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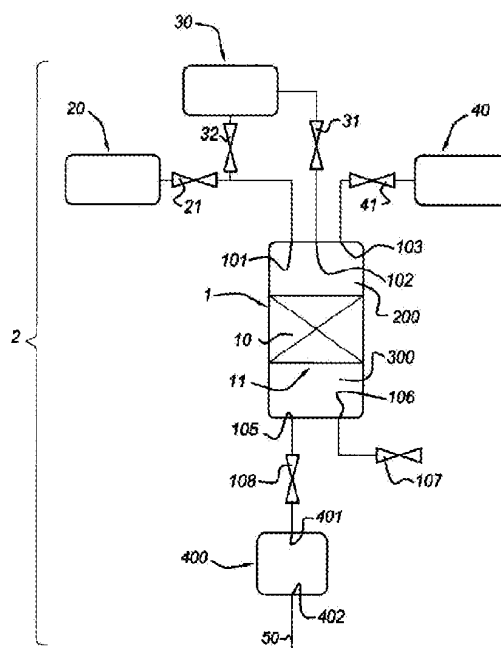
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(54) Water gas shift process.

(57) The invention provides a water gas shift process comprising a reaction stage. The reaction stage comprises (a) providing a gas mixture comprising CO, H₂O and an acid gas component to a reactor containing an adsorbent, and (b) subjecting the gas mixture to water gas shift reaction conditions to perform the water gas shift reaction. The adsorbent comprises an alkali promoted alumina based material. The acid gas component comprises H₂S. The gas mixture comprises a H₂S reactor inlet concentration of at least 200 ppm H₂S relative to the gas mixture.



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Dit octrooi is verleend ongeacht het bijgevoegde resultaat van het onderzoek naar de stand van de techniek en schriftelijke opinie. Het octrooischrift komt overeen met de oorspronkelijk ingediende stukken.

Water gas shift process

Field of the invention

The invention relates to a water gas shift (WGS) process. The invention further
5 relates to the use of an alkali promoted alumina based material (as adsorbent) for the removal of (multiple) acid gas components from a gas mixture.

Background of the invention

The use of adsorbents to remove SO_2 from certain gas streams is known in the
10 art. For instance, US5358701 describes a process for removing noxious sulphur oxides, nitrous oxides, and chlorine from gas streams, particularly from flue gases of coal-burning power plants, using layered double hydroxide (LDH) sorbents. The sorbents are particularly useful for SO_2 absorption at temperatures in the range of 100°C to less than 400°C . The SO_2 gas absorbs into the hydrotalcite structure as SO_3^{2-} anions by
15 replacing most of the gallery CO_3^{2-} anions. The adsorbed SO_2 is driven-off by calcination at elevated temperatures (500°C) and the LDH sorbents are regenerated by hydrolyzing the calcined product optionally in the presence of CO_2 or CO_3^{2-} .

Further, methods to fixate carbon dioxide are also known in the art. WO2005102916 for instance, describes apparatus and methods for converting
20 hydrocarbon fuels to hydrogen-rich reformat that incorporate a carbon dioxide fixing mechanism into the initial hydrocarbon conversion process. The mechanism utilizes a carbon dioxide fixing material within the reforming catalyst bed to remove carbon dioxide from the reformat product. The removal of carbon dioxide from the product stream shifts the reforming reaction equilibrium toward higher hydrocarbon conversion
25 with only small amounts of carbon oxides produced. Fixed carbon dioxide may be released by heating the catalyst bed to a calcination temperature. A non-uniform distribution of catalysts and carbon dioxide fixing material across catalyst bed yields higher conversion rates of hydrocarbon to hydrogen-rich reformat.

US2004081614 describes a process for producing a high temperature CO_x -lean
30 product gas from a high temperature CO_x -containing feed gas, which includes providing a sorption enhanced reactor containing a first adsorbent, a shift catalyst and a second adsorbent; feeding into the reactor a feed gas containing H_2 , H_2O , CO and CO_2 ; contacting the feed gas with the first adsorbent to provide a CO_2 depleted feed gas;

contacting the CO₂ depleted feed gas with the shift catalyst to form a product mixture comprising CO₂ and H₂; and contacting the product mixture with a mixture of second adsorbent and shift catalyst to produce the product gas, which contains at least 50 vol. % H₂, and less than 5 combined vol. % of CO₂ and CO. The adsorbent is a high temperature adsorbent for a Sorption Enhanced Reaction process, such as K₂CO₃ promoted hydrotalcites, modified layered double hydroxides, spinels, modified spinels, and magnesium oxides.

US6322612 describes a pressure or vacuum swing adsorption process and apparatus used for the separation and recovery of certain gaseous components, such as carbon dioxide from hot gas mixtures containing water vapour. The process comprises introducing the feed gas mixture at an elevated temperature into a feed end of an adsorber column containing an adsorbent. The adsorbent preferentially adsorbs at least one adsorbable component. An adsorber effluent, depleted of the at least one adsorbable component, is withdrawn from a product end of the adsorber column. The adsorber column is depressurized below atmospheric pressure and then purged with steam to withdraw an effluent comprising a mixture of the at least one adsorbable component and H₂O. Next, the adsorber column is pressurized by introducing a gas that is depleted of the at least one adsorbable component. The steps are repeated in a cyclic manner.

Further, Descamps et al (Energy 33 (2008) 874-881)) and Maurstad (8th International Conference on Greenhouse Gas Control Technology, Trondheim, 2006 ("Impact of coal quality and gasifier technology on IGCC performance" (Abstract)) describe the removal of CO₂ and H₂S from coal derived syngas, wherein in the former H₂S is removed at ambient temperatures to provide a clean water gas shift (WGS) gas, followed by the WGS reaction in several reactors, and followed by CO₂ removal at ambient temperatures, and wherein in the latter a sour-gas WGS is performed in several reactors, and wherein thereafter H₂S and CO₂ are removed at ambient temperatures.

Summary of the invention

It is an aspect of the invention to provide an alternative water gas shift process, which preferably further at least partly obviates one or more drawbacks of prior art processes. Preferably, such process may be performed in a single reactor, preferably even in a single bed, with optionally even the absence of conventional WGS catalysts.

A disadvantage of prior art processes may be that for performing the WGS process from a gas that (also) comprises H_2S , H_2S has to be removed from the WGS inlet gas (or starting mixture) and/or from the WGS outlet gas (or product gas), which may require a plurality of reactors. Further, a disadvantage of prior art processes may be that conventional WGS catalysts are necessary, in addition to optional CO_2 adsorbents, which may also require a plurality of reactors and/or a plurality of (mixed) beds.

Therefore, in a first aspect, the invention provides a water gas shift process comprising a reaction stage comprising (a) providing a gas mixture comprising CO , H_2O and an acid gas component to a reactor containing an adsorbent, wherein the adsorbent comprises an alkali promoted alumina based material, and (b) subjecting the gas mixture to water gas shift reaction (WGSR) conditions to perform the water gas shift reaction, wherein the acid gas component may comprise H_2S , and wherein the gas mixture comprises a H_2S reactor inlet concentration of at least about 200 ppm H_2S relative to the gas mixture, more especially at least about 500 ppm. Characteristic ranges will be about 200-20.000 ppm, such as 500-20.000 ppm H_2S .

It surprisingly appears that the adsorbent may be suitable for the abatement (capture) of CO_2 and H_2S in the gas, while on the other hand, the adsorbent may also have suitable water gas shift (WGS) activity. Hence, the adsorbent may be used as coadsorber of two or more acid gas components and/or for the catalysis of the WGS reaction.

An advantage of the process of the invention may be that this process may be applied in one single reactor and optionally even with one single bed. Hence, in an embodiment, the reaction stage is performed in a single reactor and especially in a single bed. A further advantage of the process may be that the adsorbent may easily be regenerated, i.e. the adsorption of CO_2 and H_2S is reversible. Via (partial) pressure swing and/or temperature swing, the adsorbent may be regenerated. Hence, in an embodiment the process further comprises an adsorbent regeneration stage, wherein CO_2 and optionally the acid gas component are at least partially removed from the adsorbent. Therefore, the invention also provides a cyclic process comprising a plurality of alternating reaction stages and regeneration stages.

Hence, advantages of the invention may be that no specific catalyst may be needed but only a sorbent, and nevertheless WGS is performed, and/or the co-capture

of CO₂ with H₂S and optionally other acid gases may be possible. Thereby, potentially costs related with traditional gas cleaning sections may be avoided.

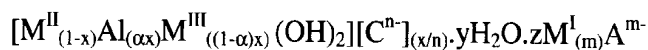
The term “adsorbent” may also indicate a combination of adsorbents.

In a specific embodiment, the adsorbent (comprising an alkali promoted alumina based material) comprises one or more alkali-promoted aluminas, wherein alkali is an element selected from the group consisting of K, Na, Li, Cs, and Rb. Especially, the alkali content is ≥ 5 wt.% calculated as carbonate, preferably 5-30 wt.% calculated as carbonate, relative to the total amount of the alkali promoted alumina.

In yet another embodiment, the adsorbent comprises one or more promoted alkali-promoted aluminas, wherein alkali is an element selected from the group consisting of K, Na, Li, Cs, and Rb (“first promotor”). Especially, the alkali content is ≥ 5 wt.% calculated as carbonate, preferably 5-30 wt.% calculated as carbonate, relative to the total amount of the alkali promoted alumina.

The alkali-promoted alumina may be further promoted, and is then indicated as “promoted alkali-promoted alumina”. The alkali-promoted alumina may be further promoted with one or more elements selected from the group consisting of Mg, Mn, Ti, Ag, Cu, Co, Pb, Fe and Cd (“second promotor”). The alumina may be promoted first with the first promotor and thereafter with the second promotor, but in another embodiment, the alumina may also be promoted first with the second promotor and thereafter with the first promotor; in yet another embodiment, the alumina is promoted with the first and second promotor substantially at the same time. Especially, the promotor (second promotor) content is about 5 wt.% or more calculated as oxide, preferable about 5-50 wt.% calculated as oxide, relative to the total weight of the promoted alkali-promoted aluminas. Preferably, Mg, Mn or Fe are used as promotor (i.e. second promotor).

In a further specific embodiment, the adsorbent comprises one or more alkali-promoted hydrotalcites, wherein alkali is an element selected from the group consisting of K, Na, Li, Cs, and Rb. The hydrotalcite may have the chemical formula



wherein

M^I is one or more selected from the group consisting of Li, Na, K, Rb and Cs;

M^{II} is one or more selected from the group consisting of Mg, Mn, Cu, Co, Fe, Cd and Cr;

Al is aluminium;

M^{III} is optionally one or more of the group consisting of Fe, Cr and Mn;

5 C^{n-} is one or more anions selected from the group consisting of NO_3^- , SO_4^{2-} , CO_3^{2-} , $CH_3CO_2^-$, Cl^- , Br^- , F^- and I^- ;

A^{m-} is one or more anions, such as selected from CO_3^{2-} , $CH_3CO_2^-$, $C_2O_4^{2-}$, NO_3^- , SO_4^{2-} , CO_3^{2-} , $CH_3CO_2^-$, OH^- , Cl^- , Br^- , F^- and I^- etc...

$n=1$ or 2 ; $x=0.01-0.99$; $y=0-4$; $z=0.001-7$; and $\alpha=0.5-1$.

10 Preferably, the alkali promotor is an element selected from the group consisting of K, Na, Li, Cs, and Rb. Especially, the alkali promotor content is ≥ 5 wt.% calculated as carbonate, preferably 5-30 wt.% calculated as carbonate, relative to the total amount of the alkali promoted hydrotalcite. The value of z is preferably at least about 0.033 and in another embodiment preferably not more than about 0.17

15 Preferably, the molar ratio $M^{II}:(Al+M^{III})$ is in the range of about 0:1 – 1:0, preferable 30:70 -70:30. The actual oxidation state of some of the M^{II} and M^{III} ions can be changed during operation, e.g. Fe^{II} and Fe^{III} exist. Further, Al can be the only element present with 3+ oxidation state ($\alpha=1$). Further, the elements with a 3+ oxidation state, can be a mixture of Al^{3+} and M^{III} , such as Fe^{III} , Cr^{III} , and Mn^{III} . The
20 molar ratio of $Al^{3+}:M^{3+}$ is preferably 1:1 – 1:0 (i.e. $0.5 \leq \alpha \leq 1$).

Herein, hydrotalcite is indicated as alumina based material, since, under the reaction conditions, hydrotalcite is at least partly converted to a mixed-metal oxide comprising alumina (more precisely, promoted alumina). M^I can be considered as first promotor and M^{II} and M^{III} can be considered as second promotor.

25 Therefore, in the invention a promoted alumina based material may be used as adsorbent. The promotor(s) may be selected from the group consisting of K, Na, Li, Cs, Rb, Mg, Mn, Ti, Ag, Cu, Co, Pb, Fe and Cd. More than one type of promotor may be applied. Especially, the adsorbent comprises a promoted alkali promoted alumina based material, wherein the alumina based material is promoted with one or more first
30 promoters selected from the group consisting of K, Na, Li, Cs, and Rb, and one or more second promoters selected from the group consisting of Mg, Mn, Ti, Ag, Cu, Co, Pb, Fe and Cd. It appears that the second promotor advantageously (further) promotes CO_2

capture by the adsorbent. Alternatively or additionally, the adsorbent comprises the alkali promoted hydrotalcite, as defined above.

The phrase “one or more alkali-promoted aluminas” (or alumina-based material) (thus) indicates that in an embodiment a mixture of differently promoted aluminas etc.

5 may be applied. The phrase “wherein alkali is an element selected from the group consisting of K, Na, Li, Cs, and Rb” indicates that the alumina etc. may be promoted with one or more types of alkali elements. Likewise, this applies to promoted alkali-promoted aluminas etc. Further, the phrase “promoted with one or more elements selected from the group consisting of Mg, Mn, Ti, Ag, Cu, Co, Pb, Fe and Cd”, and
10 similar phrases, indicates that the (promoted) alumina etc. may be promoted with one or more types of these elements. Preferably, one or more of Mg, Fe and Mn are used as promotor (i.e. second promotor). Preferably, Fe is used as promotor (i.e. second promotor). More preferably, Mg, and Mn are used as promotor (i.e. second promotor), yet even more preferably, Mg.

15 The terms “alkali-promoted alumina”, “promoted alkali-promoted alumina”, and “alkali-promoted hydrotalcite” may also include a thermally treated alkali-promoted alumina, thermally treated promoted alkali-promoted alumina, and thermally treated alkali-promoted hydrotalcite, respectively. The thermal treatment may be performed before use as adsorbent or under the reaction conditions to perform the method of the
20 invention (see also below).

Promoting the materials may be performed by mixing or impregnation of a salt of the alkali (and/or other) element with the alumina based material and thermally treating the product thus obtained. Suitable salts are hydroxides, carbonates, nitrates, halides, oxalates etc., especially carbonates. As mentioned above, the thermal treatment may in
25 an embodiment be performed in the reactor for performing the method of the invention.

Yet a further advantage may be that the invention may allow the use of coal-derived syngas (synthesis gas) as feed to the WGS reactor, whereas in prior art (sweet shift) processes, coal derived syngas could not easily, or could not be used at all without further measures, as WGS reactor inlet gas. Surprisingly, no substantial sulphur deactivation, such as by H₂S, may take place, and thus no pre-desulphurization step
30 may be necessary (although such pre-desulphurization is not excluded in an embodiment).

The terms “reactor inlet gas” or “WGS reactor inlet gas” refer to the gas (and optionally its composition) that is provided to the reactor. In principle, different components of the gas mixture might be provided within the reactor via different inlets. Therefore, the term “reactor inlet gas” or “WGS reactor inlet gas” refer to the gas (and optionally its composition) not yet adsorbed and/or reacted (including subjecting to the WGS conditions) according to the invention; or, in other words, the terms “reactor inlet gas” or “WGS reactor inlet gas” can also be indicated as starting mixture.

The terms “coal-derived syngas” or “coal-derived synthesis gas” refer to synthesis gas derived from coal gasification, and which especially includes sulphur compounds, such as H_2S . The phrase “not yet adsorbed and/or reacted” does not exclude that before entering a reactor wherein the method of the invention is performed, the gas may have been subjected to other reactions, such as in a pre-shift reactor.

This acid gas component may further (thus in addition to H_2S) comprise one or more components selected from the group consisting of HCN, COS, CS_2 , NO_x , SO_x and HCl. The total acid gas component concentration (not including CO_2) may be in the range of about 200-50.000 ppm, such as 500-50.000 ppm. In this concentration, CO_2 is not included; CO_2 may be present in an amount ranging from for instance 5000 - 500000 ppm.

Although the adsorbent may be the sole adsorbent-catalyst system within the reactor, optionally the reactor may further contain a (conventional) water gas shift catalyst, wherein preferably the weight ratio of the adsorbent to catalyst is about ≥ 5 , even more preferably about ≥ 20 . For instance, the weight ratio may be in the range of about 5-50, such as about 5-20, especially about 10-20, or in the range of about 20-100, such as 20-50, especially about 25-50. However, in a specific embodiment, the reactor does not contain a further (WGS) catalyst (in addition to the adsorbent as defined herein).

According to a further aspect, the invention provides the use of an alkali promoted alumina based material (as adsorbent) for the removal of acid gas components of a gas mixture comprising acid gas components, wherein the acid gas components comprise (a) a sulphur containing compound selected from the group consisting of H_2S , COS, CS_2 and SO_x and (b) another compound selected from the group consisting of HCN, NO_x and HCl. More especially, the invention provides the

use of an alkali promoted alumina based material for the removal of acid gas components of a gas mixture comprising acid gas components, wherein the acid gas components comprise H_2S and one or more components selected from the group consisting of H_2S , CO_2 , HCN , COS , CS_2 , NO_x , SO_x and HCl . Especially, the acid gas components at least comprise H_2S and CO_2 . Hence, the adsorbent comprising the alkali promoted alumina based material may be used as co-adsorbent.

After having removed the acid gas components, the gas mixture (thus provided) may be used for a Fischer-Tropsch reaction but also for other processes. The reaction mixture, enriched in H_2 , may thus be provided to a further reactor, which may for instance be a Fischer-Tropsch reactor, or a gas turbine for combustion, or a methanol synthesis reactor, or a CO preferential oxidizer for low-grade H_2 production lean in $\text{CO}+\text{CO}_2$, or a PSA (pressure swing adsorber) system for high grade H_2 production, or a methanol production unit, or an ammonia synthesis reactor, etc. Note that the term “remove” here refers to reducing or abating, and does not necessarily imply the complete removal of one or more acid gas components.

Hence, especially the gas mixture further comprises CO and H_2O , and the alkali promoted alumina based material may further also be used for the simultaneous removal of H_2S and CO_2 and the water gas shift reaction of CO and H_2O from the gas mixture. Especially, the gas mixture may comprise coal derived syngas, to which H_2O is added or has been added.

The term “ NO_x ” relates to compounds wherein x is equal to or larger than 1, such as NO , N_2O_3 , NO_2 , N_2O_4 , N_2O_5 , etc., especially at least NO and/or NO_2 . The term “ SO_x ” relates to compounds wherein x is equal to or larger than 1, such as SO , S_2O_2 , SO_2 , SO_3 , S_6O_2 , S_7O_2 , etc., especially at least SO_2 .

Brief description of the drawings

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying schematic drawings in which corresponding reference symbols indicate corresponding parts, and in which:

Figure 1 schematically depicts an embodiment of an arrangement comprising a reactor for performing the process of the invention; and

Figures 2a-2f show experimental results.

Description of preferred embodiments

Figure 1 schematically depicts an arrangement 2 comprising an embodiment of a reactor 1 for performing the process of the invention. The reactor 1 in this embodiment encloses a single bed 11, which comprises an adsorbent 10 (and optionally a catalyst).

5 Within this reactor 1, at least part of the process of the invention may be applied, especially at least the water gas shift reaction (WGSR) (i.e. the herein indicated reaction stage is especially performed within the reactor 1). The process of the invention is however not confined to the herein schematically depicted arrangement 2 and the schematically depicted reactor 1. Further, the term reactor may also relate to a plurality of reactors, which may especially be arranged parallel. Therefore, also the term "single reactor" may relate to a plurality of reactors arranged in parallel.

The process that may be applied, the water gas shift process, may comprise a reaction stage comprising (a) providing a gas mixture 200 comprising CO, H₂O and an acid gas component to reactor 1 containing adsorbent 10 and (b) subjecting the gas mixture 200 to water gas shift reaction conditions to perform the water gas shift reaction.

The adsorbent 10 may comprise an alkali promoted alumina based material, such as potassium promoted alumina. Alumina may for instance be promoted with K₂CO₃. The term "promoted" relates to the intimate mixture of a compound with another compound that acts like a promoter. Alumina may for instance be promoted with K₂CO₃ by mixing an (aqueous) slurry of both components and removing water by drying, and optionally calcining the dried product. Other alkali promoted alumina based materials may for instance comprise sodium or lithium promoted aluminas. The alumina may for instance comprise α alumina, but may also comprise gibbsite or gamma alumina.

The adsorbent 10 may also comprises an alkaline earth alkali promoted alumina. This may imply that in addition to promotion with the alkali element, also the alumina is promoted with the alkaline earth element (sometimes also indicated as "earth alkaline element"). Especially, the adsorbent 10 may comprise a magnesium alkali promoted alumina. For instance, the alumina may be potassium and magnesium promoted. Alumina may for instance be promoted with K₂CO₃ and Mg(NO₃)₂ by mixing an (aqueous) slurry of both components and removing water by drying, and optionally calcining the dried product. Other alkali and alkaline earth promoted aluminas may for

instance comprise aluminas promoted with one or more of potassium, sodium or lithium and promoted with one or more of magnesium, (calcium,) strontium and barium. The promotion can be performed with most commonly available salt of the promoters, not necessarily carbonates, or oxides, as these may be formed under reaction conditions in any case.

Yet in addition, the adsorbent 10 may comprise a transition metal promoted alumina. Hence, the alumina may not only be promoted with an alkali element, and optionally with an alkaline earth element, but may optionally also be promoted with a transition metal element. Such transition metal element may be selected from the groups 3-12, especially from the groups 6-11, such as for instance one or more of Mn, Fe, Co, Ni, Cu and Zn.

Especially, the adsorbent 10 may comprise a promoted layered double hydroxide (LDH), especially alkali promoted layered double hydroxide, and even more especially the adsorbent 10 comprises a promoted hydrotalcite, especially alkali promoted hydrotalcite.

The term “the product of a thermally treated” relates to a product that has been heated at a temperature above about 200°C, even more especially above about 400°C. For instance, assuming a hydrotalcite, when heating this hydrotalcite in the reactor before the WGS reaction or during the WGS 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 hydrotalcites and layered double hydroxide. This is well known in the art and is for instance described in US5358701, US6322612 and WO2005102916.

The term “metal promoted compound” refers to compounds to which these metals, in any form, are attached and/or included. The metal will in general be present on the compound as oxide and/or as hydroxide. The difference between a mixed bed of a catalyst of a metal oxide and a compound is that such mixed bed may essentially consist of discrete particles (especially granules or extrudates) of the metal oxide and of the compound (respectively), whereas when a promoted compound is used in a (single) bed, the bed will essentially consist of particles (especially granules or extrudates) which comprise an intimate mixture of the compound and its promotor(s).

In an embodiment, the acid gas component may comprises H_2S , but may also (alternatively or additionally) comprise one or more components selected from the group consisting of HCN , COS , CS_2 , NO_x , SO_x and HCl . The gas mixture 200 comprising the starting components CO and H_2O (for the WGSR) and the acid gas components may be introduced to the reactor 1 via one or more inlets. In an embodiment, a mixture comprising at least CO and H_2S originates from a first supply 20, for instance from a coal gasifier, an oil gasifier, a petcoke gasifier, a natural gas reformer, from biomass gasification, etc. can be introduced to a first inlet 101 to the reactor 1. H_2O , for instance from a second supply 30, can be added to this mixture, either via the same supply line, such that the complete gas mixture is introduced at inlet 101, or via a separate supply line, such that H_2O may be introduced at a second inlet 102 in the reactor 1. The supply of the gas mixture 200 or gas components from first and second supplies 20, 30 may be controlled by for instance valves 21 and 32, respectively. The gas mixture 200 before a reaction and before adsorption in the reactor 1 has a composition, which can be predetermined, and which composition is also indicated as "inlet composition".

The complete gas mixture 200 may be introduced via one supply line into reactor 1. For instance, the gas mixture may originate from supply 20. However, one or more of the components may also be introduced to a gas mixture comprising at least CO and H_2S before entering the reactor, such as in the example above wherein H_2O is introduced in the gas mixture from supply 30 via valve 32. Alternatively or additional, one or more components of the gas mixture 200 may also be introduced to the reactor separate from the mixture 200 comprising at least CO and H_2S , such as in the example above wherein H_2O is introduced in the gas mixture from supply 30 via valve 31. Optionally, (further) gas components of the gas mixture 200 may also introduced from a third supply 40, which may be introduced for instance in reactor 1 via opening 103 (and optional valve 41). Such further supply 40 may also for instance be used to provide gasses for pressure swing, like steam (see also below). Alternatively, gasses for pressure swing can be provided counter current to the feed stream 20.

Below, some characteristic compositions and some example compositions (including example conditions) are indicated:

Table 1: characteristic compositions and example compositions

	comp.1	comp.2	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6
CO ₂	1%	24%	24 %	24 %	24 %	24%	-	24%
CO	29%	6%	-	-	-	6%	6%	6%
H ₂ S	0.2%	0.2%	2000 ppm	2000 ppm	1000 ppm	2000 ppm	-	2000 ppm
H ₂	12%	35%	-	-	-	35%	12%	35%
H ₂ O	57%	34%	34 %	34 %	34 %	34%	34%	34%
Ar	0.8%	0.8%	42%	42%	42%	0.8%	48%	0.8%
P (bar)	20/40	20/40	2	5	5	5	5	5
T (°C)	300- 500	300/500	400	400	400	400	400	400
Fig.			2a	2b	2c	2d	2e	2f
K- hydrotalcite			+	+	+	+	+	-
K-alumina			-	-	-	-	-	+

Examples 1-5 relate to potassium promoted hydrotalcite, $\text{Mg}_{0.81}\text{Al}_{0.19}(\text{OH})_2(\text{CO}_3)_{0.095} \cdot 0.13[\text{K}_2\text{CO}_3]$ and example 6 relates to K promoted alumina, $\text{Al}_2\text{O}_3 \cdot 0.185[\text{K}_2\text{CO}_3]$. The first comparative example (comp. 1) indicates a gas composition comparable to a coal derived syngas at the inlet of pre-shift section (or without pre-shift section). The second comparative example (comp. 2) shows a gas composition comparable to a coal derived syngas at the outlet of pre-shift section (or with pre-shift section).

The gas mixture 200 may comprise a H₂S reactor inlet concentration of at least 200 ppm, especially at least about 500 ppm H₂S relative to the gas mixture 200. In a specific embodiment, the gas mixture 200 comprises coal-derived synthesis gas.

The gas mixture 200 is fed to reactor 1 (or is composed at the inlets) and is subjected to water gas shift conditions (also indicated herein as WGSR conditions).

This may mean introducing a predetermined amount of H₂O such that the WGSR may take place, providing the gas mixture 200 an elevated temperature or bringing the gas mixture 200 to an elevated temperature (in the reactor 1), wherein the elevated temperature is preferably at least about 300°C, even more preferably at least about 400°C, and further preferably below about 700°C, even more preferably below about

650°C, such as equal to or below about 600°C. Advantageously, it appears that the adsorbent alone already provides the WGS reaction in addition to the advantageous adsorption of CO₂ (i.e. sorption enhanced WGS) and in addition to the advantageous H₂S and/or other acid gas component adsorption. Hence, subjecting the gas mixture
 5 200 to water gas shift reaction conditions to perform the water gas shift reaction may comprise subjecting the gas mixture 200 to a temperature in the range of 300-600°C.

The adsorbent 10 may be comprised in one or more beds 11; the schematic picture indicates one single bed 11. Further, additional catalyst may be present, in other beds or mixed with the adsorbent 10. When the reactor 1 further contains a WGS
 10 catalyst, the weight ratio of the adsorbent 10 to the catalyst is preferably ≥ 5 . Conventional WGS catalysts are for instance Iron-Chromium based catalyst, high temperature shift catalysts, Copper-Zinc-Aluminium mixed oxide catalysts, low temperature shift catalysts, sulphided Cobalt Molybdenum catalysts, sour shift catalysts or any noble metal based catalyst. However, in a specific embodiment, the reactor 1
 15 only contains the adsorbent 10 as active species (i.e. here adsorbent and WGS catalyst). Thus, in a specific embodiment, the reactor 1 does not contain a further catalyst (and/or no other adsorbent). Hence, in a specific embodiment, the reaction stage is performed in a single reactor 1, preferably in a single bed 11.

In this way, a water gas shifted reaction mixture is provided, indicated with
 20 reference 300. The reaction mixture 300, enriched in H₂, may be provided to a further reactor, here indicated as second reactor 400, which may for instance be a Fischer-Tropsch reactor or a gas turbine for combustion or a methanol synthesis reactor, or a CO preferential oxidizer for low-grade H₂ production lean in CO+CO₂, or a PSA (pressure swing adsorber) system for high grade H₂ production, or a methanol
 25 production unit, or an ammonia synthesis reactor, etc. Products thereof, indicated with reference 402, may be released from the second reactor 50 via outlet 402. Reference 105 indicates an opening or outlet in the reactor 1, arranged to be in gaseous communication with the optional second reactor 400. A valve 108 may be present in the gas channel between the reactor 1 and the optional second reactor 400. Optional
 30 second reactor 400 may have an opening or inlet 401, arranged to be in gaseous contact (via the gas channel) with the reactor 1.

An advantage of the application of the invention may also be for instance that the downstream reactors for H₂ production may be smaller (such as a methanator, PrOx,

PSA) and/or that the H_2 purity can be increased because the present invention already removes significant amounts of impurities (CO_2 , H_2S , etc).

After the reaction stage (i.e. the WGS stage), a regeneration stage may be applied. Hence, in a specific embodiment, the process of the invention further comprises an adsorbent regeneration stage, wherein CO_2 and optionally the acid gas component are at least partially removed from the adsorbent 10. Regeneration may be applied by pressure-swing and/or thermal swing, processes known in the art. Pressure-swing herein also comprises partial pressure swing, i.e. the partial pressure of a gas component is controlled. During the regeneration stage steam may be provided to the adsorbent 10. Hence, the partial pressure of H_2O may be increased in the reactor 1. In this way, CO_2 and H_2S and/or other acid gas components may substantially release from the adsorbent 1. Other gases, like N_2 or Air could also be used; in a pressure swing unit the sorbent can also be regenerated using CO_2 . Combinations of two or more gasses may also be applied. The off-gasses may be released from the reactor 1, for instance via an exhaust 107, such as via a further outlet 106 to exhaust 107. The regeneration stage is preferably performed at a temperature in the range of about 200-600°C, even more preferably above about 250°C, yet even more preferably in a range of about 300-500°C. The reaction stage and regeneration stage may be performed in a cyclic way, wherein the reaction stage is followed by one or more regeneration stages. Outlets 105 and 106 may also be connected to a parallel reactor 1 (see above) for e.g., pressure equalisation.

Therefore, the invention also provides the use of an alkali promoted alumina based material, i.e. adsorbent 10, for the removal of acid gas components of a gas mixture 200 comprising (a) a sulphur containing compound selected from the group consisting of H_2S , COS, CS_2 and SO_x and (b) another compound selected from the group consisting of HCN, NO_x and HCl. More especially, the invention provides the use of an alkali promoted alumina based material for the removal of acid gas components of a gas mixture comprising acid gas components, wherein the acid gas components comprise H_2S and one or more components selected from the group consisting of H_2S , CO_2 , HCN, COS, CS_2 , NO_x , SO_x and HCl. Especially, the acid gas components at least comprise H_2S and CO_2 . Hence, the adsorbent 10 may also be used for the co-adsorption of CO_2 and H_2S in gas mixtures. Therefore, such adsorbent 10 may be used for the purification of natural gas.

Thus, in an embodiment, the adsorbent 10 may be used for the simultaneous removal of one or more sulphur containing acid gas components, especially H_2S , and CO_2 and (for performing) the water gas shift reaction of CO and H_2O from the gas mixture 200 comprising CO , CO_2 , H_2O and sulphur containing acid gas components, especially H_2S .

Examples

Examples were performed, with gas mixtures 200 with compositions as described in the above table, and under the therein indicated conditions.

Figures 2a-2e show a number of experiments, wherein on the x-axis the number of cycles (i.e. a time scale with time on stream (T.O.S.) in minutes) is indicated, and on the y-axis the normalized response is indicated. In figure 2e, on the right y-axis, the non-normalized CO_2 -response is indicated in arbitrary units. From these data it can be concluded that there is co-adsorption of CO_2 and H_2S . Further, it appears that the material has water gas shift activity while still having the ability to co-adsorb CO_2 and H_2S , even after initial saturation with CO_2 .

In figure 2a, the sorbent is periodically exposed to $\text{He}/\text{H}_2\text{S}/\text{CO}_2/\text{H}_2\text{O}$ and $\text{H}_2\text{O}/\text{N}_2$ at conditions specified in the table above. The responses for He , H_2S and CO_2 are represented by 201, 202 and 203, respectively. The response of the inert tracer 201 is added as reference for the hydrodynamics of the experimental reactor. From this figure it can be concluded that there is a reversible co-adsorption of CO_2 and H_2S because of the reproducible delayed responses for 202 and 203 with respect to 201. If there was no adsorption taking place then CO_2 and H_2S would breakthrough at the same time as the non-reactive trace gas He . This is clearly not the case. If there was no co-adsorption the CO_2 and H_2S would breakthrough at different times relative to the tracer gas. It is clear to those skilled in the art that this is not the case.

In figure 2b, the experiment is repeated at 5 bara pressure (instead of 2 bara in figure 2a). From this figure it can again be concluded that there is reversible co-adsorption of CO_2 and H_2S . The number of sites for CO_2 and H_2S adsorption may increase in the same fashion as a function of pressure, thus there is more evidence of true co-adsorption.

In figure 2c, experiment 2b is repeated using a halved H_2S content. Despite the lower H_2S content, there still is reversible co-adsorption of CO_2 and H_2S . The CO_2 and

H₂S still breakthrough at the same time relative to each other. The figures 2a-2c taken together show that co-adsorption is occurring.

In figure 2d, the sorbent is periodically exposed to H₂S rich syngas and H₂O/N₂ at conditions specified in the table above. The responses for H₂ and CO are represented by 204 and 205 respectively. Besides the evident reversible co-adsorption of CO₂ and H₂S, it can be concluded that the sorbent is active for the WGS reaction. This is apparent from the delayed response for 205 compared to that of the inert tracer 201. While the sorbent is adsorbing CO₂ and H₂S, it simultaneously converts CO into CO₂ via the WGS reaction. The resulting CO₂ is immediately adsorbed. Accordingly, 205 displays breakthrough at about the same time as 202 and 203.

In figure 2e, the sorbent is periodically exposed to i) syngas free of CO₂ and H₂S and ii) H₂O/N₂ at conditions specified in the table above. In agreement with the experiment of figure 2d, it can be concluded that the WGS reaction proceeds to completion in the period before the sorbent is saturated by CO₂. Moreover, the sorbent displays some WGS activity following breakthrough of CO₂. This is evidenced by the observation that the H₂ response is higher than in the feed, while the CO response is lower than in the feed.

Other examples

Other examples of promoted alumina based materials are for instance selected from K-Al₂O₃, Cs-Al₂O₃, K-MgO-Al₂O₃, Li-MgO-Al₂O₃, K-MnO-Al₂O₃, K-Fe-Al₂O₃, Li-HTC, K-(Mn-Al)HTC, K-(Fe-Al)HTC (with HTC being hydrotalcite).

Alumina promoted with potassium was tested for its CO₂ capacity. The alumina (γ -Al₂O₃) was promoted by impregnation with a solution of potassium carbonate as follows: the material was first dried at 80 °C for 16h and 5.0 g of dried material were further impregnated by incipient wetness method with a aqueous solution containing 1.41g of K₂CO₃. The resulting wet powder was dried at 120 °C for 16h. Further, alumina was also promoted with potassium and magnesium, potassium and iron or potassium and manganese according to the following procedures:

- Mg,K-Al₂O₃: γ -Al₂O₃ was dried at 80 °C for 16h. 6.37g Mg(NO₃)₂·6H₂O dissolved in 5.70 g deionised water were used for impregnating 9.00g of γ -Al₂O₃. The resulting wet powder was dried at 120 °C for 16 h and further calcined at 400 °C for 4 hours. 5.00 g of the resulting material were further

impregnated by incipient wetness method with an aqueous solution containing 1.41 g of K_2CO_3 . The resulting wet powder was dried at 120 °C for 16 h.

- Fe,K- Al_2O_3 : $\gamma-Al_2O_3$ was dried at 80 °C for 16 h. 8.48g $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in 5.70 g deionised water were used for impregnating 9.00g of $\gamma-Al_2O_3$. The resulting wet powder was dried at 120 °C for 16h and further calcined at 400 °C for 4 hours. 5.00 g of the resulting material were further impregnated by incipient wetness method with an aqueous solution containing 1.41 g of K_2CO_3 . The resulting wet powder was dried at 120 °C for 16 h.
- Mn,K- Al_2O_3 : $\gamma-Al_2O_3$ was dried at 80 °C for 16 h. 6.23g $Mn(NO_3)_2 \cdot 4H_2O$ dissolved in 5.70 g deionised water were used for impregnating 9.00g of $\gamma-Al_2O_3$. The resulting wet powder was dried at 120 °C for 16h and further calcined at 400 °C for 4 hours. 5.00 g of the resulting material were further impregnated by incipient wetness method with an aqueous solution containing 1.41 g of K_2CO_3 . The resulting wet powder was dried at 120 °C for 16 h.

The CO_2 sorption capacities were measured under the following conditions:

2 grams of the material in a U-shaped glass reactor were first treated with a flow of N_2 with 10.7% water at 400 °C during one hour. Then, CO_2 was added to the gas mixture for 45 minutes (gas mixture: 5.8% CO_2 , 10.7% H_2O and balance N_2). Desorption stage under a flow of N_2 with 10.7% water was then carried out at 400 °C for one hour. This adsorption/desorption cycle was repeated two times, while the CO_2 flow in the outlet was continuously monitored using the mass spectrometer.

The following table summarises the CO_2 adsorption capacities measured after the third cycle for the corresponding compounds:

Material	CO_2 capacity (mmol/g)
K- Al_2O_3	0.27
Mg,K- Al_2O_3	0.35
Fe,K- Al_2O_3	0.39
Mn,K- Al_2O_3	0.26

Hence, in an embodiment the invention provides a water gas shift process comprising a reaction stage comprising (a) providing a gas mixture comprising CO ,

H₂O and an acid gas component to a reactor containing an adsorbent, wherein the adsorbent comprises an alkali promoted alumina based material and (b) subjecting the gas mixture to water gas shift reaction conditions to perform the water gas shift reaction, wherein the acid gas component comprises H₂S, and wherein the gas mixture comprises a H₂S reactor inlet concentration of at least 200 ppm H₂S relative to the gas mixture.

Further, the invention provides such process, wherein the acid gas component further comprises one or more components selected from the group consisting of HCN, COS, CS₂, NO_x, SO_x and HCl.

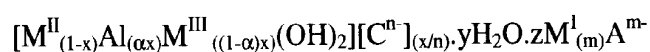
In addition, the invention provides such process, wherein subjecting the gas mixture to water gas shift reaction conditions to perform the water gas shift reaction comprises subjecting the gas mixture to a temperature in the range of 300-600°C.

Yet, the invention provides such process, wherein the adsorbent comprises potassium promoted alumina.

In addition, the invention provides such process, wherein the adsorbent is further promoted with one or more elements selected from the group consisting of Mg, Mn, Ag, Cu, Co, Pb, Fe and Cd, especially selected from Mg, Fe and Mn.

Further, the adsorbent may comprises an alkaline earth alkali promoted alumina. Yet, the invention provides such process, wherein the adsorbent comprises magnesium alkali promoted alumina.

Especially, the adsorbent comprises an alkali promoted hydrotalcite having the chemical formula



wherein

M^I is one or more selected from the group consisting of Li, Na, K, Rb and Cs;

M^{II} is one or more selected from the group consisting of Mg, Mn, Cu, Co, Fe, Cd and Cr;

Al is aluminium;

M^{III} is optionally one or more of the group consisting of Fe, Cr and Mn;

Cⁿ⁻ is one or more anions selected from the group consisting of NO₃⁻, SO₄²⁻, CO₃²⁻, CH₃CO₂⁻, Cl⁻, Br⁻, F⁻ and I⁻;

A^{m-} is one or more anions, such as selected from CO_3^{2-} , CH_3CO_2^- , $\text{C}_2\text{O}_4^{2-}$, NO_3^- , SO_4^{2-} , CO_3^{2-} , CH_3CO_2^- , OH^- , Cl^- , Br^- , F^- and Γ etc...

$n=1$ or 2 ; $x=0.01-0.99$; $y=0-4$; $z=0.001-7$; and $\alpha=0.5-1$.

Yet, the invention provides such process, wherein the reactor further contains a
5 water gas shift catalyst, wherein the weight ratio of the adsorbent to catalyst is ≥ 5 .

In an embodiment, the reactor does not contain a further catalyst.

The invention further provides the use of an alkali promoted alumina based material for the removal of acid gas components of a gas mixture comprising acid gas components, wherein the acid gas components comprise H_2S and one or more
10 components selected from the group consisting of CO_2 , HCN , COS , CS_2 , NO_x , SO_x and HCl .

The invention further provides such use, wherein the acid gas components at least comprise H_2S and CO_2 .

Yet, the invention provides such use, wherein the gas mixture further comprises
15 CO and H_2O , for the simultaneous removal of H_2S and CO_2 and the water gas shift reaction of CO and H_2O from the gas mixture.

In addition, the invention provides such use, wherein the gas mixture comprises coal-derived synthesis gas.

20

The term “substantially” herein, such as in “substantially all emission” or in “substantially consists”, will be understood by the person skilled in the art. The term “substantially” may also include embodiments with “entirely”, “completely”, “all”, etc. Hence, in embodiments the adjective substantially may also be removed. Where
25 applicable, the term “substantially” may also relate to 90% or higher, such as 95% or higher, especially 99% or higher, even more especially 99.5% or higher, including 100%. The term “comprise” includes also embodiments wherein the term “comprises” means “consists of”.

Furthermore, the terms first, second, third and the like in the description and in
30 the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of

the invention described herein are capable of operation in other sequences than described or illustrated herein.

The arrangement herein is amongst others described during operation. As will be clear to the person skilled in the art, the invention is not limited to methods of operation
5 or arrangements in operation.

It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as
10 limiting the claim. Use of the verb "to comprise" and its conjugations does not exclude the presence of elements or steps other than those stated in a claim. The article "a" or "an" preceding an element does not exclude the presence of a plurality of such elements. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be
15 used to advantage.

Claims

1. Een water gas shift proces omvattende een reactiestadium dat (a) het inbrengen van een gasmengsel, dat CO, H₂O en een zure gascomponent bevat, in een reactor, die een adsorbens bevat, waarbij het adsorbens een alkali gepromoot alumina-gebaseerd materiaal bevat, en (b) het onderwerpen van het gasmengsel aan water gas shift reactiecondities om de water gas shift reactie te ondergaan omvat, waarbij de zure gascomponent H₂S bevat, en waarbij het gasmengsel een H₂S reactorinlaat concentratie van ten minste 200 ppm ten opzichte van het gasmengsel bevat.
2. Het proces volgens conclusie 1, waarbij de zure gascomponent verder een of meer componenten, gekozen uit de groep bestaande uit HCN, COS, CS₂, NO_x, SO_x en HCl, bevat.
3. Het proces volgens een of meer van de voorgaande conclusies, waarbij het onderwerpen van het gasmengsel aan water gas shift reactiecondities om de water gas shift reactie te ondergaan het onderwerpen van het gasmengsel aan een temperatuur in het bereik van 300-600°C omvat.
4. Het proces volgens een of meer van de voorgaande conclusies, waarbij het adsorbens kalium gepromoot alumina bevat.
5. Het proces volgens een of meer van de voorgaande conclusies, waarbij het adsorbens verder gepromoot is met een of meer van de elementen gekozen uit de groep bestaande uit Mg, Mn, Ag, Cu, Co, Pb, Fe en Cd, in het bijzonder gekozen uit Mg, Fe en Mn.
6. Het proces volgens een of meer van de voorgaande conclusies, waarbij het adsorbens een aardalkali alkali gepromoot alumina bevat.
7. Het proces volgens conclusie 6, waarbij het adsorbens magnesium alkali gepromoot alumina bevat.
8. Het proces volgens een of meer van de voorgaande conclusies, waarbij het adsorbens een alkali gepromoot hydrotalciet met de chemische formule

$$[M^{II}_{(1-x)}Al_{(x)}M^{III}_{((1-x)x)}(OH)_2][C^{n-}]_{(x/n)} \cdot yH_2O \cdot zM^I_{(m)}A^{m-}$$
 waarbij
 M^I is een of meer gekozen uit de groep bestaande uit Li, Na, K, Rb en Cs;

M^{II} is een of meer gekozen uit de groep bestaande uit Mg, Mn, Cu, Co, Fe, Cd en Cr;

Al is aluminium;

M^{III} is optioneel een of meer gekozen uit de groep bestaande uit Fe, Cr en Mn;

C^{n-} is een of meer anionen gekozen uit de groep bestaande uit NO_3^- , SO_4^{2-} , CO_3^{2-} , $CH_3CO_2^-$, Cl^- , Br^- , F^- en I^- ;

A^{m-} is een of meer anionen, zoals gekozen uit CO_3^{2-} , $CH_3CO_2^-$, $C_2O_4^{2-}$, NO_3^- , SO_4^{2-} , CO_3^{2-} , $CH_3CO_2^-$, OH^- , Cl^- , Br^- , F^- en I^- etc.

$n=1$ or 2 ; $x=0.01-0.99$; $y=0-4$; $z=0.001-7$; en $\alpha=0.5-1$

omvat.

9. Het proces volgens een of meer van de conclusies 1-9, waarbij de reactor verder een water gas shift katalysator bevat, waarbij de gewichtsverhouding van het adsorbens tot de katalysator ≥ 5 is.

10. Het proces volgens een of meer van de conclusies 1-9, waarbij de reactor geen verdere katalysator bevat.

11. Het gebruik van een alkali gepromoot alumina-gebaseerd materiaal voor het verwijderen van zure gascomponenten uit een gasmengsel dat zure gascomponenten bevat, waarbij de zure gascomponenten H_2S en een of meer componenten gekozen uit de groep bestaande uit CO_2 , HCN , COS , CS_2 , NO_x , SO_x en HCl omvatten.

12. Het gebruik volgens conclusie 11, waarbij de zure gascomponenten ten minste H_2S en CO_2 omvatten.

13. Het gebruik volgens een of meer van de conclusies 11-12, waarbij het gasmengsel verder CO en H_2O bevat, voor de simultane verwijdering van H_2S en CO_2 en de water gas shift reactie van CO en H_2O uit het gasmengsel.

14. Het gebruik volgens een of meer van de conclusies 11-13, waarbij het gasmengsel van kool afgeleid synthesesgas bevat.

Fig 1

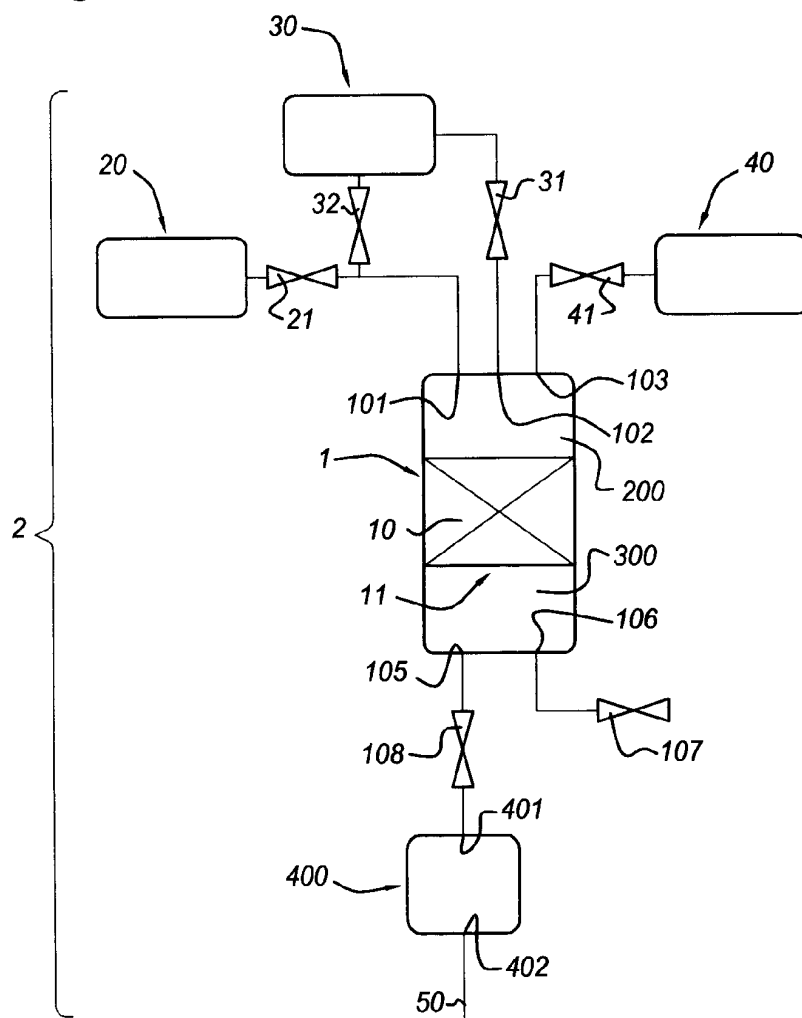


Fig 2a

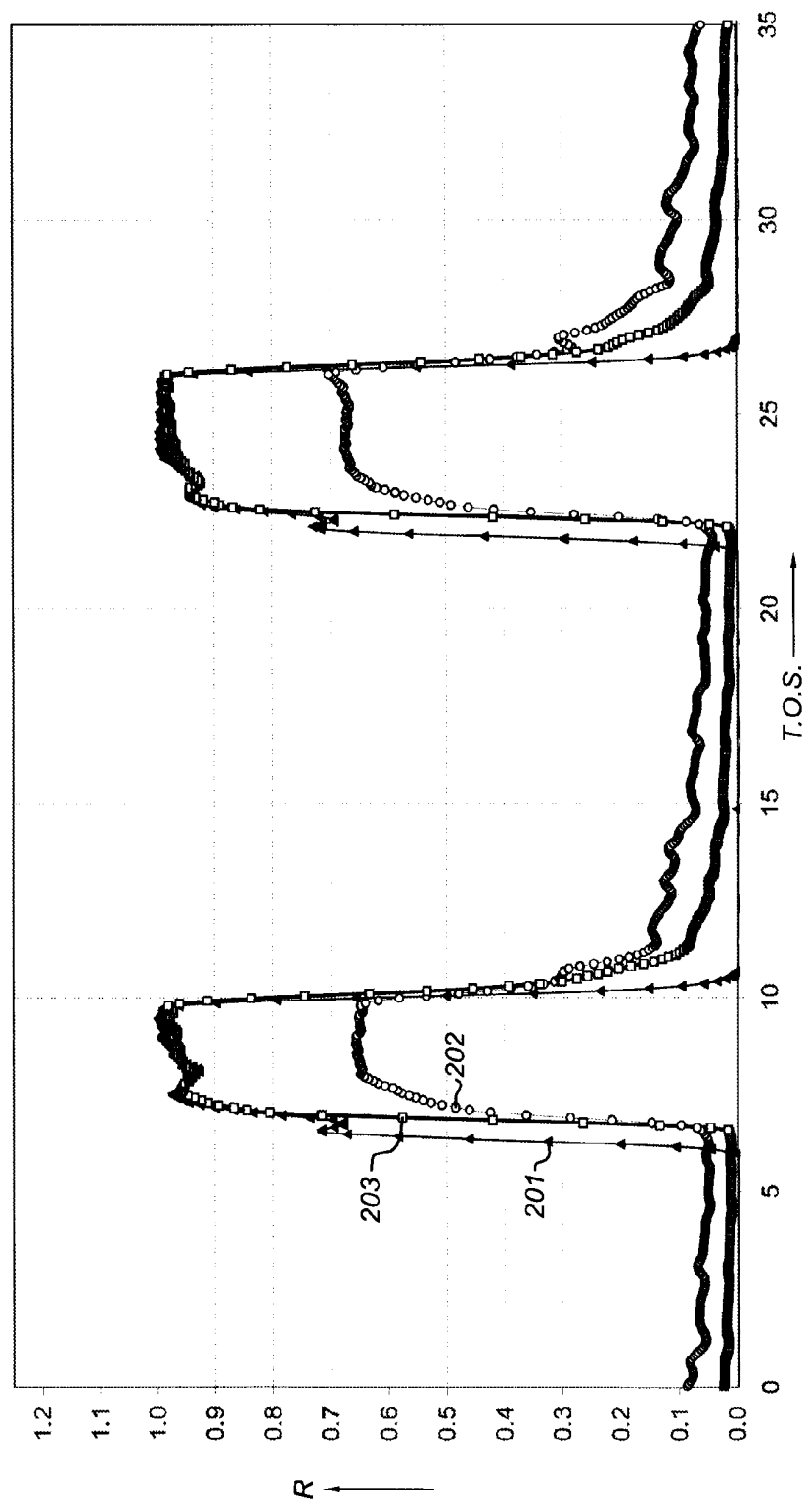


Fig 2b

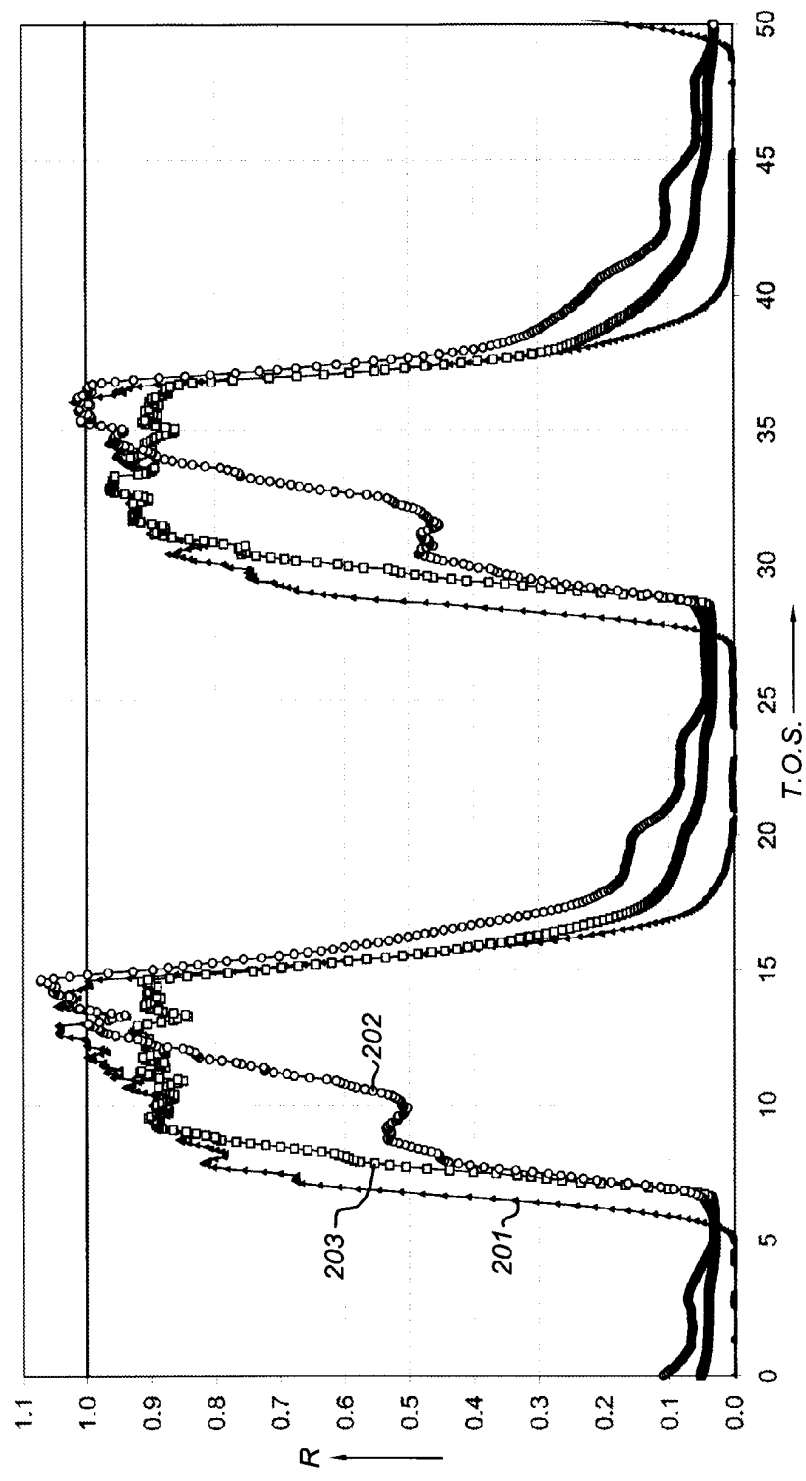


Fig 2c

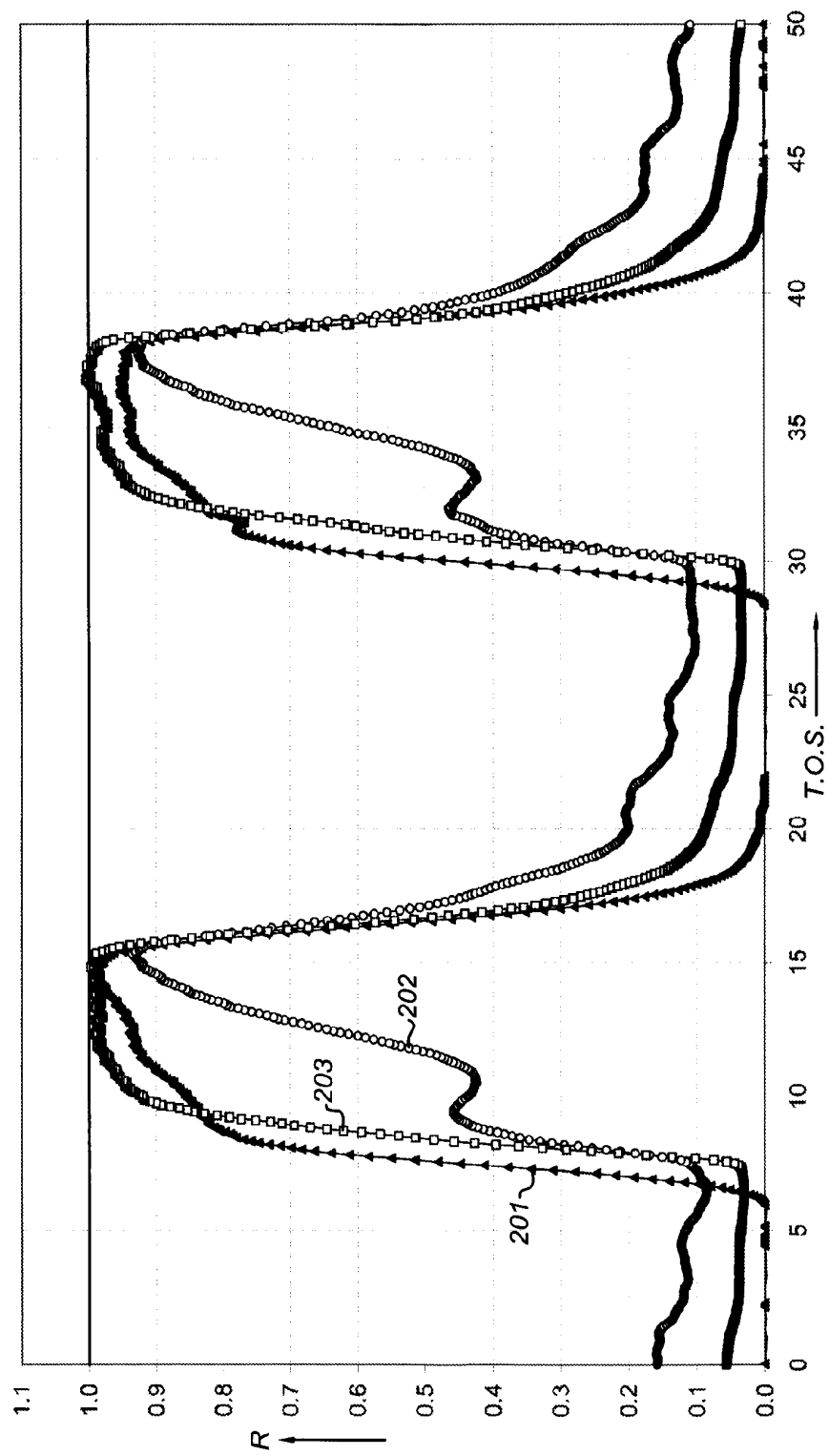


Fig 2d

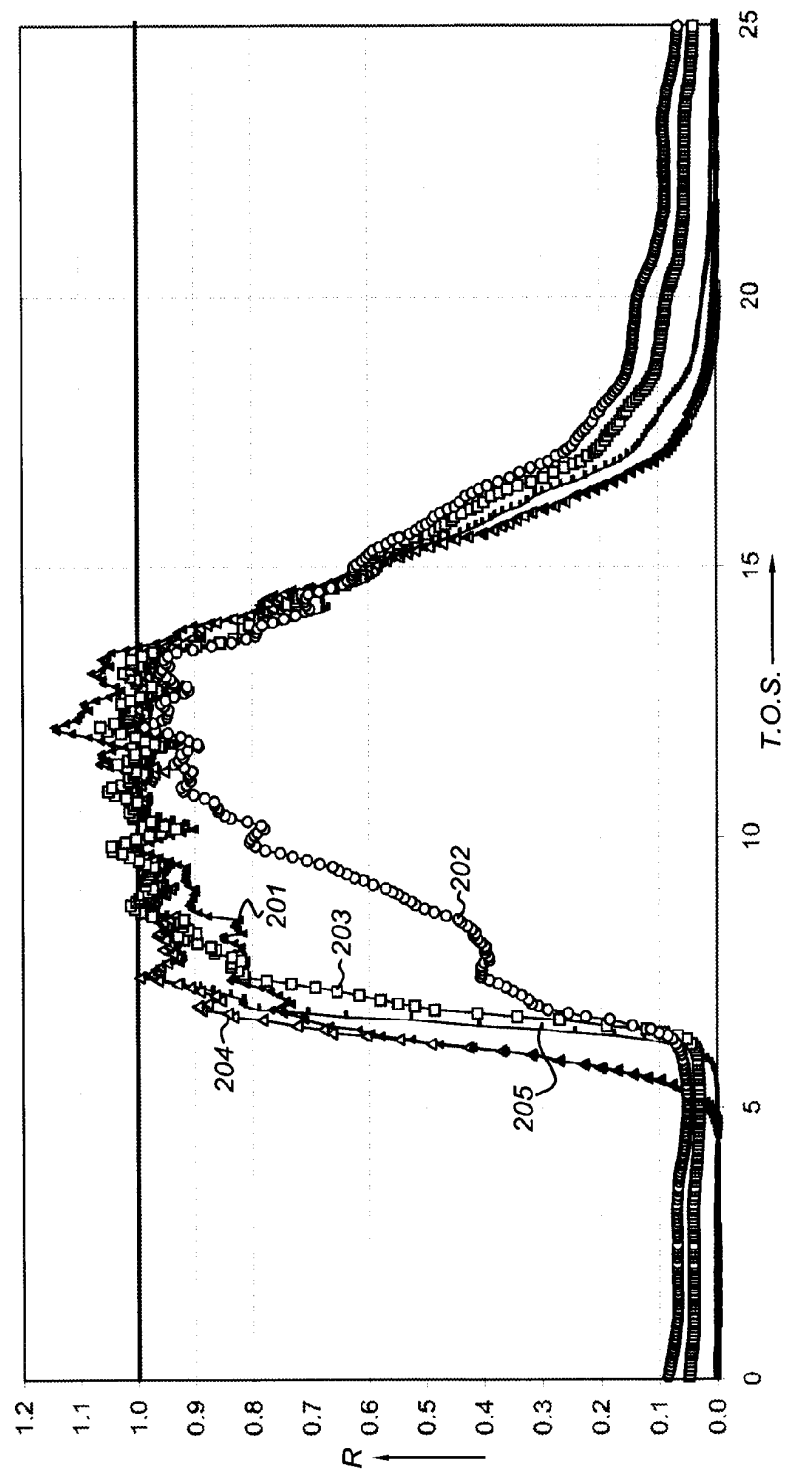
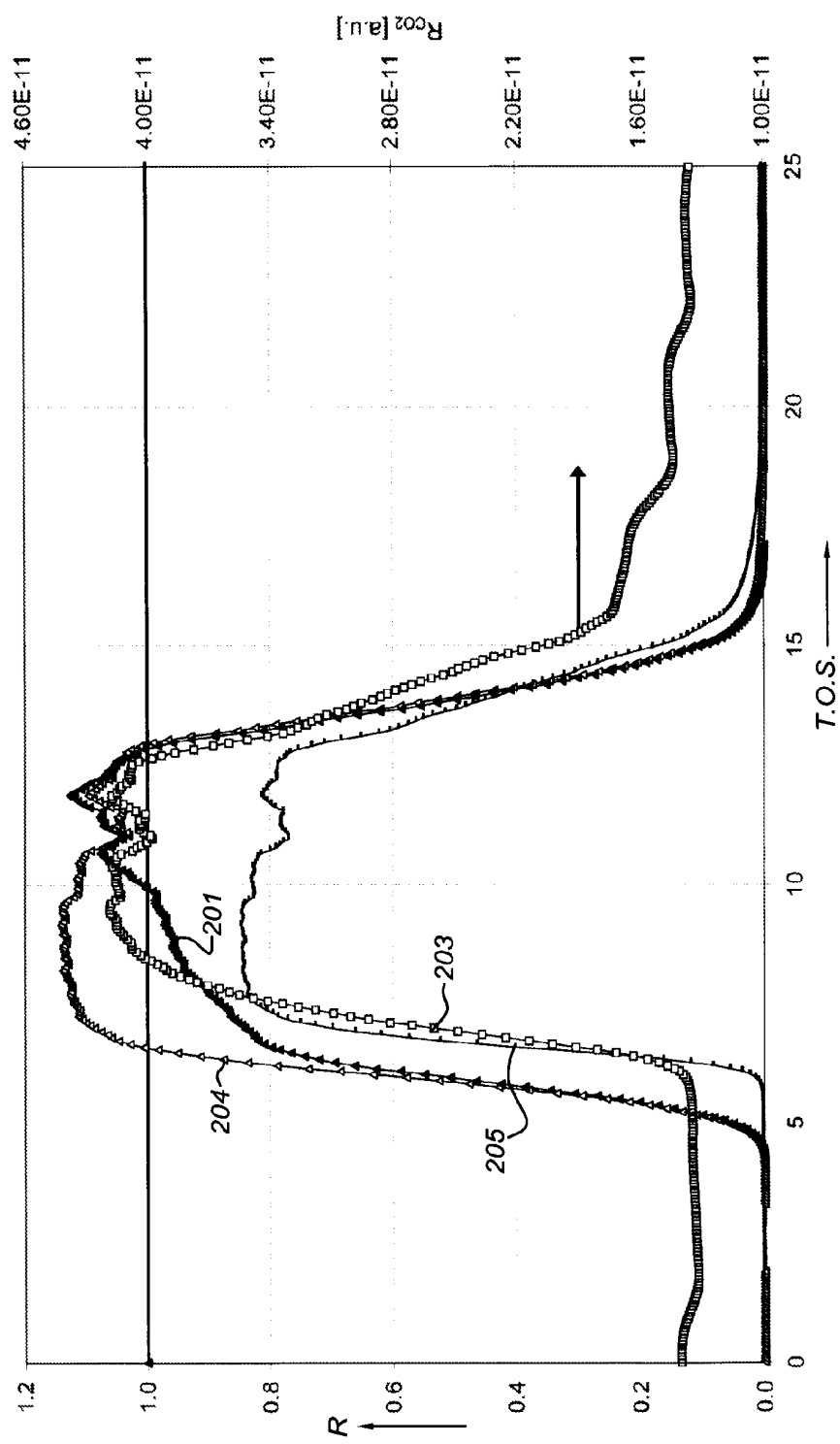


Fig 2e



SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE P6021183NL
Nederlands aanvraag nr. 1036224	Indieningsdatum 21-11-2008
	Ingeroepen voorrangsdatum
Aanvrager (Naam) Stichting Energieonderzoek Centrum Nederland	
Datum van het verzoek voor een onderzoek van internationaal type 03-02-2009	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. SN 51596
I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)	
Volgens de internationale classificatie (IPC) C01B3/16 C01B3/56 B01D53/52	
II. ONDERZOCHE GEBIEDEN VAN DE TECHNIEK	
Onderzochte minimumdocumentatie	
Classificatiesysteem	Classificatiesymbolen
IPC 8	C01B B01D
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)

**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 1036224

A. CLASSIFICATIE VAN HET ONDERWERP

INV. C01B3/16 C01B3/56 B01D53/52

Volgens de Internationale Classificatie van octroolen (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimum documentatie (classificatie gevolgd door classificatiesymbolen)

C01B B01D

Onderzochte andere documentatie dan de minimum 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, API Data, CHEM ABS Data, WPI Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	US 4 002 720 A (WHELOCK KENNETH S ET AL) 11 januari 1977 (1977-01-11)	11-12
Y	* voorbeeld *	1-7, 9-10, 13-14
Y,D	----- DESCAMPS C ET AL: "Efficiency of an Integrated Gasification Combined Cycle (IGCC) power plant including CO2 removal" ENERGY, PERGAMON PRESS, OXFORD, GB, deel 33, nr. 6, 1 juni 2008 (2008-06-01), bladzijden 874-881, XP022634870 ISSN: 0360-5442 [gevonden op 2008-04-30] in de aanvraag genoemd	1-7, 9-10, 13-14
A	* bladzijde 875, rechter kolom - bladzijde 877, linker kolom; figuur 1 * ----- -/--	11

☒ Verdere documenten worden vermeld in het vervolg van vak C. ☒ Leden van dezelfde octroolfamilie 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 octroolaanvraag vermeld

"E" eerdere octrool(aanvraag), 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 octroolaanvraag, 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 octroolfamilie of overeenkomstige octroolpublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid

Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type

23 juli 2009

Naam en adres van de instantie

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De bevoegde ambtenaar

Van der Poel, Wim

**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 1036224

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN		
Categorie *	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
A	WO 2008/068305 A2 (SHELL INT RESEARCH [NL]; DIERICKX JAN LODEWIJK MARIA [NL]; HESSELINK M) 12 juni 2008 (2008-06-12) * conclusies *	1,11
A	WAKKER J P ET AL WAKKER J P ET AL: "High-temperature H ₂ S and COS removal [from coal gases] with MnO and FeO on (GAMMA)-Al ₂ O ₃ acceptors High-temperature H ₂ S and COS removal [from coal gases] with MnO and FeO on (GAMMA)-Al ₂ O ₃ acceptors" INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH V32 N.1 139-49 (JANUARY 1993). ISSN: 0888-5885. INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH V32 N.1 139-49 (JANUARY 1993). ISSN: 0888-5885., deel 32, nr. 1, 1993, bladzijden 139-149, XP002538496 * het gehele document *	1,11
A	KO ET AL: "A study of Zn-Mn based sorbent for the high-temperature removal of H ₂ S from coal-derived gas" JOURNAL OF HAZARDOUS MATERIALS, ELSEVIER, deel 147, nr. 1-2, 26 juli 2007 (2007-07-26), bladzijden 334-341, XP022385524 ISSN: 0304-3894 * bladzijde 338, rechter kolom *	1,11
A	WO 03/020406 A2 (TEXACO DEVELOPMENT CORP [US]) 13 maart 2003 (2003-03-13) * bladzijde 12, alinea 2 *	1,11
A,D	US 6 322 612 B1 (SIRCAR SHIVAJI [US] ET AL) 27 november 2001 (2001-11-27) in de aanvraag genoemd * kolom 6, regel 65 - kolom 7, alinea 54 *	1,8,11

**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 1036224

In het rapport genoemd octroolgeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
US 4002720	A	11-01-1977	CA 1069678 A1 15-01-1980
			DE 2519236 A1 27-11-1975
			GB 1500811 A 15-02-1978
			JP 50150686 A 03-12-1975
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WO 2008068305	A2	12-06-2008	AU 2007328925 A1 12-06-2008
WO 03020406	A2	13-03-2003	CZ 20040426 A3 10-11-2004
			EP 1434643 A2 07-07-2004
			TW 533265 B 21-05-2003
			US 2003181314 A1 25-09-2003
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			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



OCTROOICENTRUM NEDERLAND

WRITTEN OPINION

File No. SN51596	Filing date (day/month/year) 21.11.2008	Priority date (day/month/year)	Application No. NL1036224
International Patent Classification (IPC) INV. C01B3/16 C01B3/56 B01D53/52			
Applicant Stichting Energieonderzoek Centrum Nederland te Pe			

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 Van der Poel, Wim

WRITTEN OPINION

Application number

NL1036224

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

1. Statement

Novelty	Yes: Claims	1-10, 13-14
	No: Claims	11-12
Inventive step	Yes: Claims	8
	No: Claims	1-7, 9-14
Industrial applicability	Yes: Claims	1-14
	No: Claims	

2. Citations and explanations

see separate sheet

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 US 4 002 720 A (WHEELLOCK KENNETH S ET AL) 11 januari 1977 (1977-01-11)
- D2 DESCAMPS C ET AL: "Efficiency of an Integrated Gasification Combined Cycle (IGCC) power plant including CO₂ removal" ENERGY, PERGAMON PRESS, OXFORD, GB, deel 33, nr. 6, 1 juni 2008 (2008-06-01) , bladzijden 874-881, XP022634870 ISSN: 0360-5442 [gevonden op 2008-04-30] in de aanvraag genoemd
- D3 WO 2008/068305 A2 (SHELL INT RESEARCH [NL]; DIERICKX JAN LODEWIJK MARIA [NL]; HESSELINK M) 12 juni 2008 (2008-06-12)
- D4 US 6 322 612 B1 (SIRCAR SHIVAJI [US] ET AL) 27 november 2001 (2001-11-27) in de aanvraag genoemd

- 1 Document D1 discloses a process for removing acidic gases from a gas mixture. The acidic gases comprise hydrogen sulfide and carbonyl sulfide. As an adsorbent alumina impregnated with lanthanum and potassium hydroxide is used. The gas to be purified contains H₂S, CH₄, CO, CO₂, H₂, N₂ and H₂O. (see example).

The material described falls under the definition alkali-promoted alumina.

The subject-matter of claims 11 and 12 are not novel.

- 2 Document D2 is considered to be the closest prior art for claim 1. This document discloses a coal gasification process after which H₂S, COS and mercaptans are removed, the H₂S in a MDEA unit. After the desulfuration the gases are subjected to water gas shift reaction and some further steps (see 3. Description of the process).

Document D2 thus discloses a water gas shift process with an upstream removal of hydrogen sulfide. Since the hydrogen sulfide in D2 also originates from the gasification of coal, the concentration of H₂S is also considered to be more than 200 ppm.

The only difference between claim 1 and document D2, therefore, lies in the fact that in claim 1 the hydrogen sulfide is removed by adsorption on an alkali-promoted alumina, whereas in D2 the hydrogen sulfide is removed using an absorption in MDEA.

A technical effect is not apparent from this difference and the objective technical problem therefore should be formulated as the provision of an alternative water gas shift process.

From document D1 the person skilled in the art knows that alumina with potassium hydroxide and lanthanum is a good adsorbent for hydrogen sulfide. The person skilled in the art will, therefore, certainly replace MDEA absorption step with the adsorption step of D1.

The subject-matter of claim 1 does not involve an inventive step.

It is noted that document D3 could also have served as closest prior art. This document also discloses hydrogen sulfide removal followed by water-gas shift (see claims).

- 3 The subject-matter of claims 2-7, 9, 10, 13 and 14 is either disclosed in D1 or D2 or is well-known to the person skilled in the art. The subject-matter of these claims, therefore, also lacks inventive step.
- 4 The subject-matter of claim 7 is not rendered obvious in view of the prior art. Even though the materials are known (see for example D4), there is no indication that these materials would be useful as adsorbents for hydrogen sulfide. Furthermore, it has not been disclosed in the prior art that these materials also exhibit activity for the water-gas shift reaction.