

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) IMPROVEMENTS IN OR RELATING TO SULPHUR TRIOXIDE

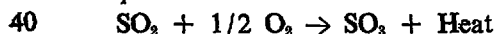
(71) We, THE RALPH M. PARSONS COMPANY, a corporation organised and existing under the laws of the State of Nevada, United States of America, residing at 617 5 West Seventh Street, Los Angeles, California, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in or relating to sulfur trioxide manufacture.

It is an object of the invention to provide a multi-stage oxidation and absorption process wherein gas fed from an intermediate absorption stage into a successive oxidation stage is more efficiently pre-heated to its required initiation temperature.

Sulfur dioxide-containing gas is currently produced in a wide variety of industrial processes. Considerable concern has arisen over the problem of lowering the content of sulfur oxides in waste gas in view of the obvious pollution problems. At present, sulfur dioxide-containing gas is treated both to lower the content of sulfur oxides in stack gas and to provide usable products, such as sulfuric acid, oleum, and liquid sulfur trioxide.

Sulfuric acid and other important products originate by reacting sulfur dioxide-containing gas with excess air while passing the gas at a suitable temperature over oxidation catalysts. At a predetermined minimum temperature, referred to as the initiation temperature, the following reaction takes place:



As is widely known, a final higher conversion can be obtained if the sulfur dioxide-containing gas is freed of sulfur trioxide during the above oxidation reaction. Thus, a series of oxidation stages are utilized with intermediate and final absorption stages in order to accomplish this result. Sulfur trioxide is removed from the gas in the absorption stages, e.g. by washing with sulfuric acid, before the gas is passed to a succeeding oxidation stage. On principle, this technique should yield exceptionally high conversion. In practice, however, difficulties have arisen in obtaining the desired initiation temperature from one oxidation stage to the next without the use of large amounts of heat transfer area.

A conventional multiple-stage oxidation and absorption process, as disclosed in U.S. Patent 3,259,459, utilises heat exchange from the exit gas of the penultimate oxidation stage to pre-heat gas entering the final oxidation stage, with an intermediate absorption stage being provided between the last two oxidation stages. The process of the U.S. Patent 3,259,459 however, in order to transfer heat, requires that the temperature of gas exiting from the penultimate oxidation stage be higher than the temperature of gas entering the final oxidation stage, a requirement which prevents the most efficient operation of the process. That is, high temperatures reduce the effective conversion efficiency, such that maximum or optimum conversion cannot be achieved. In the technique of the U.S. Patent 3,259,459, the heat exchanger surface employed between the final two oxidation stages becomes extremely large when the temperature of the gas leaving the penultimate oxidation stage approaches the temperature of the gas entering the final oxidation stage. When the exit temperature of the penultimate stage is equal to the inlet temperature of the final stage, the surface area of the heat exchanger would have to be infinite.

Conventional multiple oxidation stage processes utilising intermediate absorption between stages for production of sulfuric acid are therefore deficient in that they fail

to allow the desired flexibility of optimum inlet or exit temperatures for each of the oxidation stages. As a result, less than the highest conversion efficiency is obtainable.

5. Elaborate and costly apparatus for correcting this problem in the form of large heat exchange apparatus, generally has been less than satisfactory.

We have found for example that a portion of the heat (derived from exothermic reaction) in gas exiting from the first of at least three successive oxidation stages, there being an intermediate absorption stage between the second and third stages thereof, can be utilised to pre-heat gas passing from such intermediate absorption stage into the third oxidation stage. The temperature of gas introduced into the third oxidation stage can thereby be maintained at any desired temperature and is completely independent of the temperature of gas exiting from the preceding oxidation stage.

The invention provides a process for the production of sulfur trioxide comprising the steps of subjecting sulfur dioxide-containing gas to catalytic oxidation in a plurality of successive oxidation stages with an intermediate absorption stage between two successive oxidation stages, and utilising a portion of the heat (derived from exothermic reaction) in gas exiting from an oxidation stage other than one of the two successive oxidation stages between which the intermediate absorption stage is carried out, to pre-heat gas passed from the intermediate absorption stage into the following oxidation stage.

The invention also provides a process for the production of sulfur trioxide by the catalytic oxidation of sulfur dioxide-containing gas in at least three successive oxidation stages, with an intermediate absorption stage between two successive oxidation stages, comprising the steps of (a) introducing pre-heated sulfur dioxide-containing gas into the first of the three successive oxidation stages, there being an intermediate absorption stage between the second and third stages; (b) utilising a portion of the heat (derived from exothermic reaction) in gas leaving the first oxidation stage to pre-heat gas passing from the intermediate absorption stage into the third oxidation stage; (c) utilising the remaining portion of the heat derived from the exothermic reaction in the gas leaving the first oxidation stage to effect the pre-heating of gas introduced into the first oxidation stage; (d) passing the cooled gas from steps (b) and (c) into the second oxidation stage for further conversion (e) utilising the exit gas from the second oxidation stage to pre-heat gas introduced into the first oxidation stage; (f) passing the cooled gas from step (e) through the intermediate absorption stage (g) passing

the gas from the intermediate absorption stage, after having been pre-heated in accordance with step (b) into the third oxidation stage; (h) utilising the exit gas from the third oxidation stage to pre-heat gas introduced into the third oxidation stage; and (i) passing the cooled exhaust gas from step (h) to a final absorption stage.

It is another object of the invention to provide plant adapted for use in producing sulfur trioxide by a process according to the invention.

The invention also provides sulfur trioxide when produced using a process according to the invention.

The invention also provides sulfuric acid when produced from sulfur trioxide produced using a process according to the invention.

The exit gas from the first oxidation stage is preferably split into two streams, one stream being fed to a heat exchange to pre-heat gas to be fed into the first oxidation stage, the other stream being utilised to pre-heat gas passing from the intermediate absorption stage to the third oxidation stage. Alternatively for example, the exit gas from the first oxidation stage can be fed into a single heat exchange utilised for the combined pre-heating of the two gas streams to be fed into the first and third oxidation stages respectively.

We believe that the improved process of this invention is particularly advantageous for use in a multiple catalytic process having three oxidation stages with an intermediate absorption stage between the second and third stage oxidation stages. For example, in such system, the exit gas from the first oxidation stage is split into two streams and employed as described above; additional pre-heating of the gas to be fed into the first oxidation stage is obtained by heat exchange with exit gas from the second oxidation stage; the two streams split from the exit gas of the first oxidation stage, after heat exchange, are then fed into the second oxidation stage, which preferably has two or more catalyst beds, with intermediate cooling between beds; the exit gas from the second oxidation stage, after exchanging heat with the gas fed to the first oxidation stage, is then fed into the intermediate absorption apparatus; the cooled gas emerging from the absorption apparatus is first preheated in a heat exchanger using exhaust gas from the final oxidation stage and then preheated to the desired initiation temperature in a heat exchanger utilising a portion of the stream of the exit gas emanating from the first oxidation stage, as noted; the exit gas from the final oxidation stage is then cooled in the above-mentioned heat exchanger and fed to a final absorption stage.

Sulfur dioxide-containing gas can be produced by a variety of reactions, e.g. by the oxidation of hydrogen sulfide or hydrocarbon mercaptans, or by metallurgical smelting. It appears that roasting gas and other sulfur dioxide-containing gas having a sulfur dioxide content of less than 9% by volume, and an oxygen-to-sulfur dioxide molar ratio of about 1.0, can be most efficiently treated in accordance with the improved process of this invention. High content sulfur dioxide gas can be purified, diluted, dried, and preheated prior to being fed into the conversion system. High strength purified sulfur dioxide gas is usually diluted with air to provide the required oxygen-to-sulfur dioxide ratio. The sulfur dioxide-containing gas is preferably fed into the conversion system, prior to the pre-heating operations, at a temperature of about 150°F.

We believe that it is a significant advantage of this process that optimum additional catalysis can be carried out in the oxidation stage immediately preceding the intermediate absorption stage, and excellent results can be obtained with only minor modification of conventional multiple catalysts systems and at minimum original and operational cost. As a result, sulfuric acid, oleum, or liquid sulfur trioxide can be manufactured under significantly improved economic conditions. It appears that conversion efficiencies in excess of 99.8 percent are possible.

We believe that the improved process of this invention is unique in that it provides a surprisingly simple and yet highly economical means for maintaining each of the gaseous streams, introduced into successive oxidation stages, at its required initiation temperature without excessive heat transfer area, and being thermally independent of the exit temperatures of a previous catalyst bed. In the process disclosed in U.S. Patent 3,259,459, discussed above, it is evident that the temperature of gas exiting from the second oxidation stage must be higher than the temperature of gas introduced into the third oxidation stage, if any heat exchange is to occur. Thus, the temperature of exit gas from the second oxidation stage must be at a higher temperature than the initiation temperature of gas passed into the final oxidation stage. In the improved process of this invention, however, the exit gas from the second oxidation stage can be at a higher temperature, an equal temperature, or a lower temperature than the gas fed into the final oxidation stage. This allows optimum conversion and complete flexibility.

There now follows a description to be read with reference to the accompanying drawing of an embodiment of the invention. This description, which is illustrative of

both plant and process aspects of the invention, is given by way of example of the invention only and not by way of limitation thereof.

The drawing is a flow diagram of a multiple stage oxidation and absorption plant embodying the invention.

Referring to the drawing, sulfur-dioxide containing gas, which is previously purified, diluted and dried to form in-feed gas having an oxygen-to-sulfur dioxide molar ratio of about 1.0 and a sulfur dioxide content of less than 9% by volume, is introduced into the conversion system at a temperature of between 120°F. and 180°F. with 150°F. being a preferred in-feed temperature. The sulfur dioxide containing gas is pre-heated to a temperature within a range of from 790°F. to 840°F. in heat exchangers 1 and 2 using the exothermic reaction heat from oxidation stage 4 and a portion of gas from stage 3. The gas is preferably fed into a catalytic oxidation stage 3 at a temperature of about 820°F. Only a portion of the exit gas from the first oxidation stage 3, is used in pre-heating the in-feed gas in heat exchanger 2. That is, the gas issuing from the first stage 3, which can be at a temperature of approximately 1130°F., is split into two streams, only one of which is employed in heat exchanger 2. The second gas stream is passed through a heat exchanger 5, utilized for pre-heating gas to be fed into the final oxidation stage 9. The two gas streams from 2 and 5 are then combined and fed into multipass catalyst bed oxidation stage 4 for further conversion of sulfur dioxide to sulfur trioxide. Intermediate cooling of gas in the multiple catalyst bed oxidation stage 4 can be accomplished using a heat exchanger, economizer, or boiler 12, provided between two or more of the oxidation stages. Also, cooling could be provided at this point by dilution with cold dried gas or air.

An intermediate absorption stage 6 is provided between oxidation stages 4 and 9. Exit gas from converter 4, typically at a temperature of about 850°F., is cooled in heat exchanger 1, where it gives heat derived from exothermic reaction to pre-heat incoming gas, and is then passed to absorption apparatus 6. Acid entrained in the gas leaving the absorption apparatus 6 is removed by a suitable medium 7 and the clarified gas is pre-heated before being fed to the final oxidation stage 9. The pre-heating of the gas from absorption stage 6 can be accomplished using two heat exchangers: the first being heat exchanger 8 using the heat content of exit gases from the final oxidation stage 9, and the second being heat exchanger 5 using a portion of the heat content of gas exiting from the first oxidation stage 3. In such manner, gas leaving the intermediate absorption stage 6,

which is typically at a temperature of about 185°F., can be easily pre-heated with minimum heat transfer surface to the final initiation temperature required.

- 5 In the process of this invention, the temperature of gas leaving the penultimate oxidation stage 4 need not be greater than the initiation temperature required in the final oxidation stage 9. Gas leaving oxidation stage 4 can be at a higher temperature, an equal temperature, or a lower temperature in relation to the final initiation temperature of the gas passing to 9. The initiation temperature required for each of the oxidation stages can therefore be easily obtained with only minor alteration of existing processing apparatus. The significantly improved flexibility of available temperatures afforded by means of the process of this invention thus makes possible high conversion efficiencies.

It is noted that exit gas from the first oxidation stage 3 need not be split into two streams for effecting the heat exchange operation of this invention. For example, heat exchangers 2 and 5 can be incorporated into a single heat exchanger, with exit gas from oxidation stage 3 flowing into and out of the heating exchanger in a single stream. It is only that a portion of the exothermic reaction heat from the first oxidation stage 3 be utilised in pre-heating gas introduced into oxidation stage 9, following the intermediate absorption stage 6.

- 35 After final catalysis in oxidation stage 9, the converter gas is passed through heat exchanger 8 and to a second absorp-tion tower 10 for final absorption. Gas exiting from such final absorption stage is demisted in a conventional demisting medium 11, to reduce any entrained acid mist, and vented to the atmosphere.

Conventional oxidation apparatus, such as that employing vanadium pentoxide catalyst beds, can be used in accordance with the improved process of this invention. Similarly, presently available absorption and heat exchange equipment, as well as any other necessary units, can be utilised.

- 50 It will be noted that although item 4 comprises two catalyst beds with cooling at 12 of the gas passing between the catalyst beds, nevertheless item 4 is regarded herein as a single oxidation stage, since in the passage of the gas between the catalyst beds there is no interaction by heat exchange, intermediate absorption or otherwise of the gas with either the SO₂-containing gas itself or with the absorption liquor. References herein to "oxidation stages" are to be construed accordingly.

WHAT WE CLAIM IS:—

1. A process for the production of sulfur trioxide comprising the steps of subjecting 65 sulfur dioxide-containing gas to catalytic

oxidation in a plurality of successive oxidation stages with an intermediate absorption stage between two successive oxidation stages, and utilising a portion of the heat (derived from exothermic reaction) in gas exiting from an oxidation stage other than one of the two successive oxidation stages between which the intermediate absorption stage is carried out, to pre-heat gas passed from the intermediate absorption stage into the following oxidation stage.

2. A process according to claim 1 wherein the gas passed from the intermediate absorption stage to the following oxidation stage is pre-heated in a heat exchanger utilising a stream of part only of the exit gas from the oxidation stage other than one of those between which the intermediate absorption stage is carried out.

3. A process according to claim 1, wherein three only oxidation stages are employed the sulfur dioxide-containing gas passing successively through first, second and third oxidation stages and the intermediate absorption stage being provided between the second and third oxidation stages and wherein exit gas from the first oxidation stage is split into two streams, one stream being used for pre-heating gas fed to the first oxidation stage and the other stream being used for pre-heating gas passed from the intermediate absorption stage, into the third oxidation stage.

4. A process according to claim 1, wherein three only oxidation stages are employed the sulfur dioxide-containing gas being passed successively through first, second and third oxidation stages and wherein the exit gas from the first oxidation stage is passed into a single heat exchanger utilised for pre-heating two separate gas streams passing respectively into the first and third oxidation stages, the intermediate absorption stage being provided between the second and third oxidation stages.

5. A process according to claim 1 or claim 2 wherein the sulfur dioxide-containing gas is pre-heated before introduction into its first oxidation stage by means of exit gas from said first oxidation stage and the oxidation stage preceding the intermediate absorption stage, the temperature of the gas prior to said pre-heating being between 120°F and 180°F.

6. A process according to any one of the preceding claims wherein the molar oxygen-to-sulfur dioxide ratio of the sulfur dioxide ratio of the sulfur dioxide-containing gas introduced into the process is about 1.0.

7. A process according to any one of the preceding claims wherein the sulfur dioxide content of the sulfur dioxide-containing gas introduced into the process is less than 9 per cent by volume.

8. A process according to any one of 130



which is typically at a temperature of about 185°F., can be easily pre-heated with minimum heat transfer surface to the final initiation temperature required.

5 In the process of this invention, the temperature of gas leaving the penultimate oxidation stage 4 need not be greater than the initiation temperature required in the final oxidation stage 9. Gas leaving oxidation stage 4 can be at a higher temperature, an equal temperature, or a lower temperature in relation to the final initiation temperature of the gas passing to 9. The initiation temperature required for each of the oxidation stages can therefore be easily obtained with only minor alteration of existing processing apparatus. The significantly improved flexibility of available temperatures afforded by means of the process of this invention thus makes possible high conversion efficiencies.

It is noted that exit gas from the first oxidation stage 3 need not be split into two streams for effecting the heat exchange operation of this invention. For example, heat exchangers 2 and 5 can be incorporated into a single heat exchanger, with exit gas from oxidation stage 3 flowing into and out of the heating exchanger in a single stream. It is only that a portion of the exothermic reaction heat from the first oxidation stage 3 be utilised in pre-heating gas introduced into oxidation stage 9, following the intermediate absorption stage 6.

After final catalysis in oxidation stage 9, the converter gas is passed through heat exchanger 8 and to a second absorp-tion tower 10 for final absorption. Gas exiting from such final absorption stage is demisted in a conventional demisting medium 11, to reduce any entrained acid mist, and vented to the atmosphere.

Conventional oxidation apparatus, such as that employing vanadium pentoxide catalyst beds, can be used in accordance with the improved process of this invention. Similarly, presently available absorption and heat exchange equipment, as well as any other necessary units, can be utilised.

It will be noted that although item 4 comprises two catalyst beds with cooling at 12 of the gas passing between the catalyst beds, nevertheless item 4 is regarded herein as a single oxidation stage, since in the passage of the gas between the catalyst beds there is no interaction by heat exchange, intermediate absorption or otherwise of the gas with either the SO₂-containing gas itself or with the absorption liquor. References herein to "oxidation stages" are to be construed accordingly.

WHAT WE CLAIM IS:—

1. A process for the production of sulfur trioxide comprising the steps of subjecting sulfur dioxide-containing gas to catalytic

oxidation in a plurality of successive oxidation stages with an intermediate absorption stage between two successive oxidation stages, and utilising a portion of the heat (derived from exothermic reaction) in gas exiting from an oxidation stage other than one of the two successive oxidation stages between which the intermediate absorption stage is carried out, to pre-heat gas passed from the intermediate absorption stage into the following oxidation stage.

2. A process according to claim 1 wherein the gas passed from the intermediate absorption stage to the following oxidation stage is pre-heated in a heat exchanger utilising a stream of part only of the exit gas from the oxidation stage other than one of those between which the intermediate absorption stage is carried out.

3. A process according to claim 1, wherein three only oxidation stages are employed the sulfur dioxide-containing gas passing successively through first, second and third oxidation stages and the intermediate absorption stage being provided between the second and third oxidation stages and wherein exit gas from the first oxidation stage is split into two streams, one stream being used for pre-heating gas fed to the first oxidation stage and the other stream being used for pre-heating gas passed from the intermediate absorption stage, into the third oxidation stage.

4. A process according to claim 1, wherein three only oxidation stages are employed the sulfur dioxide-containing gas being passed successively through first, second and third oxidation stages and wherein the exit gas from the first oxidation stage is passed into a single heat exchanger utilised for pre-heating two separate gas streams passing respectively into the first and third oxidation stages, the intermediate absorption stage being provided between the second and third oxidation stages.

5. A process according to claim 1 or claim 2 wherein the sulfur dioxide-containing gas is pre-heated before introduction into its first oxidation stage by means of exit gas from said first oxidation stage and the oxidation stage preceding the intermediate absorption stage, the temperature of the gas prior to said pre-heating being between 120°F and 180°F.

6. A process according to any one of the preceding claims wherein the molar oxygen-to-sulfur dioxide ratio of the sulfur dioxide ratio of the sulfur dioxide-containing gas introduced into the process is about 1.0.

7. A process according to any one of the preceding claims wherein the sulfur dioxide content of the sulfur dioxide-containing gas introduced into the process is less than 9 per cent by volume.

8. A process according to any one of



(12)

the preceding claims wherein gas exiting from the oxidation stage preceding the intermediate absorption stage is at a lower temperature than that entering the following oxidation stage.

9. A process according to any one of claims 1 to 7 wherein gas exiting from the oxidation stage preceding the intermediate absorption stage is at a temperature substantially equal to that entering the following oxidation stage.

10. A process according to any one of claims 1 to 7, wherein gas exiting from the oxidation stage preceding the intermediate absorption stage is at a higher temperature than that entering the following oxidation stage.

11. A process for the production of sulfur trioxide by the catalytic oxidation of sulfur dioxide-containing gas in at least three successive oxidation stages, with an intermediate absorption stage between two successive oxidation stages, comprising the steps of (a) introducing preheated sulfur dioxide-containing gas into the first of the three successive oxidation stages, there being an intermediate absorption stage between the second and third stages; (b) utilising a portion of the heat (derived from exothermic reaction) in gas leaving the first oxidation stage to preheat gas passing from the intermediate absorption stage into the third oxidation stage; (c) utilising the remaining portion of the heat derived from exothermic reaction in the gas leaving the first oxidation stage to effect the preheating of gas introduced into the first oxidation stage; (d) passing the cooled gas from steps (b) and (c) into the second oxidation stage for further conversion; (e) utilising the exit gas from the second oxidation stage to preheat gas introduced into the first oxidation stage (f) passing the cooled gas from step (e) through the intermediate absorption stage (g) passing the gas from the intermediate absorption stage, after having been pre-

heated in accordance with step (b) into the third oxidation stage; (h) utilising the exit gas from the third oxidation stage to preheat gas introduced into the third oxidation stage; and (i) passing the cooled exhaust gas from step (h) to a final absorption stage.

12. A process for the production of sulfur trioxide substantially as hereinbefore described with reference to the accompanying drawing.

13. Plant adapted for use in producing sulfur trioxide by a process according to claim 1 comprising (a) a plurality of successive catalytic oxidation stages adapted to subject sulfur dioxide-containing gas to catalytic oxidation (b) an intermediate absorption stage between two successive oxidation stages, (c) heat exchange means, and (d) means interconnecting the oxidation stages, the intermediate absorption stage and the heat exchange means so that in the operation of the plant a portion of the heat (derived from exothermic reaction) in gas exiting from an oxidation stage other than one of the two successive oxidation stages between which the intermediate absorption stage is carried out, is utilised to pre-heat gas passed from the intermediate absorption stage into the following oxidation stage.

14. Plant adapted for use in producing sulfur trioxide constructed, arranged and adapted to operate substantially as hereinbefore described with reference to the accompanying drawing.

15. Sulfur trioxide when produced using a process according to claim 1.

16. Sulfuric acid when produced from sulfur trioxide produced using a process according to claim 1.

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