

BeschreibungHydrogen production from refinery acid gas and sour water stripper

This invention relates to the production and capture of hydrogen from the partial oxidation and/or cracking of hydrogen sulphide and ammonia.

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Several different industrial and chemical processes produce waste gas streams comprising amongst other gases hydrogen sulphide, ammonia, carbon dioxide and moisture. The Claus process is one that is conventionally used to treat such waste streams. In the Claus process the waste gas stream comprising hydrogen sulphide is fed to an upstream furnace, termed as "Claus reaction furnace", in which a part of the hydrogen sulphide is oxidised in a flame region to form sulphur dioxide and thermal reaction takes place between the sulphur dioxide and hydrogen sulphide at least in part downstream of the flame region to form water vapour and sulphur vapour. Accordingly, there is a net partial oxidation of some of the hydrogen sulphide to sulphur vapour.

Other reactions typically take place in the furnace including the thermal cracking of hydrogen sulphide to form hydrogen and sulphur vapour, depending on reaction furnace temperature. At a temperature typical of the operating temperature of the Claus reaction furnace between 1000 and 1400°C, it would be expected that a significant quantity of the hydrogen sulphide has either reacted with oxygen to form sulphur dioxide or dissociated to hydrogen and sulphur. An effluent gas stream containing hydrogen sulphide, sulphur dioxide, hydrogen, sulphur vapour and water vapour leaves the furnace through a Waste Heat Boiler (WHB). The purpose of the WHB is to cool the gas from the Claus reaction furnace to a suitable temperature for condensation of liquid sulphur for further catalytic processing of the effluent gas stream and the generation of medium pressure steam, typically in the range 30-60 barg. The design of the WHB is such that the gas exiting the Claus reaction furnace at a temperature typically in the range of 1000-1400°C, is quenched to the temperature of the steam system, at typical temperatures in the range 230-275°C, within residence time typically in the range of 50 to several hundred milliseconds, depending on throughput and the velocity of the gases through the WHB's heat transfer tubes. During the slow quench of the gases exiting the Claus reaction furnace, sulphur will react and recombine with hydrogen to form

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hydrogen sulphide. Typically, the hydrogen levels in the effluent gas after the WHB are in the range 2-6% vol (wet).

If air is used to support the combustion of the hydrogen sulphide, the effluent gas stream also contains nitrogen and argon. The amount of nitrogen in the effluent gas stream can be kept down by using commercially pure oxygen or oxygen-enriched air instead of air unenriched in oxygen to support the combustion. In addition, the hydrogen sulphide-containing feed gas stream typically includes carbon dioxide as a component, so the effluent gas stream also contains carbon dioxide. The effluent gas stream is cooled in the WHB and has sulphur extracted therefrom. The resulting sulphur vapour depleted effluent gas stream is subjected to a train of treatment stages in which it is reheated, passed over a catalyst of the reaction between hydrogen sulphide and sulphur dioxide, the so-called "Claus" reaction, in order to form further water vapour and sulphur vapour, and the resulting sulphur vapour is extracted, again conventionally by condensation. A conventional Claus plant typically has two or three such trains of stages in series.

For a 3-stage configuration the resulting effluent gas typically contains less than 3% of the original content of sulphur atoms in the feed gas. If a higher standard of purification is required, the effluent gas may be treated in a tail gas clean up unit, where SO₂, CS₂ and COS formed in the Claus process are hydrogenated on a hydrodesulphurisation bed (typically Cr-Mo catalyst) to H₂S, prior to water removal, typically by direct quench. The hydrogen sulphide is captured from the Claus gas exhaust stream in an amine absorber, and regenerated for recycle to the inlet feed to the Claus reaction furnace. Hydrogen is required for the hydrogenation reactions and is typically generated with a reducing gas generator, firing natural gas or other hydrocarbon fuel sub-stoichiometrically. This generation supplements the hydrogen in the Claus gas exiting the Waste heat boiler. The hydrogen demand is highly dependent on the SO₂ in the exhaust gas stream to the tail gas clean-up unit, and can be reduced by controlling the SO₂ exiting the final Claus catalytic bed, via the control of air/oxygen to the Claus reaction furnace.

The use of oxygen-enriched air or commercially pure oxygen to support the combustion of the hydrogen sulphide is particularly advantageous because it makes possible a throughput of feed gas at a higher rate than would be possible were air unenriched in

oxygen to be the sole gas used for supporting the combustion of hydrogen sulphide. Oxygen enriched conditions promote higher reaction furnace temperatures and the almost complete destruction of contaminants such as ammonia. Under oxygen enriched combustion at higher temperature there is also a much higher level of dissociation of hydrogen sulphide to hydrogen and sulphur.

The Claus process is particularly used in oil and gas refineries. For example, in an oil refinery, the Claus process may be used to treat a waste acid gas stream. One example of such a stream is so-called amine gas which typically comprises hydrogen sulphide and carbon dioxide, hydrocarbons, and water vapour. Another example is sour water stripper, a gas which typically comprises hydrogen sulphide, water vapour and ammonia. The sour water stripper can be treated in the Claus furnace with the hydrogen sulphide-containing feed gas. Given enough reaction furnace temperature ($> 1300^{\circ}\text{C}$) and residence time, the ammonia can be thermally dissociated, into nitrogen and hydrogen in the reaction furnace.

The hydrogen sulphide in amine acid gas and sour water stripper treated in the Claus reaction furnace is produced in refinery processing, in the desulphurization of various refinery hydrocarbon fractions. Hydrogen is required to desulphurize the different hydrocarbons fractions. It is typically produced using carbon intensive technologies like the steam methane reforming of natural gas, whereby significant quantities of carbon dioxide are generated, typically around 9-10 tonnes of carbon dioxide per tonne of hydrogen produced, and as such has been termed as "grey hydrogen". As the sulphur level in the crude to the refinery increases, due to the global reduction in the amount of lower sulphur sweet crude available, and the level of sulphur in the refinery hydrocarbon products decreasing, a higher level of desulphurization is required, consuming greater quantities of grey hydrogen.

It is the aim of the invention to provide a method to generate hydrogen from hydrogen sulphide and ammonia present in amine acid gas and sour water stripper in a Claus sulphur recovery unit and therefore minimize the production of grey hydrogen from carbon intensive technologies. Such hydrogen generation from the sulphur recovery unit can be deemed as "blue hydrogen" since it is produced without significant generation of greenhouse gases, including carbon dioxide. In effect the hydrogen is recycled in a chemical looping process from the Claus sulphur recovery unit, thereby

reducing the on-purpose hydrogen produced from carbon intensive technologies, such as the steam methane reforming of natural gas, thereby reducing greenhouse gases such as carbon dioxide from a refinery.

5 The invention provides apparatus for the partial oxidation of hydrogen sulphide comprising a burner such as a SURE® burner (as described in detail in e.g. EP974552, EP1240460, and EP1483199) arranged to fire into a furnace. The burner having a first inlet communicating with a source of a first feed stream comprising primarily hydrogen sulphide, ammonia, carbon dioxide and moisture, a second inlet for a second feed
10 stream of pure oxygen (> 99.7%vol) and a third inlet for air or oxygen enriched air as third feed stream. In use, the burner oxidises a part of the hydrogen sulphide content of the first feed stream to sulphur dioxide. The furnace being arranged such that, in use, some so formed sulphur dioxide reacts with residual hydrogen sulphide to form sulphur vapour and water vapour.

15 The limiting factor for the use of a single reaction furnace in order to achieve all the oxidation reactions is typically determined by the high temperature resistance of the refractory in the furnace. For a single reaction furnace the adiabatic flame temperatures would typically be controlled below 1500°C, provided high temperature
20 refractory is used in the furnace exposed to the flame.

The temperature of the Claus reaction furnace can be controlled via the volumetric flow of pure oxygen relative to air, or oxygen enrichment level, to meet the stoichiometric requirements of oxygen for the Claus reaction. Typically for a refinery acid gas stream
25 the oxygen enrichment level can be increased from 21%vol to 28%vol via simple addition of oxygen to the air, before oxygen must be added separately to the burner, for levels 28 to 100%vol. Up to a level of 40-50%vol oxygen enrichment the reaction furnace temperatures can be maintained within safe operating limits of the refractory, typically less than 1500°C. For higher levels of oxygen enrichment temperatures can
30 be controlled for example via the addition of oxygen to two or more reaction furnace zones, with waste heat recovery in-between, as licensed in the Linde SURE® Double Combustion process.

At these elevated Claus reaction furnace temperatures hydrogen sulphide dissociates
35 into hydrogen and sulphur, to a higher level than > 40%vol in the hot flame region. The

level of highest dissociation of hydrogen sulphide, measured as hydrogen, closely matches with the region of highest flame temperature within the furnace.

Investigations of the chemistry within the Claus reaction furnace used sampling probes
5 to take small samples of the furnace gas and quench them from about 800-1400°C to
below 150°C within a few milliseconds (< 6ms). This made it possible to freeze the
chemistry and avoid recombination reactions such as those of hydrogen and sulphur to
hydrogen sulphide, which are normal within the long residence time typical of
commercial waste heat boiler operation. The sampling probe had a water-cooled jacket
10 to protect from the furnace environment, steam jacket to quench the sample, at a
temperature to avoid solidification of sulphur, and quartz lining to prevent reactions
within the probe.

The fast quench of the Claus reaction furnace chemistry, has shown that it is possible
15 to avoid the recombination of hydrogen and sulphur, thereby maintaining a high
concentration of hydrogen in the exit stream from the reaction furnace. Once the exit
stream is cooled to a temperature in the range 150-300°C, the hydrogen will largely be
maintained through the downstream catalytic stages, since hydrogen is relatively
unreactive at these temperatures.

20 The invention relates to the fast quench of the chemical species present in the reaction
furnace at high temperature, typically in the range 1300-1500°C, from a high level of
oxygen enrichment, typically in the range 45-100%vol, thereby avoiding chemical
recombination. The invention provides several options to rapidly quench the Claus
25 reaction furnace gas.

In a first option, described with reference to figure 1, the exit stream 7 from the Claus
reaction furnace C is subjected to rapid quench via a conventional waste heat boiler
tube configuration W, which is operated at a high mass flux of more than 5kg/m²s. This
30 can be achieved using narrower diameter waste heat boiler tubes, at internal diameter
0.5 to 2 inches, than the current design of internal diameter 2 to 4 inches. An increased
number of tubes will be required for the tube sheet, to minimize the increase in
pressure drop, which may require a large tube sheet, relative to current design. It may
also be necessary to include a blower or compressor to increase the pressure of the
35 amine acid gas and sour water stripper 1 to the Claus reaction furnace C, thereby

allowing for a higher pressure drop, higher velocities and faster quench through the waste heat boiler W. The oxygen 2 used in the Claus reaction furnace C can typically be made available at a much higher pressure of 5-10 barg.

5 It is proposed to operate the Claus reaction furnace with an oxygen supply that is less than the oxygen supply usually used to achieve a $\text{H}_2\text{S}:\text{SO}_2$ ratio of 2:1 for the downstream Claus reaction on the catalytic stages K, and to control the oxygen supply in such a way that the $\text{H}_2\text{S}:\text{SO}_2$ ratio at the exit of the final Claus catalytic stage (K) is 20:1 or higher. This reduction in oxygen has the effects of reducing the temperature of
10 the Claus reaction furnace C to a level that can be controlled with a single reaction furnace, depending on acid gas strength and of maximising the hydrogen generation under much more reducing conditions in the Claus reaction furnace C and minimizing the hydrogen demand to convert SO_2 to H_2S in the hydrodesulphurisation reactor H of the tail gas clean-up unit T, thereby maximizing the hydrogen generated.

15 The exit gas 8 from the catalytic stages K, is treated in a hydrodesulphurisation unit H to form a hydrotreated stream 9, which is cooled in a direct water quench Q and passed through the amine wash A of the tail gas clean-up unit T, to absorb H_2S and some CO_2 , and to receive an acid gas recycle stream 3 consisting predominantly of
20 H_2S , as well as an exit stream 4, rich in hydrogen. Unlike in the prior art, the exhaust gas stream 4 is not combusted but fed to a separation unit P to recover "blue hydrogen" 5, preferably with purity higher than 99.9%vol, by pressure swing absorption and/or in a membrane process. The also produced residual stream 6, consisting mainly of nitrogen and carbon dioxide, can be fed to an incinerator I or used as fuel.

25 In a second option, described with reference to figure 2, the exit stream 7 from the Claus reaction furnace C is subjected to rapid direct water quench D. In such a concept the Claus reaction furnace C is vertically mounted, with a burner B firing in a downward direction into a refractory lined reaction chamber. A refractory choke ring R is located at
30 the bottom of the Claus reaction furnace C to accelerate the gas flow prior to entry into the direct water quench D. At the top of the quench section water 11 is injected through a quench ring E built into the refractory of the choke ring R. The quench ring is a cylindrical pipe with orifices positioned to provide a high velocity water spray, reducing the temperature of the hot gases exiting the Claus reaction furnace C, to 100-120°C,
35 depending on the operating pressure of the direct water quench D. The gas flows

through a dip tube F and exits as quenched gas 12 from the side of the quench section D for reheat, prior to transfer to the downstream catalytic sections (not shown). The quench water 11 at a temperature, typically 10-50°C is routed at sufficient pressure and flow for direct water quench. A stream 13, comprising quench water, condensed water
5 from the Claus reaction and solid sulphur in suspension, is drained off from the bottom of the quench section D. After flashing to atmospheric conditions (not shown), the sulphur can be removed either from settling tanks, before further drying or passing through pressurised filter presses to produce sulphur filter cake as product and quench water for recycling to the direct water quench D.

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In a third option, described with reference to figure 3, the exit stream 7 from the Claus reaction furnace C is subjected to rapid quenching by expansion through an orifice O using Fristoms technology.

15 Such a quench can be combined with a traditional waste heat boiler, where a restriction is added just downstream of the tube sheet, providing a rapid expansion downstream and improved quench rate. Such an option would require additional pressure drop and therefore the acid gas, sour water stripper, air and oxygen would need to be routed to the reaction furnace at increased pressure via blower or compressor.

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The above three options provide a means to quench the Claus reaction furnace gas within a few milliseconds, maintaining a high level of hydrogen in the exit gas (as shown by pilot plant results). Once sulphur has been condensed or filtered given the use of water quench, the Claus reaction furnace gas can be routed through 2-3
25 catalytic Claus reactors to continue the Claus reaction and yield of sulphur prior to the hydrodesulphurisation unit of the tail gas clean-up unit. Hydrogen levels are maintained through the catalytic stages and consumption in the hydrodesulphurisation unit minimized, given operation at a H₂S:SO₂ ratio higher than 20:1, without have a significantly detrimental impact of sulphur conversion.

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Using pure oxygen in the Claus reactor furnace minimizes the flow of nitrogen inert through the plant and allows for cost effective pressure swing absorption and/or membrane process for recovering of hydrogen. The "blue hydrogen" stream from the pressure swing absorption and/or membrane process can be used in a refinery, for
35 desulphurisation, hence chemically looping the hydrogen.

Patent Claims

1. A method for the production of hydrogen (5) from a hydrogen sulphide and ammonia containing first feed stream (1), comprising:
 - 5 (a) oxidizing part of the hydrogen sulphide content of said first feed stream (1) in a flame region in a Claus furnace (C) to form sulphur dioxide, and reacting hydrogen sulphide and sulphur dioxide in the furnace (C) and in downstream catalytic reactors (K) to form sulphur;
 - 10 (b) introducing into the Claus furnace (C) as second feed stream (2) pure oxygen or oxygen enriched air to achieve a temperature to within a range of 1300-1500°C, and providing conditions for a high level of hydrogen sulphide dissociation into hydrogen and sulphur;
 - 15 (c) controlling the Claus furnace temperature, so not to cause refractory damage;
 - (d) quenching the Claus reaction furnace exhaust gas (7) upstream the catalytic reactors (K) in less than 6 milliseconds to a temperature below 150°C;
 - 20 (e) extracting sulphur from the gas downstream the quench and downstream the catalytic reactors (K);
 - (f) hydrotreating the sulphur depleted gas (8) in a hydrodesulphurisation unit (H) to form a hydrotreated gas (9), and
 - 25 (g) separating off hydrogen (5) from the hydrotreated gas (9).
2. The method according to Claim 1, wherein the Claus reaction furnace exhaust gas (7) is quenched via a waste heat boiler (W), whose heat transfer tubes have
30 internal diameter of 0.5-2 inches.
3. The method according to Claim 1, wherein the Claus reaction furnace exhaust gas (7) is quenched via direct water quench (D).
4. The method according to Claim 1, wherein the Claus reaction furnace exhaust gas (7) is quenched via an expansion orifice (O).

5. A method according to any of Claims 1 to 4, wherein the amount of oxygen supplied to the Claus reactor furnace (C) is controlled in such a way that the $\text{H}_2\text{S}:\text{SO}_2$ ratio at the exit of the final Claus catalytic stage (K) is 20:1 or higher.
- 5 6. A method according to any of Claims 1 to 5, wherein the hydrotreated gas (9) is cooled in a direct water quench (Q) before it is passed through an amine wash (A) to receive an acid gas stream (3) consisting predominantly of H_2S for recycle to the Claus reaction furnace (C), as well as an exit stream (4), rich in hydrogen.
- 10 7. The method according to Claim 6, wherein the hydrogen-rich exit stream (4) is treated by pressure swing absorption or a membrane process (P) to receive a hydrogen product (5).