

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 November 2011 (03.11.2011)

(10) International Publication Number
WO 2011/134847 A2

(51) International Patent Classification:
F01K 3/24 (2006.01)

(21) International Application Number:
PCT/EP2011/056261

(22) International Filing Date:
19 April 2011 (19.04.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10161374.3 28 April 2010 (28.04.2010) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: PROCESS FOR PRODUCING POWER FROM A SOUR GAS

(57) Abstract: A process for producing power from a sour gas comprising H₂S, the process comprising the steps of: (a) providing a sour gas stream comprising natural gas and H₂S to an acid gas removal unit, resulting in a cleaned natural gas and an acid gas stream comprising H₂S; (b) combusting the cleaned natural gas stream with an oxygen containing gas in a gas turbine to produce power and a hot flue gas; (c) sending the hot flue gas to a first heat recovery steam generator to generate steam and a clean flue gas; (d) combusting at least part of the H₂S in the acid gas stream comprising H₂S in the presence of an oxygen containing gas to obtain a hot gas effluent comprising SO₂; (e) sending the hot gas effluent comprising SO₂ to a second heat recovery steam generator to generate steam and a cooled gas effluent comprising SO₂; (f) leading the cooled gas effluent comprising SO₂ to a sulfuric acid unit to produce sulfuric acid, steam and a cleaned flue gas stream.



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PROCESS FOR PRODUCING POWER FROM A SOUR GAS

The present invention relates to a process for producing power from a sour gas comprising H₂S, particularly a hydrogen sulphide containing gaseous stream derived from natural gas. The method is particularly useful when combined with a sulfuric acid unit.

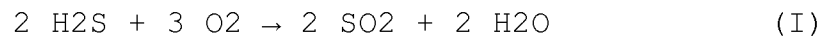
Sour gas comprising H₂S can originate from various sources. For example, numerous natural gas wells produce sour natural gas, i.e. natural gas comprising H₂S and optionally other contaminants. Natural gas is a general term that is applied to mixtures of light hydrocarbons and optionally other gases (nitrogen, carbon dioxide, helium) derived from natural gas wells. The main component of natural gas is methane. Further, often other hydrocarbons such as ethane, propane, butane or higher hydrocarbons are present.

It is desirable to reduce the amount of hydrogen sulphide in sour gas for a number of reasons. Sulphur-containing compounds, such as hydrogen sulphide and oxides of sulphur, are controlled by emission standards in many countries. Furthermore, especially hydrogen sulphide can cause erosion of equipment.

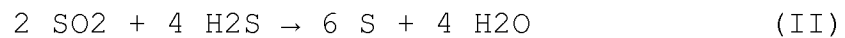
The Claus process is frequently used for the treatment of hydrogen sulphide recovered from various gas streams, such as hydrocarbon streams, for example natural gas. The multi-step process produces sulphur from gaseous hydrogen sulphide.

The Claus process comprises two steps, a first thermal step and a second catalytic step. In the first thermal step, a portion of the hydrogen-sulphide in the

gas is oxidised at temperatures above 850 °C to produce sulphur dioxide and water:



In the second catalytic step, the sulphur dioxide produced in the thermal step reacts with hydrogen sulphide to produce sulphur and water:



The gaseous elemental sulphur produced in step (II) can be recovered in a condenser, initially as liquid sulphur before further cooling to provide solid elemental sulphur. In some cases, the second catalytic step and sulphur condensing step can be repeated more than once, typically up to three times to improve the recovery of elemental sulphur.

The second catalytic step of the Claus process requires sulphur dioxide, one of the products of reaction (I). However, hydrogen sulphide is also required. Typically approximately one third of the hydrogen sulphide gas is oxidised to sulphur dioxide in reaction (I), in order to obtain the desired 1:2 molar ratio of sulphur dioxide to hydrogen sulphide for reaction to produce sulphur in the catalytic step (reaction (II)). The residual off-gases from the Claus process may contain combustible components and sulphur-containing compounds, for instance when there is an excess or deficiency of oxygen (and resultant overproduction or underproduction of sulphur dioxide). Such combustible components can be further processed, suitably in a Claus off-gas treating unit, for instance in a Shell Claus Off-gas Treating (SCOT) unit.

The overall reaction for the Claus process can therefore be written as:



As conventional Claus installations are costly, both in terms of capital expenditure as well as in terms of operational costs, alternative processes have been reported.

5 It is an object of the invention to provide a process for generating power more efficiently from a sour gas comprising hydrogen sulphide.

10 It is a further object of the invention to provide a process wherein the generation of power from a sour gas is combined with the production of sulphuric acid.

15 To this end, the invention provides a process for producing power from a sour gas comprising H₂S, the process comprising the steps of: (a) providing a sour gas stream comprising natural gas and H₂S to an acid gas removal unit, resulting in a cleaned natural gas and a
20 acid gas comprising H₂S; (b) combusting the cleaned natural gas stream with an oxygen containing gas in a gas turbine to produce power and a hot flue gas; (c) sending the hot flue gas to a first heat recovery steam generator to generate steam and a clean flue gas; (d) combusting at
25 least part of the H₂S in the acid gas comprising H₂S in the presence of an oxygen containing gas to obtain a hot gas effluent comprising SO₂; (e) sending the hot gas effluent comprising SO₂ to a second heat recovery steam generator to generate steam and a cooled gas effluent
30 comprising SO₂; (f) leading the cooled gas effluent comprising SO₂ to a sulfuric acid unit to produce sulfuric acid, steam and a cleaned flue gas stream.

30 The process according to the invention uses the thermal energy used for power generation more efficiently from highly contaminated sour gases. The invention is suitable for sour gases wherein the sour gas comprises preferably in the range of from 1 to 50 vol% H₂S, more

preferably in the range of from 10 to 35 vol% H₂S. In addition the invention allows to produce sulphuric acid by leaving out the production of sulphur. This reduces the amount of process steps and the related process equipment.

5 According to prior art processes a sour gas is treated to generate a cleaned natural gas stream for power generation in a so-called combined cycle involving a gas turbine and a steam turbine. The resulting acid gas containing most of the H₂S is sent to a sulphur recovery
10 unit for the production of solid sulphur that is then degassed, pelletized, stored and shipped. The combustion energy of H₂S, that can be as much as 30% of the chemical energy of the sour gas, is not being used for power generation in the line-up.

15 One of the uses for the produced sulphur pellets is sulphuric acid production. In for example US-A-20090077944 the use of elemental sulphur is described, wherein the solid sulphur is combusted. The sulphur-burning combustor generates hot sulphur dioxide while a pressure-exchanging
20 ejector mixes the hot combustion gases with a cooler gas (e.g. pressurized air, pressurized N₂ or recycled sulphur dioxide to form a mixed working gas having a temperature below the maximum allowable temperature (metallurgical limit) of the blades of the turbine. The formed sulphur
25 dioxide is delivered to a sulphuric acid plant to produce sulphuric acid.

 Thus one of the main differences of the current invention with processes according to the prior art is that in prior art processes elemental sulphur is being
30 produced, that might be used in a second process for the production of sulphuric acid on a different location, while the current invention preferably fully converts all H₂S to SO₂ in one step, followed by the conversion in

sulphuric acid. The process according to the present invention is therefore much more energy efficient.

Sour gas streams are commonly hydrocarbon streams, for instance natural gas streams. Natural gas is comprised substantially of methane, normally greater than 50 mol%, typically greater than 70 mol% methane. Depending on the source, the natural gas may contain varying amounts of hydrocarbons heavier than methane such as ethane, propane, butanes and pentanes as well as some aromatic hydrocarbons. The natural gas may also contain various amounts of hydrogen sulphide. For instance, some natural gas fields contain natural gas having 15-30% hydrogen sulphide by volume. The gas may also contain other non-hydrocarbon impurities such as H₂O, N₂, CO₂ and the like.

The impurity content of extracted natural gas has tended to gradually increase over time in association with the decreasing availability of good quality of natural gas. In addition, environmental legislation is becoming stricter in terms of the impurity content of burned gases. As a result, it is becoming increasingly necessary to treat the natural gas to remove the impurity gases therefrom in order to produce a product gas having a desired specification. In the process according to the invention the sour gas is first treated in an acid gas removal unit.

There are known methods for separating a gaseous stream comprising hydrogen sulphide from a gaseous hydrocarbon stream in an acid gas removal unit, such as natural gas, to provide a gaseous stream comprising hydrogen sulphide and purified natural gas.

In step b) of the process according to the invention the cleaned natural gas stream is combusted with an

oxygen containing gas. The oxygen containing gas might be pure oxygen, or air, or oxygen-enriched air. In order to omit the need to separate air to provide oxygen-enriched air or pure oxygen it is preferred to use air to combust the hydrogen sulphide. There are known methods and apparatuses for operating a gas turbine. The hot flue gas that is being generated has a temperature in the range of from 400 to 700°C.

Step (c) of the process described herein uses the heat of the hot flue gas to generate steam in a heat recovery steam generator. Thus the steam formed is used to drive one or more steam turbines. The steam streams used to drive the steam turbines may be saturated steam streams, or the steam streams may be superheated.

The steam turbines may be selected from the group consisting of: backpressure turbines, condensing turbines, backpressure/condensing turbines, condensing/extracting turbines, condensing/admission turbines, and condensing/extraction/admission turbines. In another embodiment, the steam turbines may be used to drive one or more of the group consisting of electrical generators, pumps and compressors.

In another embodiment, heat may be cogenerated with power by extracting steam from the steam turbines. The steam may be extracted at a pressure of 5 bara, and may be fed to any steam consumer (such as reboilers, live steam injection, general heat exchangers). The extraction pressure level is typically dictated by the requirements of the consumers.

In step d) of the process a hot gas effluent comprising SO₂ is being generated by combusting at least part of the H₂S that is present in the acid gas. Preferably at least 50% of the H₂S of the acid gas

comprising H₂S is being combusted, more preferably at least 70% of the H₂S is being combusted, even more preferably at least 90% of the H₂S is being combusted. The temperature of the hot gas effluent comprising SO₂ is preferably in the range of from 400 to 700°C. This heat is used in step e) in a second heat recovery steam generator to generate steam. The reason for using a second steam generator and not the same steam generator of step c) is that the flue gas generated in step b) is already a cleaned flue gas, that requires no further treatment before sending it to the stack. Thus according to the invention the gas effluent comprising SO₂ remains as concentrated as possible, to keep the stream that needs further treatment as small as possible.

In step f) the gas effluent is being sent to a sulfuric acid unit, which removes sulphur dioxide from the gas effluent and uses it to generate sulphuric acid. The sulphuric acid unit can produce sulphuric acid from the sulphur dioxide in the gas effluent in a manner known in the art. For example, the sulphur dioxide can first be oxidised to sulphur trioxide, SO₃, with oxygen from an oxygen-comprising stream such as air. A catalyst, such a vanadium (V) oxide catalyst may be present.

The gaseous sulphur trioxide may then be treated with water, to produce sulphuric acid in an exothermic reaction. In order to control the heat evolved, it is preferred to treat the sulphur trioxide with 2-3 wt% water comprising 97-98 wt% sulphuric acid to produce 98-99 wt% concentrated sulphuric acid.

In an alternative embodiment, the sulphur trioxide can be treated with oleum, H₂SO₄, to form concentrated sulphuric acid. Such processes together with other methods for manufacturing sulphuric acid from sulphur

dioxide are well known to the skilled person. The concentrated sulphuric acid can then be added to water to provide aqueous sulphuric acid.

5 The resulting combustion product of step e), the cooled gas effluent comprising SO₂, is a gaseous mixture comprising predominantly sulphur dioxide, nitrogen, carbon dioxide and optionally residual oxygen. This gaseous mixture may be partly separated or partly concentrated to increase the sulphur dioxide content, e.g. by removing the nitrogen. It is preferred to subject at least part of the cooled gas effluent comprising SO₂ to an SO₂ concentration step between step (e) and step (f), thereby generating a gas stream comprising at least 70% SO₂ on dry basis.

15 The advantage of having a sulphur dioxide concentration step between step (e) and (f) is that the size of the sulfuric acid unit can be decreased, in the preferred case that the gas stream comprising at least 70% SO₂ on dry basis is send to the sulfuric acid unit. Furthermore, by tailoring the composition of the cooled effluent comprising SO₂, one becomes more flexible in the choice of the sulfuric acid unit to be used for the production of sulphuric acid. The sulfuric acid unit may comprise a dry sulphuric acid process, or the contact H₂SO₄ process, or a wet sulphuric acid process, or both next to each other. Preferably, tailoring the composition of the cooled effluent comprising SO₂ might be done by combining the gas stream comprising at least 70% SO₂ on dry basis with the non-treated part of the cooled gas effluent comprising SO₂ before step (f).

30 The sulphur dioxide can be concentrated by any process know in the art such as for example by using liquid absorption, e.g. the CanSolv process, adsorption,

membrane separation or by condensation of the sulphur dioxide. Sulphur dioxide condenses at much higher temperatures, i.e. at approximately -10°C , than for instance nitrogen. Due to the high condensation temperature of sulphur dioxide, the post combustion separation of sulphur dioxide and nitrogen is preferred to the pre combustion separation of oxygen and nitrogen.

A most preferred manner for sulphur dioxide concentration is by contacting the gas effluent comprising sulphur dioxide (i.e. the mixture comprising sulphur dioxide and nitrogen) with an absorbing liquid for sulphur dioxide in a sulphur dioxide absorption zone to selectively transfer sulphur dioxide from the combustion gas effluent to the absorbing liquid to obtain sulphur dioxide-enriched absorbing liquid and subsequently stripping sulphur dioxide from the sulphur dioxide-enriched absorbing liquid to produce a lean absorbing liquid and the sulphur dioxide-containing gas.

One preferred absorbing liquid for sulphur dioxide comprises at least one substantially water immiscible organic phosphonate diester.

Another preferred absorbing liquid for sulphur dioxide comprises tetraethyleneglycol dimethylether.

Yet another preferred absorbing liquid for sulphur dioxide comprises diamines having a molecular weight of less than 300 in free base form and having a pKa value for the free nitrogen atom of about 3.0 to about 5.5 and containing at least one mole of water for each mole of sulphur dioxide to be absorbed.

Stripping of sulphur dioxide from the sulphur dioxide-enriched absorbing liquid is usually done at elevated temperature. To provide a more energy-efficient process, steam generated in a heat recovery steam

generator unit can be used to provide at least part of the heat needed for the stripping of sulphur dioxide from the sulphur dioxide-enriched absorbing liquid.

Preferably, steam generated in steps (c), (e) or (f) may be used for the sulphur dioxide concentration.

In a preferred embodiment of the invention, the steam generated in step (c), (e) and (f) are being collected in one steam collecting vessel. The steam can be distributed to various locations in the process, where heat or power is being required.

In a further preferred embodiment of the invention, the clean flue gas of step (c) and the cleaned flue gas stream of step (f) are being combined and send to one common stack.

Depending on the concentration of the H₂S of the sour gas and the SO₂ concentration step, one might choose the process for the production of sulphuric acid. Preferably, when the sour gas comprises in the range of from 1-20 vol%, more preferably in the range of from 10-20 vol%, even more preferably in the range of from 15-20 vol% H₂S, the sulfuric acid unit of step (f) comprises a wet sulfuric acid process. In another preferred embodiment, when the sour gas comprises more than 15 vol% H₂S, more preferably in the range of from 20 to 50 vol% H₂S, even more preferably in the range of from 20-35 vol% H₂S, the sulfuric acid unit of step (f) comprises a dry sulfuric acid process.

C L A I M S

- 5 1. A process for producing power from a sour gas
comprising H₂S, the process comprising the steps of:
(a) providing a sour gas stream comprising natural gas
and H₂S to an acid gas removal unit, resulting in a
cleaned natural gas and a acid gas comprising H₂S;
10 (b) combusting the cleaned natural gas stream with an
oxygen containing gas in a gas turbine to produce power
and a hot flue gas;
(c) sending the hot flue gas to a first heat recovery
steam generator to generate steam and a clean flue gas;
15 (d) combusting at least part of the H₂S in the acid gas
comprising H₂S in the presence of an oxygen containing
gas to obtain a hot gas effluent comprising SO₂;
(e) sending the hot gas effluent comprising SO₂ to a
second heat recovery steam generator to generate steam
20 and a cooled gas effluent comprising SO₂;
(f) leading the cooled gas effluent comprising SO₂ to a
sulfuric acid unit to produce sulfuric acid, steam and a
cleaned flue gas stream.
- 25 2. A process according to claim 1, wherein between step
(e) and step (f) at least part of the cooled gas effluent
comprising SO₂ is subjected to an SO₂ concentration step,
thereby generating a gas stream comprising at least 70%
SO₂ on dry basis.
- 30 3. A process according to claim 2, wherein the gas
stream comprising at least 70% SO₂ on dry basis is send
to a sulfuric acid unit to produce sulfuric acid, steam
and a cleaned flue gas stream.

4. A process according to claim 3, wherein the sulfuric acid unit comprises a dry sulphuric acid process.

5. A process according to claim 2, wherein the gas stream comprising at least 70% SO₂ on dry basis is combined with the non-treated part of the cooled gas effluent comprising SO₂ before step (f).

6. A process according to anyone of claims 1-5, wherein in step (d) at least 50% of the H₂S in the acid gas comprising H₂S is being combusted, preferably at least 70% of the H₂S is being combusted, more preferably at least 90% of the H₂S is being combusted.

7. A process according to anyone of claims 1-6, wherein the steam generated in step (c) and the steam generated in step (e) are being collected in one steam collecting vessel.

8. A process according to anyone of claims 1-7, wherein the clean flue gas of step (c) and the cleaned flue gas stream of step (f) are being combined and send to one common stack.

9. A process according to anyone of claims 1-8, wherein the sour gas comprises in the range of from 1 to 50 vol% H₂S.

10. A process according to anyone of claims 1-8, wherein the sour gas comprises in the range of from 10 to 20 vol% H₂S and the sulfuric acid unit of step (f) comprises a wet sulfuric acid process.

11. A process according to anyone of claims 1-8, wherein the sour gas comprises in the range of from 20 to 35 vol% H₂S and the sulfuric acid unit of step (f) comprises a dry sulfuric acid process.