

METHOD FOR MAKING SULFUR TRIOXIDE, SULFURIC ACID, AND OLEUM FROM SULFUR DIOXIDE

FIELD OF THE INVENTION

This invention relates to a novel process for preparing sulfur trioxide (SO_3) by oxidizing sulfur dioxide (SO_2). This invention also relates to a process for preparing liquid sulfuric acid (H_2SO_4) and/or oleum from SO_3 by the contact process, wherein SO_2 is oxidized to form SO_3 , which, in turn, is contacted with water or a solution of sulfuric acid to produce additional sulfuric acid and/or oleum. This invention further relates to recovering high grade energy from the heat produced during such a contact process.

BACKGROUND OF THE INVENTION

Sulfuric acid is the highest volume chemical manufactured in the world. Much of the sulfuric acid is used to produce phosphoric acid in integrated fertilizer complexes. Sulfuric acid is also used, for example, in dyes and pigments, industrial explosives, etching applications, alkylation catalysis, electroplating baths, and nonferrous metallurgy. Current worldwide production is reported to be about 570,000 tons per day, with about 30% being produced in the United States.

The contact process has been one of the most popular methods for making sulfuric acid and oleum ("oleum" is a solution of SO_3 in sulfuric acid, and also is known as "fuming sulfuric acid" or " $\text{H}_2\text{S}_2\text{O}_7$ "). This process generally comprises 3 steps: (1) forming SO_2 from a sulfur-containing raw material, (2) catalytically oxidizing the SO_2 to form SO_3 and (3) contacting the SO_3 with water or concentrated sulfuric acid to hydrate the SO_3 and form sulfuric acid and/or oleum.

A wide variety of sulfur-containing raw materials have been used in the contact process to form SO_2 . Most sulfuric acid plants, for example, form SO_2 by oxidizing an oxidizable sulfur-containing material (e.g., elemental sulfur or metal ores containing sulfides) in a thermal combustion zone. A significant number of other

plants (e.g., sulfuric acid regeneration plants), in contrast, burn a carbonaceous material (i.e., a fuel) in the presence of a decomposable sulfate to provide the heat necessary to decompose the sulfate into SO_2 and various byproducts.

After being formed, the SO_2 is normally oxidized to SO_3 by contacting it with
5 a catalyst (e.g., a vanadium pentoxide (V_2O_5) catalyst) at a temperature effective for catalytic oxidation of SO_2 (e.g., at least about 410 to about 420°C for a V_2O_5 catalyst) in the presence of molecular oxygen. This reaction is often conducted in a catalytic converter which comprises a plurality of catalyst beds in series (conventionally, 4 or more catalyst beds). One of the difficulties with this reaction stems from the fact that
10 it is a highly exothermic reaction. This requires that the reaction conditions be controlled so that the heat evolved from the oxidation reaction does not overheat the catalyst to a temperature which may lead to thermal damage and premature deactivation of the catalyst and/or adversely affect the reaction equilibrium. The oxidation reaction can be controlled, for example, by limiting the concentration of
15 SO_2 or oxygen fed into the catalytic converter, or by using a converter comprising a tube-in-shell device such as that disclosed by Daley et al. in U.S. Patent No. 4,643,887 wherein the catalyst is cooled by indirect heat exchange with a cooling medium (e.g., air or molten salts). In processes using a V_2O_5 catalyst, for example, the reaction conditions are typically controlled so that the temperature of the catalyst
20 bed(s) is maintained at less than about 650°C, and more typically less than about 630°C.

The formation of sulfuric acid and/or oleum is normally conducted in an absorption zone within an SO_3 absorption tower, in which the conversion gas containing the SO_3 is contacted with water, or, more typically, a concentrated solution
25 of sulfuric acid (e.g., a solution containing about 98.5 weight% sulfuric acid) to form sulfuric acid and/or oleum. Water is normally less preferred because it tends to form an acid mist of H_2SO_4 that is difficult to condense.

While the reaction of SO_3 with the concentrated H_2SO_4 is rapid and virtually complete, the oxidation of SO_2 to SO_3 is typically less complete. Thus, the tail gas
30 leaving the SO_3 absorption tower will typically contain residual SO_2 . In most countries, H_2SO_4 plants are limited by the amount of SO_2 that they are allowed to emit into the atmosphere. The U.S. Environmental Protection Agency, for example,

currently limits SO₂ emissions to 4 pounds per short ton (2 kg per metric ton) of H₂SO₄ produced. This is equivalent to a minimum SO₂ to SO₃ conversion of 99.7% in the catalytic oxidation step (*i.e.*, no greater than 0.3% of the entering SO₂ may exit the system in the SO₃ absorber tail gas).

5 Increasing the concentration of SO₂ in the gas fed to the catalytic converter generally tends to reduce the efficiency of the reaction. This, in turn, leads to more SO₂ remaining in the tail gas discharged from the plant. Consequently, as a sulfuric acid plant operator seeks to increase production by increasing the concentration of SO₂ in the gas fed to the converter, the SO₂ emissions from the plant will tend to
10 increase. As a result, sulfuric acid plants have generally been forced to limit their rate of production or risk non-compliance with environmental regulations.

 In some instances, sulfuric acid plants have been able to increase their production by using tail-gas scrubbers to remove SO₂ before it is emitted to the atmosphere. Tail-gas scrubbers have been particularly useful in conjunction with
15 low-conversion, single-stage SO₃ absorption plants. A number of SO₂ tail-gas scrubbing processes are available, many of which use non-regenerable scrubbing mediums such as ammonia, sodium hydroxide, or hydrogen peroxide. Such techniques, however, have various disadvantages. For example, they require expensive equipment (*e.g.*, a separate scrubbing tower). Such equipment takes up
20 valuable space and produces an additional pressure drop in the overall gas system, which decreases the gas handling capacity of the system. In addition, the scrubbing processes using a base often produce a by-product which must be properly disposed of (*e.g.*, when ammonia is used to scrub the tail gas, a side stream of ammonium sulfate is produced; and when sodium hydroxide is used, a side stream of sodium sulfate is
25 produced). And the use of ammonium salt scrubbing solutions, in particular, typically results in the formation of submicron aerosol fumes which must be removed using sophisticated and expensive mist eliminators.

 Sulfuric acid plants have also controlled SO₂ emissions by using a dual SO₃ absorption process. In such a process, an SO₃ absorption tower containing an
30 intermediate SO₃ absorption zone is positioned between two of the catalyst beds of the converter. For example, in many conventional systems using a 4 bed catalytic converter, gas exiting the second or third catalyst bed is passed through an

intermediate SO_3 absorption zone wherein the gas is contacted with a concentrated solution of H_2SO_4 to form product acid. Gas exiting the intermediate SO_3 absorption zone is returned to the next bed of the converter. Because the oxidation of SO_2 to SO_3 is an equilibrium-controlled reaction, removal of SO_3 in the intermediate absorption zone helps drive the reaction forward in the succeeding beds of the converter to achieve higher conversions and thereby reduce SO_2 emissions in the tail gas exiting the final SO_3 absorption tower. Such a process is disadvantageous, however, because the intermediate absorption zone contributes substantially to the capital and operating costs of the system. In addition, even with the dual absorption, plant capacity may still be limited to assure high conversions and low SO_2 emissions.

In addition to the goal of increasing capacity while controlling SO_2 emissions, another goal related to sulfuric acid contact plants has been to maximize the recovery of useable energy from the heat produced during the exothermic steps of the contact process. Until recently, only from about 55 to about 60% of the heat generated in the contact sulfuric acid process was recovered in useful form. A major improvement in energy recovery, however, was provided by McAlister et al. in U.S. Patent Nos. 5,503,821; 5,118,490; 4,670,242; and 4,576,813. These patents describe processes which can, for example, recover heat of SO_3 absorption in the form of medium pressure steam. In each process, an SO_3 absorption tower is operated at high temperature, and heat is transferred from the absorption acid to produce steam. By maintaining the acid concentration in the range of 99 to 100%, alloy heat exchangers may be used for recovery of the absorption heat. These processes allow the process heat energy recovery capability to be increased to greater than 90%.

SUMMARY OF THE INVENTION

This invention provides for an improved process for making SO_3 which comprises oxidizing SO_2 in a catalytic converter. More particularly, this invention provides for a process for making SO_3 which can be implemented with relatively low capital and operating costs; a process for making SO_3 which allows for a minimal volume of gas to be handled upstream of the catalytic converter, thus allowing for smaller equipment (*i.e.*, equipment having lower capital and operating costs) to be used upstream of the converter; a process for making SO_3 from an SO_2 source gas that



has a relatively low SO_2 gas strength; a process for making SO_3 wherein the catalytic converter can be operated without the use of an extraneous energy source to bring the SO_2 converter feed gas to the activation temperature of the SO_2 oxidation catalyst (*i.e.*, a process wherein the catalytic converter operates "autothermally"); a process for making SO_3 wherein the catalytic converter may be operated autothermally even when a weak source gas (*e.g.*, a source gas having an SO_2 concentration of less than about 5 mole%) is used; a process for making SO_3 from spent sulfuric acid; a process for making SO_3 from sulfidic metal oxidation off gases; and a process for the production of sulfuric acid and/or oleum wherein the recovery of heat energy is enhanced.

10 Briefly, therefore, the present invention is directed to a process for making SO_3 from a source gas comprising SO_2 . In one embodiment, the process comprises contacting the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent. Sulfur dioxide is then
15 stripped from the SO_2 -enriched solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas having an SO_2 gas strength greater than the SO_2 gas strength of the source gas. A reaction gas comprising a first portion of the SO_2 -enriched stripper gas is then formed. An oxidation product gas (comprising SO_3 and residual SO_2), in turn, is formed by a
20 process comprising passing the reaction gas through a plurality of catalyst beds in series (this plurality comprises at least 2 and no greater than 4 catalyst beds which contain a catalyst effective for oxidizing SO_2 into SO_3). In this embodiment, a second portion of the SO_2 -enriched gas is introduced into at least one catalyst bed downstream of the most upstream catalyst bed to increase the amount of SO_2 being
25 fed into the downstream bed.

In another embodiment for making SO_3 from a source gas comprising SO_2 , the process comprises contacting the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent. Sulfur
30 dioxide is then stripped from the SO_2 -enriched solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas having an SO_2 gas strength greater than the SO_2 gas strength of the source gas. A reaction gas is

then formed which comprises a first portion of the SO_2 -enriched stripper gas (this first portion comprises at least about 30% of the SO_2 in the SO_2 -enriched stripper gas).

Afterward, an oxidation product gas (comprising SO_3 and residual SO_2) is formed by a process comprising passing the reaction gas through a plurality of catalyst beds in series (this plurality comprises at least 2 catalyst beds which contain a catalyst effective for oxidizing SO_2 into SO_3). In this embodiment, a second portion of the SO_2 -enriched gas is introduced into at least one catalyst bed downstream of the most upstream catalyst bed to increase the amount of SO_2 being fed into the downstream bed.

10 In another embodiment for making SO_3 from a source gas comprising SO_2 , the process comprises contacting the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent. Sulfur dioxide is then stripped from the SO_2 -enriched solvent in an SO_2 stripping zone to
15 form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas having an SO_2 gas strength greater than the SO_2 gas strength of the source gas. A reaction gas is then formed which comprises a first portion of the SO_2 -enriched stripper gas. Afterward, an oxidation product gas (comprising SO_3 and residual SO_2) is formed by a process comprising passing the reaction gas through a plurality of catalyst beds in
20 series (this plurality comprises at least two catalyst beds which comprise a catalyst effective for oxidizing SO_2 into SO_3). In this embodiment, a second portion of the SO_2 -enriched gas is introduced into at least one catalyst bed downstream of the most upstream catalyst bed to increase the amount of SO_2 being fed into the downstream bed. In addition, the molar ratio of O_2 to SO_2 is greater than about 0.2:1 in the gas
25 entering each of the catalyst beds in the plurality.

In another embodiment for making SO_3 from a source gas comprising SO_2 , the process comprises contacting the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent. Sulfur
30 dioxide is then stripped from the SO_2 -enriched solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas. A converter feed gas is formed which comprises a first portion of the SO_2 -enriched

stripper gas. This converter feed gas is divided into a first portion and a second portion. A first partial conversion gas and a second partial conversion gas (both comprising SO_3 and residual SO_2) are then formed by passing the first portion of the converter feed gas through a catalyst bed, and passing the second portion through a different catalyst bed in parallel with the catalyst bed through which the first portion of the converter feed gas is passed (both catalyst beds comprise an oxidation catalyst effective for oxidizing SO_2 to SO_3). A first portion of the remainder of the SO_2 -enriched stripper gas is then combined with the first partial conversion gas to fortify the SO_2 gas strength of the first partial conversion gas. Likewise, a second portion of the remainder of the SO_2 -enriched stripper gas is combined with the second partial conversion gas to fortify the SO_2 gas strength of the second partial conversion gas. The fortified first partial conversion gas and the fortified second partial conversion gas are then passed through at least one further catalyst bed (also comprising an oxidation catalyst effective for oxidizing SO_2 to SO_3), thereby oxidizing additional SO_2 to SO_3 and forming a conversion gas comprising SO_3 and SO_2 .

This invention also provides for an improved process for making sulfuric acid and/or oleum. More particularly, this invention provides for a process for making sulfuric acid and/or oleum which meets SO_2 emissions standards; a process for making sulfuric acid and/or oleum having greater SO_2 oxidation capacity than typical conventional sulfuric acid plants without having greater SO_2 emissions; a process for making sulfuric acid and/or oleum in which SO_2 emissions are confined to a single purge stream for simple control and monitoring; a process for making sulfuric acid and/or oleum which achieves at least about 99.7% recovery of SO_2 , even at low single pass SO_2 conversions (*e.g.*, SO_2 single-pass conversions of as low as about 75% or lower); a process for making sulfuric acid and/or oleum which can be implemented with relatively low capital and operating costs; a process for making sulfuric acid and/or oleum which allows for a lesser volume of gas to be handled upstream of the catalytic converter than typical conventional sulfuric acid contact plants, thus allowing for smaller equipment to be used upstream of the converter; a process for making sulfuric acid and/or oleum which achieves low SO_2 emissions without requiring the installation of separate SO_2 non-regenerable tail gas scrubbing treatments and/or an SO_3 intermediate absorption zone (*i.e.*, low emissions may be

achieved using a single SO_3 absorber); a process for making sulfuric acid and/or oleum from an SO_2 source stream that has an $\text{H}_2\text{O}/\text{SO}_2$ molar ratio greater than the desired $\text{H}_2\text{O}/\text{SO}_3$ molar ratio in the product acid stream; a process for making sulfuric acid and/or oleum from an SO_2 source gas that has a relatively low SO_2 gas strength; a process for making sulfuric acid and/or oleum wherein the catalytic converter operates autothermally; a process for making sulfuric acid and/or oleum wherein the catalytic converter can be operated autothermally even when a weak source gas is used; a process for making sulfuric acid and/or oleum from spent sulfuric acid; a process for making sulfuric acid and/or oleum from sulfidic metal oxidation off gases; a process for making sulfuric acid and/or oleum in which process energy is recovered in high grade form; a process for making sulfuric acid and/or oleum from a wet source gas; a process for making sulfuric acid and/or oleum from a wet source gas without first requiring the source gas to be passed through a drying tower; and a process for making sulfuric acid and/or oleum from a wet source gas in which heat generated by vapor phase formation of sulfuric acid (*i.e.*, sulfuric acid formation from water vapor in the source gas reacting with SO_3 in the conversion gas) is recovered.

Briefly, therefore, the present invention is directed to a process for making sulfuric acid and/or oleum from a source gas comprising SO_2 . In one embodiment, the process comprises contacting at least a portion of the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the portion of the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent. Sulfur dioxide is then stripped from the SO_2 -enriched solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas having an SO_2 gas strength greater than the SO_2 gas strength of the source gas. An oxidation product gas (comprising SO_3 and residual SO_2) is then formed by a process comprising passing the SO_2 -enriched stripper gas through a plurality of catalyst beds in series (each comprising an oxidation catalyst effective for oxidizing SO_2 to SO_3). The oxidation product gas, in turn, is combined with water vapor to form an acid product gas comprising: (a) sulfuric acid formed by a gas phase reaction between SO_3 from the oxidation product gas and water vapor, thereby generating the heat of formation of sulfuric acid in the gas phase; (b) SO_3 ; and (c) SO_2 . Heat energy from the gas phase heat of formation of sulfuric acid is recovered

by transfer of heat from the acid product gas to steam or feed water in an indirect heat exchanger. The cooled acid product gas is then contacted with liquid sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or oleum and an SO_3 -depleted gas comprising SO_2 .

- 5 In another embodiment for making sulfuric acid and/or oleum from a source gas comprising SO_2 , the process comprises forming an oxidation product gas (comprising SO_3 and residual SO_2) by a process comprising passing a first portion of the source gas through a plurality of catalyst beds in series (this plurality comprises at least 2 catalyst beds which contain a catalyst effective for oxidizing SO_2 into SO_3).
- 10 Here, a second portion of the source gas is introduced into at least one catalyst bed downstream of the most upstream catalyst bed to increase the amount of SO_2 being fed into the downstream bed. The oxidation product gas, in turn, is combined with water vapor to form an acid product gas comprising: (a) sulfuric acid formed by a gas phase reaction between SO_3 from the oxidation product gas and water vapor, thereby
- 15 generating the heat of formation of sulfuric acid in the gas phase; (b) SO_3 ; and (c) SO_2 . Heat energy from the gas phase heat of formation of sulfuric acid is recovered by transfer of heat from the acid product gas to steam or feed water in an indirect heat exchanger. The cooled acid product gas is then contacted with liquid sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or oleum and an SO_3 -
- 20 depleted gas comprising SO_2 .

- Another embodiment of this invention is directed to an improved process for making sulfuric acid and/or oleum from a source gas comprising SO_2 and water vapor. This process comprises forming a reaction gas comprising SO_2 , and then forming an oxidation product gas (comprising SO_3 and residual SO_2) by a process comprising
- 25 passing the reaction gas through a plurality of catalyst beds in series (each catalyst bed comprises an oxidation catalyst effective for oxidizing SO_2 into SO_3). The oxidation product gas, in turn, is combined with water vapor to form an acid product gas comprising: (a) sulfuric acid formed by a gas phase reaction between SO_3 from the oxidation product gas and water vapor, thereby generating the heat of formation of
- 30 sulfuric acid in the gas phase; (b) SO_3 ; and (c) SO_2 . Heat energy is recovered from the gas phase heat of formation of sulfuric acid by transferring heat from the acid product gas to steam or feed water in an indirect heat exchanger. Afterward, the cooled acid

product gas is contacted with a solution comprising sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or oleum and an SO_3 -depleted gas comprising SO_2 . The improvement in this process comprises combining at least a portion of the source gas with the oxidation product gas to form the acid product gas, and forming the reaction gas from the SO_3 -depleted gas.

Other objects and features of this invention will be in part apparent and in part pointed out hereinafter.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a schematic flow sheet illustrating various features of one embodiment of the process of the present invention.

Fig. 2 is a schematic flow sheet showing a 4 bed catalytic converter of a contact sulfuric acid plant modified in accordance with the present invention.

Fig. 3 is a schematic flow sheet illustrating various features of another embodiment of the process of the present invention for use with a wet SO_2 source gas.

Fig. 4 is a schematic flow sheet illustrating an embodiment of the process of the present invention described in the Example below.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A. Formation of the Source Gas Containing Sulfur Dioxide

Referring to **Fig. 1**, a source gas 3 containing SO_2 is formed from a sulfur-containing raw material 6. A wide variety of sulfur-containing raw materials may be used. For example, a decomposable sulfate is often suitable. Such a sulfate may include, for example, calcium sulfate, ammonium sulfate, or spent H_2SO_4 (*i.e.*, contaminated or diluted H_2SO_4). To form SO_2 , the sulfate is typically injected as a liquid spray into a combustion zone 9, along with a carbonaceous material (*i.e.*, a fuel) and an oxygen source 12 (normally air). This mixture is then burned to provide the heat necessary to evaporate water and decompose the sulfate. For example, in a spent acid recovery plant where spent H_2SO_4 is used as the raw material 6, a gas 3 is formed which typically contains sulfurous acid (H_2SO_3), SO_2 , O_2 , CO_2 , N_2 , and water vapor.

In a particularly preferred embodiment, the sulfur containing raw material 6 is an oxidizable material, such as elemental sulfur, hydrogen sulfide (H_2S), or iron pyrite

(FeS₂) or another sulfide-containing metal ore. In this embodiment, the sulfur-containing material 6 is typically burned with an oxygen source 12 in a kiln or other suitable thermal combustion zone 9 to produce a source gas 3 containing SO₂. The most economically practical oxygen source 12 is normally air, which, when
5 burned with the oxidizable sulfur material 6, produces a source gas 3 containing SO₂, O₂, and N₂ (and water vapor if, for example, the air and/or the raw sulfur material contains water, or the sulfur-containing raw material is H₂S).

It should be recognized that the process of this invention may be practiced with a wide range of SO₂ concentration in the source gas 3 (*i.e.*, the source gas 3 may
10 contain from about 0.1 to about 100 mole% SO₂). In some embodiments, for example, the process is used in conjunction with other manufacturing processes which either need to reduce or eliminate the sulfur content in a particular material, or need to reduce or eliminate a sulfur-containing material in a waste stream. As suggested above, this process provides, for example, a practical way to utilize the SO₂ which is
15 produced as an off-gas when a metal ore is roasted or smelted during a metal recovery operation. This process also, for example, provides a practical way to utilize spent H₂SO₄. In most of these SO₂ salvage processes, the SO₂ concentration in the source gas 3 is typically less than about 11 mole%, and more typically from about 0.1 to about 5 mole%.

20 Because there are greater operational and capital costs associated with larger process equipment, it is often preferable to minimize the volume of the SO₂ source gas 3, while also increasing the concentration of SO₂ in the source gas 3. In a particularly preferred embodiment, this is achieved by using elemental sulfur as the raw material 6. When elemental sulfur is burned in air, for example, SO₂
25 concentrations of from about 11 to about 21 mole% (and more typically, from about 15 to about 20 mole%) may be obtained.

Regardless of the content of the oxygen source 12, it is also preferable to minimize the volume of the source gas 3 by burning the elemental sulfur in the least amount of O₂ necessary to allow substantially complete conversion of the elemental
30 sulfur. In other words, the amount of the oxygen source 12 fed into the combustion zone 9 of the sulfur burner preferably is the amount necessary to maintain the molar ratio of O₂ to elemental sulfur at slightly greater than about 1.0, more preferably from

about 1.05 to about 1.3, and most preferably about 1.05 to about 1.1. In most embodiments, it is preferred for the O₂ concentration in the source gas 3 to be from about 0.5 to about 5 mole%, more preferably from about 0.5 to about 3 mole%, and most preferably from about 0.5 to about 2 mole%.

5 **B. Sulfur Dioxide Gas Strengthening**

The SO₂-containing source gas 3 is preferably introduced into an SO₂ absorption/stripping zone to remove and recover SO₂ in the form of an SO₂-enriched gas (*i.e.*, a gas having an increased SO₂ content relative to the source gas 3).

10 If the source gas 3 is at an elevated temperature (*i.e.*, greater than about 50°C) and/or contains entrained particulate impurities, it is generally preferred to first condition the source gas 3 to cool the gas 3 and remove particulates from the gas 3 before introducing it into the SO₂ absorption/desorption zone. There are a variety of well-known techniques which may be used to condition the source gas 3. For example, if the source gas 3 is a combustion gas exiting a sulfur burner, its
15 temperature is typically from about 900 to about 1600°C, and more typically from about 1050 to about 1600°C. This gas 3 may, for example, be cooled by: (a) passing the gas 3 through an indirect heat exchanger where heat from the gas 3 is used, for example, to preheat the oxygen source 12 (*e.g.*, air) being used in the combustion chamber 9, thereby reducing fuel costs in heating the oxygen source 12 with an
20 external source; (b) by passing the gas 3 through a waste heat boiler where it is cooled by generation of high pressure steam (*i.e.*, steam having a pressure of at least about 27 bar (gauge)); and/or (c) passing the gas 3 through a humidifying tower and one or more indirect heat exchangers, where it is further cooled with, for example, cooling tower water. Particularly where the source gas 3 is formed from spent sulfuric acid or
25 is the off-gas from a metal roasting or smelting operation, an electrostatic precipitator is often used to remove particulates from the gas after it is cooled. Alternatively, such a gas 3 may be conditioned by passing the gas 3 through one or more reverse jet scrubbers of the type, for example, sold by Monsanto Enviro-Chem Systems, Inc. (St. Louis, MO, USA) under the trademark "DYNAWAVE". It should be noted that a
30 portion (*e.g.*, 5-10%) of the conditioned source gas 3 may be recycled back to the

combustion zone 9 (particularly a sulfur burner) to control the temperature in the combustion zone 9 below a desired maximum temperature.

Preferably, in the first step of the SO₂ absorption/desorption process, the SO₂-containing source gas 3 is contacted with a liquid SO₂ absorption solvent 15 in an SO₂ absorption zone 18. The liquid SO₂ absorption solvent 15 selectively absorbs SO₂ from the source gas 3, thereby transferring SO₂ from the source gas 3 to the SO₂ absorption solvent 15 and producing an SO₂-depleted exhaust stripper gas 21 (from which the SO₂ has been substantially removed) and an SO₂-enriched absorption solvent 24. The SO₂-enriched absorption solvent 24, in turn, is stripped of SO₂ in an SO₂ stripper zone 27 to yield an SO₂-enriched stripper gas 30 and an SO₂-depleted solvent 33 (which preferably is subsequently recycled back to the SO₂ absorption zone 18 for further selective absorption of SO₂ from the source gas 3).

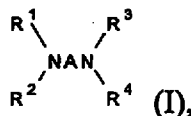
The liquid SO₂ absorption solvent 15 may be either a physical or a chemical solvent. Physical solvents, however, are generally more preferred. Suitable absorbents include various organic absorbents (e.g., tetraethylene glycol dimethyl ether), and aqueous solutions of alkali metals (e.g., a sodium sulfite/bisulfite solution).

An example of a suitable physical sulfur dioxide absorption solvent is one comprising tetra ethylene glycol diethyl ether such as that disclosed and utilized in the sulfur dioxide recovery processes described in U.S. Patent No. 4,659,553 (Line) and U.S. Patent No. 4,795,553 (Hensel et al.), the entire disclosures of which are incorporated herein by reference. The liquid sulfur dioxide absorbent preferably contains more than 50% by weight tetra ethylene glycol diethyl ether. Such a liquid sulfur dioxide absorbent suitably comprises, on a dry weight basis, from about 60% to about 80% tetra ethylene glycol diethyl ether, from about 15% to about 25% triethylene glycol diethyl ether, from about 2.5% to about 7.5% pentaethylene glycol diethyl ether and from about 2.5% to about 7.5% mono ethers. The circulating tetra ethylene glycol diethyl ether-containing absorbent may contain water, for example, up to about 10% by weight. Use of sulfur dioxide absorbents based on tetra ethylene glycol diethyl ether in the absorption and stripping stages of a sulfur dioxide recovery system, including the process equipment and operating conditions employed, is described in U.S. Patent Nos. 4,659,553 (Line) and U.S. Patent No. 4,795,553 (Hensel

et al.) and may be applied by one skilled in the art in the practice of the present invention.

Another example of suitable SO₂ absorption solvents include aqueous solutions of various amines. Exemplary amine absorbing agents include, for example, aniline derivatives (e.g., dimethylaniline), alkanolamines (e.g., diethanolamine, triethanolamine, tripropanolamine, and tributanolamine), tetrahydroxyethylalkylenediamines (e.g., tetrahydroxymethylenediamine, tetrahydroxyethylethylenediamine, tetrahydroxyethyl-1,3-propylenediamine, tetrahydroxyethyl-1,2-propylenediamine, tetrahydroxyethyl-1,5-pentylpentylenediamine), and heterocyclic diamines (e.g., piperazine; dimethylpiperazine; N,N'-bis(2-hydroxyethyl)piperazine; -methylpyrrolidone; and sulfonate as disclosed in U.S. Patent No. 3,764,665, Groenendaal et al. the entire disclosure which is herein incorporated by reference).

An even more preferred traditionally used absorbing agent is a half salt of a diamine having the following formula (I):



wherein A is alkylene having 2 or 3 carbon atoms; R¹, R², R³, and R⁴ may be the same or different, and can be hydrogen, alkyl (preferably having from 1 to about 8 carbon atoms, and including cycloalkyls), hydroxyalkyl (preferably having from 2 to about 8 carbon atoms), aralkyl (preferably having from about 7 to about 20 carbon atoms), aryl (preferably monocyclic or bicyclic), or alkylaryl (preferably having from about 7 to about 20 carbon atoms). It should be noted that any of R¹, R², R³, and R⁴ may together form cyclic structures. The free nitrogen of the half salt preferably has a pK_a of from about 4.5 to about 7.3. Examples of particularly preferred diamines include the sulfite half salts of N,N',N'-(trimethyl)-N(2-hydroxyethyl)ethylenediamine; N,N,N',N'-tetramethylethylenediamine; N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine; N-(2-hydroxyethyl)ethylenediamine; N,N'-dimethylpiperazine; N,N,N',N'-tetrakis(2-hydroxyethyl)-1,3-diaminopropane; and N,N'-dimethyl-N,N-bis(2-hydroxyethyl)ethylenediamine. These half-salt diamine

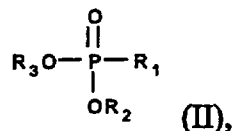
absorbents are described by Hakka in U.S. Patent No. 5,019,361 (incorporated herein by reference).

In the embodiments using an aqueous solution comprising an amine or an amine salt, the absorption solvent 15 preferably comprises an aqueous solution
5 containing from about 20 to about 40 weight% of the absorbing agent on an amine (rather than an amine salt) basis. The SO₂-enriched absorption solvent 24, in turn, preferably has an SO₂/amine-absorbing-agent weight ratio of from about 0.1:1 to about 0.25:1.

The above-listed traditional SO₂ absorbents are often hampered by one or
10 more shortcomings. These shortcomings include, for example, relatively low SO₂ absorption capacity and the tendency to absorb substantial quantities of water vapor from the source gas 3. Absorption of substantial quantities of water, in turn, can lead to a significant reduction in the SO₂ absorption capacity of the SO₂ absorption solvent 15, thereby requiring a greater flow of the SO₂ absorption solvent 15. Such water
15 absorption can also lead to excessive corrosion of the equipment used in the SO₂ absorption/stripping process. Further, such absorption requires energy and capital input for the water to be separated from the SO₂-depleted solvent 33 so that the solvent 33 may be recycled back to the SO₂ absorption zone 18 and used for further SO₂ absorption.

20 In a particularly preferred embodiment, the SO₂ absorption solvent 15 comprises an organic phosphorous compound, as described in U.S. Patent No. 5,851,265 (Burmaster et al.) which the entire disclosure is herein incorporated by reference). In this embodiment, the SO₂ absorption solvent 15 preferably comprises a phosphate triester, phosphonate diester, phosphinate monoester, or a mixture thereof.
25 The substituents bonded to the phosphorous atom, as well as the organic radicals of the ester functionality, in the compounds are preferably independently aryl or C₁ to C₈ alkyl (*i.e.*, an alkyl group containing from 1 to 8 carbon atoms). Examples of suitable phosphate triesters include: tributyl phosphate, tripentyl phosphate, trihexyl phosphate, and triphenyl phosphate. Examples of suitable phosphinate monoesters
30 include: butyl dibutyl phosphinate, pentyl dipentyl phosphinate, hexyl dihexyl phosphinate, and phenyl diphenyl phosphinate.

In accordance with an even more preferred embodiment of the present invention, the SO₂ absorption solvent 15 comprises at least one substantially water-immiscible organic phosphonate diester having formula (II)



5 wherein R¹, R², and R³ are independently aryl or C₁ to C₈ alkyl, with R¹, R², and R³ being selected such that (1) the organic phosphonate diester has a vapor pressure of less than about 1 Pa at 25° C, and (2) the solubility of water in the organic phosphonate diester is less than about 10 weight% at 25° C. Preferably, the organic phosphonate is a dialkyl alkyl phosphonate, and R¹, R², and R³ are independently C₁ to C₆ alkyl. More preferably, to simplify preparation and reduce the manufacturing costs of the phosphonate deter solvent, R¹, R², and R³ are identical, with each containing at least 4 carbon atoms. Examples of suitable organic phosphonate deter for use in the practice of the present invention include dibutyl butyl phosphonate, dipentyl pentyl phosphonate, dihexyl hexyl phosphonate and diphenyl phenyl phosphonate. In accordance with an especially preferred embodiment of the present invention, the SO₂ absorption solvent 15 comprises dibutyl butyl phosphonate. Dibutyl butyl phosphonate is a neutral diester of phosphonic acid, and is a clear, colorless liquid with a relatively low viscosity and very mild odor. Dibutyl butyl phosphonate has a molecular weight of 250.3 and a vapor pressure of about 0.1 Pa at 25° C. The solubility of water in dibutyl butyl phosphonate is about 5.5 weight% at 25° C.

An SO₂ absorption solvent comprising at least one organic phosphonate diester as defined above tends to be more preferred because such a solvent typically possesses a combination of characteristics which renders it particularly useful in an SO₂ absorption/desorption process, including: (1) increased SO₂ solubility, especially at low partial pressures of SO₂ in the source gas 3; (2) high heats of solution, which reduce the amount of energy required for stripping SO₂ from the SO₂-enriched absorption solvent 24; (3) low melting points, so that the solvent 15 will remain a liquid over a wide range of process temperatures; (4) low viscosity, which allows the

size of both thermal and absorption/stripping equipment to be reduced; (5) low vapor pressure, which reduces solvent 15 losses; (6) decreased tendency to react with water and undergo hydrolysis; and (7) being substantially water immiscible (*i.e.*, non-hygroscopic) such that the solubility of water in the solvent 15 is decreased. The fact that the organic phosphonate diesters are substantially water immiscible is particularly advantageous in the practice of the present invention. This characteristic provides an SO_2 absorption solvent 15 which does not absorb excessive amounts of water from the SO_2 -containing source gas 3.

The SO_2 absorption zone 18 preferably comprises a means for promoting mass transfer between the gas and liquid phases, and more preferably comprises a bed of random packings such as saddles or rings in a vertical tower. Preferably, the source gas 3 is contacted countercurrently with the SO_2 absorption solvent 15. In such an embodiment, the source gas 3 is preferably introduced through an inlet near the bottom of the SO_2 absorption zone 18, and the SO_2 absorption solvent 15 is introduced through an inlet near the top of the SO_2 absorption zone 18 and distributed over the packing. The SO_2 -enriched absorption solvent 24 is then withdrawn from an outlet near the bottom of the SO_2 absorption zone 18, and the exhaust gas substantially free of SO_2 (*i.e.*, the SO_2 -depleted gas 21) is removed from an outlet near the top of the SO_2 absorption zone 18. Although the SO_2 absorption zone 18 may comprise a conventional, randomly packed tower, those skilled in the art will appreciate that other configurations may be suitably used as well. For example, the tower may contain structured packing or comprise a tray tower, in either of which the process streams preferably flow countercurrently.

When the above-described solvents comprising an organic phosphorus compound are used, the SO_2 absorption zone 18 preferably is operated at an average temperature of from about 10 to about 60°C (more preferably from about 10 to about 50°C, and most preferably from about 30 to about 40°C), and a pressure of from about 50 to about 150 kPa (absolute). It should be recognized that although pressure increases the amount of SO_2 that the SO_2 absorption solvent 15 can absorb, the absorption can alternatively be carried out at a relatively low pressure, thereby reducing equipment costs.

Condensation of water vapor from the source gas 3 in the SO₂ absorption zone 18 may lead to formation of a separate water phase, which could increase the corrosion rate of metallic process equipment and complicate later removal of the absorbed SO₂ in the subsequent solvent regeneration step. To avoid such
5 condensation, the temperature of the solvent 15 introduced into the absorption zone 18 preferably is above the dew point temperature of the source gas 3 fed into the absorption zone 18.

The mass flow rate ratio (L/G) of the SO₂ absorption solvent 15 and the source gas 3 necessary to achieve substantial transfer of SO₂ from the source gas 3 to the SO₂
10 absorption solvent 15 in the absorption zone 18 may be determined by conventional design practice. Preferably, the SO₂ absorption zone 18 is designed and operated such that the SO₂ content of the SO₂-depleted gas 21 is less than about 400 ppmv, more preferably less than about 200 ppmv, and most preferably less than about 150 ppmv. This trace amount of SO₂, along with most of the O₂, inert gases (e.g., N₂), and water
15 vapor contained in the source gas 3, are eliminated from the system as part of the SO₂-depleted gas 21 vented from the top of the SO₂ absorption zone 18. If necessary to achieve satisfactory emission standards, the SO₂-depleted gas 21 may be passed through a mist eliminator for recovery of entrained liquid before being discharged through a stack.

20 Use of the highly efficient organic phosphorous solvents discussed above allows the concentration of the SO₂ in the SO₂-enriched stripper gas 30 exiting the stripper zone 27 to be significantly greater than the concentration of the SO₂ in the source gas 3 fed to the system. For example, for source gases containing from about 0.1 to about 5 percent by volume SO₂, the process of the present invention may be
25 operated such that the ratio of the SO₂ molar concentration in the in the SO₂-enriched stripper gas 30 to the SO₂ molar concentration in the source gas 3 is greater than about 1.1:1, preferably at least about 2.75:1, more preferably at least about 4:1, even more preferably at least about 7:1, and most preferably at least about 10:1. It should be recognized that even greater ratios may often be achieved, depending on the SO₂
30 concentration of the source gas 3. Generally, it is preferred that at least 67 mole% (more preferably at least about 75 mole%, still more preferably at least about 85

mole%, and most preferably at least about 90 mole%) of the SO₂-enriched stripper gas 30 consist of SO₂.

Various methods for stripping SO₂ from the SO₂-enriched absorption solvent 24 may be used. For example, SO₂ may be stripped by contacting the SO₂-enriched absorption solvent 24 with a non-condensable, oxygen-containing stripping gas 36 such that SO₂ is transferred from the SO₂-enriched absorption solvent 24 to the stripping gas 36 to produce the SO₂-enriched stripper gas 30 and the SO₂-depleted absorption solvent 33. Preferably, the non-condensable, oxygen-containing stripping gas 36 comprises air. It should be recognized that one of the advantages provided by the above-described solvents comprising organic phosphorous compounds (and especially solvents comprising phosphonate diesters) is their inherent flame retarding property and resistance to oxidation. Thus, unlike some organic solvents used in conventional SO₂ absorption/desorption cycles (e.g., tetraethylene glycol dimethyl ether), the organic solvents utilized in the present invention can be readily stripped of SO₂ using an oxygen-containing stripping gas with minimal risk of solvent degradation or explosion.

The SO₂ stripper zone 27 preferably comprises a means for promoting mass transfer between the gas and liquid phases. Like the SO₂ absorption zone 18, the SO₂ stripper zone 27 preferably comprises a bed of conventional random packing in a vertical tower. To maximize transfer of SO₂, the SO₂-enriched absorption solvent 24 is preferably contacted countercurrently with the SO₂ stripping gas 36. In this embodiment, a non-condensable, oxygen-containing SO₂ stripping gas 36 preferably is introduced through an inlet near the bottom of the SO₂ stripper zone 27, and the SO₂-enriched absorption solvent 24 is introduced through a liquid inlet near the top of the SO₂ stripper zone 27 and distributed over the packing material. The SO₂-depleted absorption solvent 33 is then preferably withdrawn from an outlet near the bottom of the SO₂ stripper zone 27, and the SO₂-enriched stripper gas 30 is removed from an outlet near the top of the SO₂ stripper zone 27. In a particularly preferred embodiment, the SO₂-depleted absorption solvent 33 is recycled back to the solvent inlet near the top of the SO₂ absorption zone 18, thereby serving as the SO₂ absorption solvent 15 for further absorption of SO₂ from the source gas 3. Although a conventional packed tower is typically preferred, those skilled in the art will

appreciate that the SO₂ stripper zone 27, like the SO₂ absorption zone 18, may have other suitable configurations, including structured packing or a tray tower.

The mass flow rate ratio (L/G) of the SO₂-enriched absorption solvent 24 to the stripping gas 36 necessary to achieve substantial transfer of SO₂ from the SO₂-enriched absorption solvent 24 to the stripper gas 36 may be determined by conventional design practice. Preferably, essentially all (*i.e.*, at least about 90%, and more preferably at least about 95%) of the SO₂ contained in the SO₂-enriched absorption solvent 24 is transferred to the stripper gas 36.

The SO₂-enriched stripper gas 30 exiting the top of the SO₂ stripper zone 27 is preferably passed to an overhead condenser, and a portion of any water vapor contained in the SO₂-enriched stripper gas 30 is condensed by transfer of heat in the SO₂-enriched stripper gas 30 to cooling water. This condensate and the remainder of the SO₂-enriched stripper gas 30 are then preferably transferred to liquid/gas phase separator. In this instance, the cooled SO₂-enriched stripper gas 30 exits the separator and a liquid stream comprising the condensate is refluxed and introduced into an upper section of the tower containing the SO₂ stripper zone 27 over a second bed of packing material. Solvent that may have been vaporized in the SO₂ stripper zone 27 may also be condensed in the overhead condenser and form part of the refluxed condensate. However, to avoid formation of two liquid phases in the separator, it is preferred to operate the condenser such that the condensate refluxed to the stripper consists essentially of water vapor condensed from the SO₂-enriched stripper gas 30.

Alternatively, the SO₂-enriched absorption solvent 24 can be stripped by steam distillation (*i.e.*, contacting the SO₂-enriched absorption solvent 24 with live steam introduced into the bottom of the SO₂ stripper zone 27) to recover the SO₂ from the SO₂-enriched absorption solvent 24. Regardless of how the SO₂ stripping/solvent regeneration step is conducted, the SO₂ preferably is stripped from the SO₂-enriched absorption solvent 24 under non-reducing conditions.

To promote desorption of SO₂ and avoid thermal degradation of the SO₂ absorption solvent 15, the SO₂ stripper zone 27 preferably is operated at an average temperature of from about 80 to about 120°C, and more preferably from about 90 to about 110°C. When air stripping is employed, the preferred operating pressure in the SO₂ stripper zone 27 is from about 20 to about 150 kPa (absolute).

Temperature control within the SO₂ absorption zone 18 and SO₂ stripper zone 27 may be achieved by controlling the temperature of the various process streams fed to these apparatus. Preferably, the temperature in the SO₂ stripper zone 27 is maintained within the desired range by controlling only the temperature of the SO₂-enriched absorption solvent 24, while air is introduced at from about 20 to about 120°C as the non-condensable, oxygen-containing stripping gas 36. As noted above, the SO₂-enriched absorption solvent 24 exiting the SO₂ absorption zone 18 preferably is at a temperature of from about 10 to about 60°C, more preferably from about 10 to about 50°C, and most preferably from about 30 to about 40°C. This SO₂-enriched absorption solvent 24 is preferably passed through a solvent heat interchanger 39 where it is preheated by indirect transfer of heat from the SO₂-depleted solvent 33 being recycled from the SO₂ stripper zone 27 to the SO₂ absorption zone 18 (this, in turn, cools the SO₂-depleted solvent 33 exiting the SO₂ stripper zone 27, which is typically at a temperature from about 80 to about 120°C). If further heating is required to achieve the desired temperature in the SO₂ stripper zone 27, the preheated SO₂-enriched absorption solvent 24 leaving the interchanger 39 may be passed through a solvent heater, where it is further heated by indirect heat exchange with steam. If further cooling of the SO₂-depleted solvent 33 is required to maintain the desired temperature in the SO₂ absorption zone 18, the SO₂-depleted solvent 33 leaving the interchanger 39 may be passed through a solvent cooler where it is further cooled by indirect heat exchange with cooling tower water. It should be recognized that the use of a solvent interchanger 39 reduces the energy demands of the solvent heater, and reduces the cooling water required in the solvent cooler.

During the course of operation, inorganic salts and strong acids may accumulate in the solvent circulated between the SO₂ absorption zone 18 and the SO₂ stripper zone 27. When this occurs, a purge stream may be periodically or continuously removed from the SO₂-depleted solvent 33 and directed to a solvent purification vessel. An aqueous wash stream, such as water or a mildly alkaline aqueous solution (*e.g.*, a sodium bicarbonate solution), is also introduced into the purification vessel and contacted with the purge stream. The resulting two-phase mixture is then decanted to separate the aqueous phase containing the inorganic salt contaminants from the organic phase comprising SO₂-depleted solvent 33 having a

reduced contaminant concentration. A waste stream comprising the aqueous waste is discharged from the purification vessel, while a liquid stream comprising the purified SO₂ absorption solvent is returned to the remaining SO₂-depleted solvent 33 routed back to the SO₂ absorption zone 18. The quantity of solvent 33 treated in this manner preferably is sufficient to maintain the contaminant concentration in the circulating solvent 33 at a level low enough to provide low process equipment corrosion rates and not materially compromise SO₂ absorption efficiency. It should be understood that the washing of the SO₂-depleted solvent 33 may be carried out in a batch or a continuous fashion. If the SO₂-depleted solvent 33 is washed continuously, a suitable liquid-liquid phase separator (e.g., a centrifugal contactor) may be used to separate the aqueous waste and purified organic phases.

It should be recognized that the SO₂ absorption/stripping zones are particularly useful when the source gas 3 has a relatively weak SO₂ concentration (*i.e.*, from about 0.1 to about 11 mole%, and even more so at from about 0.1 to about 5 mole%) because they can be used to remove the inert gases (most notably, N₂) from the source gas 3 and thereby significantly increase the SO₂ concentration. One advantage of having a greater SO₂ concentration is that it allows for a smaller volume of gas to be handled during the process, thereby permitting the use of smaller equipment (which has cheaper capital and operational costs). Also, by removing inert gases during the SO₂ absorption/stripping process and then combining the SO₂-enriched stripper gas 30 with a fresh oxygen source 42 (and/or providing oxygen by way of the stripper gas 36 itself), the oxygen concentration in the gas 30 can be increased without necessarily increasing the total volume of the SO₂-containing gas. This process also provides a mechanism for delaying the introduction of the oxygen needed for the SO₂ oxidation until the oxygen is actually needed (*i.e.*, in the catalytic converter 45). This is particularly advantageous because, under such a scheme, only the amount of oxygen needed for producing the SO₂ has to be introduced into combustion zone 9. Thus, the combustion zone 9 and other equipment upstream of the converter 45 does not have to be sized to handle the oxygen-containing gas which is required for the SO₂ oxidation. Because smaller equipment can be used upstream of the catalytic converter 45, significant capital and operational expenses can be avoided.

Because the SO_2 absorption/stripping zones may be used to remove water from the source gas 3, they are particularly useful in embodiments where it is desirable to remove water vapor from the source gas 3 so that the SO_2 -containing gas fed to the catalytic converter 45 contains essentially no water vapor. Such

5 embodiments include, for example, embodiments where the converter 45 and/or equipment downstream of the converter 45 are made of material which is vulnerable to corrosion caused by sulfuric acid formed by the vapor phase reaction of water vapor with SO_3 . The SO_2 absorption/stripping zones are also particularly useful in

10 embodiments where the $\text{H}_2\text{O}/\text{SO}_2$ molar ratio in the source gas 3 is greater than the molar ratio of $\text{H}_2\text{O}/\text{SO}_3$ in the desired acid product 51 (this situation may especially occur when the source gas 3 is prepared from spent acid, the off-gas of a metal roasting or smelting operation, or H_2S). For example, if the desired product acid concentration is 98.5 weight%, the $\text{H}_2\text{O}/\text{SO}_3$ molar ratio in the conversion gas 54 fed to the SO_3 absorption zone 57 cannot exceed about 1.08. Consequently, if there is no

15 water removal in the system between the source gas 3 and the SO_3 absorption zone 57, the $\text{H}_2\text{O}/\text{SO}_2$ molar ratio in the source gas 3 also preferably does not exceed about 1.08. The SO_2 absorption/stripping zone may be used (alone or together with, for example, a drying tower and/or a cooling tower(s) which condenses liquid out of the source gas 3) to ensure that the $\text{H}_2\text{O}/\text{SO}_3$ molar ratio is maintained below this value.

20 **C. Oxidation of Sulfur Dioxide to Sulfur Trioxide**

The SO_2 -enriched stripper gas 30 is preferably combined with a source of molecular oxygen 42 to form a converter feed gas 48, which is then passed through a catalytic converter 45 to oxidize the SO_2 to form a conversion gas 54 containing SO_3 .

The oxygen source 42 may be any oxygen-containing gas. As used herein, an

25 "oxygen-containing gas" is a gas comprising molecular oxygen (O_2), which optionally may also comprise one or more diluents which are non-reactive with O_2 , SO_2 , SO_3 , and sulfuric acid under the reaction conditions. Examples of such gases are air, pure molecular oxygen, or molecular oxygen diluted with nitrogen and/or another inert gas(es). For economic reasons, the oxygen source 42 preferably is air or essentially

30 pure molecular oxygen, with air being most preferred. It should be recognized that the stripper gas 36 advantageously may provide part (or, in some instances, all) of the

oxygen required in the converter feed gas 48 if the stripper gas 36 is air or another O₂-containing gas.

In a particularly preferred embodiment, the converter feed gas 48 contains essentially no water vapor, thereby reducing the risk of corrosion to process equipment downstream. Here, if the SO₂-enriched stripper gas 30 is wet, it preferably is dried, such as by being contacted with concentrated sulfuric acid in a drying tower before being introduced into the catalytic converter 45. If the SO₂ absorption solvent 15 is an organic phosphorous solvent as described above and dry air is used to strip the SO₂ from the SO₂-enriched absorption solvent 24, the SO₂-enriched stripper gas 30 often does not need to be dried before being routed to the converter 45.

The catalytic converter typically comprises at least two catalyst beds in series through which the converter feed gas 48 passes. The catalyst in each of the catalyst beds may generally be any material which catalyzes the oxidation reaction of SO₂ to SO₃. Conventionally used catalysts include, for example, various vanadium compounds, platinum compounds (*e.g.*, platinized asbestos), silver compounds, ferric oxide, chromium oxide, etc. In a particularly preferred embodiment, the catalyst comprises vanadium or a combination of vanadium and cesium. In the most preferred embodiment, the catalyst comprises vanadium pentoxide (V₂O₅).

As noted above, in the more preferred embodiments of this invention, the SO₂-enriched stripper gas 30 is normally at a temperature of no greater than about 120°C upon exiting the SO₂ stripper zone 27. And this temperature is typically decreased when the SO₂-enriched stripper gas 30 is combined with the oxygen source 42, which is often near ambient temperature. The more preferred oxidation catalysts, however, have an activation temperature which is significantly greater than 120°C. Thus, the converter feed gas 48 is often preferably heated before being introduced into the first catalyst bed 60 of the converter 45. On the other hand, because the oxidation of SO₂ to SO₃ is an exothermic reaction, the reaction is also preferably controlled so that the temperature of the catalyst bed 60 does not increase so much as to deactivate the catalyst and/or shift the reaction equilibrium to favor the reverse reaction.

When, for example, a vanadium-containing catalyst (*e.g.*, V₂O₅) is used, it is typically preferred for the converter feed gas 48 and partial conversion gas 69 and 72 entering catalyst beds 60, 63 and 66, respectively, to have a temperature of from



about 410 to about 450°C (even more preferably from about 415 to about 435°C), and then to control the temperature in each bed so that the gas temperature approaches, but does not exceed, about 650°C (more preferably about 630°C). Temperature control in the converter 45 is preferably accomplished by maintaining the SO₂ strength (*i.e.*, the SO₂ concentration) in the converter feed gas 48 and partial conversion gas 69 and 72 introduced into catalyst beds 60, 63 and 66, respectively, at no greater than about 15 mole%, more preferably no greater than about 13.5 mole%, and still more preferably no greater than about 12 mole%. It is also preferred that the amount of the oxygen source 42 combined with the SO₂-enriched stripper gas 30 be such that the molar ratio of O₂ to SO₂ in the gas converter feed gas 48 and partial conversion gas 69 and 72 introduced into catalyst beds 60, 63 and 66, respectively, be greater than about 0.2:1, more preferably at least about 0.5:1, even more preferably at least about 0.7:1, still even more preferably from about 0.7:1 to about 1.4:1, and most preferably from about 0.9:1 to about 1.2:1.

Because the SO₂ oxidation reaction is exothermic, it is often advantageous to use an indirect heat exchanger(s) 75 and 78 to heat the converter feed gas 48 with the partial conversion gas 81 and 84 exiting the catalyst beds 60 and 63 of the catalytic converter 45. Generally, if the converter feed gas 48 contains at least about 5 mole% SO₂ (and particularly at least about 8 mole%) and an excess amount of O₂, the oxidation reaction can evolve sufficient heat for increasing the temperature of the converter feed gas 48 to the activation temperature of the oxidation catalyst, thus avoiding the need for any extraneous heat source for heating the converter feed gas 48 after startup (*i.e.*, making the converter 45 energy self-sustaining or "autothermal"). Thus, the converter feed gas 48 preferably has an SO₂ concentration of from about 7 to about 15 mole%, more preferably from about 7 to about 13.5 mole%, even more preferably from about 7 to about 12 mole%, still even more preferably from about 10 to about 12 mole%, and most preferably about 11.5 mole%. The converter feed gas 48 preferably is preheated using two indirect heat exchangers in series: first, a cold heat exchanger 78 in which the converter feed gas 48 is preheated by transfer of heat from the partial conversion gas 84 leaving the second bed 63 of the converter 45; and, second, a hot heat exchanger 75 in which the converter feed gas 48 is further heated by transfer of heat from the partial conversion gas 81 leaving the first catalyst bed 60

of the converter 45. In the embodiments where the source gas 3 is a hot gas exiting from a combustion chamber 9, the converter feed gas 48 may also (or alternatively), for example, be heated by passing it through an indirect heat exchanger to transfer heat from the source gas 3 to the converter feed gas 48.

5 In a particularly preferred embodiment, the SO₂-enriched stripper gas 30 is split into at least two streams. Preferably, a portion, preferably at least about 30% (more preferably at least about 40%, and even more preferably at least about 50%) of the SO₂-enriched stripper gas 30 is combined with the oxygen source 42 (either before or after being preheated, and preferably before) to form the converter feed gas 48,
10 which, in turn, is introduced into the first catalyst bed 60 of the converter 45 wherein a portion of the SO₂ content of the gas 48 is oxidized to SO₃ to form a partial conversion gas 81 containing SO₃ and residual SO₂. The cooled partial conversion gas exiting indirect heat exchanger 75 is then combined with a second portion 31 of the SO₂-enriched stripper gas 30 to fortify the SO₂ concentration in the partial
15 conversion gas. The fortified partial conversion gas 69 is then passed through at least one additional catalyst bed (63 and 66 in Fig. 1) to oxidize further SO₂ in the gas 69. Fortifying the SO₂ gas strength of the partial conversion gas is advantageous because it significantly increases the capacity of the converter 45. As noted above, the maximum SO₂ concentration of the gas fed into the first catalyst bed 60 is normally
20 limited (in the presence of excess oxygen) to about 15 mole% (more typically about 13.5 mole%, and even more typically about 12 mole%) because greater SO₂ concentrations will typically cause too much heat to be released during the oxidation reaction, thereby causing the catalyst to deactivate and/or the reaction equilibrium to shift unfavorably. However, by adding additional SO₂ to the partial conversion gas
25 fed into the second catalyst bed 63 (and, in some embodiments, a subsequent catalyst bed as well), that additional SO₂ may be oxidized without causing the temperature in any bed to increase to an undesirable level (as long as the amount of SO₂ added does not cause the SO₂ concentration in the fortified partial conversion gas 69 to be greater than about 15 mole%). Preferably, the amount of SO₂ added to the partial conversion
30 gas increases the SO₂ concentration to no greater about 15 mole%, more preferably from about 7 to about 13.5 mole%, even more preferably from about 7 to about 12

mole%, still even more preferably from about 10 to about 12 mole%, and most preferably about 11.5 mole%.

Although it is especially preferred for the partial conversion gas to be fortified with the entire portion of the SO₂-enriched stripper gas 31 which is not fed into the first catalyst bed 60, it should be recognized that this invention also encompasses embodiments wherein the SO₂-enriched stripper gas 30 is split into more than 2 portions and subsequently used to fortify the feed gas to more than one catalyst bed of the converter. Thus, where the catalytic converter has 4 catalyst beds in series, the SO₂-enriched stripper gas may, for example, be split into three portions. To illustrate, in one such embodiment, the first portion of the SO₂-enriched stripper gas is combined with the oxygen source to form the converter feed gas, which, in turn, is introduced into the first catalyst bed of the converter where SO₂ in the gas is oxidized to form a partial conversion gas. This partial conversion gas is then combined with the second portion of the SO₂-enriched stripper gas to fortify the SO₂ strength in the partial conversion gas. The fortified partial conversion gas is then passed through the second catalyst bed to oxidize further SO₂ and form a second partial conversion gas. This second partial conversion gas is then combined with the third portion of the SO₂-enriched stripper gas to fortify the SO₂ strength in the second partial conversion gas. This fortified second partial conversion gas is then passed through the third catalyst bed to oxidize still further SO₂ and form a third partial conversion gas. This third partial conversion gas is then passed through the fourth (*i.e.*, the final) catalyst bed to oxidize at least a portion of any remaining SO₂.

D. Production of Sulfuric Acid and/or Oleum from Sulfur Trioxide

The conversion gas 54 exiting the catalytic converter 45 preferably is contacted with water or, more preferably, concentrated sulfuric acid 87 (preferably an aqueous solution containing from about 96 to about 99.5 weight% H₂SO₄, more preferably from about 98.5 to about 99.5 weight%, and most preferably from about 99 to about 99.5 weight%) in an SO₃ absorption zone 57 to absorb SO₃ from the conversion gas 54, thereby forming an SO₃-depleted gas 90 and additional sulfuric acid and/or oleum 51. There is preferably also a heat recovery zone 93 associated with the SO₃ absorption zone 57. This heat recovery zone 93 preferably recovers

energy from the heat of absorption of the SO_3 in the SO_3 absorption zone 57. Sulfur trioxide absorption zones and heat recovery zones suitable for use in accordance with this invention are well-known in the art. *See, e.g.,* McAlister et al., U.S. Patent Nos. 4,670,242 and 4,576,813 (both incorporated herein by reference).

5 In a particularly preferred embodiment employing a heat recovery zone 93 in association with an SO_3 absorption zone 57, the conversion gas 54 is cooled in an economizer to a temperature which is above the dew point of the conversion gas 54, and then introduced into the lower portion of a vertical tower comprising the SO_3 absorption zone 57. The SO_3 absorption zone 57 preferably comprises a bed of
10 random packing (although the SO_3 absorption zone 57 may alternatively comprise another gas-liquid contacting device, such as a tray tower). Preferably, the cooled conversion gas 54 flows upward through the SO_3 absorption zone 57. At the same time, hot, concentrated liquid sulfuric acid 87 is sprayed from the top of the absorption zone 57 and flows downward through the packing. As the concentrated
15 sulfuric acid 87 and SO_3 countercurrently contact each other, the SO_3 is absorbed into the concentrated sulfuric acid 87. This concentrated sulfuric acid 87 preferably has a temperature of greater than about 120°C . Such conditions tend to reduce sulfuric acid corrosiveness to alloys used in many conventional absorption towers, while providing a high degree of SO_3 absorption.

20 After passing through the absorption zone 57, the sulfuric acid concentration in the sulfuric acid solution 96 is preferably greater than about 98 weight% (more preferably greater than about 98.5 weight%, even more preferably greater than about 99 weight%, and most preferably from about 99 to about 100 weight%). It should be recognized that these preferred concentrations can be greater if the SO_3 absorption
25 zone 57 is operated at pressure significantly greater than atmospheric pressure.

Because the absorption of SO_3 into the concentrated liquid sulfuric acid is an exothermic process, the temperature of the liquid sulfuric acid increases as the liquid sulfuric acid becomes more concentrated while passing through the absorption zone 57. In fact, while passing through the absorption zone 57, the temperature of the
30 concentrated sulfuric acid preferably increases to a temperature of up to about 250°C (this preferred maximum temperature is greater at absorber pressures greater than atmospheric pressure). Consequently, the liquid sulfuric acid 96 preferably is passed

through a heat recovery zone 93 (which may either be physically inside or outside of the absorption zone 57, and most preferably comprises an indirect heat exchanger outside the absorption zone 57) to remove the heat of absorption of the SO_3 . This heat may, in turn, be used, for example, to generate low to medium pressure steam
5 (typically up to about 10.5 bar (gauge)) for use within the manufacturing complex surrounding the sulfuric acid plant or to generate electricity.

To minimize corrosion of the heat exchanger in the heat recovery zone 93, the liquid sulfuric acid concentration preferably is at least about 99 weight% throughout the course of the heat transfer. It is also preferred that the temperature of the liquid
10 sulfuric acid 96 throughout the heat exchanger be greater than about 130°C (more preferably greater than about 140°C , and most preferably greater than about 150°C) where low pressure steam is desired (*i.e.*, up to about 3.5 bar (gauge)), and be greater than about 150°C (more preferably greater than about 175°C , and most preferably greater than about 200°C) where medium pressure steam is desired (*i.e.*, from about
15 6.5 to about 10.5 bar (gauge)). A portion of the sulfuric acid stream 96 preferably is recovered as product 51. The remainder 99 preferably is diluted with water 102 (in either liquid or vapor form) or dilute sulfuric acid, and reticulated to the top of the SO_3 absorption zone 57 to again be passed through the SO_3 absorption zone 57.

After the SO_3 -depleted gas 90 exits from the top of the SO_3 absorption zone
20 57, the gas 90 may optionally be passed through a second SO_3 absorption zone which may be a second stage of the tower containing the first SO_3 absorption zone 57, or may be located in a separate tower. The purpose of such a second stage or tower is to remove any residual SO_3 that remains in the SO_3 -depleted gas 90. It should be recognized, however, that in many instances, essentially all the SO_3 is absorbed in the
25 primary SO_3 absorption zone 57, rendering a second stage or a second tower unnecessary. And, even if a second stage or tower is used, it is typically not economically productive to incorporate a heat exchanger to recover energy from the heat of absorption of the SO_3 in the second stage or second tower, given the small amount (if any) of SO_3 being absorbed there. Use of a second SO_3 absorption zone is
30 described, for example, by McAlister, et al. in U.S. Patent No. 4,996,038 (incorporated herein by reference).

It should be recognized that the process of this invention may comprise more than one SO₃ absorption zone such that partial conversion exiting an intermediate catalyst bed of the converter is contacted with water or a liquid comprising sulfuric acid to absorb SO₃ from the gas before the gas is passed through one or more subsequent catalyst beds of the converter (*i.e.*, the process may be used with a system comprising an intermediate SO₃ absorber). For example, where a catalytic converter comprising 4 catalyst beds is used, the partial conversion gas leaving the second or third bed may be passed through an intermediate SO₃ absorption zone (*i.e.*, an interpass absorption zone) for removal of SO₃ in the form of product acid and/or oleum. Gas exiting the intermediate absorption zone is then returned to the next downstream catalyst bed of the converter. Because the conversion of SO₂ to SO₃ is an equilibrium reaction, removal of SO₃ in the interpass absorption zone helps drive the reaction forward in the succeeding bed or beds of the converter to achieve higher conversions. Use of an intermediate SO₃ absorption zone, however, is normally less preferred in the practice of the present invention because it substantially adds to the capital and operating costs.

E. Recycling the Tail Gas

In a particularly preferred embodiment of this invention, at least a portion of the SO₃-depleted gas 90 exiting the SO₃ absorption zone 57 (*i.e.*, the tail gas) is recycled back to the SO₂ absorption zone 18 and contacted with the SO₂ absorption solvent 15 along with the source gas 3. In this manner, unconverted SO₂ in the tail gas 90 is thereby recaptured in the SO₃-enriched absorption solvent 24 exiting the SO₂ absorption zone 18, stripped from the SO₃-enriched absorption solvent 24 in the SO₂ stripper zone 27, and returned to the catalytic converter 45 as part of the SO₂-enriched stripper gas 30 for ultimate recovery as product acid 51. In such an embodiment, at least a substantial portion of the inert gases and excess O₂ in the recycled tail gas 90 will be purged from the process in the SO₂-depleted gas 21 exiting the SO₂ absorption zone 18.

Those skilled in the art will recognize that, depending on the efficiency of the converter 45, emission standards may be met by recycling less than all of the tail gas 90 from the SO₃ absorption zone 57. In fact, depending on local prevailing emission

standards, target emissions may be met by recycling 90%, 75%, or even 50% of the tail gas 90, with some resultant savings in energy costs for gas compression. It is ordinarily preferred, however, that substantially all the tail gas 90 be recycled. While non-condensable gases separated from the process gas in both the SO₂ and SO₃ absorption zones must be purged to the atmosphere, emissions are confined to a single location (*i.e.*, the SO₂-depleted gas from the SO₂ absorption zone) when the entire tail gas 90 is recycled back to the SO₂ absorption zone 18. This facilitates both monitoring and control of SO₂ emissions. Moreover, by recycling all the tail gas 90 to the SO₂ absorption zone 18, 99.7 percent or more of the SO₂ in the source gas 3 fed to the SO₂ absorption zone 18 may ultimately be recovered as product acid 51, even where single-pass conversion efficiencies in the sulfuric acid plant are relatively low. In other words, by recycling all the tail gas 90 to the SO₂ absorption zone 18, SO₂ emissions from the contact sulfuric acid plant may be essentially eliminated. And, recycle of the entire tail gas 90 allows the acid plant to be operated with a single SO₃ absorption zone 57, entirely eliminating the interpass SO₃ absorption step that has become standard throughout much of the sulfuric acid industry as a means of controlling SO₂ emissions. And, even with single rather than dual absorption, the converter 45 may be operated at a single-pass efficiency of less than 98 percent. Where the tail gas 90 is recycled, it is typically preferred that the SO₂ conversion per single pass through the entire converter 45 (*i.e.*, the total amount of SO₂ consumed during a single pass through the entire converter ÷ total amount of SO₂ fed into the converter x 100%) be at least 75%, more preferably at least about 85%, even more preferably at least about 90%, and most preferably at least about 95%.

In one embodiment, instead recycling all the tail gas 90 to the SO₂ absorption zone 18, only a portion (*e.g.*, from about 80 to about 90%) of the tail gas 90 is recycled to the SO₂ absorption zone 18, while another portion (preferably the entire remainder of the tail gas 90) is routed directly to the converter feed gas 48, and thereby fed back into the converter 45. This allows for a smaller SO₂ absorption zone 18 to be used.

Advantageously, the process of this invention may be implemented using only two (or, more preferably, three (as shown in Fig. 1)) catalyst beds in the catalytic converter 45. It should be recognized, however, that this process may also be

implemented using a double SO_3 absorption plant and/or 4 or more catalyst beds in the catalytic converter. For example, an existing contact acid plant (having, for example, a 4-catalyst-bed converter) can be retrofitted with the features of this invention to operate at greater than design throughput without exceeding emission limits.

In another embodiment of the present invention, an already-existing contact sulfuric acid production plant including a catalytic converter with 4 catalyst beds in series and at least two associated indirect heat exchangers for cooling the partial conversion gas passing between catalyst beds is modified (*i.e.*, retrofitted) so that the converter comprises 2 parallel sets of 2 catalyst beds in series. The flow scheme for such a retrofitted catalytic converter is schematically illustrated in Fig. 2. In the retrofitted converter 45A, the parallel sets of catalyst beds are typically contained within the single vessel which housed the serial catalyst beds of the original converter. However, it should be understood that the parallel sets of catalyst beds could be housed in separate vessels. In the modified flow scheme, the SO_2 -enriched stripper gas 30 is preferably ultimately divided into 4 portions. A first portion of the SO_2 -enriched stripper gas 30 is combined with an oxygen source 42 to form a converter feed gas 48, which is subsequently divided to form a first converter feed gas 48A and a second converter feed gas 48B. The first converter feed gas 48A is heated in indirect heat exchanger 75 and passed through the first catalyst bed 60 of the first set of catalyst beds to form a first partial conversion gas 81A, and the second converter feed gas 48B is simultaneously heated in indirect heat exchanger 78 and passed through the first catalyst bed 65 of the second set of catalyst beds to form a second partial conversion gas 84A. The remainder of the SO_2 -enriched stripper gas 31 is divided and a first portion 31A is combined with the cooled first partial conversion gas exiting indirect heat exchanger 75 to fortify the SO_2 concentration in the first partial conversion gas and produce a fortified first partial conversion gas 69A. The second portion 31B of the remainder of the SO_2 -enriched stripper gas 31 is likewise combined with the cooled second partial conversion gas exiting indirect heat exchanger 78 to fortify the SO_2 concentration in the second partial conversion gas and produce a fortified second partial conversion gas 72A. The first fortified partial conversion gas 69A is passed through the second catalyst bed 63 of the first set of

catalyst beds to form a first conversion gas 54A, and the second fortified partial conversion gas 72A is passed through the second catalyst bed 66 of the second set of catalyst beds to form a second conversion gas 54B. The first and second conversion gases 54A and 54B may then be combined to form conversion gas 54 and introduced into a single SO₃ absorption zone. Where the existing contact sulfuric acid plant is a dual SO₃ absorption plant, however, the first conversion gas 54A preferably is introduced into one of the SO₃ absorption zones, while the second conversion gas 54B is introduced into the other SO₃ absorption zone (*i.e.*, the two SO₃ absorption zones are operated in parallel). In either case, it is particularly preferred to recycle the SO₃-depleted tail gas exiting the SO₃ absorption zone (or zones) to the SO₂ absorption zone.

F. Particularly Preferred Embodiments for High Grade Energy Recovery

Water vapor may be introduced into the conversion gas 54 exiting the catalytic converter 45. In such embodiments, upon mixing, the water vapor reacts with the SO₃ in the conversion gas 54 to produce gaseous sulfuric acid. A portion of the energy from the heat of formation of the gaseous sulfuric acid may, in turn, be recovered by, for example, passing the resulting gas through a heat exchanger. Substantial additional energy may be recovered by also (or alternatively) passing the gas through a condensing economizer.

The source of the water vapor may, for example, be low pressure steam (*i.e.*, up to about 6.5 bar (gauge), more preferably up to about 3.5 bar (gauge), and most preferably from about 0.2 to about 1 bar (gauge)). This low pressure steam may be obtained from a variety of sources at a sulfuric plant, such as, for example, a low pressure port on a steam turbine for an electrical generator, steam generated from low temperature sulfuric acid, etc.

In a particularly preferred embodiment, a wet SO₂ source gas 3 is used, and at least a portion (often preferably all) of the source gas 3 is combined with the conversion gas 54 to supply at least a portion (preferably all) of the water vapor. An example of such an embodiment is illustrated in Fig. 3. In this embodiment, the water vapor in the wet source gas 1003 reacts with the SO₃ in the conversion gas 1006 to produce gaseous sulfuric acid. The vapor phase formation of gaseous sulfuric acid

generates heat which preferably is recovered as energy by, for example, transferring the heat to steam or feed water in an indirect heat exchanger 1012. In addition, more energy is preferably recovered by condensing at least a portion of the gaseous sulfuric acid into liquid sulfuric acid in a condensing economizer 1015. The gas 1018 exiting the condensing economizer 1015 is then preferably passed through an SO₃ absorption zone 1021 (which preferably is associated with a heat recovery means 1024 which recovers the energy from the heat of absorption produced in the SO₃ absorption zone 1021) where SO₃, water vapor, and any additional gaseous sulfuric acid is separated from the gas 1018 to form a dry SO₃-depleted gas 1066. This dry SO₃-depleted gas 1066, in turn, is a/the source of SO₂ for the converter feed gas 1030.

Suitable methods for recovering energy using an indirect heat exchanger, a condensing economizer, and/or a heat-recovery/SO₃-absorption tower are described, for example, by McAlister et al. in U.S. Patent Nos. 5,503,821; 5,130,112; and 5,118,490 (all incorporated herein by reference).

The condensing economizer 1015 preferably comprises an indirect heat exchanger in which heat is transferred to a heat transfer fluid (*e.g.*, boiler feed water). This indirect heat exchanger preferably comprises heat transfer wall means (*e.g.*, the tubes of a shell and tube type heat exchanger), preferably constructed of an alloy (*e.g.*, an Fe/Cr or Fe/Cr/Ni alloy) which is resistant to corrosion by condensing sulfuric acid. Preferably, at least a portion of the wall means on the gas stream side of the exchanger is at a temperature which is less than the dew point of the gas stream in the exchanger. Thus, sulfuric acid condenses on the heat transfer wall, and the heat of formation of the condensing acid is transferred to the boiler feed water.

The condensing economizer 1015 may be operated to condense as sulfuric acid as much as from about 5 to about 20% of the SO₃ generated in the catalytic converter 1009. Table 1 shows the heat evolved when SO₃ and water react to form sulfuric acid under various phase conditions.

Table 1

Sulfuric Acid Heat of Reaction from Standard Heat of Formation (25°C)

<u>No.</u>	<u>Reaction Conditions</u>	<u>Heat of Reaction</u>
1)	$\text{SO}_3 (\text{g}) + \text{H}_2\text{O} (\text{l}) \longrightarrow \text{H}_2\text{SO}_4 (\text{l})$	-31.7 kcal/mole
5	2) $\text{SO}_3 (\text{g}) + \text{H}_2\text{O} (\text{g}) \longrightarrow \text{H}_2\text{SO}_4 (\text{g})$	-23.3 kcal/mole
	3) $\text{SO}_3 (\text{g}) + \text{H}_2\text{O} (\text{g}) \longrightarrow \text{H}_2\text{SO}_4 (\text{l})$	-42.2 kcal/mole

The gas phase reaction (Equation 2) produces 74% of the heat produced by the normal liquid phase reaction (Equation 1). Transferring the heat from condensing sulfuric acid to boiler feed water results in the ultimate recovery of both the heat of formation and heat of condensation of the sulfuric acid. The boiler feed water, in turn, may be further heated with the source gas 1003 as the source gas 1003 exits the SO_2 -producing combustion zone 1002 to form high grade energy, i.e., steam at a pressure of at least about 30 bar (gauge), and more preferably from about 40 to about 60 bar (gauge). This steam may be further heated by, for example, the conversion-gas/source-gas mixture 1039 in the indirect heat exchanger 1012.

The conversion of SO_3 to sulfuric acid in the vapor phase increases as the temperature of the vapor phase decreases. Thus, it is advantageous to decrease the temperature in the condensing economizer 1015 to the maximum extent compatible with effective operation of the SO_3 absorber 1021 downstream. Not only is the reaction forced to the maximum degree of completion and generation of the heat of formation, but the maximum proportion of the heat of formation and condensation of sulfuric acid is recovered in high grade form by transfer to high pressure boiler feed water for the waste heat boiler. Fortuitously, the condensing economizer 1015 can be operated to extract a maximum amount of the vapor phase energy of formation of sulfuric acid without the necessity for close control of the fluid flow rates or wall temperatures within the economizer 1015. The concentration of acid in the condensate 1033 varies only slightly with the $\text{H}_2\text{O}/\text{SO}_3$ molar ratio in the gas 1036, and consequently does not vary significantly with either the temperature to which the gas 1036 is cooled or the wall temperature of the condensing economizer 1015. Thus, it is not necessary to closely control the operation of the condensing economizer 1015 to avoid corrosive conditions therein. And, variations in inlet air humidity, or

excursions in sulfur flow rate, do not materially affect the concentration of the acid condensate 1033 on the tube walls of the condensing economizer 1015. As much as 140% of the stoichiometric amount of water vapor may be present in the gas 1036 without reducing the concentration of the condensing acid condensate 1033 to less than 98%.

The energy equivalent of from about 40 to about 70% (most typically about 60%) of the heat of formation of sulfuric acid vapor may be recovered by cooling the gas 1039 before it enters the SO₃ absorption zone 1021. Where both an initial heat exchanger 1012 and a condensing economizer 1015 are used, typically from about 70% to about 90% (and more typically about 75%) of the recovered heat of formation is recovered in the condensing economizer 1015.

Preferably, the boiler feed water enters the condensing economizer at a temperature of from about 110 to about 180°C, and the gas 1036 enters the condensing economizer 1015 at a temperature of from about 320 to about 470°C, and with an H₂O/SO₃ mole ratio of from about 0.2 to about 1.05. The gas 1018 leaving the condensing economizer 1015, on the other hand, preferably has a temperature of from about 240 to about 300°C.

It should be understood that a substantial portion of the vapor phase heat of formation of sulfuric acid can be extracted without condensation in the economizer 1015. In some circumstances, for example, it may be desirable to operate the economizer 1015 under conditions which preclude condensation because this allows the economizer 1015 to be constructed of carbon steel instead a more costly material (e.g., a Fe/Cr or Fe/Cr/Ni alloy) which is resistant to sulfuric acid corrosion. Thus, for example, recovery of a substantial fraction of the heat of formation may be achieved without condensation by transferring heat from the gas 1036 to boiler feed water in a co-current heat exchanger. Nevertheless, in most instances, it is preferred that an alloy exchanger be used and that the tube walls be operated at a temperature low enough to cause condensation thereon (though not so low as to cause nucleation and mist formation within the bulk gas). By such means, a substantial portion of the heat of formation and a significant portion of the heat of condensation may be recovered in the form of high pressure steam.

The wet gas 1018 leaving the condensing economizer 1015 preferably is directed to an SO₃ absorption zone 1021 where it is contacted countercurrently with a concentrated solution of sulfuric acid 1048. Preferably, the SO₃ absorption zone 1021 comprises a means in a vertical tower for promoting mass transfer and heat transfer between the gas and liquid phases within the tower (preferably a bed of random packings such as saddles or rings, although it should be understood that other gas liquid contacting devices, e.g., a countercurrent tray tower or a co-current venturi absorber, may be used in lieu of random packing). The inlet gas 1018 to the absorption zone 1021 comprises SO₃ and sulfuric acid vapor. Contact of the gas 1018 with the liquid sulfuric acid 1048 causes absorption of SO₃, condensation and absorption of any water vapor, and condensation and absorption of sulfuric acid vapor into the sulfuric acid solution. It should be understood that, within the context of this disclosure, the terms "heat of absorption" and "energy of absorption" include all these various heat effects, and may also include energy of formation of sulfuric acid in the vapor phase that has not been recovered in condensing economizer 1015.

The use of hot acid for SO₃ absorption provides at least two advantages. First, the heat of absorption is generated at relatively high temperature which allows subsequent recovery of this energy at high temperature. Additionally, the use of high temperature acid avoids shock cooling of the gas 1018 and consequently minimizes the formation of acid mist in the wet gas. Preferably, the temperature of the acid 1051 at the exit of the absorption zone 1021 is no greater than about 40°C less than (and more preferably no greater than about 20°C less than) the dew point of the inlet gas 1018. The gas 1018 can typically be at a temperature of up to about 300°C as it enters the SO₃ absorption zone 1021, thereby allowing recovery of the maximum amount of the energy of vapor phase formation and condensation of sulfuric acid in the form of high pressure steam as a result of the transfer of this heat to the high pressure boiler feed water for waste heat boiler.

In a particularly preferred embodiment, the concentrated sulfuric acid contact solution 1048 is introduced at an inlet near the top of the SO₃ absorption zone 1021, while the gas 1018 is introduced at an inlet near the lower end of the SO₃ absorption zone 1021. The acid solution 1048 at the acid inlet preferably has a temperature of from about 170 to about 220°C, and a sulfuric acid concentration of from about 98.5

to about 99.5%, and more preferably from about 99 to about 99.5%. The gas 1018 at the gas inlet, on the other hand, preferably has a temperature of from about 240 to about 300°C, and an $\text{H}_2\text{O}/\text{SO}_3$ molar ratio which preferably is less than the $\text{H}_2\text{O}/\text{SO}_3$ molar ratio in the acid solution 1048, and equals from about 0.2 to about 1.05 (more preferably from about 0.7 to about 1.0). If the water vapor concentration in the source gas 1003 is so great that the $\text{H}_2\text{O}/\text{SO}_3$ molar ratio in the gas 1018 entering the SO_3 absorption zone 1021 exceeds the $\text{H}_2\text{O}/\text{SO}_3$ molar ratio in the concentrated sulfuric acid contact solution 1048 when the entire source gas 1003 is combined with the conversion gas 1006, the $\text{H}_2\text{O}/\text{SO}_3$ molar ratio in the gas 1018 entering the SO_3 absorption zone 1021 preferably is reduced by either partially drying the source gas 1003 in a drying tower before it is combined with the conversion gas 1006; or by only combining a portion 1042 of the source gas 1003 with the conversion gas 1006, and routing the remaining portion 1045 directly to the SO_2 absorption/stripper zones (and, optionally a drying tower, if the SO_2 absorption/stripper zone is unable to remove essentially all the water content).

The acid solution 1051 preferably is discharged from the SO_3 absorption zone 1021 at a temperature of at least about 190°C, more preferably from about 190 to about 250°C, and even more preferably from about 210 to about 250°C. At least a major portion of this solution preferably flows to a circulating pump, and passed through an indirect heat exchanger 1024 where the energy of absorption is recovered by transfer of heat to another fluid. Preferably, the indirect heat exchanger 1024 comprises a heat recovery system boiler, and the heat energy is ultimately recovered in the form of low to medium pressure (*i.e.*, up to about 10.5 bar (gauge)).

The acid solution 1054 from the indirect heat exchanger 1024 is preferably recirculated back to the SO_3 absorption zone 1021. To recover the acid product, a portion 1057 of the acid solution 1054 preferably is removed as product before the acid solution 1054 is recirculated (additional heat energy may be recovered from this acid product by, for example, passing it through one or more additional indirect heat exchangers). An equal amount of water 1060 is then added to the remaining sulfuric acid solution 1063. This water 1060 may, for example, be added in liquid or vapor form, or in the form of diluted sulfuric acid.

As a result of the high temperature operation of the SO₃ absorption zone 1021, the SO₃-depleted gas 1066 exiting the top of this zone 1021 is relatively hot. This, in turn, often results in the stripping of sulfuric acid from the acid stream into the gas stream. In other words, although the absorption efficiency of the SO₃ absorption zone 1021 is at least about 90%, high temperature operation of the absorption zone 1021 also typically results in some unabsorbed SO₃ passing through the absorption zone 1021. Gas 1066 exiting the top of the SO₃ absorption zone 1021 is therefore preferably directed to a condensing stage for absorption of residual SO₃ and condensation of sulfuric acid vapor. This condensing stage preferably contains means for promoting gas/liquid contact and mass transfer and heat transfer. For example, in one embodiment, this stage comprises a countercurrent packed section wherein relatively cool acid having a concentration of about 98.5% is fed to the top of this stage and gas 1066 leaving the main SO₃ absorption zone 1021 (which is typically at a temperature of from about 170 to about 230°C) enters the bottom of the condensing stage. In this embodiment, the acid entering the condensing stage preferably is at a temperature of less than about 120°C, most preferably from about 60 to about 80°C. On passage through the condensing stage, the gas 1066 preferably is cooled to a temperature of from about 75 to about 140°C, and more preferably from about 80 to about 120°C. Gas leaving the condensing stage is then preferably passed through a mist eliminator. The acid flow rate in the condensing stage preferably is maintained at a rate low enough so that the acid leaves the stage at a temperature which approaches the temperature of the acid entering the main SO₃ absorption packed bed.

In this wet gas embodiment, the gas 1066 exiting the SO₃ absorption zone 1021 (*i.e.*, the SO₃-depleted gas), along with any portion 1045 of the source gas 1003 that is not combined with the conversion gas 1006, is preferably used to form the converter feed gas 1030. More specifically, the SO₃-depleted gas 1066 (along with any portion 1045 of the source gas 1003 which is not combined with the conversion gas 1006) is first passed through the SO₂ absorption/stripper zones described previously. This removes the excess inert gases, and can be used to enhance the SO₂ concentration in the SO₃-depleted gas 1066 where the SO₂ concentration in the SO₃-depleted gas 1066 is less than the desired concentration. The gas exiting the SO₂ absorption/stripper zones (*i.e.*, the SO₂-enriched stripper gas 1069) is then preferably combined with a dry

oxygen source 1072 if the stripper gas 1075 does not supply the desired level of oxygen. It should be recognized that the SO₂-enriched stripper gas 1069 may also be divided into 2 or more portions in the same manner as described above wherein one portion of the SO₂-enriched stripper gas 1069 is combined with the dry oxygen source 1072 and fed into the first catalyst bed 1078 of converter 1009, and a second portion 1070 is used to fortify the SO₂ concentration of the partial conversion gas 1081 exiting the first catalyst bed 1078.

It is especially preferred for the gas passing through the converter 1009 to be essentially free of water vapor. By passing essentially moisture free gas through the converter 1009, the risk of corrosion (or the added cost of using corrosion-resistant material) in the converter 1009 (and any process equipment between the catalyst beds of the converter 1009) caused by sulfuric acid formed by the vapor phase reaction of SO₃ and water vapor is generally avoided. To ensure that the gas 1030 being fed into the converter 1009 is essentially free of water vapor, any oxygen source 1072 combined with the SO₂-enriched stripper gas 1069 preferably is dried beforehand. It is also preferred that the SO₂ absorption solvent 1084 consist essentially of a composition that transfers little or no water to the SO₂-enriched stripper gas 1069. The organic phosphorus solvents discussed above are generally suitable for this purpose, particularly where the stripper gas 1075 is dry air.

The wet-source-gas embodiment described above is advantageous because it produces a dry SO₂ gas 1030 for the converter 1009 without having to first pass the entire source gas 1003 through a drying tower, thereby avoiding the capital and operational expenses associated with such a tower (and associated equipment, *e.g.*, a pump, piping, a pump tank, and a cooler) as to the portion 1042 of the source gas 1003 that is combined with the conversion gas 1006 (as noted above, it is most often preferred that this portion 1042 be the entire source gas 1003). In addition, this process is advantageous because it produces heat (*i.e.*, the heat of formation of gaseous sulfuric acid, the heat of condensation of gaseous sulfuric acid, and the heat of condensation of water vapor) which may be transferred and used elsewhere as energy.

Although the above discussion focuses on heat recovery in the particularly preferred embodiment where a wet source gas is combined with the conversion gas to

supply all the water vapor, it should be understood that the general heat recovery principles discussed above also apply to embodiments where a different source of water vapor is used (e.g., low pressure steam), or where a wet source gas and a different source of water vapor are both combined with the conversion gas to supply the water vapor.

G. Preferred Equipment for Handling Gases Containing Sulfuric Acid

Wet SO₃-containing gas can be handled in carbon steel equipment, although the gas temperature in such equipment preferably is kept above the dew point to avoid the condensation of gaseous sulfuric acid formed from the water vapor and SO₃. In the more preferred embodiments of the present invention, however, the dew point is generally high and much of the equipment (particularly the condensing economizer) is operated at a temperature below the dew point. This equipment, therefore, preferably is made of a material that is resistant to sulfuric acid corrosion under the conditions of this invention. There are a number of conventionally used materials, particularly stainless steel and nickel alloys, that can be used in for this purpose. Alloy performance may be characterized by a corrosion index (CI), which is defined in terms of alloy composition by the following relationship:

$$CI = 0.4[Cr] - 0.05[Ni] - 0.1[Mo] - 0.1[Ni] \times [Mo]$$

wherein [Cr] is the weight percent of chromium in the alloy, [Ni] is the weight percent of nickel in the alloy, and [Mo] is the weight percent of molybdenum in the alloy. Alloys which work best in high temperature strong sulfuric acid service have been found to have a corrosion index of greater than 7, and particularly greater than 8.

The alloys most likely to exhibit low corrosion rates are those with the highest corrosion index. As indicated by the corrosion index formula, high chromium is desirable, and it is preferable to avoid alloys which have both high nickel and high molybdenum. It should be recognized, however, that alloys which contain high nickel and very low molybdenum, or low nickel and moderate amounts of molybdenum, are often acceptable. Particular alloys found suitable for use in contact with liquid phase

sulfuric acid at high temperature include, for example, those having UNS designations S30403, S30908, S31008, S44627, S32304, and S44800.

EXAMPLE

This example further illustrates and explains the invention. The invention,
5 however, should not be considered to be limited to any of the details in this example.

Using a computer model, the performance of the system shown in Fig. 4 was assessed. A source gas 2003 containing about 19 mole% SO₂, about 2 mole % O₂, and about 79 mole% N₂ is formed in a sulfur burner 2006 by burning sulfur 2009 in the presence of dry air 2012. This source gas 2003 (initially at a temperature of about
10 1538°C upon exiting the sulfur burner 2006) is cooled to about 548°C in a waste heat boiler 2002. The source gas 2004 is further cooled to about 337°C in an indirect heat exchanger 2015 (*i.e.*, Monplex™, Monsanto Environ-Chem Systems, Inc., St. Louis, MO, USA) by transferring heat from the source gas 2004 to the gas 2018 being fed into the SO₂ oxidation catalytic converter 2021. Finally, the source gas 2024 is cooled
15 even further to about 204°C in yet another indirect heat exchanger 2023 which uses heat in the source gas 2024 to form steam.

The cooled source gas 2025 is split into two portions: one portion 2026 (being about 6.6 volume% of the cooled source gas 2025) is fed back into the sulfur burner 2006 to maintain the desired temperature in the burner 2006, and the remaining
20 portion 2028 (being about 94% of the cooled source gas 2025) is introduced into the SO₂ absorption/stripping zones (*i.e.*, a Claus Master™, Monsanto Environ-Chem Systems, Inc., St. Louis, MO, USA). Here, the source gas 2028 is passed through a packed SO₂ absorption column 2027, where it is contacted with a liquid SO₂ absorption solvent comprising dibutyl butyl phosphonate 2030 flowing
25 countercurrently to the source gas 2028. The dibutyl butyl phosphonate 2030 selectively absorbs SO₂ to form an SO₂-enriched absorption solvent 2033 and an SO₂-depleted gas 2036 (the SO₂-depleted gas 2036 containing substantially all the residual O₂ and inert gases (mostly N₂) from the source gas 2028).

The SO₂-depleted gas 2036 is discharged from the system, and the SO₂-enriched
30 absorption solvent 2033 is introduced into a packed SO₂ stripper column 2039, where the SO₂-enriched absorption solvent 2033 is contacted with a countercurrent flow of

dry air 2042 (the dry stripper air 2042 entering the column 2039 has a temperature of about 110°C) to form an SO₂-enriched stripping gas 2045 (containing about 90 mole% SO₂, with the remaining being air) and an SO₂-depleted absorption solvent 2048 (which is recycled back to the SO₂ absorption column 2027 to be used again as the SO₂ absorption solvent 2030). Both the SO₂ absorption column 2027 and the SO₂ stripper column 2039 are operated at nearly atmospheric pressure.

The SO₂-enriched stripping gas 2045 is divided into two portions: one portion (*i.e.*, the primary SO₂ gas 2051) being about 54 volume% of the SO₂-enriched stripping gas 2045, and the other portion (*i.e.*, the bypass SO₂ gas 2054) being about 46 volume% SO₂-enriched stripping gas 2045 (both portions having the same composition, *i.e.*, 90 mole% SO₂, with the remaining being air). The primary SO₂ gas 2051 is combined with dry air 2057 (the dry air 2057 having a temperature of about 66°C) to form a converter feed gas 2018 containing about 12 mole% SO₂ and having a temperature of about 130°C. This converter feed gas 2018 is heated to a temperature of about 410°C by the gas 2004 coming from the sulfur burner 2006 using the MonplexTM indirect heat exchanger 2015. After being heated, the converter feed gas 2060 is passed through a first catalyst bed 2063 containing V₂O₅ which converts (*i.e.*, oxidizes) about 67% of the SO₂ in the converter feed gas 2060 into SO₃, thereby forming a partial conversion gas 2066 having a temperature of about 637°C, and containing about 4 mole% SO₂ and about 8 mole% SO₃. The V₂O₅ catalyst in the first catalyst bed 2063 is a potassium-promoted catalyst coated on a silica support, and is in the shape of rings having an outer diameter of 12.5 mm, an inner diameter of 5 mm, and an average length of 14 mm (Cat. No. LP-120, Monsanto Environ-Chem Systems, Inc., St. Louis, MO, USA). The first catalyst bed 2063 has a diameter of about 26.25 feet and contains about 50,000 liters of the catalyst. The total flowrate of the converter feed gas 2060 into the first catalyst bed 2063 is about 50,767 scfm (*i.e.*, standard cubic feet per minute (defined at 70°F and 1 atm)).

The partial conversion gas 2066 exiting the first catalyst bed 2063 is cooled to about 420°C by transferring heat to feed water in an indirect heat exchanger 2069. The cooled partial conversion gas 2072 is then combined with the bypass SO₂ gas 2054 to increase the SO₂ concentration in the partial conversion gas 2072 to about 13 mole%. The SO₂-fortified partial conversion gas 2075 (having a temperature of about

423°C) is then passed through a second catalyst bed 2078 containing V_2O_5 to oxidize more SO_2 to form a second partial conversion gas 2081 having a temperature of about 607°C, and containing about 15.4 mole% SO_3 and about 6.1 mole% un-oxidized SO_2 . The second catalyst bed 2078 has the same dimensions, the same V_2O_5 catalyst, and
5 the same volume of catalyst as the first catalyst bed 2063. The total flowrate of gas entering the second catalyst bed 2078 is about 54,366 scfm.

The second partial conversion gas 2081 is cooled to about 420°C by transferring heat to feed water in a second indirect heat exchanger 2084, and then passed through a third catalyst bed 2087 containing V_2O_5 to oxidize still more SO_2 and form a final
10 conversion gas 2090 having a temperature of about 519°C, and containing about 20.0 mole% SO_3 and about 2.1 mole% un-oxidized residual SO_2 . The V_2O_5 catalyst in the third catalyst bed 2087 is a potassium-promoted catalyst coated on a silica support and is in the shape of rings having an outer diameter of 9.5 mm, an inner diameter of 4 mm, and an average length of 13 mm (Cat. No. LP-110, Monsanto Environ-Chem
15 Systems, Inc., St. Louis, MO, USA). The third catalyst bed 2087 has a diameter of about 26.25 feet and contains about 80,000 liters of the catalyst. The total flowrate of gas entering the third catalyst bed 2087 is about 52,406 scfm.

The final conversion gas 2090 is cooled to a temperature of about 166°C in an indirect heat exchanger 2091, and then contacted in a packed SO_3 absorption column
20 2093 (having a diameter of about 12 feet and a height of about 40 feet) with a countercurrent flow of an aqueous solution 2096 containing about 98.5 weight% H_2SO_4 to form a more concentrated sulfuric acid solution 2097 having a sulfuric acid concentration of about 99.5 weight%. The flowrate of the conversion gas 2090 is about 51,349 scfm, while the flowrate of the aqueous sulfuric acid solution 2096 is
25 about 1,700 gallons per minute. The temperature of the aqueous sulfuric acid solution 2096 entering the column 2093 is about 82°C, and the temperature of the sulfuric acid solution 2097 exiting the SO_3 absorption column 2093 is about 110°C.

The gas 2102 exiting the SO_3 absorption column 2093 (*i.e.*, "the SO_3 -depleted gas" or "tail gas") is split into 2 portions: one portion 2103 (being about 80 volume%
30 of the SO_3 -depleted gas 2102) is combined with the source gas stream 2028, and thereby routed to the SO_2 absorption column 2027. The other portion 2104 (being about 20 volume% of the SO_3 -depleted gas 2102) is combined with the dry air 2057

being combined with the primary SO₂ gas 2051, thereby maintaining a smaller volume of total gas being fed into the SO₂ absorption column 2027. Thus, both portions of the SO₃-depleted gas 2102 are ultimately recycled back to the converter 2021 so that substantially all the residual SO₂ in the SO₃-depleted gas 2102 can eventually be converted into sulfuric acid.

The single pass SO₂ conversion for the whole converter 2021 is about 90.4%. The overall conversion of the SO₂ in the source gas 2003 is about 99.87%.

* * * * *

The above description of the preferred embodiments and accompanying figures are intended only to acquaint others skilled in the art with the invention, its principles, and its practical application, so that others skilled in the art may adapt and apply the invention in its numerous forms, as may be best suited to the requirements of a particular use. The present invention, therefore, is not limited to the above embodiments, and may be variously modified.

With reference to the use of the word(s) "comprise" or "comprises" or "comprising" in the above description and/or in the following claims, applicant notes that unless the context requires otherwise, those words are used on the basis and clear understanding that they are to be interpreted inclusively, rather than exclusively, and that applicant intends each of those words to be so interpreted in construing the above description and/or the following claims.

**I claim:**

1. A process for making SO_3 from a source gas comprising SO_2 , the process comprising:

contacting the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent;

stripping SO_2 from the SO_2 -enriched solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas having an SO_2 gas strength greater than the SO_2 gas strength of the source gas;

forming a converter feed gas by combining a first portion of the SO_2 -enriched stripper gas with an oxygen source;

forming a partial conversion gas comprising SO_3 and residual SO_2 by passing the converter feed gas through a first catalyst bed of a catalytic converter comprising at least 2 and no greater than 4 catalyst beds in series, each catalyst bed containing an oxidation catalyst effective for oxidizing SO_2 to SO_3 , the first catalyst bed being upstream of the remaining catalyst beds in the series with respect to the direction of gas flow through the catalytic converter; and

forming a conversion gas comprising SO_3 and residual SO_2 by passing the partial conversion gas through the remainder of the series of catalyst beds to oxidize SO_2 in the partial conversion gas to SO_3 , the SO_2 concentration in the partial conversion gas being fortified by introducing a second portion of the SO_2 -enriched stripper gas into the partial conversion gas downstream of the first catalyst bed, the fortified partial conversion passing through at least one remaining catalyst bed in the series to oxidize SO_2 in the fortified partial conversion gas to SO_3 .

2. The process as set forth in claim 1 wherein the second portion of the SO_2 -enriched stripper gas comprises the remainder of the SO_2 -enriched stripper gas which is not combined with the oxygen source to form the converter feed gas.

3. The process as set forth in claim 1 wherein the second portion of the SO_2 -enriched stripper gas is introduced into the partial conversion gas downstream of the



first catalyst bed and upstream of the next catalyst bed in the series and the fortified partial conversion gas is passed through the next catalyst bed in the series.

4. The process as set forth in claim 1 wherein the oxygen source is dry.
5. The process as set forth in claim 1 wherein the concentration of SO_2 in the converter feed gas and in the fortified partial conversion gas is no greater than about 13.5 mole%, and the molar ratio of O_2 to SO_2 in the converter feed gas and in the fortified partial conversion gas is greater than about 0.5:1.
6. The process as set forth in claim 1 wherein the source gas comprises a combustion gas formed by burning a source of sulfur in the presence of oxygen in a combustion zone to oxidize the sulfur to SO_2 , the combustion gas comprising at least about 15 mole% SO_2 .
7. The process as set forth in claim 6 wherein the source of sulfur is burned in the presence of air and the non-reacted components of the air present in the combustion gas are substantially rejected in the SO_2 absorption zone as part of the SO_2 -depleted gas.
8. The process as set forth in claim 7 wherein air is introduced into the combustion zone at a rate such that the molar ratio of O_2 to sulfur supplied to the combustion zone is maintained at from about 1.05 to about 1.3.
9. The process as set forth in claim 1 wherein the catalytic converter comprises no more than three catalyst beds in series.
10. The process as set forth in claim 1 wherein the catalytic converter comprises two catalyst beds in series.

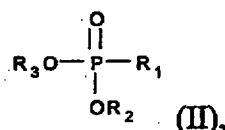


11. The process as set forth in claim 1 wherein the liquid SO₂ absorption solvent contacted with the source gas in the SO₂ absorption zone is a physical SO₂ absorbent.

12. The process as set forth in claim 1 wherein the ratio of the SO₂ molar concentration in the SO₂-enriched stripper gas to the SO₂ molar concentration in the source gas is at least about 2.75:1.

13. The process as set forth in claim 1 wherein the SO₂-enriched stripper gas comprises greater than about 70 mole% SO₂.

14. The process as set forth in claim 1 wherein the liquid SO₂ absorption solvent comprises at least one substantially water immiscible organic phosphonate dieter of the formula (II)



- 5 wherein R¹, R² and R³ are independently amyl or C₁ to C₈ alkyl, the organic phosphonate dieter having a vapor pressure less than about 1 Pa at 25° C, the solubility of water in the organic phosphonate dieter being less than about 10 weight percent at 25° C.

15. The process as set forth in claim 14 wherein the liquid SO₂ absorption solvent comprises dibutyl butyl phosphonate.

16. The process as set forth in claim 1 wherein the liquid SO₂ absorption solvent comprises tetra ethylene glycol diethyl ether.

17. The process as set forth in claim 16 wherein the liquid SO₂ absorption solvent comprises more than 50% by weight tetra ethylene glycol diethyl ether.



18. The process as set forth in claim 1 wherein the process further comprises contacting the conversion gas with a solution comprising sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or ileum and an SO_3 -depleted gas comprising SO_2 .

19. The process as set forth in claim 18 wherein the source gas comprises at least a portion of the SO_3 -depleted gas exiting the SO_3 absorption zone such that SO_2 from the SO_3 -depleted gas is recovered in the SO_2 absorption zone for ultimate conversion to sulfuric acid and/or ileum.

20. The process as set forth in claim 1 wherein the partial conversion gas is not contacted with a solution comprising sulfuric acid in an SO_3 absorption zone while passing through the remainder of the series of catalyst beds.

21. A process for making SO_3 from a source gas comprising SO_2 , the process comprising:

5 contacting the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent;

 stripping SO_2 from the SO_2 -enriched solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas having an SO_2 gas strength greater than the SO_2 gas strength of the source gas;

10 forming a converter feed by combining a first portion of the SO_2 -enriched stripper gas with an oxygen source, the first portion of the SO_2 -enriched stripper gas comprising at least about 30% of the SO_2 in the SO_2 -enriched stripper gas;

15 forming a partial conversion gas comprising SO_3 and residual SO_2 by passing the converter feed gas through a first catalyst bed of a catalytic converter comprising at least 2 catalyst beds in series, each catalyst bed containing an oxidation catalyst effective for oxidizing SO_2 to SO_3 , the first catalyst bed being upstream of the remaining catalyst beds in the series with respect to the direction of gas flow through the catalytic converter; and

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20 forming a conversion gas comprising SO_3 and residual SO_2 by passing the partial conversion gas through the remainder of the series of catalyst beds to oxidize SO_2 in the partial conversion gas to SO_3 , the SO_2 concentration in the partial conversion gas being fortified by introducing a second portion of the SO_2 -enriched stripper gas into the partial conversion gas downstream of the first catalyst bed, the fortified partial conversion passing through at least one remaining catalyst bed in the series to oxidize SO_2 in the fortified partial conversion gas to SO_3 .

22. The process as set forth in claim 21 wherein the oxygen source is dry.

23. The process as set forth in claim 21 wherein the converter feed gas comprises at least about 40% of the SO_2 in the SO_2 -enriched stripper gas.

24. The process as set forth in claim 21 wherein the converter feed gas comprises at least about 50% of the SO_2 in the SO_2 -enriched stripper gas.

25. The process as set forth in claim 21 wherein the process further comprises contacting the conversion gas with a solution comprising sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or ileum and an SO_3 -depleted gas comprising SO_2 .

26. The process as set forth in claim 25 wherein the source gas comprises at least a portion of the SO_3 -depleted gas exiting the SO_3 absorption zone such that SO_2 from the SO_3 -depleted gas is recovered in the SO_2 absorption zone for ultimate conversion to sulfuric acid and/or ileum.

27. The process as set forth in claim 21 wherein the partial conversion gas is not contacted with a solution comprising sulfuric acid in an SO_3 absorption zone while passing through the remainder of the series of catalyst beds.

28. A process for making SO_3 from a source gas comprising SO_2 , the process comprising:

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contacting the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent;

stripping SO_2 from the SO_2 -enriched solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas having an SO_2 gas strength greater than the SO_2 gas strength of the source gas;

forming a converter feed by combining a first portion of the SO_2 -enriched stripper gas with an oxygen source;

forming a partial conversion gas comprising SO_3 and residual SO_2 by passing the converter feed gas through a first catalyst bed of a catalytic converter comprising at least 2 catalyst beds in series, each catalyst bed containing an oxidation catalyst effective for oxidizing SO_2 to SO_3 , the first catalyst bed being upstream of the remaining catalyst beds in the series with respect to the direction of gas flow through the catalytic converter; and

forming a conversion gas comprising SO_3 and residual SO_2 by passing the partial conversion gas through the remainder of the series of catalyst beds to oxidize SO_2 in the partial conversion gas to SO_3 , the SO_2 concentration in the partial conversion gas being fortified by introducing a second portion of the SO_2 -enriched stripper gas into the partial conversion gas downstream of the first catalyst bed, the fortified partial conversion passing through at least one remaining catalyst bed in the series to oxidize SO_2 in the fortified partial conversion gas to SO_3 , molar ratio of O_2 to SO_2 in the converter feed gas entering the first catalyst bed and in the partial conversion gas entering each of the remainder of the series of catalyst beds being greater than about 0.2:1.

29. The process as set forth in claim 28 wherein the oxygen source is dry.

30. The process as set forth in claim 28 wherein the molar ratio of O_2 to SO_2 in the converter feed gas entering the first catalyst bed and in the partial conversion gas entering each of the remainder of the series of catalyst beds is at least about 0.5:1.

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31. The process as set forth in claim 28 wherein the molar ratio of O_2 to SO_2 in the converter feed gas entering the first catalyst bed and in the partial conversion gas entering each of the remainder of the series of catalyst beds is at least about 0.7:1.

32. The process as set forth in claim 28 wherein the molar ratio of O_2 to SO_2 in the converter feed gas entering the first catalyst bed and in the partial conversion gas entering each of the remainder of the series of catalyst beds is from about 0.7:1 to about 1.4:1.

33. The process as set forth in claim 28 wherein the molar ratio of O_2 to SO_2 in the converter feed gas entering the first catalyst bed and in the partial conversion gas entering each of the remainder of the series of catalyst beds is from about 0.9:1 to about 1.2:1..

34. The process as set forth in claim 28 wherein the process further comprises contacting the conversion gas with a solution comprising sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or ileum and an SO_3 -depleted gas comprising SO_2 .

35. The process as set forth in claim 34 wherein the source gas comprises at least a portion of the SO_3 -depleted gas exiting the SO_3 absorption zone such that SO_2 from the SO_3 -depleted gas is recovered in the SO_2 absorption zone for ultimate conversion to sulfuric acid and/or ileum.

36. The process as set forth in claim 28 wherein the partial conversion gas is not contacted with a solution comprising sulfuric acid in an SO_3 absorption zone while passing through the remainder of the series of catalyst beds.

37. A process for making SO_3 from a source gas comprising SO_2 , the process comprising:

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contacting the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent;

stripping SO_2 from the SO_2 -enriched solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas;

forming a converter feed gas, the converter feed gas comprising a first portion of the SO_2 -enriched stripper gas;

dividing the converter feed gas into a first portion and a second portion;

passing the first portion of the converter feed gas through a catalyst bed of a catalytic converter and passing the second portion of the converter feed gas through a different catalyst bed of the catalytic converter in parallel with the catalyst bed through which the first portion of the converter feed gas is passed, each catalyst bed containing an oxidation catalyst effective for oxidizing SO_2 to SO_3 , thereby forming a first partial conversion gas and a second partial conversion gas, each partial conversion gas comprising SO_3 and residual SO_2 ;

combining a first portion of the remainder of the SO_2 -enriched stripper gas with the first partial conversion gas to fortify the SO_2 concentration in the first partial conversion gas;

combining a second portion of the remainder of the SO_2 -enriched stripper gas with the second partial conversion gas to fortify the SO_2 concentration in the second partial conversion gas; and

passing the fortified first partial conversion gas and the fortified second partial conversion gas through at least one further catalyst bed of the catalytic converter containing an oxidation catalyst effective for oxidizing SO_2 to SO_3 , thereby oxidizing additional SO_2 to SO_3 and forming a conversion gas comprising SO_3 and residual SO_2 .

38. The process as set forth in claim 37 wherein the converter feed gas is formed by combining the first portion of the SO_2 -enriched stripper gas with an oxygen source.

39. The process as set forth in claim 38 wherein the oxygen source is dry.





40. The process as set forth in claim 37 wherein the fortified first partial conversion gas and the fortified second partial conversion gas are passed through only one further catalyst bed to form the conversion gas.

41. The process as set forth in claim 37 wherein the fortified first partial conversion gas is passed through one additional catalyst bed, while the fortified second partial conversion gas is passed through a separate additional catalyst bed which is parallel to the additional catalyst bed through which the first fortified partial
5 conversion gas is passed.

42. The process as set forth in claim 37 wherein the process further comprises contacting the conversion gas with a solution comprising sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or ileum and an SO_3 -depleted gas comprising SO_2 .

43. The process as set forth in claim 42 wherein the source gas comprises at least a portion of the SO_3 -depleted gas exiting the SO_3 absorption zone such that SO_2 in the SO_3 -depleted gas is recovered in the SO_2 absorption zone for ultimate conversion to sulfuric acid and/or ileum.

44. A process for making sulfuric acid and/or ileum from a source gas comprising SO_2 , the process comprising:

5 contacting at least a portion of the source gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the portion of the source gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched solvent;

stripping SO_2 from the SO_2 -enriched solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas having an SO_2 gas strength greater than the SO_2 gas strength of the source gas;

10 forming a converter feed gas by combining the SO_2 -enriched stripper gas with an oxygen source;





forming a conversion gas comprising SO_3 and residual SO_2 by passing the converter feed gas through a plurality of catalyst beds in series, each catalyst bed comprising an oxidation catalyst effective for oxidizing SO_2 to SO_3 ;

- 15 combining the conversion gas with water vapor to form an acid product gas comprising: (a) sulfuric acid formed by a gas phase reaction between SO_3 from the conversion gas and water vapor, thereby generating the heat of formation of sulfuric acid in the gas phase; (b) SO_3 ; and (c) SO_2 ;

- 20 recovering heat energy from the gas phase heat of formation of sulfuric acid by transfer of heat from the acid product gas to steam or feed water in an indirect heat exchanger; and

contacting the cooled acid product gas with liquid sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or oleum and an SO_3 -depleted gas comprising SO_2 .

45. The process as set forth in claim 44 wherein at least a portion of the SO_3 -depleted gas is recycled back to the plurality of catalyst beds.

46. The process as set forth in claim 44 wherein the indirect heat exchanger comprises an economizer in which heat is transferred from the acid product gas to feed water.

47. The process as set forth in claim 46 wherein the economizer comprises heat transfer wall means between the acid product gas and the feed water, at least a portion of the wall means on the gas side thereof being at a temperature less than the dew point of the acid product gas entering the economizer.

48. The process as set forth in claim 44 wherein the gas passing through the plurality of catalyst beds is not contacted with a solution comprising sulfuric acid in an SO_3 absorption zone.

49. A process for making sulfuric acid and/or oleum from a source gas comprising SO_2 , the process comprising:

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passing a first portion of the source gas through a first catalyst bed of a plurality of catalyst beds in series to form a partial conversion gas comprising SO_3 and residual SO_2 , the plurality of catalyst beds comprising at least 2 catalyst beds, each catalyst bed containing a catalyst effective for oxidizing SO_2 into SO_3 , the first catalyst bed being upstream of the remaining catalyst beds in the series with respect to the direction of gas flow through the catalyst beds;

forming a conversion gas comprising SO_3 and residual SO_2 by passing the partial conversion gas through the remainder of the series of catalyst beds to oxidize SO_2 in the partial conversion gas to SO_3 ;

introducing a second portion of the source gas into the partial conversion gas downstream of the first catalyst bed to fortify the SO_2 concentration in the partial conversion, the fortified partial conversion gas passing through at least one remaining catalyst bed in the series to oxidize SO_2 in the fortified partial conversion gas to SO_3 ;

combining the conversion gas with water vapor to form an acid product gas comprising: (a) sulfuric acid formed by a gas phase reaction between SO_3 from the conversion gas and water vapor, thereby generating the heat of formation of sulfuric acid in the gas phase; (b) SO_3 ; and (c) SO_2 ;

recovering heat energy from the gas phase heat of formation of sulfuric acid by transfer of heat from the acid product gas to steam or feed water in an indirect heat exchanger; and

contacting the cooled acid product gas with liquid sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or oleum and an SO_3 -depleted gas comprising SO_2 .

50. The process as set forth in claim 49 wherein at least a portion of the SO_3 -depleted gas is recycled back to the plurality of catalyst beds.

51. The process as set forth in claim 49 wherein the indirect heat exchanger comprises an economizer in which heat is transferred from the acid product gas to feed water.



52. The process as set forth in claim 51 wherein the economizer comprises heat transfer wall means between the acid product gas and the feed water, at least a portion of the wall means on the gas side thereof being at a temperature less than the dew point of the acid product gas entering the economizer.

53. The process as set forth in claim 49 the gas passing through the plurality of catalyst beds is not contacted with a solution comprising sulfuric acid in an SO_3 absorption zone.

54. In a process for making sulfuric acid and/or ileum from a source gas comprising SO_2 and water vapor, the process comprising:

forming a converter feed gas comprising SO_2 ;

forming a conversion gas comprising SO_3 and residual SO_2 by passing the converter feed gas through a plurality of catalyst beds in series, each catalyst bed comprising an oxidation catalyst effective for oxidizing SO_2 into SO_3 ;

combining the conversion gas with water vapor to form an acid product gas comprising: (a) sulfuric acid formed by a gas phase reaction between SO_3 from the conversion gas and water vapor, thereby generating the heat of formation of sulfuric acid in the gas phase; (b) SO_3 ; and (c) SO_2 ;

recovering heat energy from the gas phase heat of formation of sulfuric acid by transferring heat from the acid product gas to steam or feed water in an indirect heat exchanger; and

contacting the cooled acid product gas with a solution comprising sulfuric acid in an SO_3 absorption zone to form additional sulfuric acid and/or ileum and an SO_3 -depleted gas comprising SO_2 ,

the improvement comprising:

combining at least a portion of the source gas with the conversion gas to form the acid product gas; and

forming the converter feed gas from at least a portion of the SO_3 -depleted gas.

55. The improved process as set forth in claim 54 wherein the converter feed gas is dry.



56. The improved process as set forth in claim 55 wherein the process further comprises:

contacting the SO_3 -depleted gas with a liquid SO_2 absorption solvent in an SO_2 absorption zone to selectively transfer SO_2 from the SO_3 -depleted gas to the SO_2 absorption solvent and form an SO_2 -depleted gas and an SO_2 -enriched absorption solvent; and

stripping SO_2 from the SO_2 -enriched absorption solvent in an SO_2 stripping zone to form an SO_2 -depleted absorption solvent and an SO_2 -enriched stripper gas, wherein the dry converter feed gas is formed from at least a portion of the SO_2 -enriched stripper gas.

57. The improved process as set forth in claim 56 wherein the formation of the dry converter feed gas comprises combining a dry oxygen source with a first portion of the SO_2 -enriched stripper gas.

58. The improved process as set forth in claim 57 wherein a second portion of the SO_2 -enriched stripper gas is introduced into at least one catalyst bed in the series which is downstream of the first catalyst bed in the series through which the dry converter feed gas passes, thereby fortifying the SO_2 concentration in the gas fed to the downstream bed.

59. The improved process as set forth in claim 54 wherein the indirect heat exchanger comprises an economizer in which heat is transferred from the acid product gas to feed water.

60. The improved process as set forth in claim 59 wherein the economizer comprises heat transfer wall means between the acid product gas and the feed water, at least a portion of the wall means on the gas side thereof being at a temperature less than the dew point of the acid product gas entering the economizer.

61. The improved process as set forth in claim 54 wherein the gas passing through the plurality of catalyst beds is not contacted with a solution comprising sulfuric acid in an SO₃ absorption zone.

