

Title: Process for the recovery of sulfur from SO₂ containing gases

In a number of processes, such as the refining of petroleum, the purification of natural gas, and the production of synthesis gas from coal or from oil residue, sulfur-containing gas is released, in particular H₂S. This H₂S is to be removed before the above-mentioned gases can be used. The most important reason for H₂S removal is the prevention of SO₂ emission through combustion of H₂S. Also, it is well known that H₂S is a very toxic gas and has a nasty smell.

The most common method in the industry is to remove H₂S from gases through a liquid absorption agent, whereby the H₂S is brought into concentrated form, whereafter the regenerated H₂S gas is converted to elemental sulfur, which is harmless.

Also, in a number of cases it is possible to skip the first step, that is, bringing H₂S into concentrated form, and to convert the H₂S directly into elemental sulfur.

One of the most well-known and widely used methods for converting H₂S to elemental sulfur is the so-called

Claus process. The Claus process is carried out in different ways, depending on the H₂S content in the feed gas.

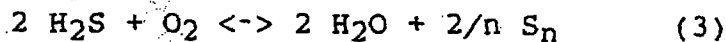
According to the most conventional embodiment, a part of the H₂S is burned to SO₂, which then proceeds to react further with the remaining H₂S to form elemental sulfur.

A detailed description of the Claus process is found in R.N. Maddox "Gas and Liquid Sweetening"; Campbell Petroleum Series (1977) pp. 239 - 243 and in H.G. Paskall "Capabilities of the Modified Claus Process", publ. Western Research & Development, Calgary, Alberta, Canada (1979).

The Claus process is based on the following reactions:



Reactions (1) and (2) result in the overall reaction



A conventional Claus plant suitable for processing gases with a H_2S content between 50 and 100% consists of a thermal stage (burner, combustion chamber, tail gas vessel and sulfur condenser) followed by a number, generally two or three, of reactor stages (gas heating, reactor filled with catalyst and sulfur condenser). In the thermal stage reactions (1) and (2) occur, in the reactor stages only reaction (2) known as the Claus reaction. In the Claus process, however, the H_2S is not completely converted to elemental sulfur, mainly as a result of the fact that the Claus equilibrium reaction (2) does not go to completion.

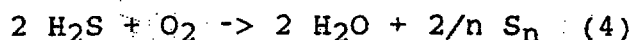
So a certain amount of H_2S and SO_2 remain. Burning this residual gas is no longer permitted in view of the stricter environmental requirements. This so-called tail gas must be further desulfurized. Tail gas processes are known to those skilled in the art and are described, for instance, in B.G. Goar, Tail Gas Clean-up Processes, a review, paper at the 33rd Annual Gas Conditioning Conference, Norman, Oklahoma, March 7-9, 1983.

The most well-known and to date most effective process for desulfurizing tail gas is the SCOT process described in Maddox "Gas and liquid sweetening" (1977). The SCOT process achieves a sulfur recovery of 99.8 to 99.9%. Drawbacks of the SCOT process are the high investment costs and the high energy consumption.

Another process for increasing the efficiency of the Claus process is the SUPERCLAUS® process. With this process the efficiency of the Claus process is increased from 94-97% to more than 99%.

5 The SUPERCLAUS® process is described in "SUPERCLAUS®, the answer to Claus plant limitations" publ. 38th Canadian Chem. Eng. Conference, Oct. 25, 1988, Edmonton, Alberta, Canada.

10 The SUPERCLAUS® process is cheaper than other known tail gas treating processes. In the SUPERCLAUS® process, reaction (2) in the thermal stage and in the Claus reactor stages is operated at excess H₂S, so that in the gas from the last Claus reactor stage the H₂S content is about 1% by volume and the SO₂ content about 0.02% by volume. In the
15 downstream reactor stage connected to it, the H₂S is selectively oxidized to elemental sulfur according to the reaction



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over a special selective oxidation catalyst.

These catalysts are described in European patents 0242920 and 0 409 353.

25 The tail gas from the SUPERCLAUS® reactor stage then still contains an H₂S content of 0.02% by volume and a SO₂ content of about 0.2% by volume and an O₂ content of 0.2-0.5% by volume.

30 Another Claus process is described in U.S. Patent 4,280,990 to Jagodzinski et al, where Claus reaction (2) occurs in liquid sulfur in the presence of standard Claus catalyst at elevated pressure, without condensation of water.

35 In this process the thermal stage is operated at pressures of 5 to 50 bar, whereafter the exiting gases are passed at the same pressure into a reactor, which is filled with a catalyst. The reaction between H₂S and SO₂ therefore occurs at pressures between 5 en 50 bar, whereby the sulfur

condenses on the catalyst. Liquid sulfur is circulated over the catalyst beds to dissipate the reaction heat. The gas from the thermal stage contains about 7.9% by volume H_2S and 3.95% by volume SO_2 , so that the ratio $H_2S : SO_2 = 2 : 1$. The reactor temperature in the first bed is set such that the exit temperature is $275^\circ C$. In a second bed the exit temperature is set at $195^\circ C$. From the examples of this method it can be derived that the conversion of these high percentages of H_2S and SO_2 proceeds better with increasing pressure. Alternatively, the same method is proposed for the desulfurization of Claus tail gas. In this case, Claus tail gas is brought to a considerable pressure.

A drawback of this process for desulfurization of both Claus process gas and Claus tail gas are, respectively, the high costs for compressors of H_2S gas (Claus feed gas) and air, and the high costs of a tail gas compressor, the high energy consumption of these compressors, the danger of leakages of toxic H_2S gas in these compressors and in other apparatus in the plant, and the operational reliability of these compressors.

That is the reason why this process so far has never found any commercial application. In the method described in U.S. Patent 4,280,990, use was made of a standard Claus catalyst. At the time of the above-mentioned patent, activated aluminas were used as Claus catalyst with a surface area of about $300 \text{ m}^2/\text{gr}$ with an average pore diameter of about 50 Angstrom. Such a catalyst is also described in U.S. Patent 4,280,990.

In the years that this process was developed, it was customary for a standard alumina catalyst to be installed in Claus reactors. It is therefore plausible that no further research was performed into other types of catalysts or that they were not available, or had not been developed yet. Nor was any research done on the required working pressure depending on the H_2S and SO_2 concentration. Most experiments described in U.S. Patent 4,280,990 are carried out with 2.5% by volume H_2S and 1.2% by volume SO_2 .

U.S. Patent 3,447,903 discloses another process, which is also based on the application of the Claus process in liquid sulfur. According to this method, the reaction is catalyzed by the presence of a slight amount of a basic
5 nitrogen compound. It appears from the examples that amounts of about 1 to 50 ppm of this compound were used. This process has never been applied commercially either.

It is an object of the invention to provide an improved method for recovering sulfur from tail gases,
10 whereby SO_2 and H_2S are removed as much as possible. More particularly, it is an object of the invention to provide a method whereby the conventional sulfur recovery methods are improved in such a manner that an industrial-scale recovery efficiency of more than 99.5% is achieved.

15 The invention provides a process for recovering sulfur from an SO_2 containing gas stream through catalytic conversion thereof to elemental sulfur, comprising converting SO_2 and H_2S in the presence of liquid sulfur and a catalyst system based on a heterogeneous catalyst which
20 catalyzes the Claus reaction, while as promoter for the Claus reaction a basic nitrogen compound is present in the liquid sulfur.

Surprisingly, it has been found that with the process according to the invention, utilizing the specific
25 promoter for the heterogeneous catalyst, a clearly improved conversion efficiency to elemental sulfur is achieved. As such, the use of liquid sulfur as a medium for the reaction had long been known. Only with the process according to the invention, however, has it become possible to carry out this
30 method at low pressures, that is, at atmospheric pressure or slightly above it.

The process can be carried out in a number of ways. Essential is that the catalyst is in direct contact
with liquid sulfur which has been supplied from an external
35 source. It is preferred that this liquid sulfur already contains an amount of the H_2S to be converted, since the conversion efficiency is then clearly higher. So, it is

possible to supply both H_2S and SO_2 from the gas phase, but this yields a lower efficiency.

In the process according to the invention, the reaction between H_2S and SO_2 to sulfur and water, in the
5 ratio of $H_2S : SO_2 = 2 : 1$, is carried out in the presence of liquid sulfur with a suitable catalyst, with the pressure being preferably between 1 and 5 bar and the temperature being preferably between 120 and 250°C.

In the process according to the invention,
10 suitable catalysts have a structure with large macropores. These include those activated aluminas that have a small micropore structure and a large volume of meso and macropores. These activated aluminas have a meso, macro and ultrastructure which contain more than 65% of the total pore
15 volume. It is also possible to use catalysts which have these properties as support material, this support material being impregnated with an active material, e.g. a metal oxide. These catalysts are often referred to as "promoted catalysts".

20 In general, it can be stated that those catalysts are useful that catalyze the Claus reaction. In addition to the activated aluminum oxide catalysts already discussed, the other catalysts known for this reaction are also suitable, such as titanium dioxide, and metal oxides on
25 support.

It was found that when water vapor is fed to the gas to be treated at pressures lower than 5 bar or when water vapor is present in the gas, this promotes the reaction between H_2S and SO_2 to sulfur and water. Also,
30 through an appropriate choice of the residence time, the efficiency can be influenced considerably.

It was also established that at pressures lower than 5 bar, when polysulfides are present in the sulfur, these react in the same manner with SO_2 to form sulfur and
35 water as does H_2S . It was found that when the gas contains oxygen, this oxygen hardly reacts, if at all, with the H_2S or sulfur present to form SO_2 .

A major advantage of the process according to the invention is the reaction at the low pressure, as a result of which all drawbacks of the process according to U.S. Patent 4,280,990 are removed.

5 In the process according to the invention, it is also possible to treat SO_2 containing gases by adding H_2S gas to these gases or by priorly dissolving H_2S in the liquid sulfur.

10 In the process according to the invention, it was established that when H_2S was priorly dissolved in the liquid sulfur, this yields a higher conversion with regard to the SO_2 and provides the advantage that the control of the required H_2S to convert the SO_2 can be simplified considerably, because the dissolved, unused H_2S remains
15 behind in the sulfur, whereafter the sulfur can be loaded with H_2S again.

Surprisingly, it was found that when in the process according to the invention a small amount of a basic nitrogen compound is present in the sulfur, the efficiency
20 of the conversion of H_2S and SO_2 to sulfur and water is improved considerably, even to the point where a practically complete equilibrium is achieved at the temperature set.

Suitable basic nitrogen compounds are amines (such as alkyl amines), alkanol amines (such as MEA, DGA, DEA,
25 DIPA, MDEA, TEA), ammonia, ammonium salts, aromatic nitrogen compounds (such as quinoline, morpholine).

Preferably, tertiary alkanol amines are used, because they do not form sulfamate, have a high boiling point, and because these amines are relatively cheap.

30 The invention will now be further clarified with reference to the drawing. In Fig. 1 H_2S - and SO_2 -containing gas is supplied via line 1 to a reactor 2 in which a catalyst 3 is present.

Liquid sulfur is supplied via line 4 and, together
35 with the entrant gas, passed over the catalyst. Liquid sulfur is produced in the catalyst bed from the reaction

between H_2S and SO_2 . The exiting gas, after reaction between H_2S and SO_2 , is discharged via line 5.

The liquid sulfur is passed via line 6 from the reactor to a cooler 7, where the reaction heat is dissipated. With the aid of pump 8, the sulfur is recirculated to the reactor 2 via line 4. The sulfur formed is discharged via line 9.

In Fig. 2 H_2S -containing gas containing more than 90% by volume H_2S is supplied via line 1 to a Claus plant 10, consisting of a thermal stage followed by two catalytic reactor stages.

The air required for the Claus reaction is supplied via line 11. The sulfur formed in the thermal stage and reactor stages is discharged via line 12. The tail gas from the second catalytic reactor stage, which still contains H_2S and SO_2 , is supplied via line 13 to a reactor 2 in which a catalyst 3 is present. Over the catalyst bed, liquid sulfur is supplied via line 4. After H_2S and SO_2 have reacted in the catalyst bed to form sulfur, the tail gas leaves the reactor via line 5. The liquid sulfur leaves the reactor via line 6 and, via a cooler 7, is recirculated to the reactor 2. The sulfur formed is discharged via line 9. Alternatively, a basic nitrogen compound can be added via line 14.

In Fig. 3 a preferred embodiment of the process according to the invention is described, where via line 1 H_2S -containing gas is supplied to a Claus plant 10, consisting of a thermal stage followed by two catalytic reactor stages.

The air required for the Claus reaction is supplied via line 11. The sulfur formed in the thermal stage and reactor stages is discharged via line 12. The tail gas from the second catalytic reactor stage, which still contains H_2S and SO_2 , is supplied via line 13 to a

SUPERCLAUS plant 15.

Via line 16 air for the selective oxidation is supplied, while via line 17 liquid sulfur is discharged. The

tail gas is supplied via line 13 to reactor 2, in which a catalyst 3 is present. Over the catalyst bed, liquid sulfur is supplied via line 4.

5 This liquid sulfur comes from column 18, in which the sulfur has been contacted with the H_2S -containing gas which was supplied to the Claus plant via line 1. In the column 18 the liquid sulfur has incorporated a part of the H_2S from the gas. After H_2S , dissolved in the liquid sulfur, and SO_2 have reacted to sulfur in the catalyst bed, the tail
10 gas leaves the reactor via line 5. The liquid sulfur leaves the reactor 2 via line 6 and is recirculated with the aid of a pump 8 via line 19 to the column 18. The sulfur formed is discharged via line 9.

In the column, the sulfur takes up H_2S again and is
15 supplied to reactor 2 again via line 20, pump 21, cooler 22 and line 4. If desired, via line 14 a basic nitrogen compound can be supplied to the liquid sulfur.

The invention is further explained in and by the following examples.

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EXAMPLE 1

Using the plant as described in Fig. 2, in a Claus plant with two catalytic stages, the Claus reaction is
25 carried out. To the thermal stage is supplied a Claus gas containing 90.0% by volume H_2S , corresponding with 36.0 kmol/h, 3.5% by volume CO_2 , 2.0% by volume hydrocarbons and 4.5% by volume H_2O and 19.5 kmol/h O_2 as air oxygen. The H_2S percentage by volume in the tail gas after the second
30 catalytic stage is 0.58% by volume, while the SO_2 content therein is 0.29% by volume and the water content therein is 33.2% by volume. The sulfur recovery efficiency of the Claus plant is 94%.

The tail gas in an amount of 120 kmol/h with a
35 temperature of $150^\circ C$, and a pressure of 1.13 bar, is supplied to the catalyst bed outlined in Fig. 2. The catalyst 3 is an activated alumina with a high meso and

macropore structure. Over the bed, liquid sulfur is circulated in an amount of 50 m³/h at a temperature of 150°C. The temperature of the circulating sulfur is kept constant by dissipating the evolved reaction heat of the process in a cooler. In order not to cause the sulfur level in the reactor to rise too far, from time to time some sulfur is drained from the system. The H₂S percentage by volume in the gas after the catalyst bed is 0.188%, while the SO₂ percentage by volume therein is 0.088%. The conversion of H₂S to sulfur in the reactor is therefore 68% and that of SO₂ is 70%.

The total sulfur recovery efficiency of the Claus plant followed by this reactor stage in which the reaction between H₂S and SO₂ occurs in liquid sulfur is thereafter more than 97.7%.

EXAMPLE 2

In the same plant as described in Fig. 2, an aromatic amine (quinoline) is added to the circulating sulfur via line 14. The amount of quinoline supplied is such that the concentration in the sulfur stream to the reactor is 500 ppm by weight.

The Claus gas to the thermal stage is the same as described in Example 1, but now 19.85 kmol/h O₂ as air oxygen is supplied in order to obtain as much SO₂ as H₂S in the tail gas after the second catalytic stage. The H₂S and SO₂ percentages by volume in the tail gas are then 0.46% each and the water content therein is 33.0% by volume. The H₂S percentage by volume in the tail gas after the catalyst bed is 0.046%, while the SO₂ percentage by volume therein is 0.018%. The conversion of H₂S to sulfur in the reactor is therefore 90% and that of SO₂ is 96%.

The total sulfur recovery efficiency of the Claus plant followed by this reactor stage in which the reaction between H₂S and SO₂ occurs in liquid sulfur is thereafter more than 99.0%.

EXAMPLE 3

In the plant as described in Fig. 3, a SUPERCLAUS reactor stage is arranged after the second catalytic stage of the Claus plant to allow selective oxidation of H_2S to sulfur in the gas from the second catalytic stage. The tail gas from the SUPERCLAUS stage is supplied to catalyst bed as outlined in Fig. 3. The Claus gas is first contacted countercurrently with a sulfur stream in a contacting vessel before the gas is passed to the thermal stage. The Claus feed gas which flows to this contacting vessel is the same as in Example 1. In the contacting vessel, 0.193 kmol/h H_2S is dissolved in the sulfur and hence withdrawn from the Claus feed gas that is passed to the thermal stage. To the thermal stage, 18.87 kmol/h O_2 as air oxygen is supplied. To the SUPERCLAUS stage, another 1.40 kmol/h O_2 as air oxygen is supplied. The H_2S percentage by volume in the tail gas after the SUPERCLAUS stage is 0.032%, while the SO_2 content therein is 0.189% by volume and the O_2 content therein is 0.50% by volume. The tail gas from the SUPERCLAUS stage in an amount of 122 kmol/h, with a temperature of 130°C and a pressure of 1.13 bar absolute is supplied to the catalyst bed outlined in Fig. 3. Over the bed is passed the liquid sulfur coming from the contacting vessel. To the liquid sulfur a tertiary alkanol amine (TEA) is added.

The sulfur is thereafter returned to the contacting vessel. The magnitude of the circulation stream is set such that sufficient H_2S with respect to the SO_2 is supplied to the catalytic bed, so that the $H_2S : SO_2$ ratio is minimally 1 : 1.

The H_2S concentration in the exiting gas after the catalyst bed is 0.015% by volume, while the SO_2 percentage by volume therein is 0.011% by volume. The conversion of H_2S to sulfur in the reactor is therefore 92% and that of SO_2 is 94%.

The total sulfur recovery efficiency of the Claus plant with SUPERCLAUS reactor stage followed by this reactor stage in which the reaction between H_2S and SO_2 proceeds in liquid sulfur, is thereupon more than 99.5%.



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CLAIMS

PART OF THIS SHEET HAS BEEN
REPLACED

1. A process for recovering sulfur from an SO_2 containing gas stream through catalytic conversion thereof to elemental sulfur, comprising converting SO_2 and H_2S in the presence of liquid sulfur and a catalyst system based on a heterogeneous catalyst which catalyzes the Claus reaction, while as promoter for the Claus reaction a basic nitrogen compound is present in the liquid sulfur.
2. A process according to claim 1, wherein the promoter is selected from the group consisting of amines, alkyl amines, alkanol amines, ammonia, ammonium salts and aromatic nitrogen compounds.
3. A process according to claim 2, wherein the promoter is selected from the group consisting of monoethanolamine, diethanolamine, DGA, DIPA, MDEA and triethanolamine.
4. A process according to claim 2 or 3, wherein a tertiary amine is used.
5. A process according to claims 1-4, wherein as Claus-active heterogeneous catalyst a porous alumina, or a porous alumina with a metal oxide provided thereon, is used.
6. A process according to claim 5, wherein the alumina has a surface area of at least $150 \text{ m}^2/\text{g}$.
7. A process according to claim 6, wherein of the pore volume, measured with nitrogen, not more than 35% by volume is present in pores of a diameter of 5 nm or less.
8. A process according to claims 1-7, which is carried out at a pressure of 1-5 bar.
9. A process according to claims 1-8, which is carried out at a temperature of 120 to 250°C .
10. A process according to claims 1-9, wherein H_2S is dissolved in liquid sulfur, which is thereafter contacted with SO_2 .
11. A process according to claim 10, wherein gas having a H_2S content of at least 0.5% by volume is contacted with liquid sulfur, whereby a part of the H_2S dissolves in

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the sulfur, thereafter the H_2S -containing gas stream is supplied to a Claus plant, whereby a part of the H_2S is thermally converted to SO_2 , whereafter in one or more stages sulfur is formed in a catalytic Claus plant, the gas mixture
5 thereby obtained, after separation of sulfur, is converted directly or, if desired, after a selective oxidation step, in the presence of the liquid sulfur which contains dissolved H_2S .

12. A process according to claims 1-10, wherein tail
10 gas of a catalytic stage of a Claus plant, having an H_2S content of at least 0.25% by volume is contacted with liquid sulfur, whereby at least a part of the H_2S dissolves in the liquid sulfur, whereafter said H_2S -containing liquid sulfur is contacted with the SO_2 -containing gas, in the presence of
15 the catalyst system based on a heterogeneous catalyst which catalyzes the Claus reaction, while as promoter for the Claus reaction a basic nitrogen compound is present in the liquid sulfur.

13. A process according to claims 1-12, wherein the
20 amount of promoter, based on the weight of the liquid sulfur, is between 1 and 1000, preferably between 1 and 50 ppm.

14. A process according to claims 1-14, wherein the
25 reaction is carried out in a fixed bed of catalyst particles or other bodies on which catalyst has been provided, and wherein these particles or bodies are irrigated with liquid sulfur.