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(71) Applicant: HALDOR TOPSØE A/S [DK/DK]; Haldor
Topsøes Allé 1, DK-2800 Kgs. Lyngby (DK).

(72) Inventor: NAVID, Asad; Askeengen 14, DK-2740
Skovlunde (DK).

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(54) Title: PROCESS FOR SULFIDATION OF GUARD CATALYST

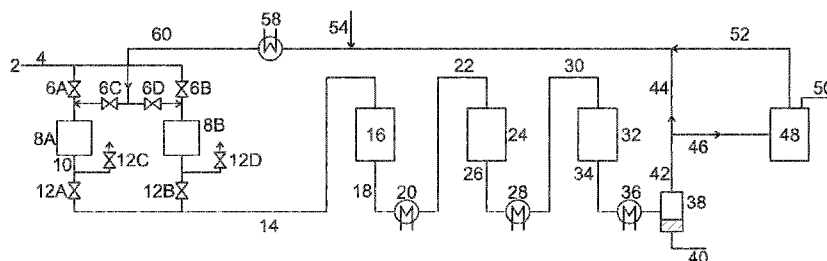


Fig. 1

(57) Abstract: The invention relates to a process plant for a chemical process according comprising a first refreshable reactor section and an second refreshable reactor section, a feed stream line, a product stream line, a sulfur stream line and a sulfidation waste line, both reactor sections being configured for containing a catalytically active material, and the process plant is configurable for either one refreshable reactor section having its inlet in fluid connection with the feed stream, and the outlet of the same refreshable reactor section being in fluid connection with the product stream and the other refreshable reactor section having its inlet in fluid connection with the sulfur stream line and the outlet of the same refreshable reactor section being in fluid connection with the sulfidation waste stream line, or one refreshable reactor section having its inlet in fluid connection with the feed stream, and the outlet of the same refreshable reactor section being in fluid connection with the inlet section of the other refreshable reactor section and the other refreshable reactor section outlet being in fluid connection with the sulfidation waste stream line.

Title: Process for sulfidation of guard catalyst

The present invention relates to a cost effective method for operation of beds of catalytically active material in chemical processes, and especially beds of catalytically active material with a short lifetime compared to other beds of catalytically active material of the same process, such as guard beds.

Impurities may cause critical failures if present in chemical processes. Some constituents such as arsenic and metal carbonyls may deactivate catalytically active materials and may even form deposits to an extent which may cause excessive pressure drop and/or fouling of equipment such as heat exchangers.

Some liquid or gaseous compounds such as water may be separated from the reactant streams and withdrawn in a side stream. However other compounds, typically metallic, are not readily removable from the gas phase. Therefore such compounds are removed from the streams by the use of a guard bed, which is an amount of catalytically active material typically having a higher void volume, enabling prolonged operation without significant influence on pressure drop, while allowing depositing on the catalytically active material, which may be exchanged often, possibly twice per year, compared to the main catalytically active material of the process, which may have a lifetime of several years.

Guard beds may be operated in "swing operation" in which one guard bed is idle, while another receives the reactant stream, until end of run where the guard capacity is used up. At the end of run, the reactant stream may be switched

to the other guard bed, and fresh catalytically active material may be filled into the first guard bed. Alternatively guard beds may be operated in a mode occasionally bypassing the first guard bed, and allowing depositing in a second guard bed, or a regular bed downstream the bypassed guard bed, while the first guard bed is refreshed by replacing the catalytically active material. Similar approaches may also be used for other beds in which there is a need for continued operation during catalyst replacement, as well as a need for catalyst activation, e.g. reactor beds containing catalytically active material which is deactivated at a higher rate compared to other beds containing catalytically active material in the chemical process, if the process allows for temporary compensation of the reduced volume of catalytically active material.

Some types of catalytically active material, typically comprising nickel, cobalt, molybdenum and tungsten requires sulfidation to be active, and these types of catalytically active material may at an extra cost be supplied in pre-sulfided form. In addition the loading of a reactor with pre-sulfided catalyst requires the loading atmosphere to be oxygen free, and additional safety requirements increase the cost of reactor loading. An alternative is the use of a reactive sulfur compound such as hydrogen sulfide or dimethyldisulfide in a separate stream of reactants, which naturally adds cost and complexity, especially due to the safety issues related to the storage, transport and handling of such compounds.

30

Now, according to the present invention it has been identified that in such processes, the existing process streams,

such as a product stream comprising sulfur or a product stream in combination with a sulfur rich stream withdrawn from an acid gas recovery (AGR) unit, may be configured to be used as presulfidation streams, allowing the activation of the catalytically active material in a more cost effective way, by connection of the idle guard bed reactor to the streams during activation.

In the following an operating reactor shall be construed as a reactor, which in the period of operation described shall be in operation, and not being activated, by e.g. sulfidation. An operating reactor, may however in other contexts be activated, and it may also be activated according to the present disclosure.

In the following a refreshable reactor or a reactor to be activated shall be construed as a reactor containing a precursor of a catalytically active material, which requires an amount of sulfides on its surface for optimal operation, and which is configured such that it may be taken out of operation in order to be refreshed or activated.

In the following an operating reactor shall be construed as a reactor which in the time of operation described is not dependent on being able to be taken out of operation in order to be refreshed or activated. However, an "operating reactor" may be configured for being a refreshable reactor during other times of operation.

In the following the water gas shift reaction, shall be construed as the exothermal conversion of water and carbon monoxide into hydrogen and carbon dioxide.

The invention relates to a procedure for operation of a reactor system involving an operating reactor and a first refreshable reactor each containing a catalytically active material and/or a precursor of a catalytically active material, in which said refreshable reactor is operable in an activation mode and an operations mode, said procedure comprising the steps of

- (a) operating the two reactors in operations mode,
- 10 (b) upon a first predetermined condition switching the operation of the refreshable reactor into activation mode,
- (c) and upon a second predetermined condition switching the operation of the refreshable reactor into operations mode,
- 15 wherein operating a reactor in operations mode involves
- (d) directing a feed stream to contact said catalytically active material providing a reacted stream, and
- 20 (e) from said reacted stream or a downstream product hereof withdrawing a stream comprising a reactive sulfur compound,
- and wherein operating a reactor in activation mode involves the steps of
- 25 (f) providing a precursor of a catalytically active material, which is activated by sulfidation into said reactor,
- (g) directing the stream comprising a reactive sulfur compound, to contact the precursor of catalytically active guard material, contained in
- 30 said reactor operating in activation mode,

with the associated benefit of reducing the requirement to shut down a process, while enabling simple and cost effective activation of catalytically active materials requiring sulfidation as activation prior to use.

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In a further embodiment the disclosure relates to a procedure for operation of a reactor system involving an operating reactor and a first refreshable reactor each containing a catalytically active material and/or a precursor of a catalytically active material, in which said refreshable reactor is operable in an activation mode and an operations mode, said procedure comprising the steps of

- (a) operating the two reactors in operations mode, either by configuring the two reactors for a serial connection or by configuring one of the two reactors for being by-passed,
- (b) upon a first condition switching the operation of the first refreshable reactor into activation mode,
- (c) and upon a second condition switching the operation of the first refreshable reactor into operations mode,

wherein operating a reactor in operations mode involves the process steps

- (i) directing a feed stream comprising sulfur to contact said catalytically active material providing a reacted stream, and
- (ii) from said reacted stream or a downstream product hereof withdrawing a stream comprising a reactive sulfur compound,

30

and wherein operating a reactor in activation mode involves the process steps of

- (iii) providing a precursor of a catalytically active material in said reactor in activation mode, in which said precursor is transformed from precursor to catalytically active material by sulfidation,
- (iv) directing said stream comprising a reactive sulfur compound, to contact the precursor of catalytically active material under sulfidation conditions,
- (v) withdrawing a stream from said reactor operating in activation mode and directing it to a sulfidation waste line.

with the associated benefit of reducing the requirement to shut down a process, while enabling simple and cost effective activation of catalytically active materials requiring sulfidation as activation prior to use.

In a further embodiment said reactor system is configurable for providing a second refreshable reactor, being equivalent to said first refreshable reactor, and according to which procedure said second refreshable reactor is at least for a period of time operating in activation mode while said first refreshable reactor is operating in operations mode, and upon said first condition said second refreshable reactor is configured for operating in operations mode while said first refreshable reactor is at least for a period of time configured for operating in activation mode,

with the associated benefit of providing a process which is minimally affected by the replacement of catalytically active material in the reactor(s) to be activated.

In a further embodiment said refreshable reactor is a guard reactor, and in which said feed stream comprises an amount of an impurity, of which a part is deposited on said catalytically active material such that the reacted stream comprises a reduced amount of said impurity compared to said feed stream, with the associated benefit of removing impurities by a chemical transformation through a process directly or indirectly involving catalysis into materials which are easily withdrawn from the reacted stream, by surface deposition on the catalytically active guard material.

In a further embodiment the feed stream is a hydroprocessing feed comprising hydrogen, a hydrocarbon mixture and one or more sulfur compounds such as mercaptans, thiophenes and in which said impurity is a metal heteroatom such as nickel, arsenic, silicon, iron or vanadium, with the associated effect of providing cost effective activation of catalytically active guard material in the context of refinery processes, where hydrogen sulfide are available as waste streams.

In a further embodiment said feed stream is a synthesis gas comprising hydrogen, carbon monoxide and one or more sulfides such as carbonyl sulfide and/or hydrogen sulfide, and in which said impurity is a metal carbonyl compound, with the associated benefit of providing a partly purified stream as reactant stream for a sour shift section.

In a further embodiment the partially purified stream is directed to contact a material catalytically active in the water gas shift reaction, operating under water gas shift conditions, providing a gas stream rich in hydrogen, with the

associated benefit of providing a gas stream rich in hydrogen suitable for a downstream synthesis or further purification into pure hydrogen.

5 In a further embodiment the stream comprising a reactive sulfur compound is directed to contact the precursor of catalytically active material at a temperature above 100°C or 120°C and below 150°C, 200°C and 300°C, above 1 and below 10, 30 or 50 bar, and which comprises at least 800 ppm hydrogen sulfide,
10 hydrogen sulfide, at least 10% hydrogen and if water is present, an amount of water which is non-condensing under the applied conditions, with the associated benefit of such a stream having a composition suited for activation of catalytically active materials by sulfidation.
15

In a further embodiment said stream comprising a reactive sulfur compound comprises an amount of the gas stream rich in hydrogen, with the associated benefit of said gas stream
20 rich in hydrogen being readily available and having a composition well suited providing the required reducing conditions for the sulfidation process.

In a further embodiment the process further comprises the
25 step of acid gas removal in which said partially purified stream or a downstream product hereof is separated in an AGR sulfur rich stream and an AGR process stream lean in sulfur compounds, and in which said stream comprising a reactive sulfur compound comprises an amount of said AGR sulfur rich
30 stream,

with the associated benefit of said AGR sulfur rich stream being available and well suited for providing additional reactive sulfur compounds if required.

5 In a further embodiment operations mode involves the further process step of combining the stream comprising a reactive sulfur compound with an amount of a substantially inert gas stream, such as a stream rich in nitrogen, with the associated benefit of providing a high flexibility
10 in concentration. Furthermore if the substantially inert gas stream is preheated, this may help in providing stream comprising sulfur at a temperature suitable for activation.

A further aspect involves a process for reducing the amount
15 of metal carbonyl compounds in a feed stream, in a reactor system operated according to the procedure above, in which the catalytically active material is a material catalytically active in conversion of carbon monoxide and water to carbon dioxide and hydrogen, and in which said material has
20 a void capacity for allowing deposition of metal derived components,
with the associated benefit of reducing the concentration of carbon monoxide in the process gas, such that the equilibrium between metal carbonyls and metal or metal sulfides
25 is shifted away from metal carbonyls, and thus towards deposition of metal or metal sulfide, and the benefit of having a void in which nickel may be deposited without the risk of excessive pressure drop in the reactor.

30 In a further embodiment said material catalytically active in conversion of carbon monoxide and water to carbon dioxide and hydrogen comprises 1-5% cobalt, 5-15% molybdenum or

tungsten and a support comprising one or more metal oxides, such as alumina, magnesia, titania or magnesium-alumina spinel,
with the associated benefit of such a material being catalytically active in sour water gas shift process.

In a further embodiment said condition is based on one or more evaluations taken from the group comprising the pressure drop across the refreshable reactor exceeding a predefined value, the amount of metal carbonyl outlet from the guard bed exceeding a predefined value or the temperature of the partly reacted stream exceeding a predefined value, with the associated benefit of the monitoring of pressure drop and metal carbonyl amount being directly correlated to catalytically active guard material capacity. The monitoring of temperature is technically simply, and it will correspond to the water gas shift activity, and thus correlate to the activity of the catalytically active guard material, and correspond to the upper potential limit of metal carbonyls, due to the relation to the nickel carbonyl equilibrium. If the criteria are combined the accuracy of the monitoring may be improved further.

In a further aspect the invention relates to a process plant for a chemical process comprising a first refreshable reactor section comprising a refreshable reactor and an operating reactor section comprising an operating reactor, a feed stream line, a product stream line, a sulfur stream line, a sulfidation waste line and either an upstream feed stream line or a downstream product stream line, both reactor sections having an inlet and an outlet, and being configured for containing a catalytically active material, and

in which the refreshable reactor is configurable for, during regular operation, having an inlet in fluid connection with a feed stream line, and an outlet in fluid connection with a product stream line, and in which the first refresh-
5 able reactor section is configurable for during activation of a precursor of catalytically active material having an inlet in fluid connection with a sulfur stream line, and an outlet in fluid connection with a sulfidation waste stream line, wherein said process plant is configurable for the
10 operating reactor and the first refreshable reactor to operate in series during regular operation by either the inlet of the operating reactor being in fluid connection with an upstream feed stream line and the outlet of the operating reactor section being in fluid connection with the feed
15 stream line, or by the inlet of the operating reactor section being in fluid connection with the product line and an outlet of the reactor section being in fluid connection with a downstream product line,
with the associated benefit of such a plant being configured for blocking and redirecting the appropriate streams,
20 in order to enable activation by sulfidation according to the process disclosed in the present application.

A further aspect of the invention relates to a process
25 plant for a chemical process according comprising a first refreshable reactor section and an second refreshable reactor section, a feed stream line, a product stream line, a sulfur stream line and a sulfidation waste line, both reactor sections being configured for containing a catalytical-
30 ly active material,
and the process plant is configurable for operation either in configuration (x) or for operation in at least one of

the configurations (y) and (z), where configurations (x), (y) and (z) are

(x) one refreshable reactor section having its inlet in fluid connection with the feed stream, and the outlet of the same refreshable reactor section being in fluid connection with the product stream and

the other refreshable reactor section having its inlet in fluid connection with the sulfur stream line and the outlet of the same refreshable reactor section being in fluid connection with the sulfidation waste stream line,

(y) one refreshable reactor section having its inlet in fluid connection with the feed stream, and the outlet of the same refreshable reactor section being in fluid connection with the inlet section of the other refreshable reactor section and the other refreshable reactor section outlet being in fluid connection with the sulfidation waste stream line

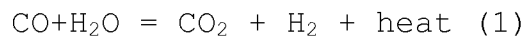
and

(z) one of the two refreshable reactor section having its inlet in fluid connection with the feed stream, and the outlet of the same refreshable reactor section being in fluid connection with the product stream, with the associated benefit of such a plant being configured for blocking and redirecting the appropriate streams, in order to enable activation by sulfidation of reactors operating in swing mode according to the process disclosed in the present application.

Catalytically active materials are often used in chemical processes, where a process feed contains undesired impurities, which are not readily converted to compounds which may be removed. Examples of such impurities include hetero-

metals in crude oils, originating from the raw material, and metal carbonyls - especially nickel carbonyls - often originating from minor release of upstream materials.

5 The removal of metal carbonyls may be carried out by exploiting the equilibrium between metal carbonyls and carbon monoxide. By shifting carbon monoxide catalytically with water, forming hydrogen and carbon dioxide the nickel carbonyl equilibrium with nickel and carbon monoxide is also
10 shifted towards nickel in the solid state such as Ni or NiS.



15 In the operation of guard reactors an important consideration is when to switch guard operation. This may be decided by a criterion based on pressure drop, by analytical detection of a breakthrough of the undesired constituent or by prediction of loss of guard activity by other means. When
20 reaction (1) takes place, the temperature increases and the CO concentration decreases, shifting reaction (2) towards the right hand side, thus leading to deposition of NiS, and thus the reduced amount of CO shifts (2) towards right hand side, thus leading to deposition of NiS. Accordingly an appropriate process criterion for cancelling guard bed operation
25 may be based on the outlet temperature of the guard reactor, which is correlated to the water gas shift conversion in the guard bed, and thus indirectly correlated to the amount of metal carbonyls present in the gas exit the
30 guard reactor. Additional appropriate process criteria for cancelling guard bed operation may be the pressure drop

across the guard bed or the amount of metal carbonyl outlet from the guard bed.

5 In the operation of the sour shift process, it is common to operate the process in three stages with intermediate cooling, since this will shift the equilibrium of (1) towards the right, with an increased amount of H_2 as a consequence.

10 The sulfidation of the catalytically active material will involve a number of practical considerations, including the environmental aspects of releasing sulfur from the sulfidation process and possibly corrosion aspects. With respect to the release of sulfur from sulfidation, initially the sulfidation waste gas will contain very small amounts of
15 sulfur, as it will all be consumed by the catalytically active material. However, when sulfidation is close to complete, an amount of sulfur may be released. In that case it may be necessary to direct the sulfidation waste gas to acid gas removal. In that case it may be beneficial that the
20 sulfidation takes place at a pressure which corresponds to the process pressure.

During sulfidation it is practical that the pressure in the stream comprising reactive sulfur is similar to the pressure in the main process. Another pressure consideration
25 relates to hydrogen sulfide withdrawn from the AGR unit. Typically the AGR unit operates close to atmospheric pressure, which adds complexity to the combination of an AGR sulfur rich stream with a process stream. If the pressure
30 during sulfidation is kept low it may be simpler to combine the process gas and an AGR sulfur rich stream.

Another aspect of sulfidation is the corrosion stability of materials. In general it is required that the materials are compatible with the process streams applied. However, as the activation procedure is only temporary the materials may be selected in a less robust quality, compared to full time operation with similar sulfur levels.

The Figure shows a process plant according to the invention. A feed gas 2 is directed through feed line 4 to valves 6A and 6B. If valve 6A is open, valves 6B, 6C and 12C are closed, and the feed gas is directed to a first guard bed 8A operating in guard mode, and outlet through outlet line 10 and valve 12A through sour shift feed line 14 to a first reactor 16 of a downstream sour shift section, which may receive a gas at 240°C, and provide a heated product at a temperature often above 400°C. The partially shifted gas is directed to heat exchanger 20 and typically cooled to around 220°C, and directed to a second sour shift reactor 24 in which it is further shifted and cooled 28, before a final sour shift 32 and cooling to around 220°C in 36. The cold product undergoes gas/liquid separation 38 into water 40 and a hydrogen rich gas 42, which is split into a stream comprising hydrogen sulfide 44 and a hydrogen rich product line 46 which is directed to acid gas removal (AGR) 48, in which a sweet hydrogen rich gas 50 is separated from a stream rich in hydrogen sulfide 52 which, especially if additional sulfur is directed to the AGR section, may be useful for providing reactive sulfur for sulfidation. The stream comprising hydrogen sulfide 44 may be combined with a nitrogen stream 54 and directed to a heater 58 before being directed 60 to valves 6C and 6D, which are configured for stream 6D to be open while 6A is open. Fur-

thermore valve 12D will be open while valve 12B is closed. By this configuration the gas comprising hydrogen sulfide will be directed to the second guard bed 8B operating in activation mode, which will contain a precursor of catalytically active guard material, which requires sulfidation to be activated. Valve 12D will direct the waste sulfidation gas to flare or an sulfur withdrawal process. When the precursor of a catalytically active guard material has been activated it is a catalytically active guard material, and reactor 8B may be put in idle mode by blocking the stream comprising hydrogen sulfide from reactor 8B by closing valves 6D and 12D, until the activity of reactor 8A drops to below a predetermined level.

When the guard activity of reactor 8A is below the predetermined level or the pressure drop has exceed the predetermined limit, reactor 8B must be put in guard mode. This is done by setting valves 6B and 12B in open position and setting valves 6A, 6D, 12A and 12D in closed position. After replacing the catalytically active guard material of reactor 8A it may be configured for activation mode by opening valves 6C and 12C, but reactor 8A may also be put in idle mode for a period if it is preferred postpone to activate the reactor shortly before being put it in guard mode.

In alternative embodiments of the process also the sour shift reactors 24 and 32 may also be bypassed during sulfidation. Such a bypass will provide modified output compositions from the sour shift section in stream 42, which may be compensated elsewhere in the process during activation.

Further alternative embodiments may involve having two "first reactor 16" in parallel, each immediately downstream the guard bed reactors 8A and 8B respectively. This may even be implemented as reactor 8A and 8B both containing an
5 initial layer of catalytically active guard material above a bed of catalytically active sour shift material, such that the number of reactors is not increased. For such a configuration the equivalent of two heat exchanger 20 is preferably positioned upstream the valves 12A, 12B, 12C and
10 12D, as these valves in this case may be designed for lower temperatures.

In an example of a process according to the present invention a shifted gas stream with addition of an AGR sulfur
15 rich stream, comprising hydrogen sulfide is used for activation of the guard bed reactors, in a setup corresponding to the Figure, with the conditions and gas compositions given in Table 1.

20 Based on a space velocity in the guard reactor of 1000 hr^{-1} and the gas compositions given in Table 1 (stream 44 comprising a reactive sulfur compound) a first step of sulfidation, which will be at temperature of 100-150 °C, is expected to be completed within 10 hours. The second step of
25 the sulfidation, is conducted while slowly increasing the temperature towards 300 °C, is completed within another 24 hours.

Table 1

Component/Stream No.	2	44
H ₂ [%]	26	56
Ar [%]	0.2	0.2
N ₂ [%]	0.6	0.6
CH ₄ [%]	1.5	1.5
CO [%]	37	1
CO ₂ [%]	9	40
H ₂ S [%]	1	1
COS [%]	0.1	0
NH ₃ [%]	0.5	0
H ₂ O [%]	24	0.2
Ni(CO) ₄ , ppm	0.5	0
Pressure, [Bar]	45	40
Temperature, [°C]	215	40

Claims:

1. A procedure for operation of a reactor system involving an operating reactor and a first refreshable reactor, each containing a catalytically active material and/or a precursor of a catalytically active material, in which said refreshable reactor is operable in an activation mode and an operations mode, said procedure comprising the steps of
- (a) operating the two reactors in operations mode, either by configuring the two reactors for a serial connection or by configuring one of the two reactors for being by-passed,
- (b) upon a first condition switching the operation of the first refreshable reactor into activation mode,
- (c) and upon a second condition switching the operation of the first refreshable reactor into operations mode,
- wherein operating a reactor in operations mode involves the process steps
- (i) directing a feed stream comprising sulfur to contact said catalytically active material providing a reacted stream, and
- (ii) from said reacted stream or a downstream product hereof withdrawing a stream comprising a reactive sulfur compound,
- and wherein operating a reactor in activation mode involves the process steps of
- (iii) providing a precursor of a catalytically active material in said reactor in activation mode, in which said precursor is transformed

from precursor to catalytically active material by sulfidation,

(iv) directing said stream comprising a reactive sulfur compound to contact the precursor of catalytically active material under sulfidation conditions,

(v) withdrawing a stream from said reactor operating in activation mode and directing it to a sulfidation waste line.

10

2. A procedure according to claim 1 in which said reactor system comprises a second refreshable reactor, being equivalent to said first refreshable reactor, and according to which procedure said second refreshable reactor is at least for a period of time operating in activation mode while said first refreshable reactor is operating in operations mode, and upon said first condition said second refreshable reactor is configured for operating in operations mode while said first refreshable reactor is at least for a period of time configured for operating in activation mode.

15

20

3. A procedure according to claim 1 or 2 in which said refreshable reactor is a guard reactor, and in which said feed stream comprises an amount of an impurity, of which a part is deposited on said catalytically active material such that the reacted stream comprises a reduced amount of said impurity compared to said feed stream.

25

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4. A process according to claim 1, 2 or 3 in which the feed stream is a hydroprocessing feed comprising hy-

drogen, a hydrocarbon mixture and one or more sulfur compounds such as mercaptan, thiophenes and in which said impurity is a metal heteroatom such as nickel, arsenic, silicon, iron or vanadium.

5

5. A procedure according to claim 1, 2 or 3 in which said feed stream is a synthesis gas comprising hydrogen, carbon monoxide and one or more sulfides such as carbonyl sulfide and/or hydrogen sulfide, and in which
10 said impurity is a metal carbonyl compound.
6. A procedure according to claim 1, 2, 3, 4 or 5 in which the partially purified stream is directed to contact a material catalytically active in the water
15 gas shift reaction, operating under water gas shift conditions, providing a gas stream rich in hydrogen.
7. A procedure according to claim 1, 2, 3, 4, 5 or 6 in which the stream comprising a reactive sulfur compound
20 is directed to contact the precursor of catalytically active material at a temperature above 100°C or 120°C and below 150°C, 200°C and 300°C, above 1 and below 10, 30 or 50 bar, and which comprises at least 800 ppm hydrogen sulfide, at least 10% hydrogen and if water
25 is present, an amount of water which is non-condensing under the applied conditions.
8. A procedure according to claim 6 or claim 7 depending on claim 6 in which said stream comprising a reactive
30 sulfur compound comprises an amount of the gas stream rich in hydrogen.

9. A procedure according to claim 1, 2, 3, 4, 5, 6, 7 or 8 in which operations mode involves the further downstream process step of acid gas removal in which said partially purified stream or a downstream product
5 hereof is separated in an AGR sulfur rich stream and an AGR process stream lean in sulfur compounds, and in which said stream comprising a reactive sulfur compound comprises an amount of said AGR sulfur rich stream.
- 10
10. A procedure according to claim 1, 2, 3, 4, 5, 6, 7, 8 or 9 in which operations mode involves the further process step of combining the stream comprising a reactive sulfur compound with an amount of a substantially inert gas stream, such as a stream rich in nitrogen.
- 15
11. A process for reducing the amount of metal carbonyl compounds in a feed stream, in a reactor system operated according to claim 5, 6, 7, 8, 9 or 10, in which
20 the catalytically active material is a material catalytically active in conversion of carbon monoxide and water to carbon dioxide and hydrogen, and in which said material has a void capacity for allowing deposition of metal derived components.
- 25
12. A process for reducing the amount of metal carbonyl compounds according to claim 11, in which said material catalytically active in conversion of carbon monoxide and water to carbon dioxide and hydrogen comprises
30 1-5% cobalt, 5-15% molybdenum or tungsten and a sup-

port comprising one or more metal oxides, such as alumina, magnesia, titania or magnesium-alumina spinel.

13. A process for reducing the amount of metal carbonyl compounds according to claim 11 or 12, in which said condition is based on one or more evaluations taken from the group comprising the pressure drop across the refreshable reactor exceeding a predefined value, the amount of metal carbonyl in the reacted stream exceeding a predefined value, or the temperature of the reacted stream exceeding a predefined value.
14. A process plant for a chemical process comprising a first refreshable reactor section and an operating reactor section, a feed stream line, a product stream line, a sulfur stream line, a sulfidation waste line and either an upstream feed stream line or a downstream product stream line, both reactor sections having an inlet and an outlet, and being configured for containing a catalytically active material, and in which the first refreshable reactor section is configurable for, during regular operation, having the inlet in fluid connection with a feed stream line, and the outlet in fluid connection with a product stream line,
- and in which the first refreshable reactor section is configurable for, during activation of a precursor of catalytically active material, having the inlet in fluid connection with a sulfur stream line, and the outlet in fluid connection with a sulfidation waste stream line,

wherein said process plant is configurable for the operating reactor and the first refreshable reactor to operate in series during regular operation by either the inlet of the operating reactor section being in fluid connection with an upstream feed stream line and the outlet of the operating reactor section being in fluid connection with the feed stream line, or by the inlet of the operating reactor section being in fluid connection with the product line and the outlet of the reactor section being in fluid connection with a downstream product line.

15. A process plant for a chemical process according to claim 14 comprising a first refreshable reactor section and a second refreshable reactor section, a feed stream line, a product stream line, a sulfur stream line and a sulfidation waste line, both reactor sections being configured for containing a catalytically active material,
- and the process plant is configurable for operation either in configuration (x) or for operation in at least one of the configurations (y) and (z), where configurations (x), (y) and (z) are
- (x) one refreshable reactor section having its inlet in fluid connection with the feed stream, and the outlet of the same refreshable reactor section being in fluid connection with the product stream and the other refreshable reactor section having its inlet in fluid connection with the sulfur stream line and the outlet of the same refreshable reactor section being in fluid connection with the sulfidation waste stream line,

(y) one refreshable reactor section having its inlet in fluid connection with the feed stream, and the outlet of the same refreshable reactor section being in fluid connection with the inlet section of the other refreshable reactor section and the other refreshable reactor section outlet being in fluid connection with the sulfidation waste stream line
5 and

(z) one of the two refreshable reactor sections having its inlet in fluid connection with the feed stream,
10 and the outlet of the same refreshable reactor section being in fluid connection with the product stream.

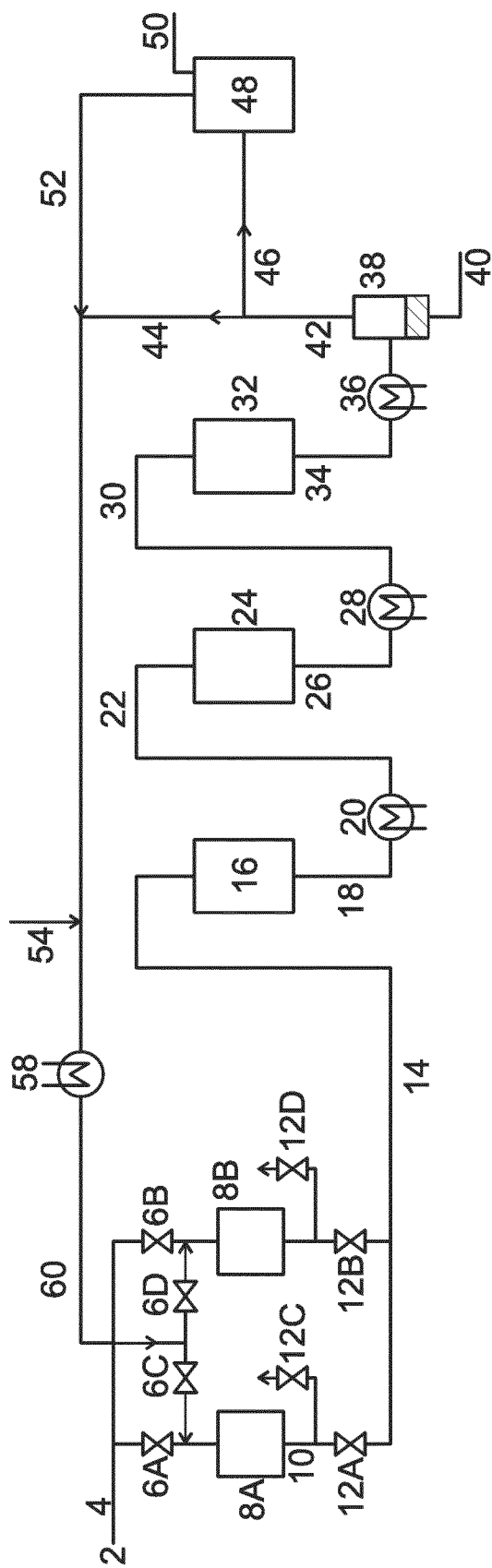


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/064857

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J8/00 B01J8/04 C10G45/02
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)
B01J C10G

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 practicable, 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.
X	US 2008/029435 A1 (UMANSKY BENJAMIN S [US] ET AL) 7 February 2008 (2008-02-07) paragraphs [0038], [0040] -----	14, 15
A	US 2004/055934 A1 (TROMEUR PASCAL [FR] ET AL) 25 March 2004 (2004-03-25) paragraphs [0001], [0004], [0031] - [0037], [0069], [0070] -----	1-10, 14, 15
A	US 4 719 006 A (GOYAL SHRI K [US]) 12 January 1988 (1988-01-12) claim 9; figure 3 -----	1-10, 14, 15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search

17 September 2015

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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

Veronesi, Sergio

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/064857

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