first reactor and receiving the oxygen-free gas, the second catalytic reactor further comprising a hydrogenation catalyst that catalyzes a reaction in which the sulfur dioxide from the oxygen-free gas and at least one of hydrogen and carbon monoxide react to form a reduced oxygen-free gas comprising hydrogen sulfide.
2. The plant of claim 1 further comprising a separator that receives the reduced oxygen-free gas to form a condensate and a hydrogen sulfide containing gas.
3. The plant of claim 2 further comprising an absorber that receives the hydrogen sulfide containing gas, and in which a lean solvent absorbs at least part of the hydrogen sulfide to form a treated gas.
4. The plant of claim 3 wherein the second gas comprises at least one of the hydrogen sulfide containing gas from the separator and the treated gas from the absorber.
5. The plant of claim 1 wherein heat is extracted from the reduced oxygen-free gas before entering a separator or absorber.
6. The plant of claim 1 wherein at least one of the effluent gas and the second gas are heated to a temperature of between 400 °F to 600 °F before entering the first catalytic reactor.
7. The plant of claim 1 wherein the catalyst in the first catalytic reactor comprises alumina, titanium oxide, or a vanadium-antimony catalyst.
8. The plant of claim 1 wherein the catalyst in the second catalytic reactor comprises a cobalt molybdenum catalyst, a ceria catalyst, or a zirconia catalyst.

9. A plant for desulfurization of a waste gas that includes oxygen and sulfur dioxide, comprising:  
a first reactor that receives the waste gas and in which a reducing agent is added to the waste gas in an amount effective to catalytically deplete the waste gas from oxygen; and  
a second reactor that receives the oxygen-depleted waste gas and in which at least one of hydrogen and carbon monoxide are added to the oxygen-depleted waste gas to catalytically reduce the sulfur dioxide to hydrogen sulfide.
10. The plant of claim 9 further comprising a separator that receives the reduced and oxygen-depleted waste gas from the second reactor to form a condensate and a hydrogen sulfide containing gas.
11. The plant of claim 10 further comprising an absorber that receives the hydrogen sulfide containing gas from the separator, and in which a lean solvent absorbs at least part of the hydrogen sulfide to form a treated gas.
12. The plant of claim 11 wherein the hydrogen sulfide is added to the waste gas is derived from at least one of the hydrogen sulfide containing gas from the separator and the treated gas from the absorber.
13. A method of desulfurizing an oxygen-containing waste gas, comprising:  
providing a waste gas that includes sulfur dioxide and oxygen;  
combining the waste gas with hydrogen sulfide in an amount sufficient to deplete the waste gas from oxygen in a catalytic reaction in which the hydrogen sulfide is oxidized to sulfur dioxide to thereby form an oxygen-depleted gas; and  
reacting the oxygen-depleted gas with at least one of hydrogen and carbon monoxide to reduce the sulfur dioxide to hydrogen sulfide to thereby form a reduced oxygen-depleted gas.
14. The method of claim 13 wherein the reduced oxygen-depleted gas is separated in a separator to form a condensate and a gas comprising the hydrogen sulfide, wherein at least a portion of the gas comprising the hydrogen sulfide is combined with the waste gas.

15. The method of claim 13 wherein the reduced oxygen-depleted gas is separated in a separator to form a condensate and a gas comprising the hydrogen sulfide, and wherein at least a portion of the gas comprising the hydrogen sulfide is fed into an absorber in which the hydrogen sulfide is absorbed by a solvent to thereby for a treated gas.
16. The method of claim 15 wherein a portion of the treated gas is combined with the waste gas.



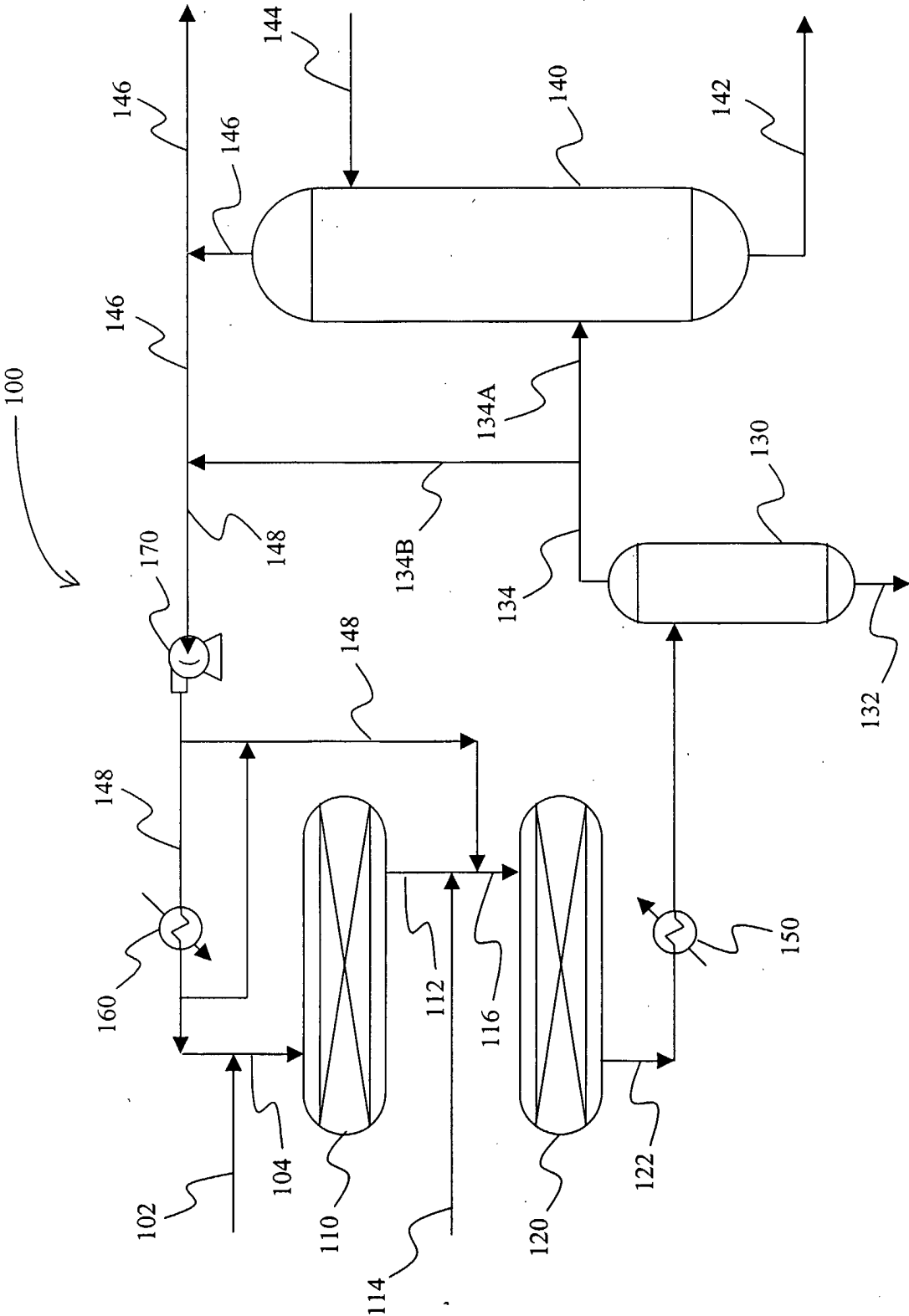


Figure 1

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/12599

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(7) : C01B 17/04; B01D 53/50; B01d 53/52 US CL : 423/573.1, 574.1 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 423/573.1, 574.1 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched sulfur dioxide, first catalytic reactor, second catalytic reactor Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS Search		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,085,199 A (SINGLETON et al.) 18 April 1978 (18.04.1978), Entire Document	1-16
X	US 5,514,351 A (BUCHANAN et al.) 07 May 1996 (07.05.1996) Entire Document	1-2, 6-10, 13-16
X	US 5,352,433 A (WATSON) 04 October 1994 (04.10.1994), Entire Document	1-2, 6-10, 13-16
X	US 4,908,201 A (CABANAW) 13 May 1990 (13.05.1990) Entire Document	1-2, 6-10, 13-16
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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