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(54) **Improved process for removing and recovering H2S from a gas stream.**

(57) A process for altering the composition of a feed gas containing H_2S equivalents is disclosed, wherein said feed gas comprises $C0_2$ and H_2S equivalents, typically H_2S and optionally COS and CS_2, preferably in a molar ratio of H_2S equivalents to $C0_2$ of below 1, preferably below 0.1, and optionally water, wherein the molar ratio of H_2O to H_2S equivalents is in the range of 0 - (5 +X), wherein X is a factor that takes into account the consumption of H_2O during conversion of an equivalent of H_2S to H_2S. The process comprises (a) contacting the feed gas with a solid adsorbent at a temperature of 250 - 500 °C, to obtain a loaded adsorbent, (b) purging the loaded adsorbent with a purge gas comprising steam, thus producing a product stream which typically contains substantially equal levels of $C0_2$ and H_2S. Preferably, the process further comprises a step (c) of drying the purged adsorbent. The adsorbent comprises alumina and one or more alkali metals, such as potassium oxides, hydroxide or the like.

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Improved process for removing and recovering H_2S from a gas stream

[0001] The present invention is in the field of removal of sour gases by adsorption, for example from syngas or Claus tail gas. Thus, the invention relates to an improved process for the selective removal of hydrogen sulphide (H_2S), and optionally further inorganic sulphide components such as carbonyl sulphide (COS) and carbon disulphide CS_2, from a gas stream by adsorption, particularly a gas stream comprising CO_2 and H_2S in a molar ratio above 0.5, and for recovering the inorganic sulphur as H_2S allowing valorisation thereof.

Background

[0002] Hydrogen sulphide removal from sour gas streams is of great industrial importance, as such gases are the main known source of H_2S. An important source of sour gases is synthesis gas (syngas) containing hydrogen, carbon monoxide, carbon dioxide and further components including H_2S, or its subsequent product obtained by water gas shift (WGS) reaction, such as described in WO 2010/059052. The WGS reaction produces H_2 and CO_2 while H_2S can be present in the feed stream. In Sorbent-enhanced WGS, CO_2 and H_2S are adsorbed onto an adsorbent such as alkali-promoted hydrotalcite and subsequently simultaneously desorbed from the adsorbent. As such, CO_2 and H_2S end up in the same effluent stream, restricting efficient reuse or requiring purification of such gaseous mixtures.

[0003] Known techniques for selective removal of H_2S from a sour gas containing CO_2 include physical, chemical and hybrid scrubbing techniques and metal oxide scavenging. Chemical scrubbing involves the use of amine-based solvents that chemically react with sour gases such as H_2S and CO_2. Physical solvents involve e.g. methanol or glycol, using the physical dissolution of the acid gases obeying Henry's law, and hybrid solvents combining the best of both chemical and physical solvents. Because these solvents favour H_2S over CO_2 only slightly, H_2S enrichment yields are relatively poor, which renders this technique unsuitable for selective removal of H_2S from a CO_2-rich, H_2S-lean stream.

[0004] EP2407227 provides a method for separating H_2S from a sour syngas stream different from the aforementioned liquid absorption processes using a pressure swing adsorption system (PSA) to produce a stream enriched in CO_2 and H_2S, after which H_2S is removed for instance by using a packed bed of ZnO that would be disposed of and replaced when saturated with H_2S, or silica gels, impregnated activated carbons and/or molecular sieves. In one embodiment, steam is used to heat the bed that has been loaded with H_2S to help removing said H_2S. Scavengers, such as Zn-, Zn/Cu- or Fe-based scavengers, bind H_2S irreversibly and thus cannot economically deal with feeds comprising relatively high amounts of H_2S, such as typically 200 ppm H_2S or even only 100 ppm H_2S. Large scale processes or H_2S levels above about 100 ppm require frequent replacement of the scavenger bed, which is usually too expensive to be economically feasible.

[0005] WO 2013/019116 discloses a process for selectively removing acidic gaseous components, in particular carbon dioxide (CO_2) and hydrogen sulphide (H_2S), from an adsorbent which has adsorbed these gaseous components from a feed gas. It involves a CO_2 purge to replace the H_2S and a subsequent H_2O purge to remove the CO_2. The process is well suited for a Sorption-Enhanced WGS process, which produces H_2 and CO_2, and wherein (small) amounts of H_2S may be present. H_2S and CO_2 are subsequently separately separated from H_2.

[0006] There remains a need for enriching a gaseous stream in H_2S from a (CO_2-rich, H_2S-lean) feed stream that comprises intermediate amounts of H_2S (e.g. 100 – 10,000 ppm), for which scavenger and scrubbing techniques are unsuited. Existing H_2S enrichment techniques as described above can only achieve about one order of magnitude enrichment at high H_2S concentrations, and two orders of magnitude increase in concentration from low H_2S concentrations, for which a marked improvement is required.

Summary of the invention

[0007] The invention relates to a process for contacting a feed gas comprising H_2S and CO_2 to an adsorbent material for altering the composition of the gas, and is particularly suited for selectively removing H_2S from a feed gas which is preferably CO_2-rich and H_2S-lean, as defined further below, or in other words for enriching such feed in H_2S. At the same time, a CO_2-containing stream may be produced which is low in H_2S. In the process of the invention, H_2S equivalents, including H_2S, carbonyl sulphide (COS) and carbon disulphide (CS_2), are preferentially adsorbed onto the sorbent, followed by purging the adsorbent with a purging gas comprising steam, which gives rise to desorption of H_2S. In view of such effective desorption with steam, intermediate CO_2 rinses are rendered superfluous.

[0008] The process according to the invention is thus capable of selectively removing hydrogen sulphide from a gas and of realising up to three orders of magnitudes H_2S concentration increase compared to the feed stream. To that end, the inventors found that selective retention of H_2S (and/or equivalents thereof) could be improved by conditioning the water concentrations at contact between feed gas and solid adsorbent for selectively adsorbing H_2S (and/or equivalents thereof). This can be achieved by either drying the solid adsorbent or providing a gaseous feed low in H_2O, or, preferably, both.

[0009] The process according to the invention thus comprises:

(a) contacting a feed gas containing H_2S equivalents, CO_2 and optionally H_2O, wherein the molar ratio of H_2O to H_2S equivalents is within the range of $0 - (5 + X)$, with a solid adsorbent at elevated temperature, to obtain a loaded adsorbent and a first product gas having a reduced ratio of H_2S equivalents to CO_2;

(b) purging the loaded adsorbent with a purge gas comprising steam to obtain a second product gas having an increased ratio of H_2S equivalents to CO_2.

[0010] Herein, the feed gas and/or the purge gas comprises a reducing agent such as hydrogen and the adsorbent comprises alumina and one or more alkali metals. In the molar ratio of H_2O to H_2S equivalents, which is in the range of $0 - (5 + X)$, X is defined as:

$$X = \sum \frac{n_i \times [H_2S\ equivalent]_i}{[H_2S\ equivalents]}$$

wherein [H_2S equivalents] indicates the total concentration (typically in ppm) of H_2S equivalents, [H_2S equivalent]$_i$ indicates the concentration (typically in ppm) of a particular H_2S equivalent i and n_i indicates the amount of water molecules n consumed when said H_2S equivalent i is converted to H_2S.

[0011] The term "H_2S equivalents" as used herein denotes H_2S and its gaseous or volatile sulphur equivalents which contain sulphur (formally) in oxidation state -2, such as carbonyl sulphide (COS) and carbon disulphide (CS_2). H_2S equivalents are preferably selected from the group consisting of H_2S, COS, CS_2 and mixtures thereof. In this respect, COS and CS_2 are referred to as equivalents of H_2S. The term "H_2S equivalents" does not includes higher valence sulphur species such as sulphur dioxide

[0012] Preferably, the process comprises a further step (c) wherein the purged adsorbent is dried, after which the adsorbent is capable of adsorbing H_2S equivalents again. As such, the adsorbent is regenerated and available for reuse in step (a) of the process again. The terms “adsorbent drying” and “adsorbent regeneration” are used interchangeably.

[0013] It was found that, advantageously, carbonyl sulphide (COS) and carbon disulphide (CS_2), if present in the feed gas, are removed together with the H_2S when using the adsorbent of the present invention, not requiring a prior hydrolysis to H_2S of these components. With the purging of step (b), all original H_2S equivalents (H_2S, COS and CS_2 and the like) are released essentially as H_2S only. The H_2S enriched effluent (second product gas) is extraordinarily high in H_2S content, thus rendering the effluent useful for further application in e.g. Claus sulphur production.

Detailed description

[0014] The invention relates in a first aspect to a process for altering the composition of a gas containing H_2S equivalents and CO_2. In a second aspect, the invention relates to a Claus process wherein the process according to the first aspect is implemented. A third aspect of the invention concerns a system designed to implement the processes according to the first and second aspects of the invention, comprising a Claus unit and an adsorption module equipped with a bed of adsorbent comprising alumina and one or more alkali metals.

Process for altering the composition of a gas

[0015] The first aspect of the invention more specifically relates to a process for selectively recovering H_2S from a feed gas or enriching said gas in H_2S, wherein said feed gas comprises CO_2 and H_2S equivalents, preferably in a molar ratio of H_2S equivalents to CO_2 of less than 2, and optionally water, wherein the molar ratio of H_2O to H_2S equivalents is in the range of $0 - (5 + X)$. The process comprises (a) contacting the feed gas with a solid adsorbent, at a temperature of 250 – 500 °C, to obtain a loaded adsorbent (the loading including H_2S) and a purified first product gas, (b) purging the loaded adsorbent with a purge gas comprising steam to obtain a gas enriched in H_2S compared to the feed gas, and preferably (c) drying the purged adsorbent. The adsorbent comprises alumina and one or more alkali metals. The alkali metals are in particular in the form of their oxides, hydroxides, carbonates, sulphides, hydrosulphides, hydroxyl-carbonates, thiols, formates, hydroxyformates or the like, the (hydro)sulphides possibly being formed in the course of the adsorption process.

[0016] In the context of the present invention, the composition of gaseous mixtures is given in percentages (%) or ppm values. Unless indicated otherwise, these always refer to mole percentages or molar ratios. In the context of the invention, the term “gas” refers to any pure compound or mixture of compounds in the gas phase. A gas should be gaseous at the processing conditions, i.e. at least at a temperature of 250 – 500 °C and at a pressure of 1 – 15 bar, even though higher or lower pressures may be feasible as well. Under such conditions, water is in gaseous form, which may also be referred to as steam. Hence, the terms “water” (or “H_2O”) and “steam” are used interchangeably in the context of the present invention. Solid compositions, such as for the adsorbent, are typically given in wt% (weight percentage) unless indicated otherwise. The adsorbent is solid at the processing conditions.

[0017] The feed gas may be referred to as “sour gas”, which is a term of art for a gas containing at least 4 ppm hydrogen sulphide and/or equivalents thereof (see e.g. http://naturalgas.org/naturalgas/processing-ng/). Sour gases may be natural gases or may for example be generated during industrial processes (e.g. gasification of coal, biomass or mixtures thereof, e.g. the tail gas of a Claus process). The “sour gas” in the context of the invention contains H_2S equivalents, CO_2 and optionally water (steam). However, large amounts of water hamper selective adsorption of H_2S equivalents to the adsorbent, so water should be present in the feed stream in a molar ratio of H_2O to H_2S equivalents in the range of 0 to $(5 + X)$, preferably 0 to $(2 + X)$, even more preferably 0 to $(1 + X)$, most preferably 0 to 1. Herein, X is a constant, the value of which depends on the type and amount of equivalents of H_2S present in the feed gas, taking into account the consumption of H_2O during conversion of such equivalent to H_2S. Each equivalent of H_2S allows for a different maximal steam content. X is further defined below. Herein, a molar ratio of 0 (zero) refers to the complete absence of steam. In absolute terms, the water (steam) level in the feed gas is preferably below 20%, more preferably below 5%, even more preferably below 2%, most preferably below 0.5%. Although it is preferred that the feed gas is completely dry without any water present, the process according to the first aspect of the invention runs sufficiently effective even when a minor amount of water is present. Typically, the molar ratio of H_2O to H_2S equivalents may be at least 0.001 or even at least 0.01, or in absolute terms, the feed gas may contain at least 50 ppm water or at least 100 ppm water or even at least 500 ppm water. This implies that source gases containing appreciable levels of water, such as Claus tail gases, may have to be dried, e.g. by condensation, adsorption, absorption or other conventional methods, to below the above levels, before being subjected to the process of the invention.

[0018] The feed gas comprises H_2S equivalents as defined herein. In the context of the present invention, the term “H_2S equivalents” denotes H_2S and its gaseous or volatile sulphur equivalents which contain sulphur (formally) in oxidation state -2, such as carbonyl sulphide (COS) and carbon disulphide (CS_2). H_2S equivalents preferably comprise H_2S, COS and/or CS_2, more preferably are selected from the group consisting of H_2S, COS, CS_2 and mixtures thereof. In this respect, COS and CS_2 are referred to as equivalents of H_2S. The term “H_2S equivalents” does not include higher valence sulphur species such as sulphur dioxide. Typically, but not mandatorily, the H_2S equivalents include H_2S as such, and preferably, they also include COS and/or CS_2. The combined content of H_2S equivalents in the feed gas typically ranges from 5 ppm to 5 % (50,000 ppm), preferably 10 – 25,000 ppm (2.5 %), more preferably 100 – 10,000 ppm, even more preferably 150 – 5000 ppm, most preferably 200 – 2000 ppm. It is noted that COS and CS_2 were found to be adsorbed in step (a) and converted to H_2S upon steam purging of step (b). Regardless of the type of H_2S equivalent(s) present in the feed gas, the second product stream, i.e. the effluent of step (b), will contain H_2S as sole sulphur species. COS and CS_2, as well as H_2S itself, are desorbed as H_2S. These species are thus considered equivalent to H_2S.

[0019] Without being bound to a theory, it is expected that during the operating conditions, two equilibria are established for which the adsorbent acts as a catalyst. These two equilibria are:

$$COS + H_2O \leftrightarrow H_2S + CO_2 \qquad (1)$$

$$CS_2 + 2\,H_2O \leftrightarrow 2\,H_2S + CO_2 \qquad (2)$$

Upon breakthrough, i.e. complete loading of the adsorbent with H_2S equivalents, H_2S equivalents end up in the first product gas, since they can no longer be adsorbed. The inventors found that regardless of whether H_2S, COS or CS_2 (or mixture thereof in any ratio) is present in the feed gas, H_2S and COS are observed in the first product gas in their equilibrium concentrations according to equilibrium (1). No CS_2 is observed, since equilibrium (2) is completely shifted to the right under the processing conditions, i.e. equilibrium concentration of CS_2 is (close to) 0.

[0020] As is clear from equilibrium (1), one molecule of COS is equivalent to one molecule of H_2S, wherein one molecule of H_2O is consumed. Thus, for each molecule (or mole) of COS present in the feed stream, one addition molecule (or mole) of H_2O

may be present therein. Likewise, as is clear from equilibrium (2), one molecule of CS_2 is equivalent to two molecules of H_2S, wherein two molecules of H_2O are consumed. Thus, for each molecule (or mole) of CS_2 present in the feed stream, two addition molecules (or moles) of H_2O may be present therein. For this reason, the allowable water content in the feed gas employs the factor X. Thus, the ratio of H_2O to H_2S equivalents is in the range of 0 – (5 + X), preferably 0 – (2 + X), even more preferably 0 – (1 + X), wherein X is defined as:

$$X = \sum \frac{n_i \times [H_2S\ equivalent]_i}{[H_2S\ equivalents]}$$

Herein, [H_2S equivalents] indicates the total concentration (typically in ppm) of H_2S equivalents, [H_2S equivalent]$_i$ indicates the concentration (typically in ppm) of a particular H_2S equivalent i and n_i indicates the amount of water molecules n consumed when said H_2S equivalent i is converted to H_2S. Thus, $n_i = 0$ for $i = H_2S$, $n_i = 1$ for i = COS and $n_i = 2$ for $i = CS_2$. For the preferred situation where the H_2S equivalents are selected from H_2S, COS, CS_2 and mixtures thereof, X simplifies as:

$$X = \frac{[COS] + 2 \times [CS_2]}{[H_2S\ equivalents]}$$

Herein, [COS] and [CS_2] indicate the concentration (typically in ppm) of COS and CS_2 respectively, and [H_2S equivalents] = [H_2S] + [COS] + [CS_2]. In case the H_2S equivalents only contain H_2S, i.e. the feed gas does not comprise detectable amounts of other H_2S equivalents, $X = 0$. Since X defines the upper limit of the allowable range of H_2O to H_2S in the feed gas, X may not exceed the above-defined values, as that would render the feed gas too wet for effective performance of the process according to the first aspect of the invention. For example, one molecule of COS requires one molecule of H_2O (or consumes one molecule of H_2O) for conversion to one molecule of H_2S, so $n_{(COS)} = 1$. Thus, when the feed gas comprises COS as the only H_2S equivalent, $X = 1$ and the maximal allowable water content of the feed gas defined as the ratio of H_2O to H_2S equivalent is 6. Similarly, a 9 to 1 H_2S to COS mixture gives $X = 0.1$ and results in a maximal allowable ratio of H_2O to H_2S equivalent of 5.1. Pure CS_2 gives $X = 2$ and results in a maximal allowable ratio of H_2O to H_2S equivalent of 7. In one embodiment, $X = 0$ and the H_2O to H_2S equivalents ratio is 0 – 5, preferably 0 – 2, more preferably 0 – 1.

[0021] The feed gas may also be referred to as a “CO_2-rich, H_2S-lean” feed gas, meaning that the molar ratio of H_2S equivalents to CO_2 is preferably below 1, more preferably below 0.1, even more preferably between 0.0001 and 0.05, most preferably in the range of 0.001 – 0.02 or even 0.002 – 0.01. CO_2 levels of the feed gas may vary greatly without negatively affecting the process. They typically range from 100 ppm to 99 %, preferably at least 500 ppm and up to 95 %, more preferably from 0.5 % (5000 ppm) up to 50 %, most preferably 3 – 25 %.

[0022] In addition to the acidic or "sour" species, other, essentially non-acidic, components may also be present, including hydrogen, carbon monoxide, hydrocarbons or other fuel gases, water, as well as any amount of inert gaseous species such as nitrogen, noble gases (e.g. helium, argon) and the like. The level of oxygen should preferably be low, e.g. below 2%, preferably below 0.5% or even below 0.1% (1000 ppm). The presence of higher levels of O_2 is undesirable, as this creates an oxidizing environment wherein SO_2 may be formed. Thus, the presence of O_2 counteracts the effect of the reducing agent which is preferably present in the feed gas. As discussed, the water content should also be kept low.

[0023] The feed gas typically further comprises a reducing agent. Although less preferred, the feed gas could also be free of a reducing agent, in which case it might be required to periodically regenerate the bed of adsorbent material. Such bed regeneration could be effected by reduction using a reducing agent as defined herein, optionally assisted by heating the bed to aid the decomposition of deactivating components. The reducing agent in the context of the present invention is a gaseous species capable of reducing oxidised species, typically capable of preventing the oxidation of H_2S to SO_2 or sulphates, under the process conditions. During the purging of step (b), the adsorbed H_2S species are in contact with great excess of H_2O molecules, which may oxidise H_2S (and/or equivalents thereof) to SO_2 or even sulphates, under the process conditions. A reducing environment suppresses such oxidation. The inventors surprisingly found that the presence of a reducing agent in the feed gas, i.e. during the contacting of step (a), suppresses such oxidation during step (b). Alternatively, the purging gas may comprise the reducing agent, as described further below, which also suppresses such oxidation. If no reducing agent is present in both the feed gas and the purging gas, significant amounts of the adsorbed H_2S are converted to sulphates during step (b), which are not capable of desorbing from the adsorbent. Preferably, the reducing agent is selected from H_2 and/or CO, more preferably the feed gas comprises at least H_2 as reducing agent. The feed gas preferably comprises 0.1 – 50 %, more preferably 0.5 – 30 %, most preferably 1 – 20 % reducing agent, most preferably H_2. The presence of a reducing agent thus suppresses the formation of sulphates on the adsorbent, for which the adsorbent may act as catalyst. The presence or formation of SO_2 is undesirable, since it is adsorbed during step (a) and when contacted with steam during step (b), SO_2 reacts to sulphate which is not readily desorbed upon purging with steam. Thus, the presence or formation of SO_2 and/or the absence of a reducing agent decreases the adsorption capacity of the adsorbent.

[0024] It is thus also preferred that the feed gas does not contain appreciable levels of SO_2 (or other sulphur oxides, together referred to as SO_x); preferably it contains less than 0.5% (5000 ppm), more preferably less than 0.05% (500 ppm), most preferably less than 50 ppm. In a particular embodiment, the feed gas contains substantially no (i.e. less than 10 ppm) of SO_2. In an especially preferred embodiment, the content of CO_2 and H_2 is substantially equal (ratio between 1:2 and 2:1). CO may also be present, e.g. in an amount of 0.05 – 30 %, more preferably 0.1 – 20 %, most preferably 0.5 – 10 %. Since the feed gas preferably contains syngas, it is preferred that the level of H_2 and CO is substantially equal, i.e. molar ratio H_2 : CO is 1:2 – 2:1.

[0025] According to a preferred embodiment of the invention the process is used for the separation H_2S from sour natural gas, syngas (e.g. general, biomass-derived or coal-derived), Claus tail gas, H_2S-containing gaseous fuels, tail gas of hydrodesulphurisation, wherein sulphur species are removed from gaseous streams (e.g. of petroleum products of refineries) by hydrogenation to H_2S. Such gases are preferably used as feed gas in step (a) of the process according to the invention. H_2S is readily separated from H_2S-containing gaseous fuels by the process according to the invention, wherein the fuel depleted in H_2S is obtained as first product gas. The adsorbent according to the invention does not adsorb hydrocarbon species, which thus leads to no loss in fuel during the adsorption of step (a). Amine scrubbing to remove sulphur species will always lead to some removal of hydrocarbons, thus leading to fuel loss. Preferred feed gases include H_2S-containing gaseous fuels, syngases and Claus tail gases, in particular, syngases and Claus tail gases having typical compositions as given in Table 1 below. Herein “inert” gases comprise nitrogen, noble gases and the like and the values for H_2S include COS and CS_2. Most preferably, a Claus tail gas is used as feed gas, since the process according to the first aspect of the invention is especially suitable to be incorporated with a Claus process. In this respect, it is especially preferred that the second product gas is used as incoming gas for a Claus process. These aspects of the invention are discussed further below.

[0026] In one embodiment, the feed gas has been pre-treated prior to being subjected to step (a) of the process according to the first aspect of the invention. Pre-treatment may be employed to lower the H_2O content and/or the SO_2 content (or the SO_x content). Pre-treatment to lower the SO_2 or SO_x content is particularly preferred for Claus tail gases and typically involves subjecting a SO_x-containing gas to a hydrogenation-hydrolysis step, as known to the art, to convert SO_x to H_2S. SO_x can also be lowered by scrubbing with an alkaline solution followed by chemical reduction, e.g. using hydrogen, or by biological reduction, e.g. using bacteria of the genera *Desulfovibrio, Desulfobacterium, Desulforomonas* or the like. Alternatively, the SO_2 or SO_x content of the Claus tail gas can be lowered by tuning of the oxidation step(s) in the Claus process itself.

[0027] Pre-treatment to lower the H_2O content is particularly preferred in case the H_2O content of a potential feed gas is too high, i.e. the molar ratio of H_2O to H_2S equivalents is above $(5 + X)$. Where necessary, the H_2O level of the feed gas is lowered e.g. by cooling and/or pressurisation resulting in condensation of water or by other conventional methods such as absorption or adsorption. Since drier feed gases give rise to increased H_2S adsorption capacity of the adsorbent, it is preferred that pre-treatment to lower the H_2O content includes a measure to lower the H_2O level to well below 1 %. Such a measure may include a glycol rinse of the feed gas and/or contacting the feed gas with molecular sieves, optionally after one or more of the above-mentioned techniques. Alternatively or additionally, the H_2O content may be lowered by selective permeation of water through a membrane (e.g. by vacuum permeation). Feed gases pre-treated as such are especially suitable to be used as feed gas for the process according to the first aspect of the invention, in view of their extremely low or even negligible water content. Pre-treatment to lower the H_2O level is also referred to as drying or “pre-drying”.

[0028] *Table 1: Typical gaseous compositions (in vol%)*

	H_2	CO	CO_2	H_2O	CH_4	inert	H_2S
Syngas general	25-45	20-60	5-25	2-30	0-15	0.5-5	0.01-1
Biomass-derived	30-45	20-30	15-25	2-10	5-15	2-5	0.002-0.05
Coal-derived	25-30	30-60	5-15	2-30	0-5	0.5-5	0.2-1
Claus tail gas	0.2-5	0-1	1-10	15-50	0-1	40-75	0.5-5

[0029] The adsorbent to be used in the process of the invention is capable of adsorbing H_2S and comprises a mixture of inorganic (hydr)oxides comprising a trivalent metal oxide, especially alumina (aluminium oxide or hydroxide). Instead or in addition to aluminium, other metals capable of adopting a trivalent state may be present, such as Fe, Mn, Cr, Ti, Pd, Ce and Zr. Apart from being highly effective in the process according to the invention, the use of alumina in the adsorbent according to the invention has further advantages. First of all, aluminas are highly stable towards reducing condition that occur during the process according to the invention, in contrast to e.g. tin oxide based materials. Also the hydrothermal stability (i.e. the inertness towards steam at high temperature) of aluminas, especially hydrotalcites, is excellent, thus preventing sintering of the adsorbent material under the process conditions. Sintering is especially disadvantageous, since it reduces the surface area of the adsorbent and thus the adsorbent capacity. The alumina of the adsorbent according to the invention is promoted with, i.e. contains, one or more alkali metals, in ionic form, e.g. as their oxides, hydroxides, carbonates, or *in situ*, sulphides and/or hydrosulphides. Preferably the adsorbent comprises one or more alkali metal oxides, hydroxides and/or carbonates, more preferably one or more alkali metal oxides or carbonates. Any alkali metal can be used, including Li, Na, K, Rb and Cs. Preferred alkali metals are Na and K, most preferably K is used as alkali metal. The alkali metal content of the adsorbent is preferably 2 – 30 wt%, more preferably 5 – 25 wt%, most preferably 10 – 15 wt%.

[0030] The adsorbent may advantageously further comprise one or more divalent metal oxides, hydroxides, carbonates, sulphides and/or hydrosulphides. The divalent metals can be an alkaline earth metal (Mg, Ca, Sr, Ba) or Co, Ni, Cu, Zn, Cd, Pb. Preferred divalent metals are Mg, Ca, Sr, Ba, Zn, Ni and Cu. More preferably, the adsorbent comprises calcium oxide and/or magnesium oxide and/or zinc oxide. In particular, the adsorbent has an atomic ratio of divalent metals (especially one or more of Mg, Ca, Zn) to Al of between 0 and 3, preferably between 0.05 and 1.5, e.g. between 0.11 and 1.0, and an atomic ratio of alkali metal (especially Na and/or K) to Al of between 0.1 and 1.0, preferably between 0.15 and 0.75, most preferably between 0.25 and 0.5. Aluminas also containing alkali metals, possibly in addition to other metals and counter ions, are referred to herein as “alkali-promoted” aluminas. Alkali-promoted alumina, not containing divalent metals, are well suitable in the present process. A specific and preferred example of a suitable adsorbent is K-promoted alumina. The K-promoted alumina preferably comprises 5 – 25 wt% K, more preferably 10 – 15 wt% K, based on total weight of the adsorbent.

[0031] When the adsorbent further comprises magnesium oxide (magnesia), it preferably has an atomic Mg to Al+Mg ratio of between 0.05 and 0.85, more preferably between 0.1 and 0.8, most preferably between 0.2 and 0.5. Aluminas that further comprise magnesia are referred to as "hydrotalcites". Where reference is made to alumina, magnesia and the like, these include the oxides, but also hydroxides and other equivalents of the oxides of aluminium, magnesium, respectively. Herein, sulphides and hydrosulphides are considered equivalent with oxides and hydroxides respectively. It is envisioned that upon adsorption of sulphur species such as H_2S metal oxides and hydroxides present in the adsorbent are converted into sulphides and hydrosulphides. When present, metal sulphides and hydrosulphides are likely to be transformed to metal oxides and hydroxides. It is however preferred that at least metal oxides are present in the adsorbent. Magnesium is particularly preferred over e.g. zinc, for feed gas mixture containing high amounts of sulphur-containing species such as H_2S, since the magnesium-based adsorbents were found to be chemically relatively insensitive to the sulphur compounds, i.e. not be deteriorated in use.

[0032] Aluminas also containing magnesium and/or other divalent metals, and also containing alkali metals, possibly with other metals and counter ions, are referred to herein as "alkali-promoted hydrotalcites". The aluminas may be used in a manner known per se, which may comprise admixing metals oxides and further additives with the alumina or hydrotalcite or other base material in a dry state or in a solution or a slurry, and optionally drying and calcining the resulting mixture. The alumina may be any form of alumina which can be rehydrated, in particular which has a level of hydroxyl groups. Examples include gamma-alumina, boehmite, gibbsite, bayerite.

[0033] The adsorbent to be used in the process according to the first aspect of the invention can be represented by the following chemical formula:

$$[\mathrm{M}^{\mathrm{II}}{}_{(1-x)}\mathrm{Al}_{(\alpha x)}\mathrm{M}^{\mathrm{III}}{}_{((1-\alpha)x)}(\mathrm{OH})_{\mathrm{y}}][\mathrm{Z}^{n-}]_{((x-y+2)/n)} \bullet p\mathrm{H_2O} \bullet q\mathrm{M}^{\mathrm{I}}(\mathrm{A}^{m-})_{1/m},$$

wherein:

- M^I is one or more metals selected from Li, Na, K, Rb and Cs, preferably from Na and K;
- M^{II} is one or more metals selected from Mg, Ca, Sr, Ba, Co, Ni, Cu, Zn, Cd and Pb, preferably from Mg, Ca, Ni, Cu and Zn;
- M^{III} is one or more metals selected from Fe, Mn, Cr, Ti and Zr;

- Z^{n-} is one or more anions selected from halide, nitrate or acetate (n = 1), or oxide, sulphate, oxalate or carbonate (n = 2);
- A^{m-} is one or more anions selected from hydroxide (m = 1) and the anions as defined for Z above, with m corresponding to n;
- m and n = 1 or 2, according to A and Z, respectively;
- $x = 0.05 - 1$, preferably 0.1 – 1.0, more preferably 0.2 – 0.95, most preferably 0.4 – 0.8;
- $\alpha = 0 - 1$, preferably 0.5 – 1, most preferably $a = 0.95 - 1$;
- $p = 0 - 15$;
- $q = 0.1 - 1$; and
- $y = 0 - 4$.

[0034] Specific examples of hydrotalcites of the above formula are referred to herein as KMG30 having an MgO : Al_2O_3 weight ratio of 30 : 70 and having the formula $[Mg_{0.35}Al_{0.65}(OH)_2][CO_3^{2-}]_{0.325} \bullet 0.5H_2O \bullet 0.32K(CO_3^{2-})_{0.5}$ with a molar ratio K : Mg : Al of about 1.0 : 1.1 : 2.0 and a molar ratio of K : (Mg + Al) in the order of 1 : 3.1 (0.32 : 1); and as KMG70 having an MgO : Al_2O_3 weight ratio of 70 : 30 and having the formula $[Mg_{0.74}Al_{0.26}(OH)_2][CO_3^{2-}]_{0.13} \bullet 0.5H_2O \bullet 0.27K(CO_3^{2-})_{0.5}$ with a molar ratio K : Mg : Al of about 1.0 : 2.7 : 0.9 and a molar ratio of K : (Mg + Al) in the order of 1 : 3.6 (0.27 : 1)

[0035] The anions in the complex metal oxides are as defined above. Preferably the adsorbent comprises hydroxide and/or carbonate anions in order to ensure sufficient alkalinity for an effective adsorption of acidic gas species. In particular, at least 50% of the anions (expressed in monovalent equivalents) consist of hydroxide and/or carbonate.

[0036] Suitable inorganic oxides can have a layered structure, wherein part of the anions is arranged in layers interposed between layers containing the cations. Examples of suitable layered oxides include the hydrotalcites having proportional formula's such as $Mg_6Al_2(CO_3)(OH)_{16} \bullet 4(H_2O)$ or similar combinations with different Mg : Al ratios. Other suitable oxides include analogues wherein magnesium is absent (e.g. scarbroite) or is replaced by calcium (e.g. alumohydrocalcites), strontium (e.g. montroyalite) or barium (e.g. dreserrites), as well as Mg/Fe, Mg/Cr, Mg/Mn, Ni/Al, etc. analogues (pyroaurite, stichtite, desautelsite, takovite).

[0037] In a preferred embodiment, the adsorbent as prepared for step (a) of the process of the invention has a H_2O content of at most 5 wt%, based on the total weight of the adsorbent. In order to obtain such H_2O contents, it may be beneficial to dry the adsorbent prior to step (a). Methods and means for drying the adsorbent are known in the art and described further below in the context of the regeneration of step (c).

[0038] The adsorbent may have been thermally treated, i.e. it may have been heated at a temperature above about 200 °C, even more especially above about 400 °C. For instance, assuming a hydrotalcite adsorbent, when heating this hydrotalcite in the reactor before or during an adsorption-desorption reaction, the hydrotalcite modifies to a promoted alumina, such as K_2CO_3 and MgO promoted alumina, since at elevated temperatures, the hydrotalcites may at least partially rearrange in mixed oxides while losing hydrotalcite crystalline structure and layered double hydroxide structure. This is well known in the art and is for instance described in US 5,358,701, US 6,322,612 and WO 2005/102916.

[0039] During step (a) of the process according to the first aspect of the invention, the feed gas is contacted with the adsorbent at a temperature of 250 – 500 °C, preferably of 280 – 450 °C, more preferably 300 – 420 °C. Step (a) is preferably performed at a pressure of below 15 bar, such as 1 – 15 bar, more preferably 1 – 10 bar, for a period of at least 5 minutes, such as 10 minutes – e.g. 12 h, preferably 30 minutes – 8 h. The flow rate of the feed gas in step (a) may be e.g. 1 – 25 m^3 per kg of sorbent per h, preferably 4 – 20 m^3/kg/h. During the contacting, certain species, in particular acidic species, are adsorbed onto the adsorbent, while other species may pass through the adsorbent material without being adsorbed (“slip through”). Such non-adsorbed species typically included inert gases such as nitrogen, argon and hydrocarbons. Together, the non-adsorbed species form a first product gas, which is depleted in acidic species, particularly in H_2S equivalents, compared to the feed gas. The first product gas is thus the off-gas of step (a). Step (a) is preferably continued until breakthrough of H_2S equivalents commences, which end up as a mixture of H_2S and COS in the first product gas as explained above.

[0040] The inventors surprisingly found that when the water content of the feed gas is sufficiently low, the adsorbent material according to the invention has an increased selectivity for H_2S (and/or equivalents thereof), when compared to adsorption by the same adsorbent with a “wet” feed gas, i.e. having a H_2O to H_2S equivalents molar ratio of above $(5 + X)$. With such a wet feed gas, the adsorbent adsorbs relatively large amounts of CO_2 while adsorbing comparatively low amounts of H_2S, e.g. as described in WO 2013/019116. Although the concentration of CO_2 of the feed gas is typically several factors higher than the concentration of H_2S equivalents in the feed stream, the molar ratio of H_2S (and/or equivalents thereof) to CO_2 that is adsorbed onto the adsorbent is surprisingly high, even above 1, when a dry feed gas is used. In this respect, it is irrelevant whether the equivalents of H_2S, typically COS and/or CS_2, are converted to H_2S when being in the gaseous state and subsequently adsorbed as H_2S, or that the equivalents of H_2S are first adsorbed as such and subsequently converted to H_2S. The sulphur species that is desorbed during step (b) is at all times H_2S, and the second product gas is substantially free of equivalents of H_2S such as COS and CS_2. Without being bound to a theory, it is believed that the adsorbent acts as catalyst for the conversion of the equivalents of H_2S to H_2S, and that the conversion occurs when an equivalent of H_2S is in adsorbed state. In the context of the present invention, reference is made to adsorption of H_2S equivalents.

[0041] The inventors found that increasing amounts of water in the feed gas decreases the selectivity for H_2S equivalents. As the amount of H_2S equivalents being adsorbed during step (a) decreases, the H_2S content in the second product gas, i.e. the off-gas of step (b), decreases. The H_2S content in the second product gas becomes unacceptably low when the ratio of H_2O to H_2S equivalents in the feed gas is above $(5 + X)$. The drier the feed gas the higher the capacity of the adsorbent for H_2S equivalents, thus it is preferred that the H_2O to H_2S equivalents ratio in the feed gas is 0 or close to 0. When the H_2O to H_2S equivalents ratio is in the range of $0 - (5 + X)$, preferably $0 - (2 + X)$, more preferably $0 - (1 + X)$, the sorbent capacity for CO_2 and H_2S equivalents is more or less similar, i.e. CO_2 to H_2S adsorption is 2:1 – 1:2, in step (a) of the process according to the first aspect of the invention. For completely dry feed gases, i.e. having a H_2O to H_2S equivalents ratio of 0 or close to 0, the ratio of CO_2 to H_2S being adsorbed in step (a) was as high as 1.5, which slightly decreased to 0.6 for a feed gas comprising H_2O and H_2S equivalents in a ratio of about 2. Such capacities for H_2S equivalents afford excellent second product gases in terms of H_2S content and H_2S to CO_2 ratios. H_2S capacities of the adsorbent were found acceptable for feed gases comprising water up to a H_2O to H_2S ratio of $(5 + X)$.

[0042] In view of the adsorption of H_2S equivalents during step (a), the first product gas, i.e. the gas issuing from step (a), is depleted in H_2S; it typically contains substantially no H_2S, i.e. less than 10 ppm, advantageously less than 5 ppm or even less than 1 ppm. The first product gas generally contains less than 0.1 times, preferably 0.05 times, most preferably less than 0.02 times the level of H_2S equivalents of the feed gas, and the level may be as low as 0.001 or even 0.0002 times the feed level. Alternatively, or additionally, the first product gas has a molar ratio H_2S equivalents to CO_2 of less than 0.005, preferably less than 0.002, down to e.g. 0.0001 or even 0.00001.

[0043] The first product gas may be emitted into the environment, which is acceptable in view of its negligible sulphur content, although incineration of the first product gas prior to emission may be desired in case it contains hydrocarbons, CO and/or H_2. In view of its low sulphur content and potentially high CO_2 content, depending on the CO_2 content of the incoming feed gas, the first product gas may also be suitable for carbon capture and storage (CCS). Alternatively, it may be used or further processed in any way conceivable, e.g. as a high-CO_2 source gas, fuel gas or syngas.

[0044] The contacting of step (a) may be performed by any means known in the art for contacting a gaseous stream with a solid material. Typically, a packed bed reactor is used, e.g. in the form of a column or tube wherein a tubular reactor is packed with the adsorbent material, although a fluidised bed may also be used. The stream of the feed gas is led over or through said reactor. In case a column is used, the feed gas is conveniently injected into the adsorbent, e.g. at the bottom or top of the column, and the first product gas is released, conveniently at the other side of the column. Alternative arrangements, including horizontal flows or flow entering and leaving the column at the long sides, are also well suitable. After contacting step (a), the adsorbent has been become loaded with acidic species, in particular H_2S and CO_2.

[0045] In step (b), the adsorbed molecules are desorbed from the adsorbent, by purging (rinsing) with a purging gas. The purging gas used in step (b) comprises steam, preferably the purging gas is steam, although minor amounts of other components such as N_2, Ar, H_2S or CO_2 may also be present in the purging gas. It is preferred that the content of other gases than steam and optionally inert gases is kept low. Preferably at least 75 % of the purging gas is steam and optionally inert gas(es), more preferably at least 90 %, most preferably at least 95 % is steam and optionally inert gas(es). Typically, the ratio of steam to inert gas is in the range of 5/95 – 100/0, more preferably 20/80 – 100/0, even more preferably 50/50 – 100/0, most preferably 90/10 – 100/0. The CO_2 content is kept low, preferably below 0.1 % (1000 ppm), especially below 100 ppm or even below 10 ppm. The presence of CO_2 is not required for effective desorption and only leads to a reduced H_2S content in the first effluent, compared to the CO_2 content (i.e. decreasing the H_2S/CO_2 molar ratio). It is also preferred to keep the H_2S content low in the purging gas, preferably 0 – 1 %.

[0046] In one embodiment, the purging gas comprises a reducing agent. The type and content of the reducing agent comprised in the purging gas is typically the same as defined above for the feed gas. The presence of a reducing agent in the purging gas ensures that any adsorbed SO_x species is reduced to H_2S upon desorption. It is preferred that the feed gas comprises a reducing agent as defined above, and the purging gas is substantially free of reducing agent (i.e. comprises < 1 % reducing agent, especially below 100 ppm or even below 10 ppm). In an especially preferred embodiment, the purging gas is substantially pure steam, i.e. comprising at least 95 % steam or even at least 99 % steam or about 100 % steam. Any further component, apart from steam, that is present in the purging gas reduces the H_2S and CO_2 content of the second product gas, based on dry weight. The potentially large amounts of water that are present in the second product gas are readily reduced by e.g. condensation. In an alternative embodiment, the purging gas is a Claus tail gas that has not been subjected to drying. The H_2O present in the Claus tail gas enables desorption of H_2S, thus giving rise to a Claus tail gas enriched in H_2S as second product gas.

[0047] The temperature at which step (b) is performed preferably ranges from 250 – 500 °C, more preferably 300 – 450 °C. Step (b) is preferably performed at a pressure of below 15 bar, such as 1 – 15 bar, more preferably 1 – 10 bar, for a period of between 10 minutes and e.g. 48 h, preferably between 20 minutes and 24 h. The flow rate of the purge gas in step (b) may be similar to the flow rate of step (a), e.g. 1 to 25 m^3 per kg of sorbent per h, preferably 4 – 20 m^3/kg/h. Although the temperatures and pressures employed in steps (a) and (b) may vary, the process is advantageously performed with steps (a) and (b) at about the same temperature and pressure. Thus, any difference in temperature between step (a) and step (b) is preferably less than 50 °C, more preferably less than 20 °C, and any difference in pressure between step (a) and step (b) is preferably less than 50 %, more preferably less than 25 %, or less than 1 bar. In other words, no pressure swing (i.e. a cycle comprising relatively high-pressure adsorption and relatively low-pressure desorption) or temperature swing (i.e. a cycle comprising relatively low-temperature adsorption and relatively high-temperature desorption) is required to obtain H_2S enrichment according to the present invention. Step (b) may be performed in co-current mode or counter-current mode with respect to adsorption step (a). For optimised desorption, it is preferred that step (b) is performed in counter-current mode with respect to step (a).

[0048] In a preferred embodiment, the process according to the first aspect of the invention runs in parallel, i.e. at least two reactor beds comprising the adsorbent according to the invention, preferably in separate reactors, are used simultaneously, one is performing step (a), i.e. is being fed with the feed gas and expels the first product gas, and the other one is performing step (b), i.e. is being fed with the purge gas and expels the second product gas. Preferably, the bed operating in step (b) subsequently performs step (c), as described below, before the beds are switched and the now loaded bed is subjected to step (b) and the now purged and preferably dried bed is subjected to step (a). Alternatively, a third bed may be used, which is subjected to step (c) while a first bed is being subjected to step (a) and a second bed is being subjected to step (b). In this embodiment, the two, three or more beds operate according to the cyclic scheme of step (a) → step (b) → step (c) → step (a) → etc.

[0049] During purging with a purging gas comprising steam, water molecules occupy adsorption sites on the adsorbent, thereby releasing the acidic species such as H_2S, CO_2 that were adsorbed during step (a). These desorbed species, together with a large part of purging gas that is not adsorbed, make up a second product gas stream (effluent). The second product gas is a main product of the process according to the first aspect of the invention, and is enriched in H_2S compared to the feed gas. Here, "enrichment" refers to the increased content of H_2S (based on dry weight) compared to the content of H_2S equivalents in the feed gas (based on dry weight) and/or to the increased molar ratio of H_2S (and/or equivalents thereof) to CO_2 compared to the feed gas. It should be noted that the second product gas is substantially free of equivalents of H_2S, since all sulphur species that are adsorbed during step (a) are desorbed as H_2S during step (b). The molar ratio of H_2S to CO_2 in the second product gas is typically increased to between about 1 and about 2, whereas the H_2S equivalents to CO_2 molar ratio in the feed gas may be as low as 0.001 or even lower. As such, an enrichment up to three orders of magnitude may be achieved, which is unprecedented in the art.

[0050] The second product gas typically contains H_2S, CO_2 and H_2O. It may further contain nitrogen as well as low levels of noble gases, carbon monoxide, hydrocarbons, depending on the composition of the purge gas, while it is preferred that the combined level of such further components, other than H_2S, CO_2 and H_2O, is less than 10%, more preferably less than 5%. Preferably, the H_2S content of the second product gas is 5 – 75 %, more preferably 10 – 70 %, most preferably 20 – 60 %, based on dry weight of the gas. Likewise, the CO_2 content of the second product gas is preferably below 70 %, more preferably below 50 %, even more preferably below 40 %, based on dry weight of the gas. Most preferably, the CO_2 content is below 30 %. Although an as low as possible CO_2 content is preferred, some CO_2 will typically end up in the second product gas, in view of adsorption thereof in step (a) and subsequent desorption in step (b). Thus, the typical CO_2 levels of the second product gas are 2 – 40 %, or 5 – 35 %, or even 10 – 30 %, based on dry weight of the gas. It is especially preferred that the H_2S content is substantially equal or higher than the CO_2 content. The second product gas of the process of the invention has a molar ratio H_2S equivalents to CO_2 of at least 0.25, preferably at least 0.5, up to e.g. 10, most preferably in the range of 0.75 – 2.

[0051] It is further preferred that the combined level of H_2S and CO_2 is between 10 and 95%, more preferably between 20 and 80%, based on dry weight of the gas. Since COS and CS_2 were found to readily adsorb and desorb under the conversion to H_2S and not to revert to COS or CS_2 upon desorption, no or only a negligible amount of COS and CS_2 is observed in the second product gas. Also hardly any or even an untraceable amount of SO_x is observed in the second product gas, in view of the presence of a reducing agent, even if the reducing agent is present in the feed gas. Thus, H_2S is the sole sulphur species which is desorbed. The level of any other sulphur species, including COS, CS_2, SO_2, in the second product gas is below 20 ppm, especially below 10 ppm; in particular, the combined levels of all such species is below 20 ppm, in particular less than 10 ppm.

[0052] The second product gas, in view of its high H_2S content, is ideally suited to be subjected to further application in e.g. Claus sulphur production. Since Claus tail, appropriately after pre-drying as described further below, gases are especially suitable as feed gas for the process according to the first aspect of the invention, and the second product gas may be recycled to the feed in a Claus process, the present process is particularly suited to be incorporated with a Claus plant. These aspects of the invention are discussed further below. Another advantageous application is the desulphurization of fuel gas in e.g. refineries. The low hydrocarbon content of the second product gas effluent is particularly advantageous, as hydrocarbons are undesirable in the downstream Claus process.

[0053] If desired, a flushing (rinsing) step may be inserted between loading step (a) and desorption step (b), so as to avoid mutual contamination of product gases issuing from steps (a) and (b). Such rinsing may be performed using the same temperatures, pressures and flow rates of steps (a) and (b), and may be continued for e.g. between 1 and 15 minutes. Suitable rinsing gases include inert gases, such as nitrogen, and may also contain carbon dioxide, hydrogen or methane, while levels of H_2O should preferably be low (preferably as defined for the feed gas in absolute terms, i.e. below 5%, more preferably below 2%, most preferably below 0.5%) and sulphur compounds should essentially be absent (less than 10 ppm).

[0054] After the purging step (b), the adsorbent is typically regenerated so as to allow its reuse in step (a) in the process of the invention. This regeneration includes removal (desorption) of H_2O from the adsorbent, to such an extent that, depending on the water content of the feed gas, the H_2O to H_2S levels during adsorption step (a) are set to the to appropriate conditions as described above. Thus, according to an especially preferred embodiment, the process according to the first aspect of the invention further comprises a step (c) wherein the purged adsorbent is regenerated by drying (i.e. removal of H_2O). The drying of step (c) may be accomplished by any means known in the art for drying a solid adsorbent material. Suitable means include reducing the pressure in the reactor (e.g. pressure swing adsorption (PSA) or vacuum pressure swing adsorption (VPSA) mode), increasing the temperature (e.g. temperature swing adsorption (TSA) mode), contacting the purged adsorbent with dry gas (e.g. passing a gas through the reactor). The dry gas should contain less than 0.1% water, and may comprise nitrogen, noble gases, carbon dioxide, and possibly low levels carbon monoxide and hydrocarbons. Combinations of drying techniques, e.g. depressurisation and heating, may also be used.

[0055] The process of the invention is preferably performed in multiple cycles of steps (a) – (c). Since contamination of the adsorbent does hardly occur, a large number of cycles, e.g. several thousands or even more, may be performed before any cleaning or exchange of adsorbent or other maintenance steps are needed.

[0056] The invention also pertains to the use of an H_2S-enriched gas as obtained in step (b) of the process of the invention as an H_2S feed gas for processes in which appreciable levels, e.g. at least 10% or even at least 25% of H_2S are required. Examples of such process include the production of elemental sulphur, e.g. in the Claus process or in biological partial oxidation (Thiopaq), or for the production of sulphuric acid or other sulphur compounds.

Claus process

[0057] According to a second aspect, the invention concerns a Claus process as known in the art, wherein the process according to the first aspect of the invention is implemented. Claus processes are known in the art and used for desulphurisation of gases, wherein H_2S is converted to elemental sulphur via the overall chemical reaction:

$$2\,H_2S + O_2 \rightarrow 2\,S + 2\,H_2O \qquad (3)$$

[0058] This overall reaction may be a combination of several subreactions, which typically occur in several stages of the Claus process. A typical Claus process includes a thermal stage wherein the feed gas comprising H_2S is heated to a temperature above 800 °C by reaction of a sub-stoichiometric amount of oxygen, wherein combustion of H_2S via SO_2 to S, and a catalytic stage, wherein H_2S reacts with SO_2 in the presence of an alumina or titania based catalyst. Side reactions that typically occur during the Claus process include the formation of H_2S, COS, CS_2 and SO_2. These species, together with unreacted H_2S make up the Claus tail gas, which is the major by-product of elemental sulphur produced in the Claus plant. Furthermore, the Claus process can be tuned as known in the art such that SO_2 is typically absent in the Claus tail gas.

[0059] Typical Claus feeds include sour natural gas, or more typically the H_2S-enriched stream obtained by amine scrubbing thereof, and gaseous by-products of refineries or other industries. Such gaseous by-products are typically obtained by desulphurization steps, wherein H_2S contaminants are removed from the main product stream, e.g. by amine scrubbers. As such gaseous steams are obtained or formed in large quantities, the Claus process is ubiquitous in present-day industry. To be suitable for conversion by Claus, the feed gas requires a minimum H_2S content of 15 %, but at least 25 % H_2S is preferred, which renders many H_2S containing gaseous stream unsuitable to be directly used as Claus feed gas. The gases that are suitable as feed gas for the process according to the first aspect of the invention are typical examples of gases that have a too low H_2S content to be suitable as Claus feed gas. However, the second product gas obtained by the process according to the first aspect of the invention contains H_2S in a sufficiently high content to be suitable as feed gas for the Claus process. The process according to the first aspect of the invention can thus be used to enrich a gaseous stream in H_2S in order to make it suitable as feed gas for a Claus process.

[0060] The process according to the second aspect of the invention concerns a process for converting H_2S to elemental sulphur (S) comprising the step of subjecting the second product gas as obtained in the process according to the first aspect of the invention, optionally after pre-drying, to a Claus process to obtain elemental sulphur and a tail gas comprising H_2S equivalents and CO_2. If needed, the second product gas is pre-dried, i.e. the H_2O content is reduced, in order to render the second product gas suitable to be subjected to a Claus process. The required composition of the second product gas to be suitable as feed gas for a Claus process depends on whether or not the second product gas is combined with a further feed gas, typically an H_2S-enriched stream obtained by amine scrubbing of sour natural gas or an H_2S-containing gaseous by-product of a refinery or other industry, before or upon being subjected to the Claus process, and to the composition of said further feed gas. The skilled person knows to what extent the second product gas needs to be dried in order to be suitable to be used as feed gas for the Claus process according to the second aspect of the invention. Any means of drying as known in the art may be used as pre-drying, such as cooling and/or pressurisation resulting in condensation of water or by other conventional methods such as absorption or adsorption. Suitable drying means include condensation of steam to liquid water, while keeping H_2S and other species such as CO_2 and inert gases gaseous. The remaining gaseous components are then fed to the Claus process. Cooling of the second product gas from a temperature of about 350 °C to about 40 °C reduces the steam content to about 7 %, which is acceptable for a Claus feed gas. In a preferred embodiment, the second product gas is combined with a further feed gas, typically an H_2S-enriched stream obtained by amine scrubbing of sour natural gas or a H_2S-containing gaseous by-product of a refinery or other industry, before or upon being subjected to the Claus process.

[0061] In a preferred embodiment, the tail gas of the Claus process according to the second aspect of the invention, comprising H_2S equivalents and CO_2, is used as feed gas in step (a) of the process according to the first aspect of the invention, optionally after pre-drying. In one embodiment, the Claus tail gas is pre-treated prior to being subjected to step (a) of the process according to the first aspect of the invention. Pre-treatment may be employed to lower the H_2O content and/or the SO_2 content (or the SO_x content). As the required H_2O content of the feed gas of the process according to the first aspect of the invention is critical, and typical Claus tail gases are too wet, it is preferred that the Claus tail gas is pre-dried, before being subjected as feed gas to the process according to the first aspect of the invention. Any means of drying as known in the art may be used as pre-drying, such as cooling and/or pressurisation resulting in condensation of water or by other conventional methods such as absorption or adsorption. Suitable drying means include condensation of steam to liquid water, while keeping H_2S equivalents and CO_2 gaseous. The remaining gaseous components are then fed to the process according to the first aspect of the invention. Since drier feed gases give rise to increased H_2S adsorption capacity of the adsorbent, it is preferred that pre-treatment to lower the H_2O content includes a measure to lower the H_2O level to well below 1 %. Such a measure may include a glycol rinse of the Claus tail gas and/or contacting the Claus tail gas with molecular sieves, optionally after one or more of the above-mentioned techniques. Alternatively or additionally, the H_2O content may be lowered by selective permeation of water through a membrane (e.g. by vacuum permeation). Claus tail gases pre-treated as such are especially suitable to be used as feed gas for the process according to the first aspect of the invention, in view of their extremely low or even negligible water content. Pre-treatment to lower the SO_2 or SO_x content is particularly preferred, since the presence of SO_2 is undesirable in the feed gas of the process according to the first aspect of the invention, as discussed above, and typically involves subjecting a SO_x-containing gas to a hydrogenation-hydrolysis step, as known to the art, to convert SO_x to H_2S. The H_2 required in this respect may originate from the Claus tail gas itself or from substoichiometric combustion of fuel (e.g. natural gas) to a mixture of CO and H_2. SO_x can also be lowered by scrubbing with an alkaline solution followed by chemical reduction, e.g. using hydrogen, or by biological reduction, e.g. using bacteria of the genera *Desulfovibrio, Desulfobacterium, Desulforomonas* or the like. Alternatively and preferably, the Claus process is tuned as known in the art such that the tail gas is substantially free of SO_x (i.e. content below 100 ppm, preferably below 10 ppm). Such tuning is typically accomplished by tuning the amount of O_2 added to the Claus feed in the thermal stage, in order to limit the amount SO_2 produced so that the off-gas of the Claus plant does not contain SO_2, but only H_2S (and optionally COS and/or CS_2).

System

[0062] In a third aspect, the invention concerns a system designed to implement the processes according to the first and second aspects of the invention, comprising (A) a Claus unit and (B) an adsorption module equipped with (b1) a bed of adsorbent comprising alumina and one or more alkali metals. Any type of Claus unit or even an entire Claus plant as known in the art may be employed as Claus unit (A) in the system according to the invention. Suitable Claus units typically include a thermal unit and a series of catalytic reactors with intermediate cooling units. In the thermal unit, the Claus feed is mixed with a substoichiometric amount of air (or oxygen) and subsequently burnt. Herein, any hydrocarbon present in the Claus feed is preferably combusted and part of the H_2S is converted into SO_2, during which some elemental sulphur is produced. The reaction mixture is transferred to a series of catalytic reactors with intermediate cooling and elemental sulphur condensation stages. Typically, at least two, preferably three or even four catalytic reactors are employed. Each catalytic reactor is employed with a catalyst bed, typically an activated alumina. Herein, the conversion of 2 H_2S and SO_2 into S and 2 H_2O is catalyzed. Since this reaction is an equilibrium reaction, multiple catalytic stages are preferred in order to obtain high yields of elemental sulphur. Remaining hydrocarbons that may still be present in this step may deactivate the catalyst. A standard Claus plant contains three catalytic reactors, which enables sulphur recoveries of 95 – 98 wt%. Claus unit (A) comprises a first inlet (a1) for receiving a gaseous feed stream and preferably a second inlet (a2) for receiving a further gaseous feed stream. The first inlet (a1) is intended for receiving the second product gas of the process according to the first aspect of the invention, while the optional second inlet (a2) is for receiving an optional further feed gas, as discussed above. Alternatively and preferably, the system according to the invention comprises means (a3) for combing the second product gas and a further feed gas to obtained a combined feed gas prior to the introduction of the combined feed gas into the Claus unit. In this embodiment, first inlet (a1) is intended for receiving the combined gas feed comprising the second product gas of the process according to the first aspect of the invention and the further feed gas. Any means for combining as known in the art can be used as means (a3), such as “in line” or “in pipe” mixing. Typically, the Claus unit comprises a third inlet (a4) for receiving air. The Claus unit further comprises a first outlet (a5) for discharging elemental sulphur (S) and a second outlet (a6) for discharging a tail gas. The Claus unit may comprise further outlets for discharging elemental sulphur and/or tail gas.

[0063] The adsorption module (B) comprises at least one bed reactor, wherein the bed (b1) comprises, preferably consists of, the adsorbent according to the invention as bed material. The adsorbent according to the invention comprises alumina and one or more alkali metals and is further described above for the process according to the first aspect of the invention. Adsorption module (B) further comprises a first inlet (b2) for receiving the feed gas and optionally the purging gas, although it is preferred that the purging gas is received via a second inlet (b3), and a first outlet (b4) for discharging the second product gas and optionally the first product gas, although it is preferred that the first product gas is discharged via a second outlet (b5). A single bed reactor may be used, the bed (b1) of which is alternately loaded in step (a), i.e. H_2S equivalents adsorb, and unloaded in step (b), i.e. H_2S desorbs, or two or more reactors in parallel may be used in module (B). Preferably, adsorption module (B) comprises two or more bed reactors, which enables performing step (a) of the process according to the first aspect of the invention in a first reactor and simultaneously step (b) of the process according to the first aspect of the invention in a second reactor. As such, a continuous process is possible, wherein a feed gas may continuously be fed to adsorption module (B), alternating to the first and second reactor, and a purge gas may continuously be fed to adsorption module (B), alternating to the second and first reactor. The reactor to which the feed gas is fed discharges the first product gas, while the reactor to which the purge gas is fed discharges the second product gas. Even more preferred is the use of three bed reactors, wherein a first bed is being subjected to step (a) while a second bed is being subjected to step (b) and a third bed to step (c). In this embodiment, the two, three or more beds operate according to the cyclic scheme of step (a) → step (b) → step (c) → step (a) → etc.

[0064] The bed reactor is preferably a packed bed reactor or a fluidized bed reactor, more preferably a packed bed reactor. The reactor is typically in the form of a column, tube or vessel, wherein preferably a reactor is packed with the adsorbent material. The reactor is designed as known in the art, typically to enable the stream of the feed gas or the purge gas, which is introduced via one of the inlets (b2) or (b3), to be led over or through the bed, towards one of the outlets (b4) or (b5). In case a column is used, the inlet (b1) for receiving the feed gas is conveniently placed at the bottom or top of the column, and the outlet (b4) for discharging the product gases is conveniently placed at the other side of the column. Alternative arrangements, including horizontal flows or flow entering and leaving the column at the long sides, are also well suitable.

[0065] In the system according to the invention, the Claus unit (A) and the adsorption module (B) are interconnected, i.e. the outlet of one is in fluid connectivity with the inlet of the other, preferably by means of a conduit. As such, the constant flow of (liquid) streams through the system is enabled. Thus, the second outlet (a6) of the Claus unit (A) is in fluid connection with the inlet (b2) of the adsorption module (B), and the first outlet (b4) of the adsorption module (B) is in fluid connection with the first inlet (a1) of the Claus unit (A). Using such arrangement, the Claus tail gas is effectively recycled to the Claus unit by increasing the H_2S content thereof. In view of legal requirements, Claus tail gases need to be treated to remove H_2S equivalents before it may be expelled into the environment after incineration. A major advantage of the recycle according to the present invention is that conventional tail gas treatments (TGT) are no longer required, which are typically less environmentally friendly and more expensive than the process according to the first aspect of the invention. For example, amine scrubbing as TGT removes H_2S together with significant quantities of CO_2, giving a typical ratio of H_2S to CO_2 of below 0.1, which renders this gas less suitable to be recycled to the Claus process. The processes according to the invention are advantageous, since a high quality recycle gases for the Claus unit are obtained. For typical Claus tail-gases having a high CO_2/H_2S ratio, conventional separation technologies are not capable to provide highly enriched H_2S streams. Moreover, conventional TGT usually create a separate sulphur-product such as sulphuric acid. Separation by adsorption gives potentially smaller TGT units compared to conventional TGT units.

[0066] In a preferred embodiment, the Claus tail gas as discharged from the Claus unit (A) via outlet (a6) is first led to a steam removal unit (C1) before being received by adsorption module (B) via inlet (b2). Steam removal unit (C1) is thus integrated in the fluid connectivity between outlet (a6) and inlet (b2). Unit (C1) comprises means for removing steam from the Claus tail gas. Any type of such means as known in the art may be used, such as means for cooling and/or pressurisation resulting in condensation of water or other conventional means such as absorption or adsorption means. More preferably, the steam removal means includes a measure to lower the H_2O level to well below 1 %. Such a measure may include a glycol rinse of Claus tail feed gas and/or contacting the Claus tail gas with molecular sieves, optionally after one or more of the above-mentioned techniques. Alternatively or additionally, the H_2O content may be lowered by selective permeation of water through a membrane (e.g. by vacuum permeation). Unit (C1) is designed for receiving the Claus tail gas originating from outlet (a6) of Claus unit (A) to the means for steam removal and for discharging the Claus tail gas which is depleted in steam from the means for steam removal. The Claus tail gas depleted in steam is then led to inlet (b2) of adsorption module (B). It is likewise preferred that a similar steam removal unit (C2) is integrated in the fluid connectivity between outlet (b4) and inlet (a1) or, if present, means (a3). Unit (C2) comprises means for removing steam from the second product gas. Any type of such means as known in the art may be used, such as means for cooling and/or pressurisation resulting in condensation of water or other conventional means such as absorption or adsorption means. Unit (C2) is designed for receiving the second product gas originating from outlet (b4) of adsorption module (B) to the means for steam removal and for discharging the second product gas which is depleted in steam from the means for steam removal. The second product gas depleted in steam is then led to inlet (a1) or means (a3) of the Claus unit (A). In the context of the present invention, units (C1) and (C2) are used for pre-drying as described for the processes according to the first and second aspects of the invention.

[0067] In a further preferred embodiment, a SO_x removal unit is integrated in the fluid connectivity between outlet (b4) and inlet (a1), preferably downstream of the unit C2 if present. The presence of such a SO_x removal unit is particularly preferred for Claus tail gases containing SO_x. The SO_x removal unit comprises means for removing SO_x from the Claus tail. Suitable means for removing SO_x include hydrogenation-hydrolysis means, which is known to the art to covert SO_x to H_2S, means for scrubbing with an alkaline solution followed by chemical reduction, e.g. using hydrogen, or means for biological reduction, e.g. using bacteria of the genera *Desulfovibrio, Desulfobacterium, Desulforomonas* or the like. The SO_x removal unit is designed for receiving the Claus tail gas originating from outlet (a6) of Claus unit (A), optionally via unit (C1), to the means for SO_x removal and for discharging the Claus tail gas which is depleted in SO_x from the means for steam removal. The Claus tail gas depleted in SO_x is then led to inlet (b2) of adsorption module (B), optionally via unit (C1).

Description of the figures

[0068] A preferred embodiment of the system according to the invention is depicted in figure 1. Claus unit (A) may be any Claus unit or Claus plant as known in the art. It comprises a first inlet (a1) for receiving a combined feed gas originating from means (a3) for combining the second product gas and a further feed gas. Unit (A) further comprises a first outlet (a5) for discharging elemental sulphur and a second outlet (a6) for discharging a Claus tail gas. Second outlet (a6) is in fluid connectivity via steam removal unit (C1) with inlet (b2) of the adsorption module (B). Adsorption module (B) comprises a bed (b1) containing the adsorbent according to the invention as bed material, a first inlet (b2) for receiving the Claus tail originating from unit (C1) and a second inlet (b3) for receiving a purge gas. Module (B) further comprises a first outlet (b4) for discharging the second product gas and a second outlet (b5) for discharging the first product gas. Module (B) is designed as such that incoming gases from inlets (b2) and (b3) are led through or over the bed towards outlets (b4) and (b5). First outlet (b4) is in fluid connectivity via steam removal unit (C2) with means (a3). Means (a3) is designed to combine the second product gas originating from unit (C2) and a further feed gas.

[0069] Figures 2 – 8 depict compositions of the tail gases obtained in examples 1 – 3.

Examples

Example 1:

[0070] A feed gas containing 10 % CO_2, 10 % H_2 and 500 ppm H_2S (balanced with N_2) was subjected to adsorption in a packed bed placed in a cylindrical reactor containing 1 g adsorbent. The feed flow was 150 Nml/min, and the bed operated at a temperature of 400 °C and a pressure of 3 bar(a). The process according to the invention was operated in a cyclic co-current mode. Cycles consisted of an adsorption stage, a flushing stage, a purging stage and a regeneration stage. The adsorption stage was continued until full breakthrough of CO_2 and H_2S was reached. Subsequently, the loaded adsorbent was flushed with 10 % Ar in N_2 (flow = 150 Nml/min) and then purged with a purging gas containing 30 % H_2O (balanced with Ar and N_2; flow = 150 Nml/min). As last step in the cycle, the adsorbent loaded with H_2O was regenerated by flushing with a dry inert gas (10 % Ar in N_2; flow = 150 Nml/min). The adsorbents used were K-promoted hydrotalcite MG30 (KMG30), K-promoted alumina (20 wt% K_2CO_2 on alumina) and unpromoted MG30 (control). A similar experiment was conducted with 0.5 g Na-promoted MG30 as adsorbent, which operated at 350 °C and 1 bar(a) and wherein the gas flows (feed, purge and flushes) were 100 Nml/min.

[0071] Figures 2 – 5 depict the tail gas (effluent) composition of a cycle of each of the four experiments: Fig. 2 shows the results for KMG30 as adsorbent, Fig. 3 for K-promoted alumina, Fig. 4 for Na-promoted MG30 and Fig. 5 for unpromoted MG30. Ar levels were also determined (data not shown), to visualise the switches between the different stages. These stages are indicated with A, D, F1 and F2, wherein "A" denotes the adsorption stage (feed gas), "D" the desorption or purging stage (purging gas), and "F1" and "F2" the first inert flush and second inert flush (regeneration), respectively. On the y-axis, the mass spectrometer (MS) response in arbitrary units is shown.

[0072] In all experiments, fast breakthrough of CO_2 was observed after the adsorption period commenced. Because of the high sorbent capacity for H_2S equivalents, breakthrough of H_2S (and COS) was observed at a later time, indicating saturation of the adsorbent with H_2S and COS at that time. For the control unpromoted adsorbent, breakthrough times for CO_2, H_2S and COS were similar (Fig. 5), indicating that significantly less H_2S (and COS) is adsorbed during the adsorption phase. For the experimental adsorbents, the H_2S+COS slip level before breakthrough as observed in the first effluent (tail gas of the adsorption phase) was less than 5 ppm, i.e. >2 orders of magnitude decrease with respect to the feed gas. It should be noted that no COS was present in the feed gas, meaning that the adsorbent promotes the $H_2S + CO_2 \leftrightarrow COS + H_2O$ equilibrium reaction at the operating conditions. In view of the simultaneous breakthrough of H_2S and COS, those species are both adsorbed. Upon steam regeneration, CO_2 was released swiftly from the adsorbent, while desorption of H_2S is spread over a longer period of time. The second effluent (tail gas of the desorption phase) contained H_2S, CO_2, H_2O and inert gases. No desorption of COS was observed, indicating that all adsorbed sulphur species are released as H_2S. For the control unpromoted adsorbent, hardly any H_2S desorption was observed (Fig. 5), reflecting the small amount of H_2S adsorbed in the adsorption period.

Example 2:

[0073] Two distinct feed gases containing 10 % CO_2, 10 % H_2 and 500 ppm or 900 ppm H_2S (balanced with N_2) were subjected to adsorption in a packed bed placed in a cylindrical reactor containing 0.5 g K-promoted hydrotalcite MG30 (KMG30) as adsorbent. The feed flow was 200 Nml/min, and the bed operated at a temperature of 350 °C and a pressure of 1 bar(a). The process according to the invention was operated in a cyclic co-current mode. Cycles consisted of an adsorption stage, a flushing stage, a purging stage and a regeneration stage. The adsorption stage was continued until full breakthrough of CO_2 and H_2S was reached. Subsequently, the loaded adsorbent was flushed with 10 % Ar in N_2 (flow = 200 Nml/min) and then purged with a purging gas containing 30 % H_2O (balanced with Ar and N_2; flow = 200 Nml/min). As last step in the cycle, the adsorbent loaded with H_2O was regenerated by flushing with a dry inert gas (10 % Ar in N_2; flow = 200 Nml/min).

[0074] Figure 6 depicts the tail gas compositions with respect to H_2S and COS for the adsorption stage of a cycle of each of the two experiments: Fig. 6a shows the results for the feed gas comprising 500 ppm H_2S and Fig. 6b for the feed gas comprising 900 ppm H_2S. Levels (in ppm) of H_2S, COS and “total S” (i.e. H_2S + COS) are depicted. The start of breakthrough is observed at about 75 min in Fig. 6a and at about 50 min in Fig.

6b. Before start of breakthrough, the level of total S in the tail gas (slip level) was below 5 ppm. Both H_2S and COS were observed at breakthrough, while only H_2S was fed. At about t = 130 min (Fig. 6a) or t = 80 min (Fig. 6b), the adsorbent reached full capacity for the H_2S equivalents, and full breakthrough was reached.

[0075] Figure 7 depicts a more detailed analysis of the tail gas composition obtained with the feed gas comprising 500 ppm H_2S. Levels (in ppm) of H_2S, COS and “total S” (i.e. H_2S + COS) are depicted. The results of a different cycle as the one presented in Fig. 6a are presented. In the cycle of Fig. 7, the slip level of total S was below 1 ppm (t = 840 – 875 min). At full breakthrough, about 500 ppm of sulphur species (H_2S to COS ratio of about 1) was observed in the tail gas, at which point the loaded adsorbent was briefly flushed (around t = 950) and the purging stage commenced. During purging, a peak in the H_2S level of the tail gas was observed, with initial H_2S levels well above 600 ppm, while COS was absent in the tail gas from the start of the purging phase. The second product gas obtained during the purging phase thus contained high levels of H_2S as sole H_2S equivalent.

Example 3:

[0076] A feed gas containing 10 % CO_2, 10 % H_2 and 100 ppm CS_2 (balanced with N_2) was subjected to adsorption in a packed bed placed in a cylindrical reactor containing 0.5 g K-promoted hydrotalcite MG30 (KMG30) as adsorbent. The feed flow was 200 Nml/min, and the bed operated at a temperature of 350 °C and a pressure of 1 bar(a). The process according to the invention was operated in a cyclic co-current mode. Cycles consisted of an adsorption stage, a flushing stage, a purging stage and a regeneration stage. The adsorption stage was continued until full breakthrough of CO_2 and H_2S was reached. Subsequently, the loaded adsorbent was flushed with 10 % Ar in N_2 (flow = 200 Nml/min) and then purged with a purging gas containing 30 % H_2O (balanced with Ar and N_2; flow = 200 Nml/min). As last step in the cycle, the adsorbent loaded with H_2O was regenerated by flushing with a dry inert gas (10 % Ar in N_2; flow = 200 Nml/min).

[0077] Figure 8 depicts the tail gas composition with respect to H_2S equivalents for a cycle of the experiment. Levels (in ppm) of H_2S, COS and “total S” (i.e. H_2S + COS + CS_2) are depicted. In the cycle of Fig. 8, the slip level of total S was below 1 ppm (t = 24770 – 24830 min). At full breakthrough, about 200 ppm of sulphur species (H_2S to COS ratio of about 7) was observed in the tail gas, while no CS_2 was completely absent in the tail gas (H_2S + COS = total S). The loaded adsorbent was briefly flushed (around t = 24910) and the purging stage commenced. During purging, a peak in the H_2S level of the tail gas was observed, with initial H_2S levels well above 250 ppm, while both COS and CS_2 were completely absent in the tail gas from the start of the purging phase. The second product gas obtained during the purging phase thus contained high levels of H_2S as sole H_2S equivalent, while CS_2 was present as sole H_2S equivalent in the feed gas.

Example 4:

[0078] Seven distinct feed gases containing 10 % CO_2, 10 % H_2, and varying amounts of H_2S and H_2O (see Table 2, balanced with N_2) were subjected to adsorption in a packed bed placed in a cylindrical reactor containing 0.5 g K-promoted hydrotalcite MG30 (KMG30) as adsorbent. The feed flow was 200 Nml/min, and the bed operated at a temperature of 350 °C and a pressure of 1 bar(a). The process according to the invention was operated in a cyclic co-current mode. Cycles consisted of an adsorption stage, a flushing stage, a purging stage and a regeneration stage. The adsorption stage was continued until full breakthrough of CO_2 and H_2S was reached. Subsequently, the loaded adsorbent was flushed with 10 % Ar in N_2 (flow = 200 Nml/min) and then purged with a purging gas containing 30 % H_2O (balanced with Ar and N_2; flow = 200 Nml/min). As last step in the cycle, the adsorbent loaded with H_2O was regenerated by flushing with a dry inert gas (10 % Ar in N_2; flow = 200 Nml/min). During cyclic steady state, both the breakthrough adsorption capacity at and the total adsorption capacity of the adsorbent for H_2S equivalents was determined, the results of which are presented in table 2. Breakthrough adsorption capacity refers to the capacity of the adsorbent during the adsorption phase until start of breakthrough, wherein start of breakthrough is defined as the point in time when the total slip level of sulphur species (H_2S + COS) in the tail gas reaches a level of 10 ppm. Total adsorption capacity refers to the capacity of the adsorbent during the adsorption phase until total breakthrough is reached, i.e. when the content of sulphur species (H_2S + COS) in the tail gas is equal to the content of sulphur species in the feed gas.

[0079] *Table 2: Feed gas compositions and adsorption capacities for H_2S*

Entry	Feed gas composition (ppm)			Adsorption capacity (mol/kg)	
	H_2S	H_2O	H_2O/H_2S	breakthrough	total
1	500	0	0	0.57	0.841
2	500	575	1.15	0.40	0.727
3	500	900	1.80	0.31	0.617
4	900	0	0	0.62	1.124
5	900	750	0.83	0.50	1.053
6	900	2100	2.33	0.33	0.816
7	25000	117000	4.68	n.d.	0.14

[0080] For both the feed gases comprising 500 ppm H_2S and the feed gases comprising 900 ppm H_2S, the adsorption capacity of the adsorbent decreased with increasing H_2O content of the feed gas. The adsorption capacity for H_2S decreased by about a factor 2 when the H_2O/H_2S ratio increased to above 2. Extrapolating the results in Table 2, the adsorption capacity for H_2S decreased to unacceptable levels in case the H_2O/H_2S ratio increases to above 5, while the best results are obtained with a H_2O/H_2S ratio of at most 2. It should be noted that since only H_2S was used as H_2S equivalent, X amounts to zero for the feed gases tested here.

Gewijzigde conclusies (schone versie)

1. Werkwijze voor het veranderen van de samenstelling van een gas welke H_2S equivalenten en CO_2 omvat, omvattende:
   (a) het in contact brengen van een voedingsgas welke H_2S equivalenten, CO_2 en eventueel H_2O omvat, waarbij de molaire verhouding van H_2O tot H_2S equivalenten in de range van 0 – (5 + X) ligt, met een vaste adsorbens bij een temperatuur van 250 – 500 °C, om een beladen adsorbens en een eerste productgas te verkrijgen;
   (b) het in contact brengen van het beladen adsorbens met een spoelgas welke H_2O bevat om een tweede productgas te verkrijgen; en
   (c) het regenereren van het adsorbens na step (b) door middel van H_2O verwijdering,

   waarbij de werkwijze in cycli van stappen (a) – (c) wordt uitgevoerd en waarbij het voedingsgas en/of het spoelgas een reduceermiddel omvat en het adsorbens alumina en één of meer alkalimetalen omvat, en waarbij X gedefinieerd is als:

   $$X = \sum \frac{n_i \times [H_2S\ equivalent]_i}{[H_2S\ equivalenten]}$$

   waarbij [H_2S equivalenten] de totale concentratie H_2S equivalenten, [H_2S equivalent]$_i$ de concentratie van een specifiek H_2S equivalent i en n_i het aantal watermoleculen n die verbruikt worden wanneer het H_2S equivalent i omgezet wordt in H_2S, aangeeft.
2. Werkwijze volgens conclusie 1, waarbij de H_2S equivalenten H_2S, COS en/of CS_2 omvatten.
3. Werkwijze volgens conclusie 1 of 2, waarbij de molaire verhouding van H_2S equivalenten tot CO_2 in het voedingsgas lager dan 1 is, bij voorkeur in de range van 0.001 – 0.1.
4. Werkwijze volgens één der conclusies 1 – 3, waarbij het voedingsgas 0.1 – 20 % H_2 omvat als reduceermiddel.
5. Werkwijze volgens één der conclusies 1 – 4, waarbij het adsorbens verder één of meer divalente metalen, bij voorkeur als hun oxides, hydroxides, carbonaten, sulfiden en/of hydrosulfiden, omvat, bij voorkeur omvat het adsorbens verder MgO.
6. Werkwijze volgens één der conclusies 1 – 5, waarbij het alkalimetaal K is en het adsorbens K-bevorderd alumina is of gebaseerd op een K-bevorderd hydrotalciet is.

7. Werkwijze volgens één der conclusies 1 – 6, waarbij de werkwijze continueert met stap (a) na de regeneratie van stap (c).
8. Werkwijze volgens één der conclusies 1 – 7, waarbij stap (b) tegenstrooms ten opzichte van stap (a) wordt uitgevoerd.
9. Werkwijze volgens één der conclusies 1 – 8, waarbij het spoelgas ten minste 75 % H_2O omvat.
10. Werkwijze volgens één der conclusies 1 – 9, Waarbij het eerste productgas minder dan 10 ppm H_2S equivalenten bevat, en/of het eerste productgas minder dan 0.1 keer de hoeveelheid H_2S equivalenten van het voedingsgas bevat, en/of de eerste productgas een molaire verhouding H_2S equivalenten tot CO_2 van minder dan 0.005 heeft.
11. Werkwijze volgens één der conclusies 1 – 10, waarbij het tweede productgas een molaire verhouding H_2S equivalenten tot CO_2 van ten minste 0.5 heeft.
12. Werkwijze volgens één der conclusies 1 – 11, waarbij het voedingsgas een eventueel voorgedroogd syngas is, welke verder H_2 en CO bevat.
13. Werkwijze volgens één der conclusies 1 – 12, waarbij het voedingsgas een eventueel voorgedroogd Claus-restgas is, welke verder N_2 bevat
14. Werkwijze voor de conversie van H_2S naar elementair zwavel, waarbij het tweede productgas als verkregen in de werkwijze volgens één der conclusies 1 – 13, eventueel na voordrogen, onderworpen wordt aan een Clausproces om elementair zwavel en een restgas welke H_2S equivalenten en CO_2 omvat te verkrijgen.
15. Werkwijze volgens conclusie 14, waarbij het restgas gebruikt wordt als voedingsgas in stap (a) van de werkwijze volgens één der conclusies 1 – 13, eventueel na voordrogen.
16. Werkwijze volgens één der conclusies 1 – 13, waarbij het tweede productgas, eventueel na voordrogen, onderworpen wordt aan een Clausproces om elementair zwavel en een restgas welke H_2S equivalenten en CO_2 omvat te verkrijgen, en waarbij het restgas gebruikt wordt als voedingsgas in stap (a) van de werkwijze volgens één der conclusies 1 – 13, eventueel na voordrogen.
17. System voor het uitvoeren van de werkwijze volgens één der conclusies 1 – 13 en de werkwijze volgens één der conclusies 14 – 16, omvattende:
    (A) een Clausunit omvattende:
        (a1) een eerste ingang voor het ontvangen van het tweede productgas;
        (a5) een eerste uitgang voor het uitstoten van elementair zwavel; en

(a6) een tweede uitgang voor het uitstoten van een Claus restgas; en

(B) een adsorptiemodule omvattende:

(b1) een reactorbed omvattende het adsorbens zoals gedefinieerd in één der conclusies 1, 5 en 6;

(b2) een eerste ingang voor het ontvangen van het Claus-restgas; en

(b4) een eerste uitgang voor het uitstoten van het tweede productgas,

waarbij uitgang (a6) in vloeiende verbinding met ingang (b2) is en uitgang (b4) in vloeiende verbinding met ingang (a1) is.

18. Gebruik van een H_2S-verrijkt gas verkrijgbaar in stap (b) van de werkwijze volgens één der conclusies 1 – 13 voor de productie van elementair zwavel, bij voorkeur in een Clausproces.

Fig. 1

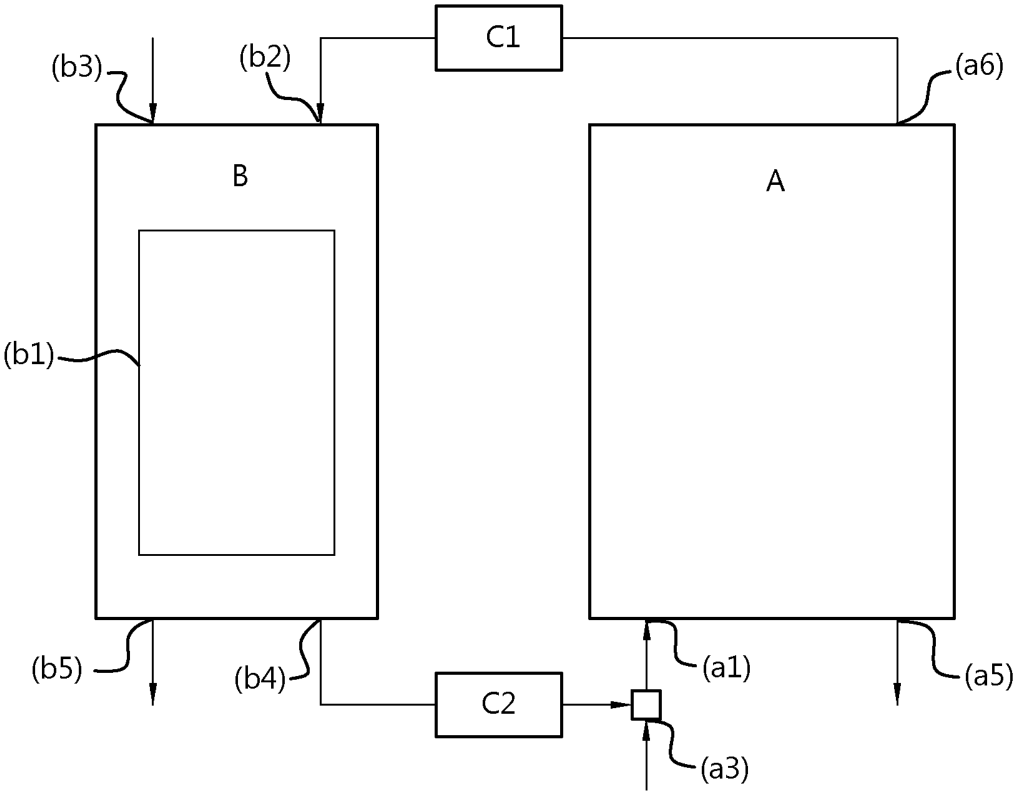
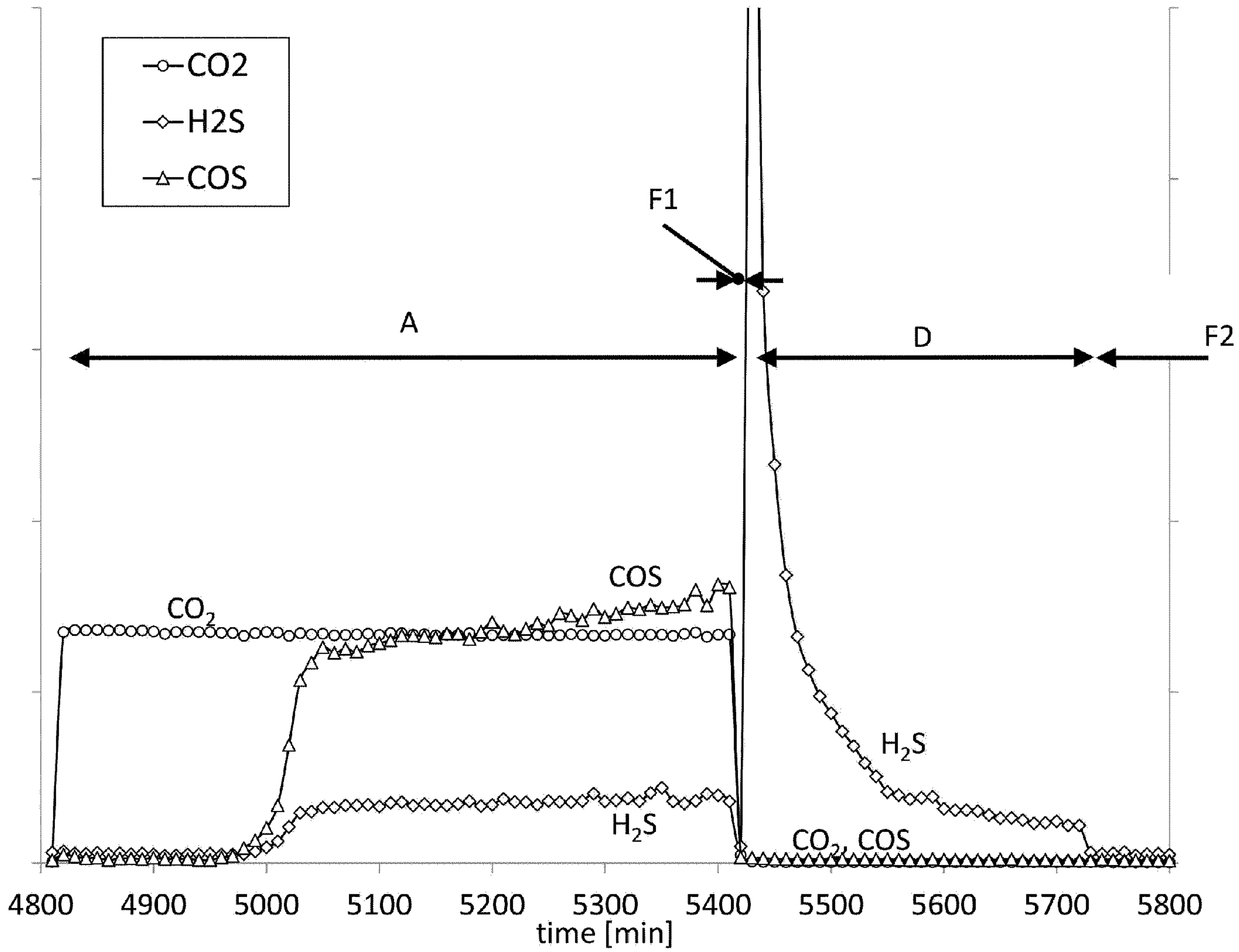
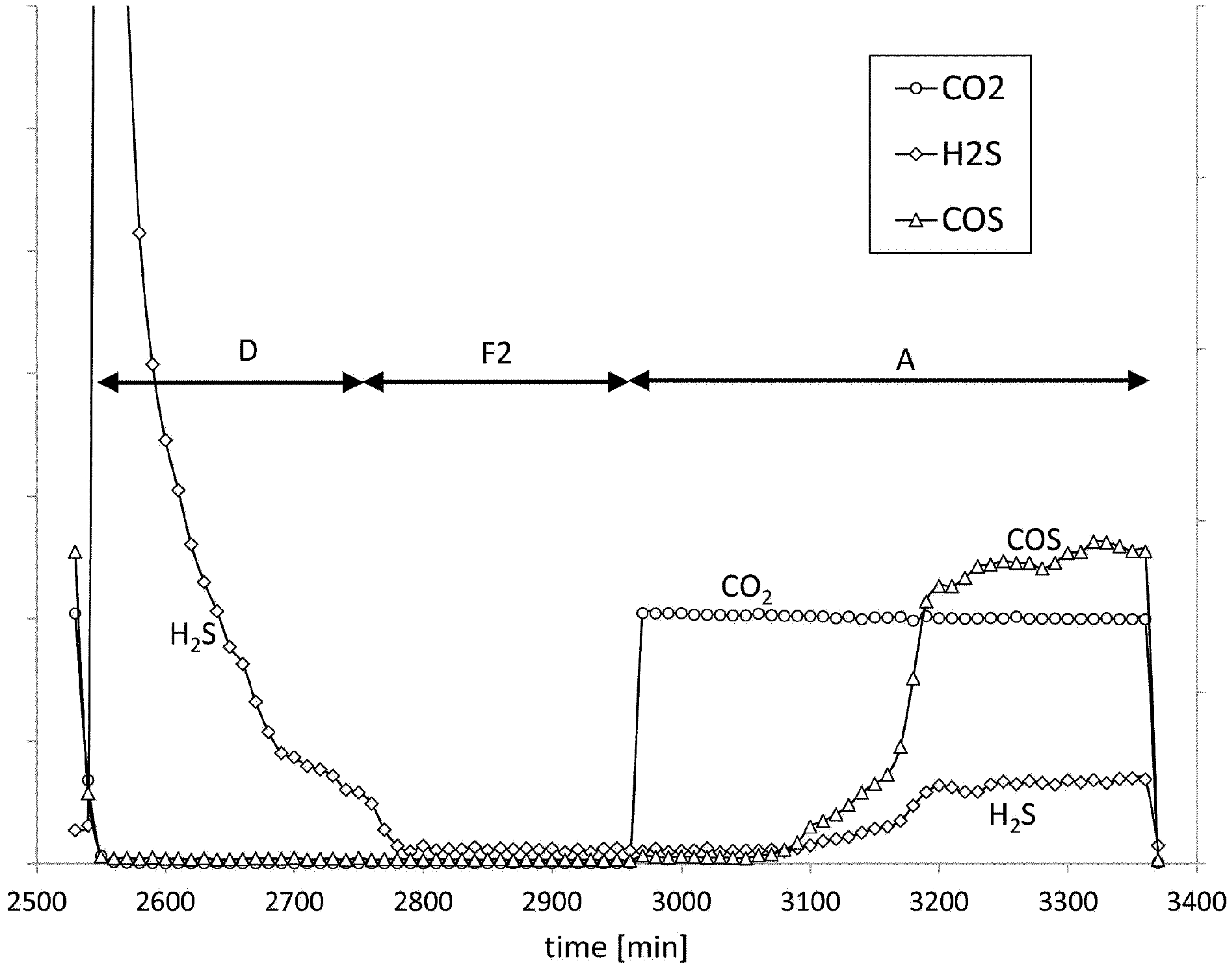


Fig. 2



CO2
H2S
COS
F1
A
D
F2
COS
CO_2
H_2S
H_2S
CO_2, COS
4800
4900
5000
5100
5200
5300
5400
5500
5600
5700
5800
time [min]

Fig. 3



-o-CO2
-◇-H2S
-△-COS
D
F2
A
H2S
CO2
COS
H2S
2500
2600
2700
2800
2900
3000
3100
3200
3300
3400
time [min]

Fig. 4

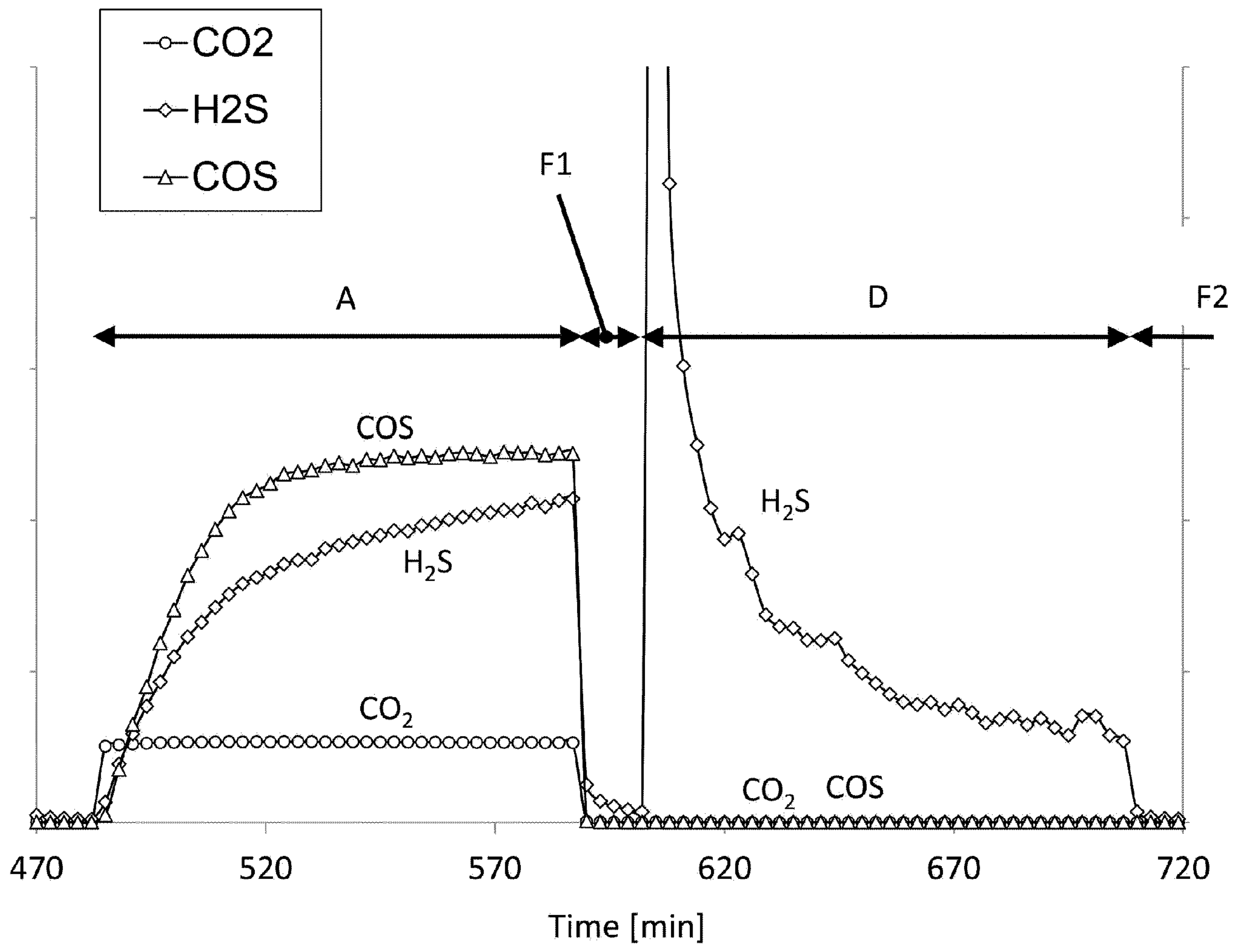

CO2
H2S
COS
F1
A
D
F2
COS
H2S
CO2
H2S
CO2
COS
470
520
570
620
670
720
Time [min]

Fig. 5

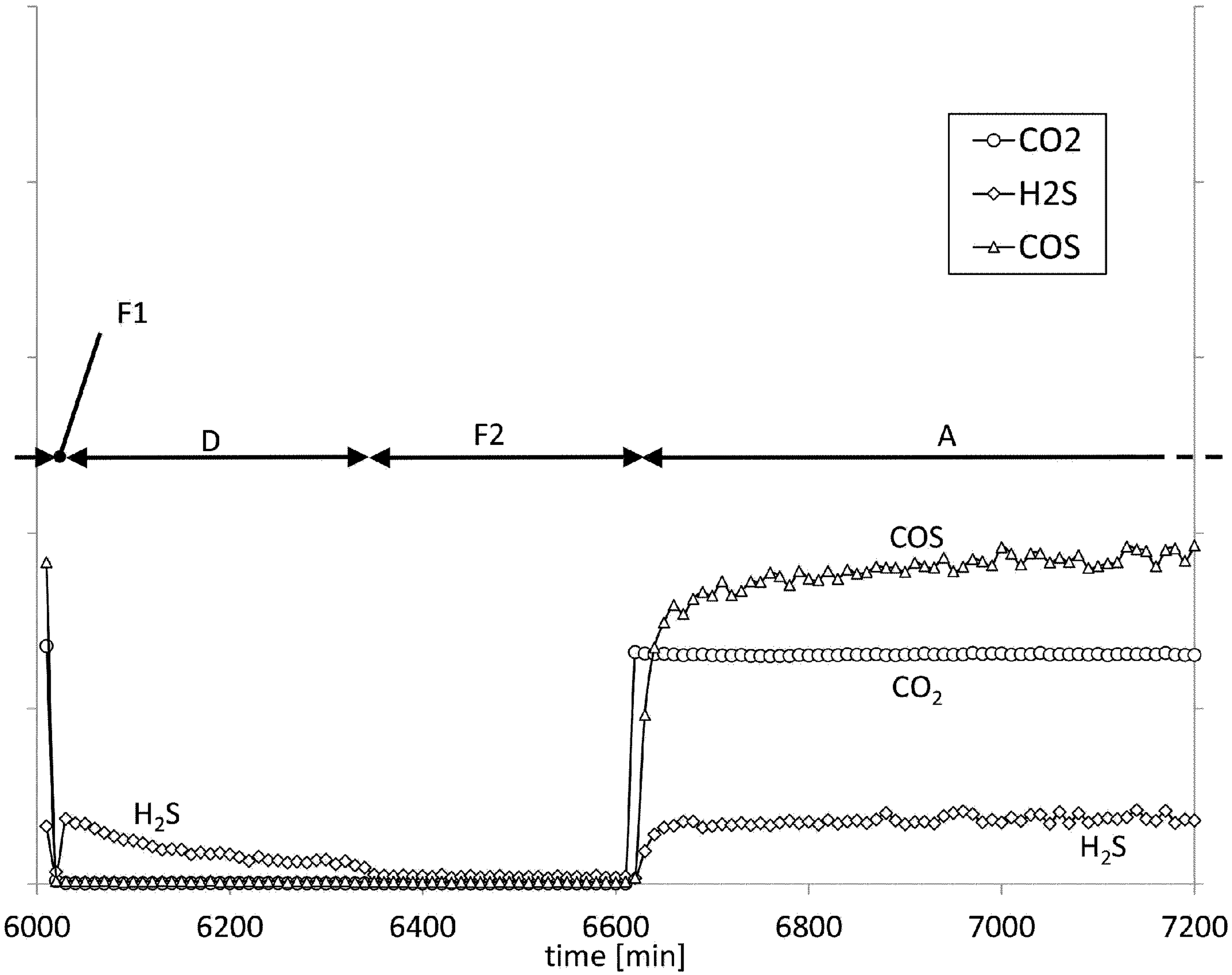
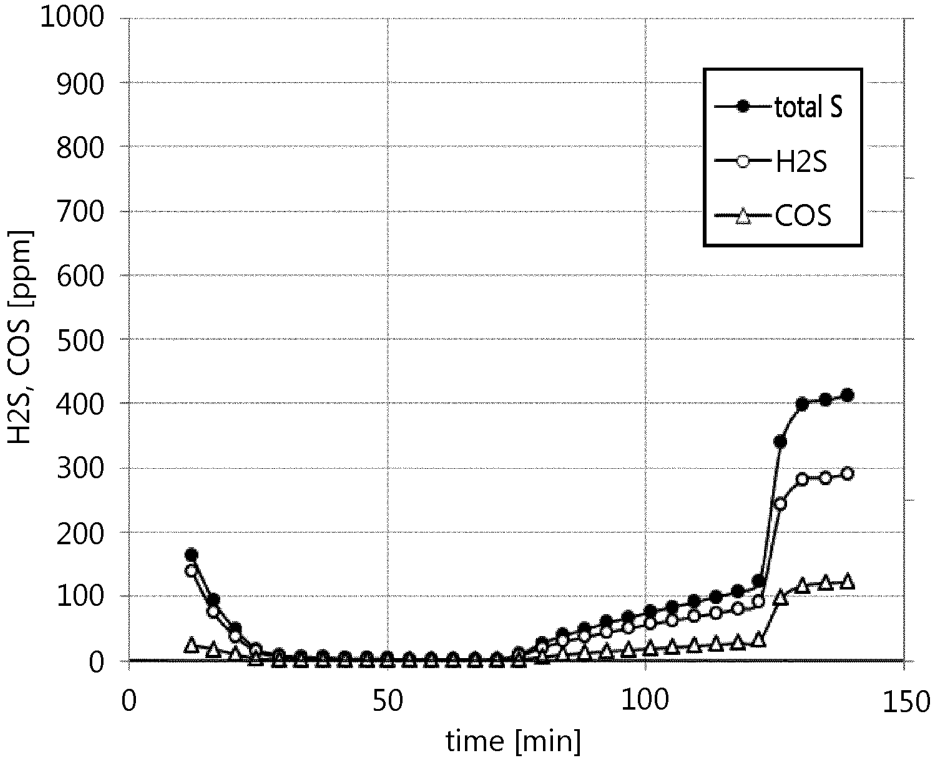
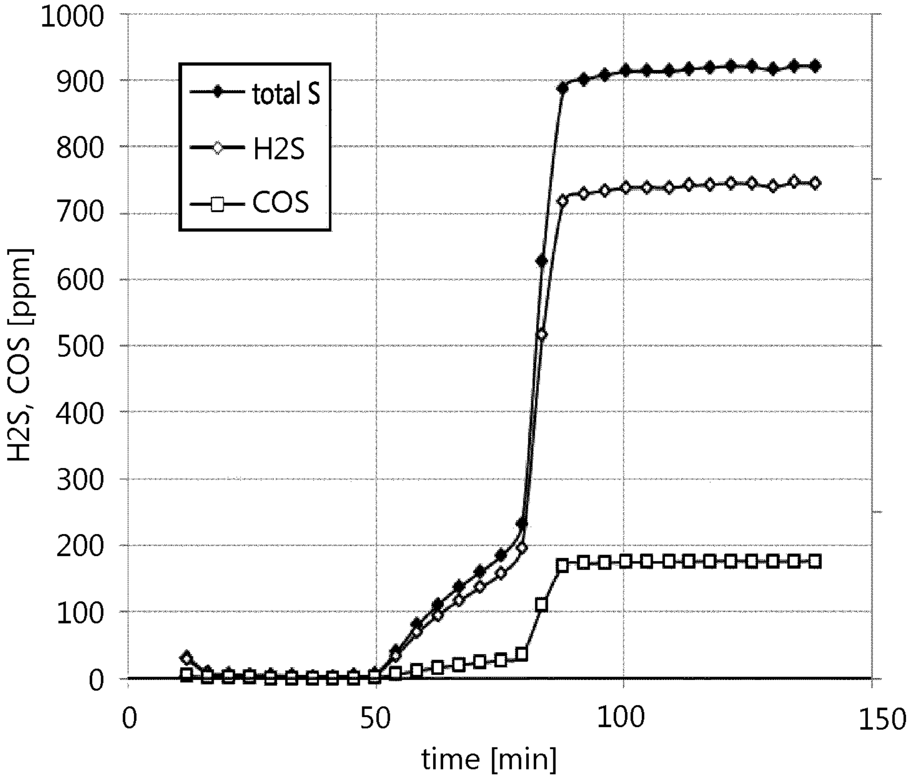

CO2
H2S
COS
F1
D
F2
A
COS
CO$_2$
H$_2$S
H$_2$S
6000
6200
6400
6600
6800
7000
7200
time [min]

Fig. 6a



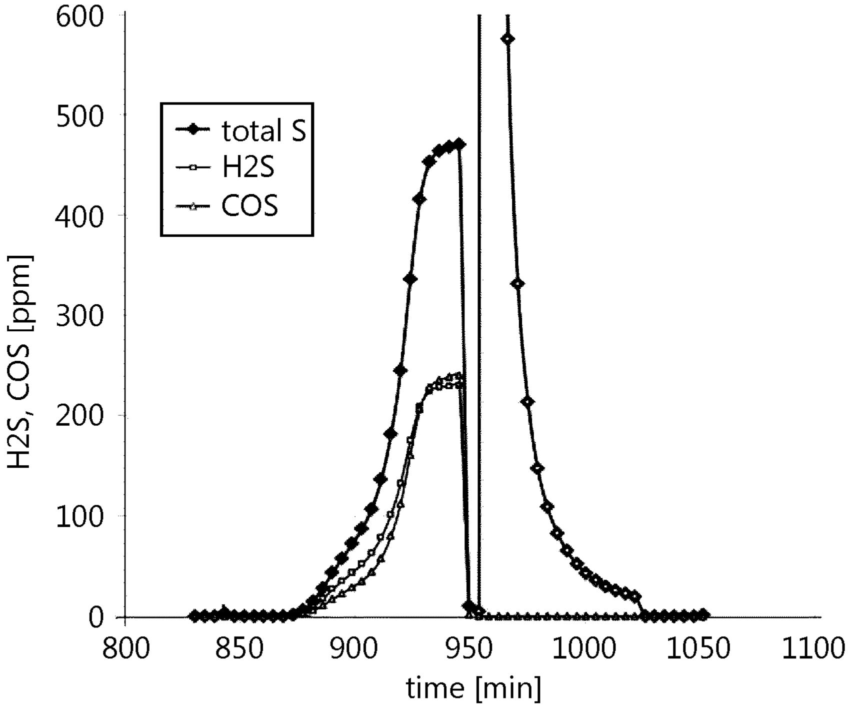
H2S, COS [ppm]
1000
900
800
700
600
500
400
300
200
100
0
0
50
100
150
time [min]
total S
H2S
COS

Fig. 6b



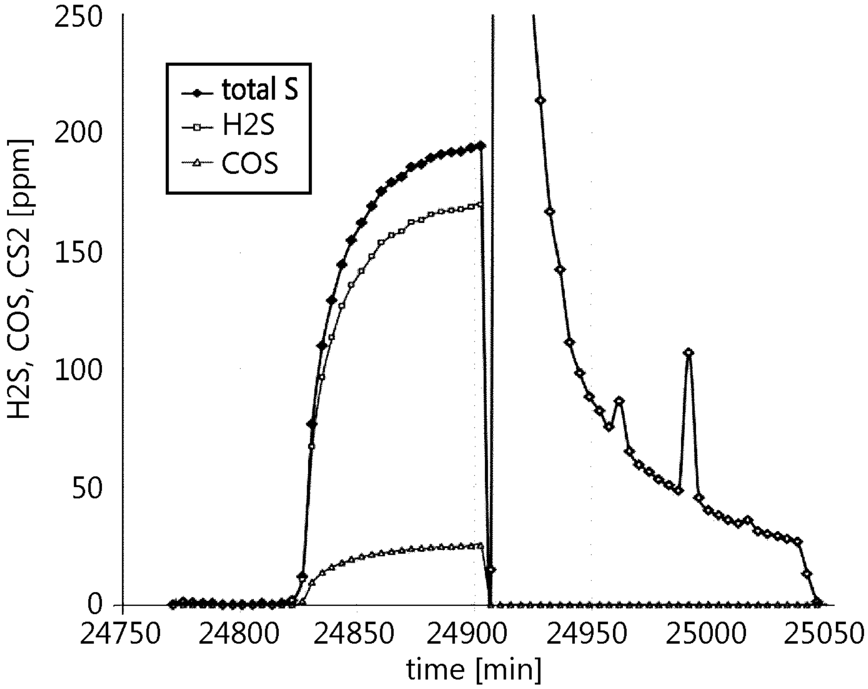
H2S, COS [ppm]
1000
900
800
700
600
500
400
300
200
100
0
0
50
100
150
time [min]
total S
H2S
COS

Fig. 7



total S
H2S
COS
H2S, COS [ppm]
600
500
400
300
200
100
0
800
850
900
950
1000
1050
1100
time [min]

Fig. 8



total S
H2S
COS
H2S, COS, CS2 [ppm]
250
200
150
100
50
0
24750
24800
24850
24900
24950
25000
25050
time [min]

Abstract

A process for altering the composition of a feed gas containing H_2S equivalents is disclosed, wherein said feed gas comprises CO_2 and H_2S equivalents, typically H_2S and optionally COS and CS_2, preferably in a molar ratio of H_2S equivalents to CO_2 of below 1, preferably below 0.1, and optionally water, wherein the molar ratio of H_2O to H_2S equivalents is in the range of 0 – (5 + X), wherein X is a factor that takes into account the consumption of H_2O during conversion of an equivalent of H_2S to H_2S. The process comprises (a) contacting the feed gas with a solid adsorbent at a temperature of 250 – 500 °C, to obtain a loaded adsorbent, (b) purging the loaded adsorbent with a purge gas comprising steam, thus producing a product stream which typically contains substantially equal levels of CO_2 and H_2S. Preferably, the process further comprises a step (c) of drying the purged adsorbent. The adsorbent comprises alumina and one or more alkali metals, such as potassium oxides, hydroxide or the like.

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	**KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE** **P6051716NL**
Nederlands aanvraag nr. **2013759**	Indieningsdatum **10-11-2014**
	Ingeroepen voorrangsdatum
Aanvrager (Naam) **Stichting Energieonderzoek Centrum Nederland**	
Datum van het verzoek voor een onderzoek van internationaal type **31-01-2015**	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. **SN63360**

I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)

Volgens de internationale classificatie (IPC)

B01D53/02;B01D53/52;B01D53/62;B01D53/86;C01B17/04;B01J20/08

II. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimumdocumentatie

Classificatiesysteem	Classificatiesymbolen
IPC	**B01D;C01D;B01J**

Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

III.	☐	**GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES**	(opmerkingen op aanvullingsblad)
IV.	☒	**GEBREK AAN EENHEID VAN UITVINDING**	(opmerkingen op aanvullingsblad)

Form PCT/ISA 201 A (11/2000)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2013759

A. CLASSIFICATIE VAN HET ONDERWERP
INV. B01D53/02 B01D53/52 B01D53/62 B01D53/86 C01B17/04
B01J20/08
ADD.
Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte mimimum documentatie (classificatie gevolgd door classificatiesymbolen)
B01D C01B B01J

Onderzochte andere documentatie dan de mimimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)

EPO-Internal, WPI Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
	EENHEID VAN UITVINDING ONTBREEKT zie aanvullingsblad B -----	
X	EP 1 142 623 A2 (AIR PROD & CHEM [US]) 10 oktober 2001 (2001-10-10)	1-13
A	* samenvatting; figuur 1 * * alineas [0001], [0015], [0017], [0019], [0020], [0031] - [0033], [0041], [0043], [0044] * -----	14-16,18
X	WO 2013/122467 A1 (STICHTING ENERGIE [NL]) 22 augustus 2013 (2013-08-22)	1-13
A	* samenvatting * * alineas [0001], [0013], [0016], [0019], [0021], [0027] - [0030], [0038] - [0042] * ----- -/--	14-16,18

☒ Verdere documenten worden vermeld in het vervolg van vak C.

☒ Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

° Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft
"D" in de octrooiaanvrage vermeld
"E" eerdere octrooi(aanvrage), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven
"L" om andere redenen vermelde literatuur
"O" niet-schriftelijke stand van de techniek
"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur
"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding
"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur
"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht
"&" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid 8 juli 2015	Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type
Naam en adres van de instantie European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	De bevoegde ambtenaar Howe, Patrick

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2013759

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
A	EP 2 412 668 A1 (AIR PROD & CHEM [US]) 1 februari 2012 (2012-02-01) * samenvatting; figuur 1 * * alineas [0001], [0024], [0034] - [0036], [0039] - [0041], [0043] - [0045], [0048], [0052], [0056], [0097] - [0099] * -----	1-16,18
A	WO 2014/005817 A1 (TOTAL SA [FR]; AIR LIQUIDE [FR]) 9 januari 2014 (2014-01-09) * samenvatting; figuren 1,2 * * bladzijde 1, regels 3-8 * * bladzijde 3, regel 3 - bladzijde 4, regel 19 * * bladzijde 6, regel 19 - bladzijde 7, regel 20 * * bladzijde 9, regels 1-19 * * bladzijde 10, regel 3 - bladzijde 11, regel 3 * -----	1-16,18
A	DE 10 2006 045379 A1 (LURGI AG [DE]) 3 april 2008 (2008-04-03) * samenvatting; figuur 1 * * alineas [0001], [0003] - [0007], [0011]; conclusie 1 * -----	1-16,18

Octrooiaanvrage Nr.:

SN 63360
NL 2013759

GEBREK AAN EENHEID VAN UITVINDING

AANVULLINGSBLAD B

De Instantie belast met het uitvoeren van het onderzoek naar de stand van de techniek heeft vastgesteld dat deze aanvrage meerdere uitvindingen bevat, te weten:

1. conclusies: 1-16, 18

   Subject-matter of claim 1

   \---

2. conclusie: 17

   Subject-matter of claim 17

   \---

Het vooronderzoek werd tot het eerste onderwerp beperkt.

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar de stand van de techniek

NL 2013759

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
EP 1142623 A2	10-10-2001	AT 264705 T	15-05-2004
		CA 2328694 A1	23-06-2001
		DE 60010037 D1	27-05-2004
		DE 60010037 T2	31-03-2005
		EP 1142623 A2	10-10-2001
		ES 2219252 T3	01-12-2004
		NO 20006556 A	25-06-2001
		US 6322612 B1	27-11-2001
WO 2013122467 A1	22-08-2013	AU 2013221020 A1	21-08-2014
		CN 104203810 A	10-12-2014
		EP 2814775 A1	24-12-2014
		KR 20140126326 A	30-10-2014
		NL 2008313 C	02-09-2013
		US 2015014595 A1	15-01-2015
		WO 2013122467 A1	22-08-2013
EP 2412668 A1	01-02-2012	CA 2747166 A1	27-01-2012
		CN 102408098 A	11-04-2012
		EP 2412668 A1	01-02-2012
		US 2012027656 A1	02-02-2012
WO 2014005817 A1	09-01-2014	CA 2878403 A1	09-01-2014
		EP 2874730 A1	27-05-2015
		WO 2014005817 A1	09-01-2014
DE 102006045379 A1	03-04-2008	CA 2663238 A1	03-04-2008
		CN 101516766 A	26-08-2009
		DE 102006045379 A1	03-04-2008
		EP 2077974 A2	15-07-2009
		US 2010111824 A1	06-05-2010
		WO 2008037315 A2	03-04-2008
		ZA 200901945 A	30-06-2010

WRITTEN OPINION

File No. SN63360	Filing date *(day/month/year)* 10.11.2014	Priority date *(day/month/year)*	Application No. NL2013759

International Patent Classification (IPC)
INV. B01D53/02 B01D53/52 B01D53/62 B01D53/86 C01B17/04 B01J20/08

Applicant
Stichting Energieonderzoek Centrum Nederland

This opinion contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☒	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☒	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the application
☒	Box No. VIII	Certain observations on the application

Examiner
Howe, Patrick

WRITTEN OPINION

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step, or to be industrially applicable have not been examined in respect of

☐ the entire application

☒ claims Nos. 17

because:

☐ the said application, or the said claims Nos. relate to the following subject matter which does not require a search *(specify)*:

☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed *(specify)*:

☒ no search report has been established for the whole application or for said claims Nos. 17

☐ a meaningful opinion could not be formed as the sequence listing was either not available, or was not furnished in the international format (WIPO ST25).

☐ a meaningful opinion could not be formed without the tables related to the sequence listings; or such tables were not available in electronic form.

☐ See Supplemental Box for further details.

Box No. IV Lack of unity of invention

1. The requirement of unity of invention is not complied with for the following reasons:

   see separate sheet

2. This report has been established in respect of the following parts of the application:

   ☐ all parts.

   ☒ the parts relating to claims Nos. (see Search Report)

WRITTEN OPINION

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	4, 10-16, 18
	No:	Claims	1-3, 5-9
Inventive step	Yes:	Claims	14-16, 18
	No:	Claims	1-13
Industrial applicability	Yes:	Claims	1-16, 18
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VIII Certain observations on the application

see separate sheet

Re Item IV

Lack of unity of invention

It is considered that there are 2 inventions covered by the claims indicated as follows:

Invention 1: claims 1-16, 18

Invention 2: claim 17

The reasons for which the inventions are not so linked as to form a single general inventive concept, are as follows:

The common or corresponding special technical feature between these two inventions, namely between claim 1 and claim 17, is a solid adsorbent comprising alumina and one or more alkali metals, possibly arranged within an enclosure and suitable for a temperature of 250-500°C, the enclosure having means to add a purging gas. However, the above feature is known from e.g. D1 or D2.

Document D1 discloses [samenvatting; figuur 1; alineas [0001], [0015], [0017], [0019], [0020], [0031] - [0033], [0041], [0043], [0044]] a process in which a solid adsorbent comprising alumina and Na/K is contacted with a gas (in an enclosure) at 260°C or 300-400°C. The sorbent is then purged.

Document D2 discloses [samenvatting; alineas [0001], [0013], [0016], [0019], [0021], [0027] - [0030], [0038] - [0042]] a process in which a solid adsorbent comprising alumina and alkali metal compounds is contacted with a gas at 350-450°C to obtain a loaded adsorbent and a first product gas. This is followed by purging the loaded adsorbent with a purge gas.

It also appears that there is a lack of corresponding technical effect between the two above inventions, since claim 1 deals with the problem of changing the composition of a gas stream with CO2 and H2S (and its equivalents) , and claim 17 deal with the production of sulfur. Consequently, neither the objective problem underlying the subjects of the claimed inventions, nor their solutions defined by the special technical features allow for a relationship to be established between the said inventions, which involves a single general inventive concept.

In conclusion, the groups of claims are not linked by common or corresponding special technical features and define 2 different inventions not linked by a single general inventive concept.

The application, hence does not meet the requirements of unity of invention.

The present search report and opinion is limited to the subject-matter of claims 1-6 and 18.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1	EP 1 142 623 A2 (AIR PROD & CHEM [US]) 10 oktober 2001 (2001-10-10)
D2	WO 2013/122467 A1 (STICHTING ENERGIE [NL]) 22 augustus 2013 (2013-08-22)
D3	EP 2 412 668 A1 (AIR PROD & CHEM [US]) 1 februari 2012 (2012-02-01)

1 The present application does not meet the criteria of patentability, because the subject-matter of claims 1-3 and 5-9 is not new.

1.1 Document D1 discloses [samenvatting; figuur 1; alineas [0001], [0015], [0017], [0019], [0020], [0031] - [0033], [0041], [0043], [0044]] a process for changing the composition of a gas containing H2S and possibly its equivalent (COS), and CO2, comprising (a) contacting the feed gas with a solid adsorbent comprising alumina and Na/K at 260°C or 300-400°C, to obtain a loaded adsorbent and a first product gas having a lower C02 content than the feed stream; (b) purging the loaded adsorbent with a purge gas comprising steam to obtain a second product gas having an increased content of C02, whereby the water content in the feed gas is either 2% or 0.1% (i.e. the molar ratio of H20 to H2S equivalents in the feed gas is within the range of 0 - (5 + X), X being the variable as defined in claim 1 of the present application). The feed gas also comprises a reducing agent (e.g. H2, CO, CH4).

D1 does not explicitly state in how far the H2S (and its equivalent COS) are adsorbed/removed from the gas stream, nor that they are desorbed during steam purging, however, since all process features are otherwise the same as in the present invention (temperature; chemical composition of the gas stream; chemical nature of the adsorbent), the same must also occur in D1 *in an implicit way*. The first product gas must therefore have a lower ratio of H2S/C02 than the feed stream and the second product gas must have a higher ratio of H2S/C02 than the feed stream.

1.2 The subject-matter of claim 1 is therefore not new.

1.3 The subject-matter of claims 2, 3 and 5-9 is also not new over D1 (claim 2: COS can also be present [§ 32]; claim 3: see § 32; claim 5: see § 40; claim 6: see § 33; claim 7: § 15; claim 8: see § 17; claim 9: see § 44).

1.4 Document D2 discloses [samenvatting; alineas [0001], [0013], [0016], [0019], [0021], [0027] - [0030], [0038] - [0042]] a process for changing the composition of a gas containing H2S and possibly its equivalent (COS), and CO2, comprising (a) contacting the feed gas with a solid adsorbent comprising alumina and alkali metal compounds, most preferably at 350-450°C, to obtain a loaded adsorbent and a first product gas having a lower C02 content than the feed stream; (b) purging the loaded adsorbent with a purge gas comprising e.g. steam to obtain a second product gas having an increased content of C02, whereby the water content in the feed gas can be very low (0-4%, i.e. the molar ratio of H20 to H2S equivalents in the feed gas is within the range of 0 - (5 + X), X being the variable as defined in claim 1 of the present application). The feed gas also comprises a reducing agent (e.g. H2, CO).

D2 does not explicitly state in how far the H2S (and its equivalent COS) are desorbed during steam purging, however, since all process features are otherwise the same as in the present invention (temperature; chemical composition of the gas stream; chemical nature of the adsorbent), the same must also occur in D2 *in an implicit way*. The first product gas must therefore have a lower ratio of H2S/C02 than the feed stream and the second product gas must have a higher ratio of H2S/C02 than the feed stream.

1.5 The subject-matter of at least claim 1 is therefore not new.

2 Dependent claims 4 and 10-13 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of inventive step, since the subject-matter of claims 4 and 10-13 is trivial, and it is not known in how far they solve any of the problems listed in the present application.

3 Claims 14-16 and 18 are considered novel and to convey an inventive step.

3.1 Document D3 can be considered the closest prior art for the subject-matter of claims 14 and 18. It discloses [samenvatting; figuur 1; alineas [0001], [0024], [0034] - [0036], [0039] - [0041], [0043] - [0045], [0048], [0052], [0056], [0097] -

[0099]] a method to convert H2S (e.g. in stream 18) to elemental sulfur (54) whereby a "second product gas" (18) of a PSA adsorption process (12) is subjected to a Claus process (32) to produce sulfur (52) and a rest gas comprising CO2 and H2S (34).

3.2 The "second product gas" (18) is produced in the adsorption process by changing the composition of a gas (10) containing H2S and possibly its equivalents (COS/CS2), and CO2, comprising (a) contacting the feed gas with a solid adsorbent comprising e.g. alumina at 10-60°C, to obtain a loaded adsorbent and a first product gas (14) having a lower C02 content than the feed stream; (b) purging the loaded adsorbent with a purge gas to obtain a second/third product gas (16/18) having an increased content of C02 and H2S compared with the feed gas, whereby the feed gas comprises water [see § 34] and reducing agents (e.g. H2, CO).

3.3 The subject-matter of claim 14/18 at least **differs** from the disclosure of D3 in that (i) the alumina adsorbent comprises alkali metal compounds; (ii) adsorption is done at 250-500°C; (iii) purging is done with steam; (iv) the molar ratio of H20 to H2S equivalents in the feed gas is within the range of 0 - (5 + X), X being the variable as defined in claim 1 of the present application.

3.4 The above differences, especially difference (i), have the effect that the H2S can be recovered during the adsorption with a higher concentrating factor compared with the process of D3. This effect can be derived from a comparison of several working examples with other examples in the present invention (see figures 2 and 5, whereby figure 2 corresponds to hydrotalcite with potassium, figure 5 uses hydrotalcite without potassium).

3.5 It does not seem obvious for the skilled person to include the above differences, known e.g. from documents D1 or D2, since these documents do not explicitly disclose that H2S can be recovered during the adsorption with a higher concentrating factor. In fact, both documents do not provide a lot of details about the removal of H2S.

3.6 The problems posed in paragraphs 3,4,6 of the present application are solved in a way that cannot be considered obvious.

3.7 The subject-matter of claims 14 and 18 involves an inventive step.

3.8 The same applies to claims 15 and 16.

Re Item VIII

Certain observations on the application

4 Claims 1-16 and 18 are not clear.

4.1 It is specified in step a) of claim 1 that the first product gas has a reduced ratio of H_2S equivalents to CO_2, but it is not known to which standard this is compared. Does it refer to the feed gas (see e.g. paragraph 49)?

A similar problem exists in step b) of claim 1, i.e. the second product gas has a higher ratio of H_2S equivalents to CO_2.

Claim 1 is unclear.

4.2 The term "H_2S equivalents" in claim 1 is unclear. The definition in claim 2 should be included into claim 1.

4.3 It is specified in claim 1 to use an adsorbent comprising alumina and one or more "alkali metals". However, it seems that alkali metals in their metallic state cannot be used in the method of claim 1 due to their extreme reactivity towards water, which is a crucial component. Claim 1 should be amended to include the definition/explanation of e.g. paragraph 15 of the description.

4.4 Claim 1 is unclear for these reasons, and also claims 2-16 and 18 due to reference to claim 1.