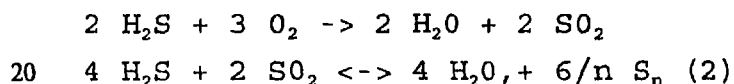


Title: A process for the recovery of sulphur from a hydrogen sulphide, containing gas

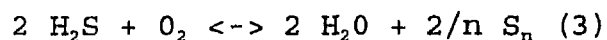
In a number of processes, such as the refining of crude oil, the purification of natural gas and the production of synthesis gas from, for example, fossil fuels, sulphur containing gas, in particular H_2S containing gas, is released. On account of its high toxicity and its smell, the emission of H_2S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

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

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



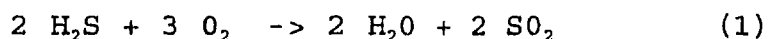
Reactions (1) and (2) result in the main reaction:



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 number of reactors generally two or three - filled with a catalyst. These last stages constitute the so-called catalytic stages.

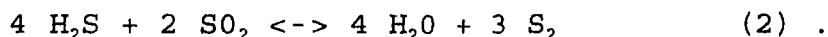
In the combustion chamber, the incoming gas stream, which is rich in H_2S , is combusted with an amount of air at a temperature of approximately $1200^\circ C$. The amount of air is adjusted so that one third of the H_2S is fully combusted to form SO_2 in accordance with the following reaction :





After this partial oxidation of H_2S the non-oxidised part of the H_2S (i.e. basically two-thirds of the amount offered) and the SO_2 formed react further as to a

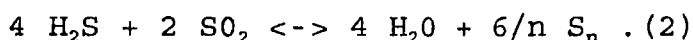
5 considerable portion, in accordance with the Claus reaction



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

The gases coming from the combustion chamber are cooled
10 to about 160°C in a sulphur condenser, in which the sulphur formed is condensed, which subsequently flows into a sulphur pit through a siphon.

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



is established.

The gases coming from this catalytic reactor are
20 subsequently cooled again in a sulphur condenser, in which the liquid sulphur 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
25 of between about 15 and 50 %, the above described "straightthrough" process is not used, but instead a variant thereof, the so-called "split-flow" process. 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.
30 Two-thirds of the feedstock is passed directly 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
35 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 sulphur condenser, in which the sulphur formed is condensed and discharged.

To dissipate the reaction heat generated in the oxidation reactor, a portion of the gas stream coming from the sulphur condenser is recirculated 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 the thermal Claus stage and the oxidation stage of the Recycle Selectox process are referred to as oxidation stages.

The sulphur recovery percentage in a conventional Claus converter is 92 - 97 %, depending on the number of catalytic stages

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 atmosphere. This has been permissible for low concentrations or small amounts of emitted SO_2 for a long time. Although SO_2 is much less harmful and dangerous than H_2S 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 $H_2S : SO_2$ ratio plays an important role. In order to obtain an optimum conversion to sulphur, this ratio should be 2 : 1. Generally speaking, this ratio is controlled by means of a so-called H_2S / SO_2 residual gas analyser. This analyser measures the H_2S and SO_2 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.

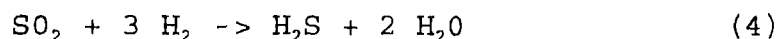
Furthermore, the sulphur recovery efficiency (calculated on the amount of H_2S supplied) is no higher than 97 %, and so the gas flowing from the last catalytic stage the residual gas - still contains substantial amounts of H_2S and SO_2 , determined by the Claus equilibrium, and this in a molar ratio of 2 : 1.

The amount of H_2S present in the residual gas can be separated by absorption in a liquid.

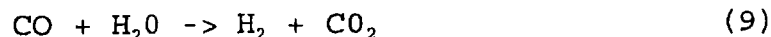
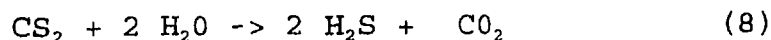
The presence of SO_2 in the residual gas, however, is a disturbing factor during the further processing thereof and must therefore be removed prior to such further processing. This removal and hence the after-treatment of the gas is complicated.

The great disadvantage of the presence of SO_2 is that this gas reacts with conventional liquid absorbents to form undesirable products. To prevent undesirable reactions of the SO_2 , therefore, the SO_2 is generally catalytically reduced with hydrogen to form H_2S over an Al_2O_3 supported cobalt-molybdenum catalyst in accordance with the so-called SCOT process. The total amount of H_2S is subsequently separated by liquid absorption in the usual manner. ,

In the SCOT process the sulphur components, other than H_2S , such as SO_2 (sulphur dioxide) and sulphur vapour (S_6 and S_8) are fully hydrogenated to H_2S according to the following reactions:



Other components, such as CO , COS and CS_2 , are hydrolysed according to:



5

Above conversions to H_2S are performed with a cobalt-molybdenum catalyst on alumina at a temperature of about 280 - 330°C. For the SCOT process it is required that sulphur vapour is hydrogenated to H_2S , and also that SO_2 is
10 completely converted to H_2S down to ppm level, to prevent plugging / corrosion in the down-stream water quench column. This type of hydrogenation can be defined as high temperature hydrogenation.

In accordance with another method, for example, the BSR
15 Selectox process, after reduction of the SO_2 in residual gas to H_2S 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 $\text{H}_2\text{S} : \text{SO}_2$ ratio of 2 : 1 is obtained, whereafter the Claus reaction
20 proceeds. Both in the SCOT process and in the BSR Selectox process, the removal of SO_2 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
25 involves an investment of another 50 - 100 % of the cost of the preceding Claus converter, can result in an increase of the sulphur recovery efficiency of up to 98 - 99.8 %.

In US patent specification No. 4,988,494, it is proposed that the H_2S concentration in the gas leaving the
30 last catalytic Claus stage is controlled to have a value ranging between 0.8 and 3 % by volume by reducing the quantity of combustion or oxidation air passed to the oxidation stage.

The increase of the H_2S concentration will result in a
35 decreased SO_2 concentration, however, not to very low levels. For an H_2S concentration of 0.8 % by volume, the SO_2

concentration will be typically 0.03 - 0.15 % by volume, and this will result in a sulphur recovery efficiency loss of typically 0.09 - 0.45 %.

In the process according to this patent, the H_2S is
5 selectively oxidised in a dry bed oxidation stage.

As SO_2 is not converted in a dry-bed oxidation stage, this will result in appreciable sulphur recovery losses, and consequently sulphur recovery efficiencies close to 100 % can not be reached.

10 A second disadvantage of operating with excess H_2S compared to SO_2 is that the temperature increase in the drybed oxidation reactor becomes higher with increasing H_2S concentration.

Higher reactor temperatures will result in an increased
15 formation of SO_2 as a result of gas-phase and catalytic oxidation of formed sulphur vapour. Also for this reason, a shifted operation towards H_2S of the Claus converter is not beneficial.

It has been experienced, that in case the catalyst
20 bottom temperature in a dry-bed oxidation reactor exceeds 250 - 260°C, the oxidation efficiency to elemental sulphur will start to drop from 94 - 96 % to lower values. Combined with a reactor inlet temperature of approximately 180 - 200°C, this results in a temperature increase of some 60 - 80°C,
25 corresponding with 1.0 - 1.2 vol.% of H_2S in the process gas.

The shifted operated sulphur plant, followed by a drybed oxidation step with an oxidation catalyst which is not effective in promoting the Claus reaction, is known as the SUPERCLAUS[™] or SUPERCLAUS[™]-99 process.

30 The SUPERCLAUS[™] process, as well as the SUPERCLAUS[™]-99.5 process, is described in "SUPERCLAUS[™]- the answer to Claus plant limitations", Lagas, J.A.; Borsboom, J; Berben, P.H., 38th Canadian Chemical Engineering Conference, Edmonton, Canada.

35 It is known, that removal of SO_2 from a process gas can be performed according to a high temperature hydrogenation

step to H₂S as applied in the SCOT process or in the SUPERCLAUS[™]-99.5 process.

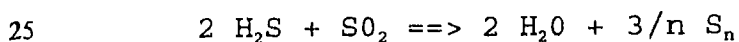
In European patent No. 669,854 the selective hydrogenation of SO₂ to elemental sulphur has been described.
5 It has been mentioned that this hydrogenation could suitably be applied downstream of a regular Claus unit, prior to dry bed oxidation.

However, the specific process conditions required according to this patent are not easily compatible with the
10 composition of gas coming from a Claus unit. This means that rather complicated, and thus costly, measures are necessary to satisfy these conditions.

Surprisingly it has now been found that it is possible to increase the sulphur recovery by very simple process
15 modifications.

According to the invention a process for the recovery of sulphur from a hydrogen sulphide containing gas comprises:

- i) oxidising part of the hydrogen sulphide in a gaseous stream with oxygen or an oxygen containing gas in an
20 oxidation stage to sulphur dioxide;
- ii) reacting the product gas of this oxidation stage in at least two catalytic stages, in accordance with the Claus equation :

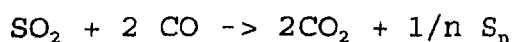
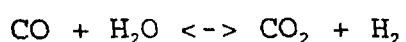


- iii) catalytically reducing SO₂ in the gas leaving the last of said at least two catalytic stages, wherein the catalytic reduction takes place in a catalyst bed
30 downstream from the last Claus catalytic stage.

One aspect of the invention is the reduction of SO₂. This reduction of SO₂ to elemental sulphur, to H₂S or to a mixture of both, by hydrogenation, requires the presence of hydrogen. In the gas leaving the last catalytic Claus stage
35 sufficient hydrogen is normally present. This hydrogen is produced in the thermal stage, by, among others, cracking of

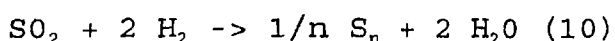
H₂S to hydrogen and sulphur vapour. In case the amount of hydrogen is insufficient, additional hydrogen may be added to the gas, by adding a stream of concentrated hydrogen, or by generating hydrogen by sub-stoichiometric combustion of fuel gas in in-line process heaters.

Also CO is usually present in the gas containing SO₂. Because of the reducing properties of CO, this component is capable of reducing SO₂. In this way CO acts in the same way as hydrogen, and a mixture of hydrogen and CO is therefore also suitable for reducing SO₂.



In the context of this invention the terms 'reduction' and 'hydrogenation' have both been used to indicate the same.

It was found that reduction of SO₂ to H₂S proceeds in two steps. The first step is the hydrogenation of SO₂ to elemental sulphur vapour, according to :



The temperature range of this reaction is typically 130 - 230°C. Complete conversion of SO₂ is achieved at approximately 200 - 230°C over a conventional cobalt-molybdenum catalyst.

The hydrogenation of sulphur vapour to H₂S starts at approximately 220°C, and is completed at approximately 260 300°C. All temperature levels depend also on space velocity, H₂O and SO₂ concentration, H₂ / SO₂ ratio and type of catalyst.

A suitable temperature range to convert SO₂ is typically above 200°C, whereas a suitable upper limit is 225°C. For an acceptable conversion of SO₂, the catalyst temperature should be high enough to stay above the sulphur vapour dewpoint. The presence of oxygen in the gas to be hydrogenated is not harmful to the catalyst or catalyst performance, as oxygen is hydrogenated to water under approximately the same reaction conditions as apply to SO₂.

The hydrogenation catalyst can be selected from the group of metals of group VI and VIII of the periodic table of elements. The catalyst may be supported and is preferably in the sulphidic form. Examples are iron, nickel and cobalt for Group VIII, and molybdenum, tungsten and chromium for Group VI. It is preferred to use cobalt-molybdenum or nickel-molybdenum.

In case the gas coming from the SO_2 hydrogenation step is not further subjected to a treatment, it has advantages to, adjust the molar ratio of H_2S to SO_2 after the final Claus stage, to a value different from 2 : 1, i.e. a higher amount of SO_2 , which results in a high sulphur recovery, with only very limited efforts. Generally it is preferred to have a ratio of from 1 : 1 to 1 : 10.

It should be noted, that complete conversion of all sulphur compounds to H_2S down to the ppmv-level as in the SCOT process, is not required. Hydrogenation of SO_2 down to a level of approximately 100 ppmv is acceptable and will result in negligible recovery efficiency losses.

It is not very critical whether the reduction of SO_2 proceeds to elemental sulphur or to H_2S . Generally a mixture of both will be obtained, which has preference.

In the SUPERCLAUS[™] process, as described in US-A 4,988,494, a residual concentration of SO_2 is left in the process gas to the dry-bed oxidation stage. This residual SO_2 not only decreases the overall sulphur recovery efficiency, because it is not converted to elemental sulphur, but also decreases the activity of the selective oxidation catalyst.

To overcome this decrease of activity, the temperature level in the dry-bed oxidation reactor has to be increased, but a higher temperature level will decrease the oxidation efficiency to elemental sulphur. Consequently, very high oxidation efficiencies in the dry-bed oxidation stage, in the range of 94 - 96 %, are not possible with process gas containing concentrations of SO_2 of more than about 250 ppmv.

It is one of the advantages of the present invention, that it allows the Claus process to be operated with a residual concentration of SO_2 which would otherwise be prohibitive for a downstream dry bed oxidation process.

5 The effect of a deactivated Claus catalyst, which results in an increased amount of SO_2 in the gas coming from the Claus unit, has the same negative effects on the overall sulphur recovery efficiency in case of a final dry-bed oxidation stage, because the SO_2 is not converted in the
10 drybed oxidation stage.

Incorporation of a hydrogenation step, as in the present invention, makes the process not sensitive anymore to Claus catalyst deactivation, which is a major advantage. In this way the reduction step also acts as a safeguard and serves to
15 maintain a constant and high sulphur recovery.

The control of the process with an incorporated hydrogenation step will also be much more flexible. A varying SO_2 content in the process gas from the last catalytic Claus reactor will not result in varying losses by SO_2 slippage,
20 because all SO_2 is converted. This makes the control on H_2S much less sensitive to process fluctuations.

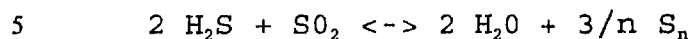
According to a further embodiment the process comprises an additional step of selectively oxidising the hydrogen sulphide in the product gas of step iii) to elemental
25 sulphur.

In this way of operation of the process it is not necessary to modify the ratio of H_2S to SO_2 , as in some of the prior art processes. Accordingly the ratio may be kept at levels close to the Claus equilibrium level of 2 : 1. A
30 suitable range for this is from 10 : 1 to 1 : 2.

In detail the process of the invention can be described as comprising:

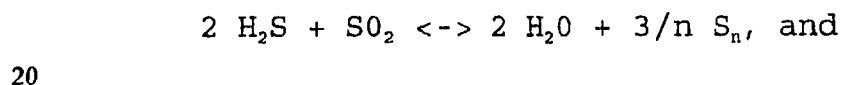
- i) oxidising part of the hydrogen sulphide in a gaseous stream with oxygen or an oxygen containing gas in an
35 oxidation stage to sulphur dioxide;

ii) reacting the product gas of this oxidation stage in at least two catalytic stages, in accordance with the Claus equation :



iii) catalytically reducing SO_2 in the gas leaving the last of said at least two catalytic stages, preferably employing for this purpose a reduction catalyst or a
10 catalytic stage including a reduction catalyst which is effective to promote reduction of SO_2

iv) selectively oxidising H_2S in the gas leaving the hydrogenation to elemental sulphur, preferably employing for this purpose a catalytic stage including a selective
15 oxidation catalyst which is substantially insensitive to the presence of water vapour in the gas stream, is ineffective in promoting establishment of the equilibrium



is effective to promote oxidation of HS to sulphur in the presence of water vapour.

It is preferred in said step iv) of selectively oxidising H_2S also employing a stoichiometric excess of
25 oxygen sufficient to result in an overall excess of oxygen being employed in the total process for the recovery of sulphur from the hydrogen sulphide-containing gas.

In the process according to the present invention, the concentration of the hydrogen sulphide gas in the residual
30 gas can be controlled in a simple way. Thus, for example, the signal from an H_2S analyser 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 reduction step can be incorporated in a commercial
35 process in several ways. The most economic way is to install a layer of hydrogenation catalyst below a layer of Claus

catalyst, in the last catalytic Claus reactor, usually the second or third Claus reactor. The process conditions should fit for the hydrogenation conditions, such as temperature, sulphur dewpoint margin, sufficient hydrogen available.

5 Usually this will be the case.

In another embodiment, the hydrogenation step is carried out in a separate (small) hydrogenation reactor, with or without prior removal of elemental sulphur from the gas to be hydrogenated.

10 Especially in case the gas contains substantial amounts of CO, it is advantageous to carry out the reduction under conditions that most of the sulphur vapour has been removed. In the presence of a hydrogenation (reduction) catalyst, CO and sulphur react, thereby producing unwanted by-products, 15 such as COS, resulting in a decrease of sulphur recovery. In these cases it is preferred that the gas coming from the last Claus reactor is first subjected to a sulphur condensation step, with removal of condensed sulphur, followed by the reduction step of the present invention, optionally after 20 reheating.

After the reduction step the gas is then further treated, such as in an oxidation stage to convert H_2S to elemental sulphur.

An alternative process route, without a final dry-bed 25 oxidation stage, may be attractive, with lower investment costs and somewhat lower sulphur recovery efficiency. This process alternative consists of a Claus converter with an oxidation stage and at least two catalytic Claus stages, the H_2S concentration in the gas leaving the last of said at 30 least two catalytic stages being controlled to have a value ranging between 0.1 and 0.4 % by volume by increasing the quantity of combustion or oxidation air passed to the oxidation stage followed by reducing SO_2 in the gas leaving the last of said at least two catalytic stages in a 35 hydrogenation step.

Depending on the number of catalytic Claus stages, a recovery efficiency of 98.0 - 99.5 % can be reached.

In the context of this application, the term 'catalytic Claus stage' refers to the actual reactor containing the Claus catalyst. Depending on the plant set-up, the usual additional equipment may be present, such as reheaters or sulphur condensers.

The hydrogenation can also be applied down-stream of the dry-bed oxidation stage (SUPERCLAUSTM reactor) , to convert the formed SO₂. This will increase the overall performance of the SUPERCLAUSTM process significantly.

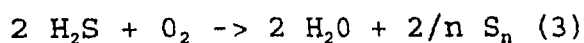
In order to unload tail gas treating units such as SCOT, it is beneficial to install a hydrogenation stage down-stream of the last Claus catalytic stage. This will reduce the amount of sulphur components to be hydrogenated in the SCOT unit significantly, and will reduce solvent circulation and stripping-steam requirements.

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

A disadvantage of operating with excess H₂S compared to SO₂ in the Claus tail gas is, that this operation mode results in less combustion air to the main (H₂S) burner compared to the conventional mode of operation with H₂S : SO₂ = 2 : 1. This will result in a decrease of temperature of combustion in the combustion chamber, which is detrimental to the destruction efficiency of ammonia, which requires high temperatures.

In the process according to the invention, the hydrogen sulphide gas remaining in the residual gas can be processed to form sulphur by a known per se method. Such methods are described in the literature. Preferably, however, the remaining gaseous hydrogen sulphide is oxidized

with air in an oxidation stage to form elemental sulphur in accordance with the following reaction :



It was found that, when the concentration of the hydrogen sulphide leaving the last catalytic hydrogenation stage is maintained at a value of between 0.5 and 1.2 % by volume, after this selective oxidation, an optimum sulphur recovery percentage of 99.6 - 99.8 can be obtained. The oxidation can in principle take place in two ways, namely, by dry-bed oxidation or by oxidation in a liquid, in which, in general, sulphur and water vapour have first been removed from the residual gas.

In the dry-bed oxidation, the H_2S concentration in the residual gas is preferably maintained between 0.5 and 1.2 by volume, because above 1.2 % by volume of H_2S the total sulphur recovery percentage is decreased.

In the dry oxidation bed, the oxidation to sulphur 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 (Hass, R.H.; Ingalis, M.N.; Trinker, T.A.; Goar, B.G.; Purgason, R.S.S. : "Process meets sulphur recovery needs", Hydrocarbon Processing, May 1981, pages 104 -107). In this process, H_2S is oxidised to S and SO_2 using a special catalyst. Approximately 80 % of the H_2S supplied is oxidised to elemental sulphur, 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 no. 71983.

In accordance with a particularly preferred embodiment of the process according to the present invention, the oxidation is carried out in a dry bed, using a catalyst, such as described in US patent specification Nos. 4,818,740 and

5,286,697 or in WO-A 9732813, the contents of which is incorporated herein by way of reference.

The use of these catalysts for the oxidation in a dry bed of the hydrogen sulphide 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 sulphur and water vapour from this residual gas is unnecessary, unless it is required for other reasons, such as described herein before.

The minimum volume percent of H_2S , corresponding with the maximum volume percent of SO_2 , in the residual gas from the last Claus stage, is determined by the ratio H_2 / SO_2 in the gas, which should be higher than two for acceptable SO_2 hydrogenation. For this reason, the H_2S volume percent cannot be lowered too much. Also, when the H_2S volume percentage to the dry-bed oxidation reactor is too low, the oxidation efficiency to sulphur in the dry-bed oxidation reactor is not at its maximum.

When the H_2S volume percentage is too high, the overall recovery efficiency will also decrease. For above reasons, the optimum H_2S volume percentage in the process gas from the hydrogenation stage, is preferably in the range of 0.5 - 1.2 Vol.%.

The liquid oxidation, too, can take place using a known process. Examples of known processes are the Stretford process (the Chemical Engineer, February 1984, pages 84 ff), the Lo-Cat process of Air Resources Inc. or the Takahax process.

The control of the oxidation air to the selective oxidation is not critical and can thus be kept 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 including a

hydrogenation step is used, a selective oxidation reactor will have to be provided in this 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 and the second Claus reactor has to be provided with a layer of a reduction catalyst. In this case, too therefore, a considerable economic benefit is obtained.

The elemental sulphur that is produced in the system can be condensed from the gas flows using conventional systems, such as condensers. In case an especially high sulphur recovery is necessary it may be advantageous to use the system disclosed in EP-A 655,414, more in particular for the treatment of the final product gas flow, after the last treatment.

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

As shown in figure 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 H₂S analyser 23, is supplied to Claus burner 2 through line 4. The heat generated during the combustion (1200°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 sulphur formed is condensed in boiler 5 (150°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°C before being supplied through line 10 to the first Claus reactor 11. In reactor 11 the Claus reaction takes place again, whereby sulphur is

formed. The gas is discharged through line 12 to the sulphur condenser 13. The condensed sulphur (150°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 sulphur condenser 18. In this reactor the Claus reaction takes place again in the top-part of the reactor on Claus catalyst layer 32. In the bottom part a layer 33 of a reduction catalyst is installed, where the residual SO₂ is hydrogenated. The condensed sulphur (150°C) is discharged through line 19. The steam generated in the sulphur condensers is discharged through lines 20 and 21.

The H₂S concentration in the residual gas line 22 is controlled by an H₂S analyser 23 to a range of from 0.5 to 1.2 % by volume. The H₂S analyser controls a control valve in combustion air line 24.

The residual gas is passed through line 22 to the sulphur removing stage 26. This sulphur removing stage may be a known sulphur removing process, such as, for example, a dry-bed oxidation stage, an absorption stage or a liquid oxidation stage. The air required for the oxidation is supplied through line 27. The sulphur formed is discharged through line 28.

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

As shown in figure 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 H₂S analyser 19 is passed to the oxidation reactor through line 4. In the oxidation reactor a portion of the H₂S is oxidised over a special catalyst to form SO₂, 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 sulphur condenser 9, where the sulphur

formed during the reaction is condensed at 150°C and discharged through line 10. The heat generated during the reaction is dissipated in sulphur condenser 9 with generation of steam, which is discharged through line 11. The gas is
5 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 in catalyst layer 29 in the top part of the reactor. In the bottom part of reactor 14, SO₂ in the process gas is
10 hydrogenated by layer 30 consisting of a reduction catalyst. In condenser 15, the sulphur is condensed at 150°C and discharged through line 16, and steam generated is discharged through line 17. The H₂S concentration in the residual gas line 18 is controlled by an H₂S analyser 19 to a range of
15 from 0.5 - 1.2 % by volume. The H₂S analyser controls a control valve in the combustion air line 20.

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

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

In figure 3a, after the removal of the sulphur from the residual gas in separator 2, which is discharged through line
30 3, and the condensation of the water in 4, which is discharged through line 5, the gas is supplied through a heater 6 to an oxidation reactor 7. The removal of sulphur and water in 2 and 4 respectively, can take place using a known method, for example, as disclosed in US patent 4526590.
35 In the oxidation reactor 7, a catalyst may be 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 sulphur condenser 9. The sulphur condensed is discharged through line 10, and
5 the steam generated through line 11. The gas next flows through line 12 to the after-burner as designated by 30 in figure 1 and 26 in figure 2.

As shown in figure 3b, the residual gas is supplied through line 1 and heater 2 direct to the oxidation stage,
10 that is to say, without a preceding sulphur 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-Claus active carrier to which at least 0.1 % by weight of a catalytically active material, in
15 particular a metal oxide, has been applied, so that the specific area of the catalyst is more than 20 m²/g, while the average pore radius is at least 25 Å. The oxidation air required is supplied through line 3. The sulphur condensed in sulphur condenser 5 is discharged through line 6 and the
20 steam generated through line 7. The gas next flows through line 8 to the after burner designated by 30, in figure 1, and by 26 in figure 2.

As shown in figure 3c the residual gas is passed through line 1 to a reactor 2 filled with an absorption mass, for
25 example, as described in European patent no. 71983. In reactor 2, the hydrogen sulphide is removed from the residual gas by absorption. The gas next flows through line 3 to the afterburner, designated by 30 in figure 1 and by 26 in figure 2. When the bed is saturated, it is regenerated. Reactor 4 is
30 connected in parallel to reactor 2 and is regenerated. By means of a circulation blower 5, a quantity of gas is circulated. This gas is heated in heater 6. The air required for the oxidation is supplied through line 7. The gas flows from reactor 4 to sulphur condenser 8. The sulphur condensed
35 is discharged through line 9 and the steam generated through line 10. To keep the system at the required pressure a small

gas stream is discharged through line 11 and recycled to the feedstock for the Claus plant (line 1 in figures 1 and 2).

As shown in figure 3d, sulphur is removed in separator 2, which is discharged through line 3. Subsequently, in
5 condenser 4, water is condensed which is removed through line 5. The gas is passed to a liquid oxidation stage 6. The oxidation stage may contain, for example, a basic solution of sodium carbonate, ADA (anthraquinone disulphonic acid) and sodium metavanadate, as used in the well-known Stretford
10 process.

H₂S is absorbed in the liquid and subsequently oxidised with air. The oxidation air is supplied through line 7 and the sulphur formed is discharged through line 8. The gas next flows through line 9 to the after-burner (30 in figure 1 and
15 26 in figure 2). Figure 4 shows an installation which is similar to that of figure 1, with the exception of the drybed oxidation stage, and including a separate hydrogenation stage. Starting with the third catalytic Claus stage comprising reheater 34, reactor 35 and sulphur condenser 36,
20 the process gas is routed via line 39 to reheater 40. Reactor 41 contains a catalyst active for the hydrogenation of SO₂. Analyser 23 in line 39 controls the content of H₂S in the process gas.

The invention is illustrated in and by the following
25 examples.

Example 1

Using the apparatus as described with reference to
30 figures 1 and 3a, the Claus reaction is performed in a Claus plant having two catalytic Claus stages and a hydrogenation stage. Supplied to the thermal stage are a Claus gas, containing 90 % by volume of H₂S, corresponding to 90 kmoles/h, 4 % Vol. CO₂, 5 Vol. H₂O and 1 % Vol C₂H₆, and 48.5
35 kmoles/h O₂ (a "deficit" of 0%) as air oxygen. The H₂S volume percentage in the residual gas after the catalytic

hydrogenation stage is 0.6, and the SO_2 content therein negligible. After the removal of sulphur and water and using a dry-bed process for the oxidation of H_2S with an oxidation efficiency of 80 %, a total sulphur recovery percentage of 99.5 is obtained.

Example 2

Using the apparatus as described with reference to figures 1 and 3b, the Claus reaction is performed in a Claus plant having two catalytic stages and a hydrogenation stage. Supplied to the thermal stage are a Claus gas containing 90 % by volume of H_2S corresponding to 90 kmol/h, 4 % by volume of CO_2 , 5 % by volume of H_2O and 1 % by volume of C_2H_6 , and 48.5 kmol/h of O_2 (a "deficit" of 0 %) as air oxygen. The H_2S volume percentage in the residual gas after the catalytic hydrogenation stage is 0.57, the SO_2 content therein is immeasurably small, and its water content is 34.3 by volume. The dry-bed oxidation is carried out using a water insensitive oxidation catalyst, comprising a silica carrier (Degussa OX-50, specific area 42 m^2/g) to which 5 by weight of Fe_2O_3 , and 0.5 % by weight of P_2O_5 have been applied as catalytically active material, which, after pelletisation and calcination has a BET area of 40.1 m^2/g , with an average pore radius of 350 Å. Using this catalyst with an oxidation efficiency of 94 %, a total sulphur recovery percentage of 99.7 is obtained.

Claims

1. A process for the recovery of sulphur from a hydrogen sulphide containing gas, which process comprises:
 - i) oxidising part of the hydrogen sulphide in a gaseous stream with oxygen or an oxygen containing gas in an oxidation stage to sulphur dioxide;
 - 5 ii) reacting the product gas of this oxidation stage in at least two catalytic stages, in accordance with the Claus equation :

$$2 \text{H}_2\text{S} + \text{SO}_2 \Rightarrow 2 \text{H}_2\text{O} + 3/n \text{S}_n$$
 - 10 iii) catalytically reducing SO_2 in the gas leaving the last of said at least two catalytic stages, wherein the catalytic reduction takes place in a hydrogenation catalyst bed downstream from the last Claus catalytic stage, which bed is installed in the reactor of the last catalytic Claus stage.
- 15 2. Process according to claim 1, said process further comprising:
 - iv) selectively oxidising H_2S in the gas obtained in step iii) to elemental sulphur and removing elemental sulphur from the product gas of this stage.
3. Process according to claim 1 or 2, wherein the process conditions in steps i) and ii) are such, that the molar ratio of H_2S to SO_2 is between 10 : 1 and 1 : 2.
- 20 4. A process as claimed in claim 2 or 3, wherein the selective oxidation is effected in a dry oxidation bed.
5. A process as claimed in claim 2 or 3, wherein the selective oxidation takes place in a liquid.
6. Process according to claim 1-5, wherein the hydrogenation catalyst is
 - 25 selected from the group of metals of group VI and VIII of the periodic table of elements, preferably cobalt-molybdenum or nickel-molybdenum.

7. Process according to claim 1-6, wherein the hydrogenation is carried out at a temperature not exceeding 250°C.