



(51) International Patent Classification:

B01D 53/14 (2006.01) **C01B 3/12** (2006.01)
B01D 53/52 (2006.01) **C01B 3/50** (2006.01)

(21) International Application Number:

PCT/EP2011/073301

(22) International Filing Date:

19 December 2011 (19.12.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10196011.0 20 December 2010 (20.12.2010) EP

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

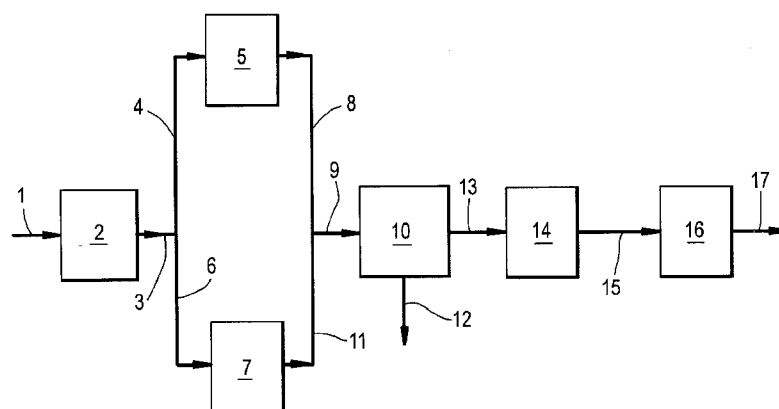
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU,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

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR REMOVING CONTAMINANTS FROM A GAS STREAM

Fig.1



(57) Abstract: The invention relates a process for removing contaminants, including sulphur compounds, from a gas stream comprising the steps of: (a) providing the gas stream which comprises a syngas; (b) subjecting at least part of the syngas to a treatment wherein the hydrogen content of the syngas is increased; (c) contacting at least part of the gas mixture as obtained in step (b) with an absorption liquid that absorbs sulphur compounds to obtain a sulphur compounds-enriched absorption liquid and a sulphur compounds-depleted gas stream; (d) passing at least part of the sulphur compounds-depleted gas stream as obtained in step (c) through a bed of a solid adsorbent for adsorbing contaminants, including metal carbonyls, to obtain a metal carbonyls-depleted gas stream; and (e) passing at least part of the metal carbonyls-depleted gas stream as obtained in step (d) through at least one bed of a solid adsorbent that comprises copper and zinc oxide for the further removal of sulphur compounds and to obtain a sulphur compounds-depleted gas stream. The invention further relates to a synthesis process for preparing hydrogen, a hydrocarbon product or a chemical product wherein the sulphur compounds-depleted gas stream as obtained in step (e) of the present process is used as a reaction component.

PROCESS FOR REMOVING CONTAMINANTS FROM A GAS STREAM

5 Field of the invention

The present invention relates to a process for removing contaminants, including sulphur compounds, from a gas stream, especially a synthesis gas stream to be used in a synthesis process.

10 Background of the invention

Synthesis gas (syngas) streams are gaseous streams mainly comprising carbon monoxide and hydrogen and further usually containing carbon dioxide, while also nitrogen, nitrogen-containing components (such as HCN and
15 NH₃), metal carbonyls and steam may be present, as well as hydrogen sulphide and some other minor constituents for example carbonyl sulphide and carbon disulphide and carbonyl compounds of iron and nickel.

Synthesis gas streams may be produced via partial
20 oxidation or steam reforming of hydrocarbons including natural gas, distillate oils and residual oil, and by gasification of coal or coke. During the production of synthesis gas, not only carbon monoxide and hydrogen are formed but also contaminants such as mentioned above.

25 Synthesis gas streams are used in many ways in industrial processes. For example, synthesis gas streams can be used for the generation of electricity via a gas turbine fired on synthesis gas. Removal of sulphur compounds is required to prevent or reduce emission of
30 SO_x and meet environmental specifications. Suitable synthesis processes in which synthesis gas streams can be used include the production of hydrogen, liquid hydrocarbons, methanol, ammonia, urea and other chemicals. In general catalysts applied in such synthesis

processes are sensitive to the various contaminants that are present in synthesis gas stream. Hence, various contaminants need to be removed from synthesis gas streams before the synthesis gas streams can be used in such synthesis processes.

A number of processes are known for the removal of contaminants, including sulphur compounds, from syngas streams which are based on physical and/or chemical absorption. Physical and/or chemical absorption processes suffer from the fact that they frequently encounter difficulties in reaching the required low concentration of the undesired contaminations in the syngas. This can lead to a fast deactivation of a synthesis catalyst, which can result in lower availability of the unit, reduced production rates and higher costs for the catalyst material. Moreover, many well-established absorption processes, such as the Rectisol process which is based on a wash with cold methanol, are capital expenditure and energy intensive. Hence, there is a need for a more energy-efficient and simple process to remove contaminants from synthesis gas streams to the low levels required by many synthesis catalysts.

Summary of the invention

It has now been found that contaminants can effectively be removed from a synthesis gas stream in a very energy-efficient manner and down to the required low levels, even to a level in the ppbv range for the different sulphur containing contaminants, when a syngas stream is subjected to a treatment wherein the hydrogen content of the syngas is increased, at least part of the gas so obtained is contacted with an absorption liquid that absorbs sulphur compounds, and a sulphur compounds-depleted gas stream is passed through a sequence of beds

of solid adsorbents. Preferably, also a part of the carbon dioxide in the gas stream is removed.

Accordingly, the present invention relates to a process for removing contaminants, including sulphur compounds, from a gas stream comprising the steps of:

- (a) providing the gas stream which comprises a syngas
- (b) subjecting at least part of the syngas to a treatment wherein the hydrogen content of the syngas is increased;
- (c) contacting at least part of the gas mixture as obtained in step (b) with an absorption liquid that absorbs sulphur compounds to obtain a sulphur compounds-enriched absorption liquid and a sulphur compounds-depleted gas stream;
- (d) passing at least part of the sulphur compounds-depleted gas streams as obtained in step (c) through a bed of a solid adsorbent for adsorbing contaminants, including metal carbonyls, to obtain a metal carbonyls-depleted gas stream; and
- (e) passing at least part of the metal carbonyls-depleted gas stream as obtained in step (d) through at least one bed of a solid adsorbent that comprises copper and zinc oxide for the further removal of sulphur compounds and to obtain a sulphur compounds-depleted gas stream.

The sulphur compounds-depleted gas stream obtained by the process according to the present invention is a highly attractive reaction component in synthesis processes to produce hydrocarbon or chemical products.

Detailed description of the invention

The present invention relates to a process for removing contaminants, including sulphur compounds, from a syngas stream. The syngas stream to be used in the

process according to the present invention may be any syngas. Suitably, the syngas to be used in the present process may be produced via partial oxidation or steam reforming of hydrocarbons including natural gas, distillate oils and residual oil, and by gasification of coal or coke. As the temperature of the syngas to be treated will typically be relatively high, preferably the gas stream is cooled prior to being subjected to step (a). Cooling of the syngas prior to being subjected to step (a) may be done by means known in the art, for example using a gas quench, a syngas cooler for production of steam or a gas-gas exchanger. Suitably, the syngas is cooled by means of a water quench or a syngas cooler for the production of high pressure steam. The syngas to be provided in step (a) can suitably have hydrogen/CO molar ratio in the range of from 0.3 to 2.3, more preferably of from 0.5 to 2.1.

In step (b) at least part of the syngas as provided in step (a) is subjected to a treatment wherein the hydrogen content of the syngas is increased. In one embodiment of the present invention in step (b) at least part of the syngas as provided in step (a) is subjected to a water gas shift reaction in which carbon monoxide and steam react to form carbon dioxide and hydrogen. The water gas shift reaction in step (b) can suitably be carried out at a temperature in the range of from 200-600 °C and a pressure in the range of from 15-100 bara, and the steam/carbon monoxide molar ratio is suitably in the range of from 0.6-3.0. A catalyst is applied in this step. A suitable catalyst comprises for instance iron oxide and/or chromium oxide.

In another embodiment of the present invention in step (b) at least part of the syngas as provided in step

(a) is contacted with a gas stream having a higher hydrogen content than the syngas as provided in step (a). This gas stream having a higher hydrogen content than the syngas as provided in step (a) can suitably be mixed with the syngas in step (b). For example this gas stream having a higher hydrogen content can suitably originate from an external source. Suitably, such a gas stream can be a syngas stream from a steam methane reformer or hydrogen rich off-gas from a steam cracker.

Preferably, in step (b) at least part of the syngas as provided in step (a) is subjected to a water gas shift reaction in which carbon monoxide and steam react to form carbon dioxide and hydrogen.

Preferably, at least part of the gas mixture as obtained in step (b) is subjected to a treatment for removing nitrogen compounds like ammonia and hydrogen cyanide, hydrogen sulphide, carbonyl sulphide and carbon dioxide to obtain a carbon dioxide, nitrogen compounds and sulphide compounds-depleted gas mixture of which at least part is passed to step (d). Preferably, at least part of the gas from (a), which has not been subjected to step (b) is also subjected to such a treatment. More preferably, the entire gas mixture as obtained in step (b) is subjected to a treatment for removing of hydrogen sulphide, and preferably also carbon dioxide, to obtain a hydrogen sulphide-depleted gas mixture which in its entirety is passed to step (c). In such a treatment the gas mixture as obtained in step (b) suitably contains hydrogen sulphide in an amount in the range of 0,005-15 mole %, based on total gas mixture. The step for the removal of the sulphur components by means of absorption can also be placed before step (b). In that case the step is placed primarily for the removal of the sulphur

components and the removal of carbon dioxide is not the primary task.

The hydrogen sulphide, other sulphur components and the ammonia components, which have been removed from the gas can be converted in a Claus process into elemental sulphur and nitrogen. Downstream the Claus process the off-gas can be treated by additional steps like for example a Shell Claus Off-gas Treatment process and subsequently in an incinerator in order to limit the emissions of hydrogen sulphur to atmosphere below the desired level.

Alternatively to the Claus process, the hydrogen sulphide can directly be converted into sulphuric acid. Alternatively, the hydrogen sulphide can be removed by absorption from the gas-stream and subsequently by way of selective biological conversion of the hydrogen sulphide into elemental sulphur, wherein use is made of microorganisms. Such treatment can be the Thiopaq process.

Alternatively, the hydrogen sulphide can be removed from the gas stream by absorption and be converted into elemental sulphur in a liquid redox process as for example the Sulferox® process.

The gas stream so treated is depleted of hydrogen sulphide. Suitably, the concentration of hydrogen sulphide in the gas stream obtained in step (c) is less than 50 ppmv, preferably less than 10 ppmv, even more preferably less than 5 ppmv.

In step (c) at least part of the gas mixture as obtained in step (b) is contacted with an absorption liquid that absorbs sulphur compounds, and preferably also carbon dioxide, to obtain a sulphur compounds

absorption liquid and a sulphur compounds depleted gas stream.

A part of the gas provided in step (a) can directly be routed to step (c). In that case the task of step (c) is primarily the removal of sulphur components.

In step (c), at least part of the gas mixture as obtained in step (b) can be contacted with an absorption liquid comprising water, and an amine. Additionally, a physical solvent can be present. Preferably, the physical solvent comprises sulfolane.

Suitable amines to be used include primary, secondary and/or tertiary amines, especially amines that are derived of ethanolamine, especially monoethanol amine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA) or mixtures thereof. A preferred amine is a secondary or tertiary amine, preferably an amine compound derived from ethanol amine, more especially DIPA, DEA, MMEA (monomethyl-ethanolamine), MDEA, or DEMEA (diethyl-monoethanolamine), preferably DIPA or MDEA.

The absorption liquid may also comprise a so-called activator compound. The addition of an activator compound to the absorption liquid system is believed to result in an improved removal of hydrogen sulphide and also of other acidic compounds such as carbon dioxide. Suitable activator compounds are piperazine, methyl-ethanolamine, or (2-aminoethyl)ethanolamine, especially piperazine.

Suitable physical solvents are sulfolane (cyclo-tetramethylenesulfone and its derivatives), aliphatic acid amides, N-methylpyrrolidone, N-alkylated pyrrolidones and the corresponding piperidones, methanol, ethanol and mixtures of dialkylethers of polyethylene glycols or mixtures thereof. The preferred physical

solvent is sulfolane. An advantage of using absorption liquids comprising both an amine and a physical solvent is that they show good absorption capacity and good selectivity for hydrogen sulphide and organic sulphur components against moderate investment costs and operational costs. Another advantage is that absorption liquids comprising both an amine and a physical solvent perform well at high pressures, especially between 20 and 90 bara. Hence, in the case that the feed gas stream is pressurised, no depressurising step is needed. Yet another advantage is that the use of a combined physical/chemical absorption liquid, rather than an aqueous chemical absorption liquid only, also results in the possibility of flashing carbon dioxide. This reduces re-compression requirements, e.g. for re-injection. A preferred absorption liquid comprises water, sulfolane and a secondary or tertiary amine, preferably an amine compound derived from ethanol amine, more especially DIPA, DEA, MMEA (monomethyl-ethanolamine), MDEA, or DEMEA (diethyl-monoethanolamine), preferably DIPA or MDEA. An especially preferred absorption liquid comprises water in the range of from 20-45 parts by weight, sulfolane in the range of from 20-35 parts by weight and amine in the range of from 40-55 parts by weight, the amounts of water, sulfolane and amine together being 100 parts by weight. The preferred ranges result in carbon dioxide removal, in addition to optimum removal of hydrogen sulphide and of other components like organic sulphur components.

Another preferred absorption liquid comprises in the range of from 15-45 parts by weight, preferably from 15-40 parts by weight of water, from 15-40 parts by weight of sulfolane, from 30-60 parts by weight of a

secondary or tertiary amine derived from ethanol amine, and from 0-15 wt %, preferably from 0.5-10 wt % of an activator compound, preferably piperazine, all parts by weight based on total absorbing liquid and the added amounts of water, sulfolane, amine and optionally activator together being 100 parts by weight. This preferred absorption liquid enables removal of hydrogen sulphide and/or COS from a gas stream comprising these compounds. When compared with the same absorption liquid without the addition of a primary or secondary amine compound, especially a secondary amine compound, one or more of the following advantages are obtained: the loading amount is higher, the solvent/gas ratio is lower, the design of the plant is smaller, the solvent has a reduced foaming tendency and the regeneration heat requirement is lower (resulting in less cooling capacity). When compared with an absorption liquid comprising aqueous amines, especially MDEA and piperazine, the addition of sulfolane enables the production of a gas stream comprising carbon dioxide having intermediate pressures, e.g. pressures in the range of from 3-15 bara, preferably in the range of from 5-10 bara. It is an advantage that step (c) can be adjusted to enable producing a gas stream depleted of hydrogen sulphide and of organic sulphur components from feed gas streams further comprising other compounds, in particular selected from the group of carbonyl sulphide and carbonyl disulphide.

Suitably, step (c) is carried out at a temperature in the range of from 0-90 °C, preferably at a temperature of at least 20 °C, more preferably in the range of from 25-80 °C, still more preferably in the range of from 40-65 °C. Step (c) is suitably carried out at a pressure in

the range of from 15-100 bara, preferably in the range of from 20-80 bara, more preferably in the range of from 30-70 bara.

Step (c) is suitably carried out in a zone having from 5-80 contacting layers, such as valve trays, bubble cap trays, baffles and the like. Structured or random packing may also be applied. A suitable solvent/feed gas ratio is from 1.0-10 (w/w), preferably in the range of from 2-6.

The gas stream obtained in step (c) is depleted of hydrogen sulphide and various other contaminants and the concentration of carbon dioxide has been reduced compared to the stream from step (b). Suitably, the concentration of hydrogen sulphide in the gas stream obtained in step (c) is less than 10 ppmv, preferably less than 5 ppmv.

In step (c), the sulphur compounds-enriched absorption liquid will comprise hydrogen sulphide, carbon dioxide and other sulphur compounds such as carbonyl sulphide or carbonyl disulphide. Step (c) will usually be carried out as a continuous process, which also comprises the regeneration of the sulphur compounds-enriched absorption liquid. Therefore, preferably a regeneration step is included wherein sulphur compounds-enriched absorption liquid is contacted with regeneration gas and/or heated and is depressurised, thereby transferring at least part of the contaminants to the regeneration gas. Typically, regeneration takes place at relatively low pressure and high temperature. The regeneration is suitably carried out by heating in a regenerator at a relatively high temperature, suitably in the range of from 70-150 °C. The heating is preferably carried out with steam or hot oil. Alternatively, a direct fired reboiler can be applied. Suitably, regeneration is

carried out at a pressure in the range of from 0.5-6 bara, more preferably at a pressure of 1-1.8 bara. After regeneration, regenerated absorption liquid is obtained and a regeneration gas stream enriched with contaminants such as hydrogen sulphide and carbon dioxide. Preferably, regenerated absorption liquid is used again in step (c). Suitably the regenerated absorption liquid is heat exchanged with contaminants enriched absorption liquid to use the heat elsewhere. Suitably, the enriched regeneration gas stream is sent to a sulphur recovery unit, for example a Claus unit, to convert the sulphur contaminants to elemental sulphur. Alternatively, the hydrogen sulphide can be removed by way of selective biological conversion of the hydrogen sulphide into elemental sulphur, wherein use is made of microorganisms.

Alternatively, liquid redox processes or direct production of sulphuric acid can be applied. An example of a biological treatment is the Thiopaq process which operates at near-ambient conditions of temperature, about 30-40 °C. The regenerator off-gas stream with or without the sulphur components and as the main components consisting of carbon dioxide is pressurised and used for example in enhanced oil recovery, suitably by injecting it into an oil reservoir where it tends to dissolve into the oil in place, thereby reducing its viscosity and thus making it more mobile for movement towards the producing well.

In another suitable embodiment, the pressurised regeneration gas stream enriched with the various contaminants with or without the sulphur components is pumped into an aquifer reservoir for storage. In yet another suitable embodiment, the pressurised regeneration gas stream enriched with the various contaminants and

with or without the sulphur components is pumped into a depleted oil or natural gas reservoir for storage. For all the above options, a series of compressors and/or pumps can suitably be used to pressurise the regeneration gas stream enriched with the various contaminants to the desired high pressures.

In one embodiment of the present process at least part of the syngas as provided in step (a) is subjected to a hydrolysis treatment for removing contaminants, including hydrogen cyanide and carbonyl sulphide, to obtain a contaminants-depleted syngas of which at least part is passed to step (c).

Preferably, at least part of the contaminants-depleted syngas as obtained from the hydrolysis treatment is passed together with at least part of the syngas as obtained in step (b) to step (c). Preferably, the entire contaminants-depleted syngas as obtained from the hydrolysis treatment is passed together with the entire syngas as obtained in step (b) to step (c).

In case use is made in step (b) of a sulphur sensitive shift catalyst to produce hydrogen, step (c) and step (d) can be applied before step (b). After step (b), step (c) can be applied a second time for the removal of carbon dioxide.

The hydrolysis treatment is suitably carried out at a temperature in the range of from 150-250 °C, a pressure in the range of from 15-100 bara, and in the presence of a steam-resistant hydrolysis catalyst. Preferably, the steam resistant catalyst comprises a metal oxide selected from the group consisting of titanium oxide, chromium oxide, aluminium oxide and cerium oxide, or any mixture thereof.

In one embodiment of the present invention at least part of the syngas as provided in step (a) is subjected to the hydrolysis treatment, at least part of the contaminants-depleted syngas as obtained from the hydrolysis treatment is subjected to a treatment for removing hydrogen sulphide to obtain a hydrogen sulphide-depleted gas stream of which at least part is passed to step (b) and at least part of the hydrogen sulphide-depleted gas stream as obtained from the treatment for removing hydrogen sulphide is passed together with at least part of the sulphur compounds-depleted gas stream as obtained in step (c) to step (d).

Preferably, the entire syngas as provided in step (a), and which is not subjected to step (b), is subjected to the hydrolysis treatment, the entire contaminants-depleted syngas as obtained from the hydrolysis treatment is subjected to a treatment for removing hydrogen sulphide to obtain a hydrogen sulphide-depleted gas stream of which at least part is passed to step (b) and at least part of the hydrogen sulphide-depleted gas stream as obtained from the treatment for removing hydrogen sulphide is passed together with the entire sulphur compounds-depleted gas stream as obtained in step (c) to step (d).

In step (d) at least part of the sulphur compounds-depleted gas stream as obtained in step (c) is routed through one or more beds of a solid adsorbent for adsorbing contaminants, including metal carbonyls, to obtain a metal carbonyls-depleted gas stream. In step (d) use can be made of one or more of beds of a solid adsorbent. The solid adsorbent can suitably be activated carbon, alumina or a zeolite, i.e. a Si and/or Al containing zeolite. Preferably, use is made of activated

carbon or a zeolite. When used carbon is made of activated carbon residual traces of metal carbonyls can suitably be removed. Alternatively or additionally an activated carbon can be applied, which is impregnated with sulphur to adsorb mercury compounds and possibly other heavy metals, in particulate those that form stable sulphides. In another embodiment the activated carbon can suitably be impregnated with copper for removing arsenic compounds. In step (d) use can suitably be made of alumina that has been impregnated with manganese oxide for removing arsenic compounds. Step (d) can suitably be carried out at a temperature in the range of from 0-90 °C and a pressure in the range of from 15-100 bara. Step (d) enables removal of iron pentacarbonyl and nickel tetracarbonyl to levels below 1 ppmv, or even below 0.1 ppmv. Even removal of nickel tetracarbonyl, which is considered to be more difficult than for example removal of iron pentacarbonyl, is possible to levels below 1 ppmv.

In step (e) at least part of the metal carbonyls-depleted gas stream as obtained in step (d) is passed through at least one bed of a solid adsorbent that comprises copper and zinc oxide for the further removal of sulphur compounds and to obtain a sulphur compounds-depleted gas stream. Preferably, in step (e) at least part of the metal carbonyls-depleted gas stream as obtained in step (c) is passed to one or more subsequent beds of a solid adsorbent that comprises copper and zinc oxide for the further removal of sulphur compounds and to obtain a sulphur compounds-depleted gas stream. In the solid adsorbent in step (e) the copper/zinc oxide weight ratio is in the range of from 0.005-0.8. Step (e) can suitably be carried out at a temperature in the range of

from 50-280 °C and a pressure in the range of from 15-100 bara. Suitably, the concentration of hydrogen sulphide in the gas stream obtained in step (e) is less than 1 ppmv, preferably less than 0.1 ppmv, even more preferably less than 0.01 ppmv.

The solid adsorbent in steps (d) and (e) is preferably in the form of pellets.

Steps (d) and (e) can be carried out in one single vessel, or may be spread over two or more vessels. The advantage of using more than one vessel is that each vessel may be used and regenerated under the most optimal conditions or may be refilled with fresh adsorbent while the rest of the unit remains in operation.

It will be understood that the solid adsorbent used in steps (d) and (e) will need to be regenerated or replaced periodically. This can be done in ways known in the art.

The present invention also relates to a synthesis process wherein the gas stream as obtained in step (e) is used as a reaction component to synthesize a hydrocarbon or chemical product. Suitable examples of hydrocarbon and chemical products include hydrogen, liquid hydrocarbons, methanol, synthetic natural gas, ammonia, urea and other chemicals.

Accordingly, the present invention also relates to a synthesis process for preparing a hydrocarbon or chemical product wherein use is made of a gas stream as a reaction component, which gas stream has been obtained by subjecting a syngas to the following process steps:

- (a) providing the syngas;
- (b) subjecting at least part of the syngas to a treatment wherein the hydrogen content of the syngas is increased;

- (c) contacting at least part of the gas mixture as obtained in step (b) with an absorption liquid that absorbs sulphur compounds to obtain a sulphur compounds-enriched absorption liquid and a sulphur compounds-depleted gas stream;
- (d) passing at least part of the sulphur compounds-depleted gas stream as obtained in step (c) through a bed of a solid adsorbent for adsorbing contaminants, including metal carbonyls, to obtain a metal carbonyls-depleted gas stream;
- (e) passing at least part of the metal carbonyls-depleted gas stream as obtained in step (d) through at least one bed of a solid adsorbent that comprises copper and zinc oxide for the further removal of sulphur compounds and to obtain a sulphur compounds-depleted gas stream; and
- (f) using the sulphur compounds-depleted gas stream as obtained in step (e) as a reaction component in a synthesis process to prepare hydrogen, a hydrocarbon product or a chemical product.

Preferably, in step (c) the absorption liquid also absorbs carbon dioxide.

In step (b) at least part of the syngas can suitably be subjected to a water gas shift reaction in which carbon monoxide and steam react to form carbon dioxide and hydrogen. In another embodiment at least part of the syngas is contacted in step (b) with a gas stream having a higher hydrogen content than the syngas as provided in step (a).

In Figure 1 is schematically shown a process in accordance with the present invention. A syngas stream as obtained by a partial oxidation process is supplied via line 1 to water quenching unit 2 where it is cooled.

The cooled syngas so obtained is discharged from unit 2 via line 3. Part of the cooled syngas is introduced via line 4 into unit 5 wherein the cooled syngas is subjected to a water gas shift reaction to form carbon dioxide and hydrogen. The remaining part of the cooled syngas is introduced via line 6 into unit 7 wherein the cooled syngas is subjected to a hydrolysis treatment to remove various contaminants. The gas stream obtained from unit 5 is via lines 8 and 9 introduced in unit 10, whereas the gas stream obtained in unit 7 is introduced via lines 11 and 9 into unit 10. In unit 10 the gas streams are contacted with an absorption liquid to remove sulphur compounds. A stream of regeneration gas enriched with the various contaminants is withdrawn from unit 10 via line 12. A stream of sulphur compounds-depleted gas stream is discharged via line 13 and introduced into unit 14 which comprises a bed of activated carbon. The metal carbonyls-depleted gas obtained in unit 14 is discharged via line 15 and introduced in unit 16 which comprises a bed of copper-zinc oxide. From unit 16 a sulphur compounds-depleted gas stream is obtained and discharged via line 17, which gas stream can subsequently be used as a reaction component in a synthesis process for preparing a hydrocarbon or chemical process.

The invention is illustrated using the following non-limiting Examples.

Example

A CTL (Coal To Liquids) process for the production of hydrocarbons from lignite is carried out as follows.

Lignite is gasified in a Shell Coal Gasification Process (SCGP) at a temperature of 1500°C and a pressure of 40 bara. The produced syngas is cooled by application of water in a quench unit. Downstream the water quench unit

the gas is at a temperature of about 215°C and at a pressure of 38 bara. The syngas will contain about 10.1 vol% hydrogen, 25 vol% carbon monoxide and 5.6 vol% carbon dioxide. The concentration for hydrogen sulphide is 0.08 vol%, but can vary significantly dependent on the feed to the gasifier. The syngas stream is split and a part is routed to a one-stage sour CO-shift unit.

Within the CO-shift unit carbon monoxide reacts at a temperature of 400°C, a pressure of 38 bara in the presence of a iron catalyst with the water in the gas stream to form hydrogen and carbon dioxide. Due to the application of a water quench to cool the syngas, the syngas contains sufficient water for the shift reaction and no additional steam needs to be added. In the CO-shift unit the hydrogen cyanide in the gas stream is hydrolysed as well as the carbonyl sulphide. Downstream the shift reactor the syngas is cooled to 40°C. With the water, which condenses during the cooling, also the ammonia in the gas is removed. Downstream of the CO shift unit the formed carbon dioxide together with the hydrogen sulphide is removed in a Sulfinol-M unit (amine absorption unit) which is operated at a temperature of 30°C and a pressure of 36.5 bara. In the absorption section of the Sulfinol-M-unit unit, carbon dioxide and hydrogen sulphide are absorbed in the Sulfinol-M solution. The remaining concentration of hydrogen sulphide is 5 ppmv. The carbon dioxide concentration is 3 vol%. In the regeneration section of the Sulfinol-M-unit, in a first step a part of the carbon dioxide in the loaded solvent is flashed off at a pressure of 1.8 bara and a temperature of 30°C.

The solvent is then routed via a pre-heating step to the regeneration section, in which the hydrogen sulphide is

removed from the solvent by means of depressurising and heating. The regenerated solvent is cooled to a temperature of 30 °C and pumped back to the absorption section of the Sulfinol-M-unit. The syngas from the

5 quench unit, which is not routed to the CO shift unit, is passed to an HCN/COS hydrolysis unit. In this unit the hydrogen cyanide and the carbonyl sulphide are reacted at a temperature of 200°C and a pressure of 38 bara over a catalyst bed which comprises a Ti/Cr/Al/Al₂O₃ catalyst to

10 form ammonia and hydrogen sulphide. The ammonia is removed with the water, which is condensed from the gas stream. Downstream the HCN/COS hydrolysis unit, the syngas is routed to a Sulfinol-M unit which is operated at a temperature of 30°C and a pressure of 36 bara. In

15 this unit hydrogen sulphide is removed from the gas stream. The two gas streams as obtained downstream of the Sulfinol-M units are combined and routed to an adsorptive purification section. In the first stage of the adsorptive purification section the gas is contacted at

20 40°C and a pressure of 35 bara in a fixed bed reactor with activated carbon. In this stage mainly iron and nickel carbonyl but also other heavy metal components are removed from the gas stream. In the next stage the gas is routed through two copper-zinc oxide beds which are

25 operated at a temperature of 200 °C and a pressure of 34.5 bara. In these two beds the remaining traces of sulphur components are removed from the gas stream. Downstream the adsorptive purification section the gas contains a total sulphur concentration of 10 ppbv. A

30 metal carbonyl concentration of 50 ppbv is achieved. A concentration of hydrogen cyanide of 20 ppbv is achieved.

It will be clear from the above that the present invention provides a very attractive process for removing contaminants from a gas stream, both from capital expenditure and energy efficiency perspective.

C L A I M S

1. A process for removing contaminants, including sulphur compounds, from a gas stream comprising the steps of:
 - 5 (a) providing the gas stream which comprises a syngas
 - (b) subjecting at least part of the syngas to a treatment wherein the hydrogen content of the syngas is increased;
 - (c) contacting at least part of the gas mixture as
10 obtained in step (b) with an absorption liquid that absorbs sulphur compounds to obtain a sulphur compounds-enriched absorption liquid and a sulphur compounds-depleted gas stream;
 - (d) passing at least part of the sulphur compounds-
15 depleted gas streams as obtained in step (c) through a bed of a solid adsorbent for adsorbing contaminants, including metal carbonyls, to obtain a metal carbonyls-depleted gas stream; and
 - (e) passing at least part of the metal carbonyls-
20 depleted gas stream as obtained in step (d) through at least one bed of a solid adsorbent that comprises copper and zinc oxide for the further removal of sulphur compounds and to obtain a sulphur compounds-depleted gas stream.
- 25 2. A process according to claim 1, wherein at least part of the gas mixture as obtained in step (b) is subjected to a treatment for removing hydrogen sulphide to obtain a hydrogen sulphide-depleted gas mixture of which at least part is passed to step
30 (c).
3. A process according to claim 2, wherein the entire syngas as obtained in step (b) is subjected to a

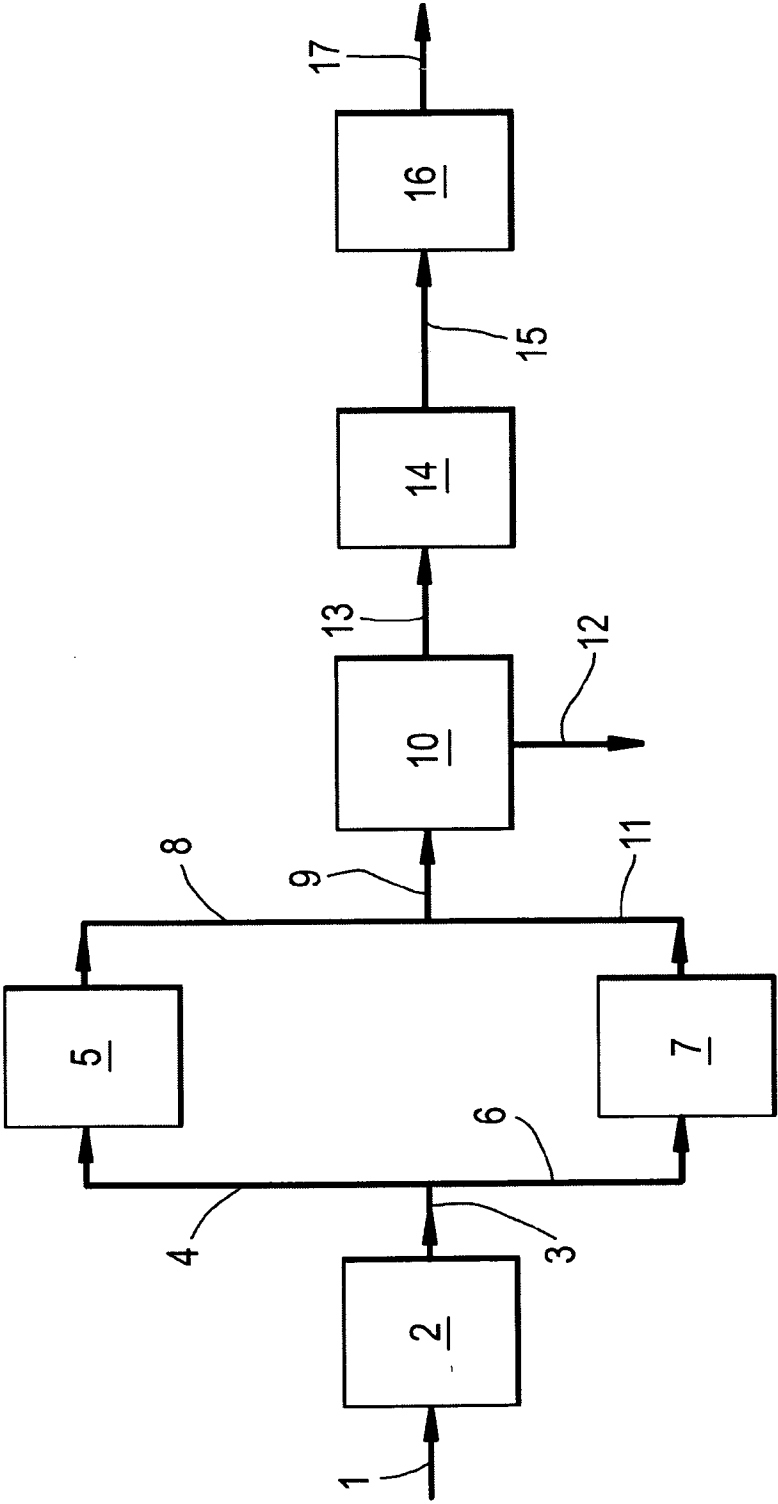
treatment for removing hydrogen sulphide to obtain a hydrogen sulphide-depleted gas mixture which in its entirety is passed to step (c).

4. A process according to any one of claims 1-3,
5 wherein at least part of the syngas as provided in step (a) is subjected to a hydrolysis treatment for removing contaminants, including hydrogen cyanide and carbonyl sulphide, to obtain a contaminants-depleted syngas of which at least part is passed to
10 step (c).
5. A process according to claim 4, wherein at least part of the contaminants-depleted syngas as obtained from the hydrolysis treatment is passed together with at least part of the gas mixture as obtained in
15 step (b) to step (c).
6. A process according to claim 5, wherein the entire contaminants-depleted syngas as obtained from the hydrolysis treatment is passed together with the entire gas mixture as obtained in step (b) to step
20 (c).
7. A process according to any one of claims 4-6, wherein at least part of the syngas as provided in step (a) is subjected to the hydrolysis treatment, at least part of the contaminants-depleted syngas as
25 obtained from the hydrolysis treatment is subjected to a treatment for removing hydrogen sulphide to obtain a hydrogen sulphide-depleted gas stream of which at least part is passed to step (b) and at least part of the hydrogen sulphide-depleted gas
30 stream as obtained from the treatment for removing hydrogen sulphide is passed together with at least part of the sulphur compounds-depleted gas stream as obtained in step (c) to step (d).

8. A process according to claim 7, wherein all or a part of the syngas as provided in step (a) is subjected to the hydrolysis treatment, the entire contaminants-depleted syngas as obtained from the hydrolysis treatment is subjected to a treatment for removing hydrogen sulphide to obtain a hydrogen sulphide-depleted gas stream of which at least part is passed to step (b) and at least part of the hydrogen sulphide-depleted gas stream as obtained from the treatment for removing hydrogen sulphide is passed together with the entire sulphur compounds-depleted gas stream as obtained in step (c) to step (d).
9. A process according to any one of claims 1-8, wherein in step (b) at least part of the syngas is subjected to a water gas shift reaction in which carbon monoxide and steam react to form carbon dioxide and hydrogen.
10. A process according to claim 9, wherein the water gas shift reaction in step (b) is carried out at a temperature in the range of from 200-600 °C and a pressure in the range of from 15-100 bara, and the steam/carbon monoxide molar ratio is in the range of from 0.6-3.0.
11. A process according to any one of claims 1-10, wherein the absorption liquid in step (c) comprises water, a physical solvent and an amine.
12. A process according to any one of claims 4-11, wherein the hydrolysis treatment is carried out at a temperature in the range of from 150-250 °C, a pressure in the range of from 15-100 bara, and in the presence of a steam-resistant hydrolysis catalyst.

13. A process according to claim 12, wherein the steam resistant catalyst comprises a metal oxide selected from the group consisting of titanium oxide, chromium oxide, aluminium oxide and cerium oxide, or any mixture thereof.
14. A process according to any one of claims 1-13, wherein in the solid adsorbent in step (e) the copper/zinc oxide weight ratio is in the range of from 0.005-0.8.
15. Synthesis process for preparing hydrogen, a hydrocarbon product or a chemical product, wherein the sulphur compounds-depleted gas stream as obtained in step (e) of the process according to any one of claims 1-14 is used as a reaction component.

Fig.1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/073301

A. CLASSIFICATION OF SUBJECT MATTER INV. B01D53/14 B01D53/52 C01B3/12 C01B3/50 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B01D C01B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	WO 2008/068305 A2 (SHELL INT RESEARCH [NL]; DIERICKX JAN LODEWIJK MARIA [NL]; HESSELINK M) 12 June 2008 (2008-06-12) page 4, line 9 - page 5, line 7 page 15, lines 11-21 page 18, lines 1-6 -----	1-15
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 22 March 2012	Date of mailing of the international search report 05/04/2012	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Hoyal, Barnaby	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/073301

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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