

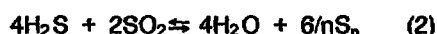
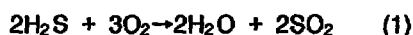
## Description

The present invention relates to a process for recovering sulfur from sulfur-containing gases

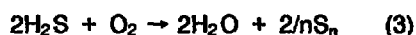
In a number of processes, such as the refining of crude oil, the purification of natural gas and the production of synthesis gas from, for example, fossil fuels, sulfur containing gas, in particular  $H_2S$  containing gas, is released. On account of its high toxicity and its smell, the emission of  $H_2S$  is not permissible.

The best known and most suitable process for recovering sulfur from hydrogen sulfide is the so-called Claus process. In this process hydrogen sulfide is converted by oxidation to a considerable extent into elemental sulfur; the sulfur thus obtained is separated by condensation. The residual gas stream (the so-called Claus residual gas) still contains some  $H_2S$  and  $SO_2$ .

The method of recovering sulfur from sulfur containing gases by the so-called Claus process is based on the following reactions:

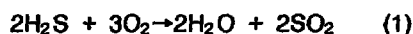


Reactions (1) and (2) result in the main reaction:



A conventional Claus converter - suitable for processing gases having an  $H_2S$  content of between 50 and 100% - comprises a burner with a combustion chamber, the so-called thermal stage, followed by a plurality of reactors - generally two or three - filled with a catalyst. These last stages constitute the so-called catalytic stages.

In the combustion chamber, the incoming gas stream, which is rich in  $H_2S$ , is combusted with an amount of air at a temperature of ca. 1200°C. This stoichiometric amount of air is adjusted so that one third of the  $H_2S$  is fully combusted to form  $SO_2$  in accordance with the following reaction



After this partial oxidation of  $H_2S$  the non-oxidized part of the  $H_2S$  (i.e. basically two-thirds of the amount offered) and the  $SO_2$  formed react further as to a considerable portion, in accordance with the Claus reaction:

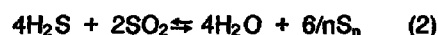


Thus, in the thermal stage, approximately 60% of the  $H_2S$  is converted into elemental sulfur.

The gases coming from the combustion cham-

ber are cooled to about 160°C in a sulfur condenser, in which the sulfur formed is condensed, which subsequently flows into a sulfur pit through a siphon.

The non-condensed gases, in which the molar ratio of  $H_2S:SO_2$  is unchanged and so still 2:1, are subsequently heated to about 250°C, and passed through a first catalytic reactor in which the equilibrium



is again established.

The gases coming from this catalytic reactor are subsequently cooled again in a sulfur condenser, in which the liquid sulfur formed is recovered and the remaining gases, after being re-heated, are passed to a second catalytic reactor.

When the gaseous feedstock contains  $H_2S$  concentrations of between about 15 and 50%, the above described 'straight-through' process is not used, but instead a variant thereof, the so-called 'split-flow' process is used. In the latter process one-third of the total amount of feedstock is passed to the thermal stage and combusted completely to  $SO_2$  therein. Two-thirds of the feedstock is passed direct to the first catalytic reactor, by-passing the thermal stage. When the feedstock contains  $H_2S$  concentrations of between 0 and 15% the Claus process can no longer be used. The process then used is, for example, the so-called Recycle Selectox process, in which the feedstock is passed with an adjusted amount of air into an oxidation reactor, the so-called oxidation stage. The reactor contains a catalyst which promotes the oxidation of  $H_2S$  to  $SO_2$ , and the amount of oxidation air is adjusted so that an  $H_2S:SO_2$  ratio of 2:1 is established, whereafter the Claus reaction proceeds. The gas from the oxidation reactor is cooled in a sulfur condenser, in which the sulfur formed is condensed and discharged.

To dissipate the reaction heat generated in the oxidation reactor, a portion of the gas stream coming from the sulfur condenser is re-supplied to the oxidation reactor.

It is clear that in the Recycle Selectox process, the oxidation stage, which is catalytic and does not lead to high temperatures, is equivalent to the thermal stage in the Claus process.

In the following, both stages are referred to as oxidation stages.

Depending on the number of catalytic stages, the sulfur recovery percentage in a conventional Claus converter is 92-97%.

By known processes, the  $H_2S$  present in the residual gas from the Claus reaction is converted, by combustion or some other form of oxidation, into  $SO_2$ , whereafter this  $SO_2$  is emitted to the at-

mosphere. This has been permissible for low concentrations or small amounts of emitted SO<sub>2</sub> for a long time. Although SO<sub>2</sub> is much less harmful and dangerous than H<sub>2</sub>S, however, this substance is also so harmful that its emission is also limited by ever stricter environmental legislation.

As has been observed, in the Claus process as described above, in view of the equilibrium reaction which occurs, the H<sub>2</sub>S:SO<sub>2</sub> ratio plays an important role. In order to obtain an optimum conversion to sulfur, this ratio should be 2:1. Generally speaking, this ratio is controlled by means of a so-called H<sub>2</sub>S/SO<sub>2</sub> residual gas analyzer. This analyzer measures the H<sub>2</sub>S and SO<sub>2</sub> concentrations in the residual gas. A controller then maintains the ratio of 2:1 constant on the basis of the equation

$$[\text{H}_2\text{S}] - 2[\text{SO}_2] = 0,$$

by varying the amount of combustion air, depending on the fluctuations in the gas composition and the resulting deviation in the above equation. Such a control of the process, however, is highly sensitive to these fluctuations.

Furthermore, the sulfur recovery efficiency (calculated on the amount of H<sub>2</sub>S supplied) is no higher than 97%, and so the gas flowing from the last catalytic stage - the residual gas - still contains substantial amounts of H<sub>2</sub>S and SO<sub>2</sub>, determined by the Claus equilibrium, and this in a molar ratio of 2:1.

The amount of H<sub>2</sub>S present in the residual gas can be separated by absorption in a liquid.

The presence of SO<sub>2</sub> in the residual gas, however, is a disturbing factor during the further processing thereof and must therefore be removed prior to such further processing. This removal and hence the after-treatment of the gas is complicated.

The great disadvantage of the presence of SO<sub>2</sub> is that this gas reacts with conventional liquid absorbents to form undesirable products. To prevent undesirable reactions of the SO<sub>2</sub>, therefore, the SO<sub>2</sub> is catalytically reduced with hydrogen to form H<sub>2</sub>S over an Al<sub>2</sub>O<sub>3</sub> supported cobalt molybdenum catalyst in accordance with the so-called SCOT process. The total amount of H<sub>2</sub>S is subsequently separated by liquid absorption in the usual manner.

In accordance with another method, for example, the BSR Selectox process, after reduction of the SO<sub>2</sub> in residual gas to H<sub>2</sub>S and after condensation of the water vapour, the gas is passed into an oxidation reactor, as in the Recycle Selectox process. The oxidation air is adjusted so that an H<sub>2</sub>S:SO<sub>2</sub> ratio of 2:1 is adjusted, whereafter the Claus reaction proceeds. Both in the SCOT process and in the BSR Selectox process, the removal of SO<sub>2</sub> from the residual gas is a relatively expensive operation.

The above-described after-treatment of the gases, carried out by means of a so-called Tail Gas Treater, which involves an investment of another 50-100% of the cost of the preceding Claus converter, can result in an increase of the sulfur recovery efficiency of up to 98-99.8%.

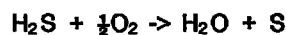
In NL-A-69 01632, it is proposed that the ratio of hydrogen sulfide to sulfur dioxide in the above reaction (1) be adjusted to between 2.5:1 to 4.0:1.

In NL-A-76 03622, it is proposed that the above reaction (1) be conducted with an insufficient amount of oxygen, that is to say, with a proportion of oxygen less than required to combust one third of the quantity of H<sub>2</sub>S supplied to the burner. Thus, relative to H<sub>2</sub>S, a substoichiometric amount of SO<sub>2</sub> is formed in reaction (1), so that ultimately, in view of the equilibrium reaction (2), the resulting ratio of H<sub>2</sub>S:SO<sub>2</sub> becomes higher than 2:1.

There is no disclosure in that patent application as regards a ratio of H<sub>2</sub>S:SO<sub>2</sub>, nor is any suggestion given as to how such a ratio must be concretely realized.

Accordingly, the methods as described in the above patent applications have the advantage that the removal of H<sub>2</sub>S from the residual gas is much easier when substantial amounts of SO<sub>2</sub> are contained therein. The methods also have substantial disadvantages, however, namely, that in the presence of sulfur vapour measuring low SO<sub>2</sub> concentrations in the residual gas is very difficult. Indeed, controlling the process on the basis of such measurements has turned out to be virtually unfeasible in practice.

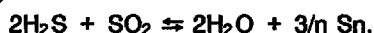
In GB-A 1,151,316, a process is described for desulfurising the residual gases from a catalytic conversion plant for production of sulphur from hydrogen sulphide, according to the equation,



which plant consists of a combustion chamber, one or more catalytic stages and one or more cooling stages to cool the reaction products and to condense the elementary sulphur formed, and is operated with a stoichiometric deficiency of oxygen, such that the residual gas produced contains hydrogen sulphide and a minor quantity of sulphur dioxide, in which process, after separation of the elementary sulphur from the residual gas, the residual gas is cooled to a few degrees centigrade above its dew point and is mixed with oxygen or air and supplied to a bed of activated carbon in which the hydrogen sulphide contained in the residual gases is converted by reaction with the oxygen or air into elementary sulphur, the elementary sulphur so formed being deposited in the activated carbon so that the remaining gases are sulphur-free, which activated carbon is subsequently regenerated by

desorbing the sulphur with a hot inert gas or with steam and the gases formed on desorption are supplied to the catalytic conversion plant.

The invention is directed to a process for the recovery of sulphur from a hydrogen sulfide containing gas, which comprises oxidizing hydrogen sulfide with oxygen, and then reacting the product gas of this oxidation further by using at least two catalytic stages, in accordance with the equation:



wherein the  $\text{H}_2\text{S}$  concentration in the gas leaving the last catalytic stage is controlled to have a value ranging between 0.8 and 3% by volume and the  $\text{H}_2\text{S} : \text{SO}_2$  ratio in that gas being larger than 2, by reducing the quantity of combustion or oxidation air passed to the oxidation stage and/or causing a portion of the hydrogen sulfide containing feedstock gas to bypass the oxidation stage and to be added to the gas flowing to a catalytic stage, the said  $\text{H}_2\text{S}$  coming from the last catalytic stage being selectively oxidized to sulphur in a dry oxidation bed, with a catalyst having an oxidation efficiency to sulphur of 80-95% whereby the gaseous sulfur thus formed is condensed after the said dry oxidation reactor and whereby

- with an oxidation efficiency to sulphur of 80-85% of the oxidation catalyst, an  $\text{H}_2\text{S}$  concentration of 0.8-1.7% by volume is selected in the gas coming from the last catalytic stage.
- with an oxidation efficiency to sulphur of 85-90% of the oxidation catalyst, an  $\text{H}_2\text{S}$  concentration of 1.0-2% by volume is selected in the gas coming from the last catalytic stage, and
- with an oxidation efficiency to sulphur of 90-95% of the oxidation catalyst, an  $\text{H}_2\text{S}$  concentration of 1.4-2.4% by volume is selected in the gas coming from the last catalytic stage.

The process according to the invention offers the advantage that no sensitive control of the process is required, because it is only the concentration of the  $\text{H}_2\text{S}$  in the residual gas and not the ratios of  $\text{H}_2\text{S}:\text{SO}_2$  therein which play a role. Claus catalysts are sensitive to sulfation under the influence of traces of oxygen in the reaction gases. In the process according to the present invention, as the Claus reaction proceeds, an ever increasing excess of  $\text{H}_2\text{S}$  is formed in the reaction gases, in particular in the last Claus reactor. This excess of  $\text{H}_2\text{S}$  reduces any sulfate that has been formed, whereby the problem of sulfation of the catalysts is counteracted and a longer service life thereof is obtained.

In the process according to the present inven-

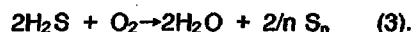
tion, the concentration of the hydrogen sulfide gas in the residual gas can be controlled in several ways. Thus, for example, the signal from an  $\text{H}_2\text{S}$  analyzer in the residual gas can be used to set or adjust the amount of combustion air or oxidation air supplied to the oxidation stage. The signal can also be used to pass, as a function thereof, a - variable - amount of  $\text{H}_2\text{S}$  direct to the first or second catalytic reactor or to both reactors.

Measurements conducted in a Claus plant comprising two catalytic stages and operated using the present invention, indicated that, to provide a proportion of 0.8-3% by volume of  $\text{H}_2\text{S}$  in the residual gas, an amount of air must be supplied that is equivalent to 86-98.5% of the stoichiometric quantity (i.e., relative to the amount of air required to combust one-third of the amount of  $\text{H}_2\text{S}$  supplied to the burner). It will be clear, where reference is made to a quantity of air, what is meant is the amount of gas containing the required amount of oxygen. When the amount of air passed to the Claus burner is not reduced but a portion of the gaseous feedstock is caused to by-pass the oxidation stage, approximately 1.5-14% of the available quantity of  $\text{H}_2\text{S}$  containing gas must be by-passed which is dictated by the reactions which occur.

According to the invention it has further been found that a concentration of  $\text{H}_2\text{S}$  in the residual gas of about 1-3% by volume corresponds to an  $\text{H}_2\text{S}/\text{SO}_2$  ratio therein of about 15-800, while with increasing percentages by volume of  $\text{H}_2\text{S}$  in the residual gas - within the range defined according to the invention - this value rapidly becomes infinitely high, so that only immeasurably small quantities of  $\text{SO}_2$  are present. This offers an additional advantage, because for the further processing of this gas the removal of  $\text{SO}_2$  is unnecessary.

The process according to the invention can be suitably applied for the treatment of gases containing hydrogen sulfide, but also for gases containing both hydrogen sulfide and substantial quantities of ammonia (cf NL-C-176160); in the latter case, the temperature in the combustion chamber should be at least 1250°C.

In the process according to the invention, the hydrogen sulfide gas remaining in the residual gas is oxidized with air in an oxidation stage to form sulfur in accordance with the following reaction:



Surprisingly it was found that, when the concentration of the hydrogen sulfide leaving the last catalytic stage is maintained at a value of between 0.8 and 3% by volume, not only is a sufficiently low  $\text{SO}_2$  concentration obtained in the residual gas, but also, after this selective oxidation, an optimum sulfur recovery percentage of 98.0-99.8 can be

obtained. This oxidation takes place by dry-bed oxidation.

In the dry-bed oxidation, the  $H_2S$  concentration in the residual gas is maintained between 0.8 and 3% by volume, because above 3% by volume of  $H_2S$  the total sulfur recovery percentage is decreased. Commonly, when the  $H_2S$  concentration is higher than 2% by volume, the oxidation bed is cooled or the  $H_2S$  concentration is reduced by dilution of the gas with, for example, a recycling gas stream to prevent that as a result of an increase in temperature from the reaction heat generated, the sulfur formed is oxidized to form sulfur dioxide in the gaseous phase.

In the dry oxidation bed, the oxidation to sulfur can be effected by a known per se method using an oxidation catalyst. One example of an oxidation catalyst and the application thereof is described in US-A-4311683.

The method described therein is the Selectox process (R.H. Hass, M.N. Ingalls, T.A. Trinker, B.G. Goar, R.S. Purgason, 'Process meets sulfur recovery needs', Hydrocarbon Processing, May 1981, pag.104-107). In this process,  $H_2S$  is oxidized to S and  $SO_2$  using a special catalyst. Approximately 80% of the  $H_2S$  supplied is oxidized to elemental sulfur, if water vapour is removed to a substantial extent. Another application of a dry-bed process which is not sensitive to water vapour in the process gas is the absorption of  $H_2S$  in an absorption mass as described, for example, in European patent application 71983.

In accordance with a particular embodiment of the process according to the present invention, the oxidation in a dry bed, is carried out using a catalyst comprising a carrier of which under the reaction conditions applied the surface exposed to the gaseous phase does not exhibit alkaline properties with a catalytically active material applied thereto or formed thereon, the specific area of the catalyst being less than  $20m^2/g$  catalyst, and less than 10% of the total pore volume having a pore radius of between 5 and 500 Å. The catalyst generally contains at least 0.1% by weight, calculated on the total mass of the catalyst, of a material that is catalytically active for the selective oxidation of  $H_2S$  to elemental sulfur. A preferred catalytically active material is a metal oxide, a mixed oxide of a plurality of metals, or a mixture of metal oxides.

The specific area of the catalyst used in accordance with the above particular embodiment of the process according to the invention is preferably no larger than  $10m^2/g$  catalyst. The substantial absence of micropores, too, is of importance for the results to be obtained by this catalyst: preferably, no more than 2% of the total pore volume will be in the form of pores having a radius of between 5 and 500 Å.

A particularly suitable carrier is alpha-alumina, but silica whose specific area satisfies the above requirements, such as hydrothermally sintered silica, can be suitably applied. It is also possible to use non-ceramic materials as carrier material, such as metal mesh, metal mouldings, or packing bodies.

As stated above, the catalytically active material used is preferably a metal oxide, a mixed oxide of a plurality of metals or a mixture of metal oxides. Preferably, however, the catalytically active material used is iron oxide or a mixed oxide of iron and chromium (with a molar ratio of Cr:Fe that is lower than 0.5 and preferably between 0.02 and 0.15).

The active component is preferably present on the carrier in a proportion of more than 1% by weight calculated on the total weight of the catalyst. Best results are obtained with catalysts in which this percentage by weight is between 3 and 10, calculated as the weight of, the metal oxide or mixed oxide of two or more metals, and calculated on the total weight of the catalyst.

In this connection it should be emphasized that this concerns the active material present on the carrier. In fact, by sintering or a different method of preparation, a portion of the active material, in particular the metal oxide, may be encapsulated within the carrier, for example, by the sintering of narrow pores. The difference between this encapsulated or embedded metal oxide and the metal oxide present on the carrier, however, can be readily determined by the so-called temperature-programmed reduction (TPR). Details of this measuring technique are described in N.W. Hurst, S.J. Gentry, A. Jones and B.D.McNicol Catal.Rev.Sci.Eng 24(2), 233-309 (1982). The amount of metal oxide present on the carrier and accessible to gases can thus be determined.

The catalysts preferably used in the particular embodiment of the process according to the present invention can in principle be prepared using known methods of preparing supported catalysts. With regard to such preparation, however, in view of the unusually small specific area and low microporosity of the catalysts, specific measures should be taken, to ensure, in particular, that the porosity is not increased during preparation.

Particular care is required in homogeneously applying the catalytically active material to the carrier material, while in addition it should be ensured that this homogeneity is maintained during and after the drying procedure.

In order to satisfy these requirements, in the preparation of the catalyst, the carrier material with a small specific area is impregnated under dry conditions with a complex solution. This method is known by the name of incipient wetness method.

The complex solution comprises the cations of the active materials complexed in the solution with an organic molecule. Also added to the solution is a quantity of a viscosity increasing compound, such as hydroxyethyl cellulose. By impregnating the carrier material with this complex solution by means of the incipient wetness method, a low-area catalyst is obtained, to which the active material is applied highly homogeneously, and whose microporosity has not increased as compared with the starting carrier material.

During the drying procedure, the temperature must be increased very slowly to maintain homogeneity. Finally a sintering treatment is carried out with the catalyst, whereby micropores are sealed. Electron micrographs, porosimetric measurements, B.E.T. measurements and reactor experiments show whether the catalysts satisfy the requirements.

The use of the catalyst described above for the oxidation in a dry bed of the hydrogen sulfide containing residual gases obtained using the process according to the present invention has the important, in particular economic advantage that such a catalyst is practically insensitive to the presence of water vapour in the residual gas, so that the removal of sulfur and water vapour from this residual gas is unnecessary.

It has been found that - with a view to a maximum sulfur recovery percentage - the choice of the optimum volume percent of  $H_2S$  in the residual gas is dependent on the extent of the efficiency of the last oxidation from  $H_2S$  to sulfur in the dry oxidation bed. When the efficiency to sulfur of the catalyst used therein is 80-85%, preferably a volume percentage of  $H_2S$  in the residual gas of 0.8-1.7 is selected. When the efficiency is 85-90%, preferably a percentage of 1.0-2 is selected, and when the efficiency is 90-95%, the volume percentage of  $H_2S$  in the residual gas is preferably adjusted between 1.4 and 2.4.

The control of the oxidation air to the selective oxidation is not critical and hence simple.

The process according to the invention can be carried out in an existing Claus plant and requires only relatively simple modifications of the existing control of the gas streams. In case a 2-stage Claus plant is used, a selective oxidation reactor will have to be provided in the specific embodiment of the present invention, which in relation to the cost involved in other residual gas processing plants is inexpensive. Thus the application of the process according to the present invention leads to considerable economic advantages.

In case a 3-stage Claus plant is used only the third catalytic reactor needs to be arranged as a selective oxidation reactor. In this case, too therefore, a considerable economic benefit is obtained.

The process according to the present invention will now be described in more detail with reference to the accompanying Figs. 1, 2 and 3.

As shown in Fig. 1, the feedstock gas (= Claus gas) is supplied through line 1 to the Claus burner with combustion chamber 2. The amount of combustion air, controlled by the quantity-proportion regulator 3 and  $H_2S$  analyzer 23, is supplied to Claus burner 2 through line 4. The heat generated during the combustion ( $1200^\circ C$ ) of the Claus gas is dissipated in a boiler heated by spent gases, producing steam that is discharged through line 6.

The Claus reaction takes place in the burner and the combustion chamber. The sulfur formed is condensed in boiler 5 ( $150^\circ C$ ) and discharged through line 7. The gas is passed through line 8 to a heater 9 where it is heated to the desired reaction temperature of  $250^\circ C$  before being supplied through line 10 to the first Claus reactor 11. In reactor 11 the Claus reaction takes place again, whereby sulfur is formed. The gas is discharged through line 12 to the sulfur condenser 13. The condensed sulfur ( $150^\circ C$ ) is discharged through line 14. Thereafter the gas is passed through line 15 to the next reactor stage, which again includes a heater 16, a reactor 17 and a sulfur condenser 18. In this reactor the Claus reaction takes place again. The condensed sulfur ( $150^\circ C$ ) is discharged through line 19. The steam generated in the sulfur condensers is discharged through lines 20 and 21.

The  $H_2S$  concentration in the residual-gas line 22 is controlled by an  $H_2S$  analyzer 23 to a range of from 0.8 to 3% by volume. The  $H_2S$  analyzer controls a control valve in combustion air line 24 or a control valve in the  $H_2S$  line 25. Through 25 a portion of the  $H_2S$  can be passed direct to the first catalytic stage 11, by-passing the thermal stage.

The residual gas is passed through line 22 to the sulfur removing stage 26. This sulfur removing stage is a dry-bed oxidation sulfur removing process. The air required for the oxidation is supplied through line 27. The sulfur formed is discharged through line 28.

The gas is then passed through line 29 to an after-burner 30 before being discharged through chimney 31.

As shown in Fig. 2, a lean Claus feedstock gas is supplied through line 1 to an oxidation reactor 2. An amount of oxidation air controlled by the quantity-ratio regulator 3 and  $H_2S$  analyzer 19 is passed to the oxidation reactor through line 4. In the oxidation reactor a portion of the  $H_2S$  is oxidized over a special catalyst to form  $SO_2$  whereafter the Claus reaction takes place.

To prevent an unduly high temperature from arising within the oxidation reactor, as a result of the reaction heat, a quantity of gas is recycled by means of blower 6 through lines 5 and 7. The gas

from reactor 2 is passed through line 8 to sulfur condenser 9, where the sulfur formed during the reaction is condensed at 150°C and discharged through line 10. The heat generated during the reaction is dissipated in sulfur condenser 9 with generation of steam, which is discharged through line 11. The gas is passed through line 12 to a heater 13, where it is heated, for example, to 220°C before being supplied to the Claus reactor 14. In reactor 14, the Claus reaction takes place again, whereby sulfur is formed. In condenser 15, the sulfur is condensed at 150°C and discharged through line 16, and steam generated is discharged through line 17. The H<sub>2</sub>S concentration in the residual gas line 18 is controlled by an H<sub>2</sub>S analyzer 19 to a range of from 0.8 to 3% by volume. The H<sub>2</sub>S analyzer controls a control valve in the combustion-air line 20, or a control valve in H<sub>2</sub>S line 21.

Through line 21, a portion of the H<sub>2</sub>S can bypass the oxidation stage and pass direct to the catalytic stage 14.

The residual gas is passed through line 18 to the sulfur removing stage 22. The air required for the oxidation is supplied through line 23. The sulfur formed is discharged through line 24. The gas is then passed through line 25 to an after-burner 26 before being discharged through chimney 27.

Fig.3 shows in greater detail the oxidation in a dry bed as indicated more generally in 26 of Fig.1 or 22 of Fig.2. In Figs. 1 and 2 the residual gas is supplied through lines 22 and 18, respectively, in Fig.3, the residual gas is supplied through line 1.

In Fig.3a, after the removal of the sulfur from the residual gas in separator 2, which is discharged through line 3, and the condensation of the water in 4, which is discharged through line 5, the gas is supplied through a heater 6 to a selective oxidation reactor 7. The removal of sulfur and water in 2 and 4 respectively, can take place using a known method, for example, as disclosed in US patent 4526590. In the selective oxidation reactor 7, a catalyst is provided, for example, as described in the French patent publications 8009126, 8105029 or 8301426. The required oxidation air is supplied through line 8.

From the reactor, the gas flows to a sulfur condenser 9. The sulfur condensed is discharged through line 10, and the steam generated through line 11. The gas next flows through line 12 to the after-burner as designated by 30 in Fig.1 and 26 in Fig.2.

As shown in Fig. 3b, the residual gas is supplied through line 1 and heater 2 direct to the selective-oxidation stage, that is to say, without a preceding sulfur and water removing stage. This embodiment can be used when a catalyst is present in the oxidation reactor 4, as described

above, consisting of a non-alkaline ceramic carrier to which at least 0.1% by weight of a catalytically active material, in particular a metal oxide, has been applied, so that the specific area of the catalyst is less than 20 m<sup>2</sup>/g, while less than 10% of the total pore volume has a pore radius of between 5 and 500 Å. The oxidation air required is supplied through line 3. The sulfur condensed in sulfur condenser 5 is discharged through line 6 and the steam generated through line 7. The gas next flows through line 8 to the after-burner designated by 30 in Fig.1 and by 26 in Fig.2.

The invention is illustrated in and by the following examples.

#### Example 1

Using the apparatus as described with reference to Figs.1 and 3a, the Claus reaction is performed in a Claus plant having two catalytic stages. Supplied to the thermal stage are a Claus gas, containing 90% by volume of H<sub>2</sub>S, corresponding to 90 kmol/h, 5% vol.CO<sub>2</sub> and 5% vol.H<sub>2</sub>O and 43.53 kmol/h O<sub>2</sub> (a 'deficit' of 3.3%) as air oxygen. The H<sub>2</sub>S volume percentage in the residual gas after the second catalytic stage is 1.2, and the SO<sub>2</sub> content therein 0.06%. After the removal of sulfur and water and using a dry-bed process for the oxidation of H<sub>2</sub>S with an oxidation efficiency of 80%, a total sulfur recovery percentage of 98.8 is obtained.

#### Example II

Using the apparatus as described with reference to Fig. 1 and 3b, the Claus reaction is performed in a Claus plant having two catalytic stages. Supplied to the thermal stage are a Claus gas containing 90% by volume of H<sub>2</sub>S corresponding to 90 kmol/h, 5% by volume of CO<sub>2</sub> and 5% by volume of H<sub>2</sub>O, and 42.30 kmol/h of O<sub>2</sub> (a 'deficit' of 6.0%) as air oxygen. The H<sub>2</sub>S volume percentage in the residual gas after the second catalytic stage is 2.03, the SO<sub>2</sub> content therein is immeasurably small, and its water content is 35.8% by volume.

The dry-bed oxidation is carried out using a water-insensitive oxidation catalyst, as defined hereinbefore, comprising an alpha-alumina carrier (Fluka, specific area 6.5 m<sup>2</sup>/g) to which 4.5% by weight of Fe<sub>2</sub>O<sub>3</sub> and 0.5% by weight of Cr<sub>2</sub>O<sub>3</sub> have been applied as catalytically active material, which, after pelletization and calcination has a BET area of 6.94m<sup>2</sup>/g, with less than 1% of the total pore volume being constituted by pores having a radius less than 500 Å. Using this catalyst with an oxidation efficiency of 90%, a total sulfur recovery percentage of 99.2 is obtained.

### Example III

Using the plant as described with reference to Fig.1 and 3b, the Claus reaction is carried out in a Claus plant having two catalytic stages.

A Claus gas containing 90% by volume of H<sub>2</sub>S, corresponding to 90 kmol/h, 5% by volume of CO<sub>2</sub> and 5% by volume of H<sub>2</sub>O and 43.53 kmol/h O<sub>2</sub> (a 'deficit' of 3.3%) as air oxygen are supplied to the thermal stage.

The H<sub>2</sub>S volume percentage in the residual gas after the second catalytic stage is 1.22, which corresponds to 3.29 kmol/h, and the SO<sub>2</sub> content therein is 0.06. Using the catalyst described in Example II, the H<sub>2</sub>S in the gas is selectively oxidized to sulfur in the presence of a considerable concentration of water vapour. The H<sub>2</sub>O content is 35.9% by volume, which corresponds to 97 kmol/h. 1.97 kmol/h O<sub>2</sub>, as air oxygen, is supplied to the selective oxidation stage, which comes down to an O<sub>2</sub>:H<sub>2</sub>S ratio of 0.6, an oxygen excess of 20%.

The gas to the selective oxidation reactor is heated to 180°C. In the selective oxidation reactor, the H<sub>2</sub>S is fully converted, with the bed temperature being 250°C. The oxidation efficiency to elemental sulfur is 90%, the balance is converted to SO<sub>2</sub>. After the condensation of the sulfur formed, the gas is mixed with a reducing H<sub>2</sub>/CO gas, heated to 280°C, and then supplied to a hydrogenation reactor in which all of the SO<sub>2</sub> in the gas and the remaining sulfur components are converted to H<sub>2</sub>S.

Subsequently the gas is re-supplied to a selective oxidation stage in which H<sub>2</sub>S is oxidized to sulfur, using the catalyst (as used in Example II). The H<sub>2</sub>S percentage by volume in this gas is 0.23, which corresponds to 0.64 kmol/h. The H<sub>2</sub>O content therein is 36.2% by volume, which corresponds to 100 kmol/h.

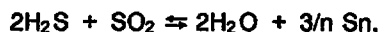
To the second selective oxidation stage, 0.51 kmol/h O<sub>2</sub> is supplied, as air oxygen, which comes down to an O<sub>2</sub>:H<sub>2</sub>S ratio of 0.8, an oxygen excess of 60%. The gas to the second selective oxidation reactor is cooled to 215°C. The H<sub>2</sub>S in the second selective oxidation reactor is again completely converted, with the bed temperature being 230°C. The oxidation efficiency of H<sub>2</sub>S to elemental sulfur in the second stage is 90%, the balance is converted to SO<sub>2</sub>.

Thus, in the overall system, a total sulfur recovery percentage of 99.8 is obtained. The spent gas is passed through an after-burner to the chimney.

### Claims

1. A process for the recovery of sulphur from a hydrogen sulfide containing gas, which comprises oxidizing hydrogen sulfide with oxygen,

and then reacting the product gas of this oxidation further by using at least two catalytic stages, in accordance with the equation:



wherein the H<sub>2</sub>S concentration in the gas leaving the last catalytic stage is controlled to have a value ranging between 0.8 and 3% by volume and the H<sub>2</sub>S : SO<sub>2</sub> ratio in that gas being larger than 2, by reducing the quantity of combustion or oxidation air passed to the oxidation stage and/or causing a portion of the hydrogen sulfide containing feedstock gas to bypass the oxidation stage and to be added to the gas flowing to a catalytic stage, the said H<sub>2</sub>S coming from the last catalytic stage being selectively oxidized to sulphur in a dry oxidation bed, with a catalyst having an oxidation efficiency to sulphur of 80-95% whereby the gaseous sulfur thus formed is condensed after the said dry oxidation reactor and whereby

- with an oxidation efficiency to sulphur of 80-85% of the oxidation catalyst, an H<sub>2</sub>S concentration of 0.8-1.7% by volume is selected in the gas coming from the last catalytic stage.
  - with an oxidation efficiency to sulphur of 85-90% of the oxidation catalyst, an H<sub>2</sub>S concentration of 1.0-2% by volume is selected in the gas coming from the last catalytic stage, and
  - with an oxidation efficiency to sulphur of 90-95% of the oxidation catalyst, an H<sub>2</sub>S concentration of 1.4-2.4% by volume is selected in the gas coming from the last catalytic stage.
2. A process as claimed in claim 1, characterized in that the quantity of combustion or oxidation air passed to the oxidation stage is about 86-98.5% of the quantity of air required to combust one third of the amount of H<sub>2</sub>S supplied to the burner.
  3. A process as claimed in claim 1, characterized in that about 1.5-14% of the available quantity of H<sub>2</sub>S containing gas is caused to bypass the oxidation stage and to be added to the gas flowing to a catalytic stage.
  4. A process as claimed in claims 1-3, characterized by using a catalyst comprising a carrier of which under the reaction conditions applied, the surface exposed to the gaseous phase does not exhibit alkaline properties, with a catalytically active material applied thereto or formed thereon, the specific area of the cata-

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The gas to the selective oxidation reactor is heated to 180°C. In the selective oxidation reactor, the H<sub>2</sub>S is fully converted, with the bed temperature being 250°C. The oxidation efficiency to elemental sulfur is 90%, the balance is converted to SO<sub>2</sub>. After the condensation of the sulfur formed, the gas is mixed with a reducing H<sub>2</sub>/CO gas, heated to 280°C, and then supplied to a hydrogenation reactor in which all of the SO<sub>2</sub> in the gas and the remaining sulfur components are converted to H<sub>2</sub>S.

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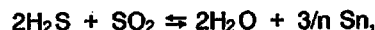
To the second selective oxidation stage, 0.51 kmol/h O<sub>2</sub> is supplied, as air oxygen, which comes down to an O<sub>2</sub>:H<sub>2</sub>S ratio of 0.8, an oxygen excess of 60%. The gas to the second selective oxidation reactor is cooled to 215°C. The H<sub>2</sub>S in the second selective oxidation reactor is again completely converted, with the bed temperature being 230°C. The oxidation efficiency of H<sub>2</sub>S to elemental sulfur in the second stage is 90%, the balance is converted to SO<sub>2</sub>.

Thus, in the overall system, a total sulfur recovery percentage of 99.8 is obtained. The spent gas is passed through an after-burner to the chimney.

### Claims

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- with an oxidation efficiency to sulphur of 80-85% of the oxidation catalyst, an H<sub>2</sub>S concentration of 0.8-1.7% by volume is selected in the gas coming from the last catalytic stage.
- with an oxidation efficiency to sulphur of 85-90% of the oxidation catalyst, an H<sub>2</sub>S concentration of 1.0-2% by volume is selected in the gas coming from the last catalytic stage, and
- with an oxidation efficiency to sulphur of 90-95% of the oxidation catalyst, an H<sub>2</sub>S concentration of 1.4-2.4% by volume is selected in the gas coming from the last catalytic stage.

2. A process as claimed in claim 1, characterized in that the quantity of combustion or oxidation air passed to the oxidation stage is about 86-98.5% of the quantity of air required to combust one third of the amount of H<sub>2</sub>S supplied to the burner.
3. A process as claimed in claim 1, characterized in that about 1.5-14% of the available quantity of H<sub>2</sub>S containing gas is caused to bypass the oxidation stage and to be added to the gas flowing to a catalytic stage.
4. A process as claimed in claims 1-3, characterized by using a catalyst comprising a carrier of which under the reaction conditions applied, the surface exposed to the gaseous phase does not exhibit alkaline properties, with a catalytically active material applied thereto or formed thereon, the specific area of the cata-

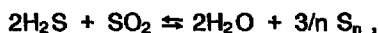


lyst being less than 20 m<sup>2</sup>/g catalyst, and less than 10% of the total pore volume having a pore radius of between 5 and 500 Å.

5. A process as claimed in claim 4, characterized by using a catalyst in which less than 2% of the total pore volume has a pore radius of between 5 and 500 Å.
6. A process as claimed in claim 4, characterized by using a catalyst having a specific area less than 10m<sup>2</sup>/g catalyst.
7. A process as claimed in claim 4, characterized by using a catalyst in which the carrier material is alpha-alumina or hydrothermally sintered silica.
8. A process as claimed in claim 4, characterized by using a catalyst in which the catalytically active material is present on the carrier in a proportion of 3-10% by weight calculated on the total mass of the catalyst.
9. A process as claimed in claim 4, characterized by using a catalyst in which the catalytically active material is a metal oxide, a mixed oxide of a plurality of metals, or a mixture of metal oxides.
10. A process as claimed in claim 9, characterized by using a catalyst in which the oxide is iron oxide or a mixed oxide of iron and chromium.

#### Revendications

1. Procédé de récupération de soufre à partir d'un gaz contenant de l'hydrogène sulfuré, qui comprend les étapes consistant à oxyder l'hydrogène sulfuré avec de l'oxygène et à faire réagir ultérieurement les produits gazeux provenant de cette oxydation, au moyen d'au moins deux étapes catalytiques, conformément à l'équation :



procédé dans lequel on règle la concentration de H<sub>2</sub>S dans le gaz quittant la dernière étape catalytique de façon à ce qu'elle ait une valeur comprise entre 0,8 et 3% en volume, le rapport H<sub>2</sub>S : SO<sub>2</sub> dans ce gaz étant supérieur à 2, en réduisant la quantité d'air de combustion ou d'oxydation envoyée à l'étape d'oxydation et/ou en faisant en sorte qu'une partie du gaz d'alimentation contenant l'hydrogène sulfuré évite l'étape d'oxydation et est ajoutée au courant gazeux allant vers une étape catalytique,

ledit H<sub>2</sub>S provenant de la dernière étape catalytique étant oxydé sélectivement en soufre dans un lit d'oxydation sec, à l'aide d'un catalyseur ayant une efficacité en ce qui concerne l'oxydation en soufre de 80 à 95%, et le soufre gazeux formé ainsi étant condensé après ledit réacteur d'oxydation par voie sèche,

une concentration de H<sub>2</sub>S de 0,8 à 1,7% en volume dans le gaz provenant de la dernière étape catalytique, étant choisie lorsque l'efficacité du catalyseur d'oxydation pour l'oxydation en soufre est de 80 à 85%,

une concentration de H<sub>2</sub>S de 1,0 à 2% en volume dans le gaz provenant de la dernière étape catalytique, étant choisie lorsque l'efficacité du catalyseur d'oxydation pour l'oxydation en soufre est de 85 à 90%, et

une concentration de H<sub>2</sub>S de 1,4 à 2,4% en volume dans le gaz provenant de la dernière étape catalytique, étant choisie lorsque l'efficacité du catalyseur d'oxydation pour l'oxydation en soufre est de 90 à 95%.

2. Procédé selon la revendication 1, caractérisé en ce que la quantité d'air de combustion ou d'oxydation envoyée à l'étape d'oxydation, est égale à environ 86-98,5% de la quantité d'air nécessaire pour effectuer la combustion d'un tiers de la quantité de H<sub>2</sub>S fournie au brûleur.
3. Procédé selon la revendication 1, caractérisé en ce que l'on fait en sorte qu'environ 1,5 à 14% de la quantité disponible de gaz contenant H<sub>2</sub>S évite l'étape d'oxydation et est ajouté au courant de gaz allant vers une étape catalytique.
4. Procédé selon les revendications 1 à 3, caractérisé en ce que l'on utilise un catalyseur comprenant un support dont la surface exposée à la phase gazeuse ne présente pas de propriétés alcalines dans les conditions de réaction utilisées, et un matériau catalytiquement actif, appliqué au support ou formé sur celui-ci, la surface spécifique du catalyseur étant inférieure à 20 m<sup>2</sup>/g de catalyseur, et moins de 10% du volume total des pores correspondant à des pores ayant un rayon compris entre 5 et 500 Å.
5. Procédé selon la revendication 4, caractérisé en ce que l'on utilise un catalyseur dans lequel moins de 2% du volume total des pores correspond à des pores ayant une rayon compris entre 5 et 500 Å.
6. Procédé selon la revendication 4, caractérisé en ce que l'on utilise un catalyseur ayant une

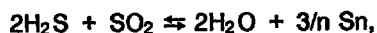


surface spécifique inférieure à 10 m<sup>2</sup>/g de catalyseur.

7. Procédé selon la revendication 4, caractérisé en ce que l'on utilise un catalyseur dans lequel le matériau support est de l'alumine-alpha ou de la silice frittée obtenue par voie hydrothermale.
8. Procédé selon la revendication 4, caractérisé en ce que l'on utilise un catalyseur dans lequel le matériau catalytiquement actif est présent sur le support en une proportion de 3 à 10% en poids par rapport à la masse totale du catalyseur.
9. Procédé selon la revendication 4, caractérisé en ce que l'on utilise un catalyseur dans lequel le matériau catalytiquement actif est un oxyde métallique, un oxyde mixte de divers métaux ou un mélange d'oxydes métalliques.
10. Procédé selon la revendication 9, caractérisé en ce que l'on utilise un catalyseur dans lequel l'oxyde est de l'oxyde de fer ou un oxyde mixte de fer et de chrome.

#### Patentansprüche

1. Verfahren zur Gewinnung von Schwefel aus einem Schwefelwasserstoff enthaltenden Gas, bei dem Schwefelwasserstoff mit Sauerstoff oxidiert und dann das Produktgas dieser Oxidation unter Verwendung von mindestens zwei katalytischen Stufen gemäß der Gleichung



weiter umgesetzt wird, wobei die H<sub>2</sub>S-Konzentration in dem die letzte katalytische Stufe verlassenden Gas auf einen Wert im Bereich zwischen 0,8 und 3 Vol.-% eingestellt wird und das Verhältnis H<sub>2</sub>S : SO<sub>2</sub> in dem Gas größer als 2 ist, indem die Menge an in die Oxidationsstufe eingeleiteter Verbrennungs- oder Oxidationsluft verringert und/oder ein Teil des Schwefelwasserstoff enthaltenden Einsatzmaterialgases an der Oxidationsstufe vorbeigeführt und dem zu einer katalytischen Stufe strömenden Gas zugeführt wird, wobei der aus der letzten katalytischen Stufe kommende Schwefelwasserstoff in einem trockenen Oxidationsbett mit einem Katalysator mit einer Oxidationswirksamkeit bezüglich Schwefel von 80 bis 95 % selektiv zu Schwefel oxidiert wird, wobei der so gebildete gasförmige Schwefel nach dem trockenen Oxidationsreaktor kondensiert wird und wobei

mit einer Oxidationswirksamkeit des Oxidationskatalysators bezüglich Schwefel von 80 - 85 % eine H<sub>2</sub>S-Konzentration von 0,8 - 1,7 Vol.-% in dem aus der letzten katalytischen Stufe kommenden Gas gewählt wird, mit einer Oxidationswirksamkeit des Oxidationskatalysators bezüglich Schwefel von 85 - 90 % eine H<sub>2</sub>S-Konzentration von 1,0 - 2 Vol.-% in dem aus der letzten katalytischen Stufe kommenden Gas gewählt wird und mit einer Oxidationswirksamkeit des Oxidationskatalysators bezüglich Schwefel von 90 - 95 % eine H<sub>2</sub>S-Konzentration von 1,4 - 2,4 Vol.-% in dem aus der letzten katalytischen Stufe kommenden Gas gewählt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Menge an Verbrennungs- oder Oxidationsluft, die in die Oxidationsstufe geleitet wird, etwa 86 - 98,5 % der Luftmenge beträgt, die erforderlich ist, um ein Drittel des dem Brenner zugeführten Schwefelwasserstoffs zu verbrennen.
3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß etwa 1,5 - 14 % der zur Verfügung stehenden Menge an H<sub>2</sub>S enthaltendem Gas an der Oxidationsstufe vorbeigeleitet und dem zu einer katalytischen Stufe strömenden Gas zugeführt werden.
4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß ein Katalysator verwendet wird, der einen Träger, bei dem unter den angewendeten Reaktionsbedingungen die der gasförmigen Phase ausgesetzte Oberfläche keine alkalischen Eigenschaften zeigt, mit einem darauf aufgebracht oder darauf gebildeten katalytisch aktiven Material umfaßt, wobei die spezifische Oberfläche des Katalysators weniger als 20 m<sup>2</sup>/g Katalysator beträgt und weniger als 10 % des Gesamtporenvolumens einen Porenradius zwischen 5 und 500 Å aufweisen.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß ein Katalysator verwendet wird, bei dem weniger als 2 % des Gesamtporenvolumens einen Porenradius zwischen 5 und 500 Å aufweisen.
6. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß ein Katalysator mit einer spezifischen Oberfläche von weniger als 10 m<sup>2</sup>/g Katalysator verwendet wird.
7. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß ein Katalysator verwendet wird,



bei dem das Trägermaterial  $\alpha$ -Aluminiumoxid oder hydrothermal gesinteres Siliciumdioxid ist.

8. Verfahren nach Anspruch 4, **dadurch gekennzeichnet**, daß ein Katalysator verwendet wird, bei dem das katalytisch aktive Material auf dem Träger in einer Menge von 3 - 10 Gew.-%, bezogen auf die gesamte Masse des Katalysators, vorhanden ist. 5  
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9. Verfahren nach Anspruch 4, **dadurch gekennzeichnet**, daß ein Katalysator verwendet wird, bei dem das katalytisch aktive Material ein Metalloxid, ein Mischoxid einer Mehrzahl von Metallen oder eine Mischung von Metalloxiden ist. 15  
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10. Verfahren nach Anspruch 9, **dadurch gekennzeichnet**, daß ein Katalysator verwendet wird, bei dem das Oxid Eisenoxid oder ein Mischoxid von Eisen und Chrom ist. 25  
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