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(54) Benævnelse: **FREMGANGSMÅDE TIL AFSVOVLING AF EN CARBONHOLDIG ENERGIBÆRESTRØM**

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METHOD FOR REMOVING SULPHUR FROM FUEL FLOW CONTAINING CARBON

The invention relates to a process for the desulphurisation of a carbon-containing energy source stream with the features of the preamble of claim 1, as well as to an installation for the desulphurisation of a carbon-containing energy source stream with the features of the preamble of claim 14.

Carbon-containing energy sources such as natural gas, for example, regularly contain a proportion of sulphur in the form of hydrogen sulphide (H_2S). Sulphur compounds of this type often cause problems during further processing of the carbon-containing energy source stream, because sulphur has a severe poisoning effect on catalysts such as nickel, for example, which could be used during further processing of the energy source stream of this type. The sulphur is absorbed by the catalyst so that the sulphur becomes bound and at the same time deactivates the catalyst. Thus, in the prior art, it is known for a carbon-containing energy source stream to undergo desulphurisation before the energy source stream is fed to further processing stages such as those of a steam reforming stage, for example.

EP 1 616 828 A2, which is known in the art, describes a device for the adiabatic pre-reforming of natural gas. Before the natural gas is fed to a reactor for adiabatic pre-reforming, the natural gas is desulphurised in a desulphurisation stage. To this end, a proportion of more than 1% of hydrogen is added to the natural gas and fed to a catalyst to be desulphurised by hydrogenation. A hydrogen recovery stage is provided downstream of the desulphurisation stage by means of which the hydrogen for the above addition can be recovered.

The disadvantage with this approach is on the one hand that, in addition to the reactor for the hydrogenation, a device also has to be provided for both the addition of the hydrogen as well as for the recovery of the hydrogen. In addition, for the desulphurisation itself, suitable process parameters have to be maintained which in particular are dependent on the proportion of sulphur. At the same time, it also has to be ensured that the desulphurisation is carried out extremely thoroughly, because even comparatively small residual concentrations could lead to catalyst poisoning in the downstream stages. As a result, this type of desulphurisation is both cumbersome as well as often unsatisfactory in the long term as regards its effect.

US 2012/0157731 A1 from the prior art describes a pre-reforming process. A first stream which contains heavy hydrocarbons is heated to a first temperature, the heated first stream is introduced into a first pre-reforming chamber, whereupon a first pre-reformed stream is produced. In addition, the first pre-reformed stream is heated to a second temperature, then the heated first pre-reformed stream is fed into a second pre-reforming chamber, whereupon a second pre-reformed stream is produced. The process also comprises heating the second pre-reformed stream to a third temperature then feeding the second pre-reformed stream into a third pre-reforming chamber, whereupon a third pre-reformed stream is produced.

US 2013/0156685 A1 from the prior art describes a process for reducing the carbon dioxide balance from a reformer furnace flue gas to the high pressure synthesis gas exit water gas shift reaction unit. A heated gas mixture is introduced into at least one pre-reforming chamber. The heating is provided by indirect heat exchange with one or more SMR furnace flue gases or SMR furnace synthesis gases which introduce the gas mixture into a standard H_2 PSA unit, wherein the gas mixture is separated into a hydrogen-enriched stream and a PSA tail gas stream; introducing the PSA tail gas stream into a CPU system, wherein the PSA tail gas stream is separated into a carbon dioxide-enriched stream, a hydrogen-rich stream and a residual stream, and introducing the residual stream as fuel into the reformer furnace along with natural gas.

US 2014/0171714 A1 from the prior art describes a process for pre-reforming a hydrocarbon-containing stream prior to admission into a steam methane reformer. This process comprises a system with two pre-reforming reactors in series, wherein an oxygen stream is combined with the partially reformed outlet stream from the first pre-reforming reactor, and then the combined stream is fed into the second pre-reforming reactor.

EP 0 921 585 A2 from the prior art describes a device for steam reforming a hydrocarbon, with a vaporizer, a pre-reforming unit, a main reformer, a CO removal unit and at least one catalytic burner unit. A first burner unit is in thermal contact with the vaporizer and a second burner unit is in thermal contact with the main reformer, and also the pre-reforming unit is in thermal contact with the CO removal unit, all via a heat-conducting separating medium. The outlet from the CO removal unit can be connected to the inlet to the respective burner unit. During a cold start-up, a heating procedure is carried out during which firstly, the two burner units are activated with an external feed of hydrogen and then the reforming operation is started up with a smaller proportion of hydrocarbon compared with normal operation and the reformate gas which is formed thereby is introduced into the burner units as fuel instead of the externally supplied hydrogen.

US 6 447 736 B1 from the prior art describes a system for steam reforming a hydrocarbon which comprises a modular reactor unit of the plate stack and/or tube bundle type and, in an integrated manner, contains a vaporizer, a pre-reforming unit, a main reformer, a CO removal unit and a catalytic burner unit. The vaporizer and the main reformer are in thermal contact with the catalytic burner unit and the pre-reforming unit is in thermal contact with the CO removal unit.

WO 2010/120962 A1, which constitutes the closest prior art to the present invention, describes a process for the production of a hydrogen-containing product gas by catalytic steam-hydrocarbon reforming with an overall steam-to-carbon molar ratio between 1.5 and 2.4 for the process. The process stream is reacted in at least two pre-reformers prior to reaction in catalyst-containing tubes in a top-fired reformer furnace. The process stream is reacted adiabatically in the first pre-reformer, while the process stream is heated prior to being introduced into the second pre-reformer. The process prevents carbon formation on the catalyst in the catalyst-containing tubes in the primary reformer.

Starting from this prior art, the aim of the invention is therefore to provide an approach for desulphurisation which is both cost-effective and also provides reliable protection of the downstream stages from sulphur in the energy source stream.

In respect of a process for the desulphurisation of a carbon-containing energy source stream with the features of the preamble of claim 1, the aim is achieved by means of the features of the characterizing portion of claim 1. In respect of an installation for the desulphurisation of a carbon-containing energy source stream with the features of the preamble of claim 14, the aim is achieved by means of the features of the characterizing portion of claim 14.

What is fundamental to the invention is the recognition that in fact, an additional, further reactor stage is employed for pre-reforming the energy source stream which is upstream of the actual reactor stage and which can be used in a particularly effective manner for desulphurising the energy source stream. An approach of this type is firstly economical because it only requires the expansion of a previously provided step of the process. In this manner, the addition of hydrogen is no longer necessary, since saturation with steam is in fact provided in any case for pre-reforming. Secondly, this approach is also particularly effective because the type of the catalyst to be protected - namely the catalyst in the reactor for the pre-reforming step - is precisely the type of catalyst for the desulphurisation step and so in addition, the mechanism for desulphurisation corresponds to that of the potential contamination of the catalyst. This prevents the desulphurisation procedure from being operated incorrectly with respect to the catalyst to be protected. In this manner, the upstream further reactor stage binds the sulphur, which leads to a progressive degradation of the catalyst in the upstream further reactor stage. In this manner, on the one hand, the catalyst in the downstream reactor stage is effectively protected and on the other hand, the remaining absorption capacity of the catalyst in the upstream further reactor stage can be assessed with the aid of the degree of degradation of the catalyst therein. Finally, other harmful substances such as mercaptans, for example, can also be reliably removed in this manner.

Here and hereinafter, the term "carbon-containing energy source stream" should be understood to mean gaseous or liquid streams containing hydrocarbons and in particular containing alkanes. In particular, this includes natural gas comprising methane, ethane, propane, butane and possibly higher hydrocarbons. In addition to these energy sources, the energy source stream may also contain inert fractions such as noble gases or nitrogen, as well as contaminants such as the sulphur compounds to be removed.

The term "pre-reforming" as used here and hereinafter should be understood to mean the procedure which is known in the art of adiabatic and catalytic steam reforming in a range of temperatures which lies below the range of temperatures for the actual steam reforming. In other words, the steam reforming which is known in the prior art can in general be divided into - as is described herein - actual steam reforming in a comparatively higher temperature range and pre-reforming in a comparatively lower temperature range. Here and hereinafter, the term "steam reforming" should be understood to mean the reforming procedure in general, the term "pre-reforming" should be understood to mean a steam reforming procedure in the comparatively low temperature range with a low conversion of methane and the term "actual steam reforming" should be understood to mean a steam reforming procedure which is not a pre-reforming procedure and during which an extensive conversion of methane takes place. Both procedures - i.e. the actual steam reforming procedure and the pre-reforming procedure - are centred on the chemical reactions which are described by the equations $C_mH_{2n} + mH_2O \leftrightarrow mCO + (m+n)H_2$ on the one hand and $C_mH_{2n} + 2mH_2O \leftrightarrow mCO_2 + (2m+n)H_2$ on the other hand. Both the actual steam reforming procedure as well as the pre-reforming procedure are catalysed by an appropriate catalyst. In addition, both the actual steam reforming procedure as well as the pre-reforming procedure occur adiabatically. The difference between the actual steam reforming procedure and the pre-reforming procedure will be explained below.

In the case of the actual steam reforming procedure, a feed stream of hydrocarbons saturated with steam is converted into a product stream substantially consisting of hydrogen, carbon monoxide and carbon dioxide. Only small residual quantities of unconverted hydrocarbons remain. In particular, the molar proportion of methane in the product stream is less than 10%. The combined molar proportion of higher hydrocarbons from the product stream is less than 1%. The actual steam reforming procedure is carried out in a temperature range of between 500°C and 850°C, preferably between 550°C and 850°C. In this regard, in addition to the reforming reactions which are given above in the form of their equations, methanisation and the water gas shift reaction regularly also occur. In the case of this actual steam reforming procedure, a steam-to-carbon ratio S/C of between 1 and 5, and in particular of substantially 3, preferably prevails.

In contrast, the pre-reforming procedure is regularly carried out - and in contrast to the actual steam reforming procedure - in a temperature range of between 400°C and 550°C, preferably between 400°C and 500°C. A reaction equilibrium exists for the methane - in contrast to the higher hydrocarbons - which is only broken down to a small extent. Preferably, therefore, the molar proportion of methane in the product stream is at least 50% and may also in particular be at least 80%. The steam-to-carbon ratio S/C in the pre-reforming procedure is preferably below 3.5 and may also in particular be below 1, wherein approximately 0.3 is a possible value. This means that during pre-reforming, hydrocarbons containing at least two carbon atoms are converted with a catalyst by steam reforming into methane, hydrogen and oxides of carbon. A conversion of the methane with water into carbon monoxide and hydrogen in accordance with the reforming reaction, $C_1H_4 + H_2O \leftrightarrow CO + 3H_2$, therefore substantially does not occur in the case of pre-reforming, but rather, the exothermic synthesis of methane in particular may occur from the products from reforming the higher hydrocarbons in the reverse reaction direction. This can in particular lead to the fact that the molar proportion of methane increases after pre-reforming, that methane is formed from the conversion of the higher hydrocarbons and that the methane per se is substantially not broken down. The pre-reforming procedure can also be characterized by the fact that by means of the reaction conditions, both the reforming reaction of methane, $C_1H_4 + H_2O \leftrightarrow CO + 3H_2$, as well as the water gas shift reaction, $CO + H_2O \leftrightarrow CO_2 + H_2$, are substantially in reaction equilibrium, so that in the pre-reformer, substantially only reforming of the higher hydrocarbons and applicable reactions occur which arise from the resulting variation in the equilibrium conditions.

The dependent claims 2 and 3 describe particularly suitable features for such a catalyst for the desulphurisation procedure.

The dependent claims 5 and 6 describe different variations in the separation of the - upstream - pre-catalyst from the - downstream - main catalyst.

The dependent claims 7 and 8 describe the possibility of operating two upstream reactor stages in alternation and therefore of being able to switch from one to the other in the case of degradation without substantial interruption.

Finally, the dependent claims 12 and 13 describe the proposed process in the context of a process for obtaining synthesis gas.

Further details, features, embodiments, aims and advantages of the present invention will be described below with the aid of the drawings which are given purely by way of exemplary embodiment. In the drawings:

Figure 1	diagrammatically shows the flow chart for an installation for the desulphurisation of a carbon-containing energy source stream from the prior art, and
Figure 2	diagrammatically shows the flow chart for an installation for implementation in the case of an exemplary embodiment of the proposed process.

The proposed process serves for the desulphurisation of a carbon-containing energy source stream 1 which, for example, may be a stream of natural gas. In particular, the proposed process is carried out by means of the proposed installation for the desulphurisation of the carbon-containing energy source stream 1 shown in Figure 2.

In accordance with the representation shown in Figure 2, the proposed installation has a pre-reformer 2 for pre-reforming the carbon-containing energy source stream 1 and for obtaining a desulphurised methane-containing stream 3, wherein in the pre-reformer 2, hydrocarbons from the energy source stream 1 which contain at least two carbon atoms are broken down into methane, hydrogen and oxides of carbon by means of a steam reforming reaction and wherein the pre-reformer 2 has a catalyst arrangement 4 for the catalysis of the steam reforming reaction. These hydrocarbons containing at least two carbon atoms comprise ethane, propane, butane, pentane and hexane. During the course of this steam reforming reaction, methanisation and the water gas shift reaction also take place.

The proposed installation is characterized in that the catalyst arrangement 4 has a pre-catalyst 5 for the catalysis of the steam reforming reaction in a pre-catalyst vessel 6 of the pre-reformer 2 and a main catalyst 7 for the catalysis of the steam reforming reaction in a main catalyst vessel 8 of the pre-reformer 2. The pre-catalyst vessel 6 and the main catalyst vessel 8 in this regard may in principle be any respective structure for the pre-reformer 2 which carries, encloses or in any other manner receives the pre-catalyst 5 or the main catalyst 7.

The proposed installation is furthermore characterized in that - as can also be seen in Figure 2 - the pre-catalyst vessel 6 is disposed remotely from the main catalyst vessel 8 and in that the energy source stream 1 passes through the pre-catalyst vessel 6 before the main catalyst vessel 8. In other words, the pre-catalyst vessel 6 is located operationally upstream of the main catalyst vessel 8.

Preferably, the steam reforming procedure, and therefore pre-reforming in the pre-reformer 2 in particular, take place adiabatically, wherein in particular, the steam reforming procedure may take place adiabatically in the pre-catalyst vessel 6 and the main catalyst vessel 8. Similarly, the molar proportion of methane in the methane-containing stream 3 is preferably higher than the molar proportion of methane in the energy source stream 1. Preferably, an increase in the molar proportion of methane in the methane-containing stream 3 compared with the energy source stream 1 occurs because of the steam reforming in the pre-reformer 2 and here, in particular, both because of the steam reforming procedure in the pre-catalyst vessel 6 as well as because of the steam reforming procedure in the main catalyst vessel 8. In particular, it may be that the molar proportion of methane in the methane-containing stream 3 is at least 50% and preferably at least 80%. Preferably, the methane-containing stream 3 is substantially free from hydrocarbons which are higher than methane.

Because sulphur rapidly leads to a deactivation of catalysts for steam reforming, in particular by means of chemisorption, and therefore acts as a catalyst poison, but is bound by the deactivated catalyst during this action as a catalyst poison, a corresponding progressive poisoning of the pre-catalyst 5 alone occurs and sulphur is efficiently prevented from gaining ingress to the main catalyst 7 to any substantial extent as long as the energy source stream 1 is fed through the pre-catalyst 5 and the latter can still absorb sulphur.

This course of action offers a series of advantages over the prior art approach which is shown in Figure 1. In the prior art, hydrogen 9 is initially fed to the carbon-containing energy source stream 1, whereupon hydrogenation then takes place in an appropriate reactor 10 making use of an appropriate catalyst, so that substantially all of the sulphur in the energy source stream 1 is converted into hydrogen sulphide. In this regard, as a rule, the hydrogen has to be obtained in a complex manner from a PSA unit and this could have been put to better use in another part of the process. Next, the energy source stream 1 is fed to a collecting reactor 11 containing zinc oxide, in which the hydrogen sulphide is removed from the energy source stream 1 by the formation of solid zinc sulphate. The disadvantage with this approach is not only that expensive hydrogen has to be used, but also that when the proportion of sulphur in the energy source stream 1 falls, the hydrogenation function could also be compromised.

In contrast, the proposed solution copes admirably, even with sharply varying proportions of sulphur in the energy source stream 1. A further advantage lies in the fact that the proposed solution is also capable of removing thioalcohols, also known as mercaptans, from the energy source stream 1, which would otherwise not be possible.

Corresponding to the proposed installation, in the proposed process, the carbon-containing energy source stream 1 is fed to the pre-reformer 2 for pre-reforming the energy source stream 1, wherein in the pre-reformer 2, hydrocarbons from the energy source stream 1 which contain at least two carbon atoms are broken down into methane, hydrogen and oxides of carbon by means of a steam reforming reaction in order to obtain a desulphurised methane-containing stream 3. Furthermore, in the proposed process, the pre-reformer 2 has a catalyst arrangement 4 for the catalysis of the steam reforming reaction.

The proposed process is characterized in that the catalyst arrangement 4 has a pre-catalyst 5 for the catalysis of the steam reforming reaction in a pre-catalyst vessel 6 and a main catalyst 7 for the catalysis of the steam reforming reaction in a main catalyst vessel 8, in that the pre-catalyst vessel 6 is disposed remotely from the main catalyst vessel 8 and in that the energy source stream 1 passes through the pre-catalyst vessel 6 before the main catalyst vessel 8.

A preferred embodiment of the proposed process and of the proposed installation is characterized in that the pre-catalyst 5 has a support material and an active metal, wherein the active metal comprises or consists of nickel, cobalt, platinum, palladium, iridium, ruthenium and/or rhodium. More preferably, the support material comprises or consists of aluminium oxide or alkaline earth aluminates. In particular, the active metal has a specific surface area per unit mass of at least 15 m^2/g.

In principle, the main catalyst 7 may also have a material composition which differs from that of the pre-catalyst 5. However, a further preferred embodiment of the proposed process and of the proposed installation is characterized in that the main catalyst 7 has an active metal which substantially corresponds to the active metal of the pre-catalyst 5. More preferably, the main catalyst 7 has a support material which substantially corresponds to the support material of the pre-catalyst 5. In particular, the material properties of the main catalyst 7 may substantially correspond to those of the pre-catalyst 5. These material properties thus not only concern the composition of the main catalyst 7, but also concern features such as pore size etc. This ensures that substances which could potentially poison the main catalyst 7 can be reliably trapped by the pre-catalyst 5.

In accordance with a preferred embodiment of the proposed process and of the proposed installation, the steam reforming reaction catalysed by the pre-catalyst 5 takes place at a temperature between 400°C and 550°C, preferably between 400°C and 500°C. In principle, steam reforming of the main catalyst may also take place at a different temperature. Preferably, however, the steam reforming reaction which is catalysed by the main catalyst 7 takes place at a temperature which substantially corresponds to the temperature of the steam reforming reaction which is catalysed by the pre-catalyst 5.

In accordance with a further preferred embodiment of the proposed process and of the proposed installation, the pre-catalyst vessel 6 has a substantially closed pre-reaction chamber for receiving the pre-catalyst 5. As an alternative or in addition, the main catalyst vessel 8 has a substantially closed main reaction chamber for receiving the main catalyst 7. Preferably, the main reaction chamber is remote from the pre-reaction chamber. In other words - as also shown in Figure 2 - the pre-catalyst vessel 5 may be a pre-reactor or a pre-reactor stage which is disposed separately from and remotely from the main reactor formed by the main catalyst vessel 8 or from the described main reactor stage.

A preferred embodiment of the proposed process and of the proposed installation is correspondingly characterized in that the pre-catalyst vessel 6 is isolated from the main catalyst vessel 8 by at least one wall. In the exemplary embodiment of Figure 2, this at least one wall is formed by the walls of the pre-reactor and of the main reactor. More preferably, the pre-reformer 2 has a section of line 12 which in particular is tubular in order to feed the energy source stream 1 from the pre-catalyst vessel 6 to the main catalyst vessel 8.

In principle, only a single pre-catalyst 5 and only a single main catalyst 7 may be present. A further preferred embodiment of the proposed process and of the proposed installation corresponding to the representation in Figure 2 is in particular characterized in that the catalyst arrangement 4 has a further pre-catalyst 13 for the catalysis of the steam reforming reaction in a further pre-catalyst vessel 14 - which is preferably contained in the pre-reformer 2 -

the further pre-catalyst vessel 14 being disposed remotely from the pre-catalyst vessel 6, and in that the energy source stream 1 is fed alternately through the pre-catalyst vessel 6 and the further pre-catalyst vessel 14 upstream of the main catalyst vessel 8 by means of a switchable valve arrangement 15 which is also contained in the pre-reformer 2. As can be seen, the further pre-catalyst vessel 14 is also remote from the main catalyst vessel 8. In this manner, in the case of progressive sulphur absorption by the pre-catalyst 5, switching to the further pre-catalyst 13 may be carried out. In principle, the further pre-catalyst 13 may differ from the pre-catalyst 5 in several respects. However, preferably, the material properties of the further pre-catalyst 13 substantially correspond to those of the pre-catalyst 5.

In accordance with a preferred embodiment of the proposed process and of the proposed installation, the geometry of the further pre-catalyst vessel 14 preferably substantially corresponds to that of the pre-catalyst vessel 6, in particular in that a mass of the pre-catalyst 5 substantially corresponds to a mass of the further pre-catalyst 13. The correspondence of the pre-catalyst 5 to the further pre-catalyst 13 is then in addition to that of the material properties.

In the proposed process and the proposed installation, preferably, a degree of degradation of the pre-catalyst 5 is measured and when the measured degree of degradation exceeds a degradation threshold, the pre-catalyst vessel 6 is isolated from the energy source stream 1. In other words, the energy source stream 1 - at least temporarily - no longer passes through the pre-catalyst vessel 6 and no more steam reforming catalysed by the pre-catalyst 5 takes place. More preferably, after isolating the pre-catalyst vessel 6 from the energy source stream 1, the pre-catalyst 5 in the pre-catalyst vessel 6 is replaced by a fresh pre-catalyst 5. In the case of degradation of the further pre-catalyst 13, the valve arrangement 15 can correspondingly be switched back again.

In principle, the isolation of the pre-catalyst vessel 6 from the energy source stream 1 may be carried out in any manner. A preferred embodiment of the proposed process and of the proposed installation is characterized in that the pre-catalyst vessel 6 is isolated from the energy source stream 1 in a manner such that by switching the valve arrangement 15, the energy source stream 1 is fed through the further pre-catalyst vessel 14. More preferably, by switching the valve arrangement 15, a steam reforming reaction in the pre-catalyst vessel 6 is stopped. In this manner, the pre-catalyst 5 in the pre-catalyst vessel 6 can be replaced.

In principle, the degree of degradation of the pre-catalyst 5 can be measured in any manner. A further preferred embodiment of the proposed process and of the proposed installation is characterized in that the measurement of the degree of degradation of the pre-catalyst 5 comprises a measurement of a temperature gradient along a flow path in the pre-catalyst 5. As long as the pre-catalyst 5 is not in fact degraded, the endothermic steam reforming reaction catalysed by it occurs, giving rise to the temperature gradient. If, on the other hand, the pre-catalyst 5 has been degraded, the temperature along the pre-catalyst 5 no longer drops to the same extent or could possibly even rise because of exothermic reactions. Thus, preferably, the degradation threshold is exceeded, and preferably a degradation is confirmed thereby, when the measured temperature gradient falls below a gradient threshold in respect of its maximum amount. In other words, a small temperature gradient indicates the presence of degradation. A degree of degradation of the further pre-catalyst 13 may be measured in an analogous manner.

In principle, the pre-catalyst 5 may have any mass and any volume. Preferably, the pre-catalyst 5 and/or the further pre-catalyst 13 has a smaller mass and/or a smaller volume than the main catalyst 7. In this manner, only a small quantity of pre-catalyst 5 has to be used.

In principle, the methane-containing stream 3 may be fed to any application. In the context of the representation in Figure 2, in accordance with a preferred embodiment of the proposed process and of the proposed installation, the methane-containing stream 3 is fed to a synthesis gas reactor arrangement 16 in order to break down the methane of the methane-containing stream 3 and to obtain a synthesis gas stream 17 with hydrogen and oxides of carbon. Preferably in this case, the stream of synthesis gas 17 has a molar proportion of methane of less than 10%. In particular, the stream of synthesis gas 17 may be substantially free from hydrocarbons.

In accordance with a further preferred embodiment of the proposed process and of the proposed installation, - as also shown in Figure 2 - the carbon-containing energy source stream 1 is fed to a saturation device 18 for enrichment with steam which is operationally upstream of the pre-reformer 2. Preferably, the carbon-containing energy source stream 1 is fed to a heating arrangement 19 which is operationally upstream of the pre-reformer 2 in order to heat the energy source stream 2. In particular, the methane-containing stream 3 is fed to a further heating arrangement 20 which is operationally upstream of the synthesis gas reactor arrangement 16 in order to heat up the methane-containing stream 2.

Patentkrav

1. Fremgangsmåde til afsvovling af en carbonholdig energibærestrøm (1), hvor den carbonholdige energibærestrøm (1) tilføres til en pre-reformer (2) til pre-reforming af energibærestrømmen (1), hvor i pre-reformeren (2) kulbrinter i energibærestrømmen (1) med mindst to carbonatomer via en dampreformering spaltes i metan, hydrogen og carbonoxider til opnåelse af en afsvovlet metanholdig strøm (3), hvor pre-reformeren (2) har en katalysatorindretning (4) til katalysering af dampreformeringen, hvor katalysatorindretningen (4) har en forkatalysator (5) til katalysering af dampreformeringen i en forkatalysatorbeholder (6) og en hovedkatalysator (7) til katalysering af dampreformeringen i en hovedkatalysatorbeholder (8), hvor forkatalysatorbeholderen (6) er anbragt med afstand til hovedkatalysatorbeholderen (8), og hvor energibærestrømmen (1) passerer forkatalysatorbeholderen (6) før hovedkatalysatorbeholderen (8), **kendetegnet ved, at** der måles en degradationsgrad af forkatalysatoren (5), og at, hvis den målte degrationsgrad overskrider en degradationstærskel, forkatalysatorbeholderen (6) isoleres fra energibærestrømmen (1).

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** forkatalysatoren (5) har et bæremateriale og et aktivt metal, hvor det aktive metal omfatter nikkel, kobolt, platin, palladium, iridium, ruthenium og/eller rhodium, foretrukket, at bærematerialet omfatter aluminiumoxid eller jordalkalimetalaluminater, særligt, at det aktive metal har en specifik overflade pr. masseenhed på mindst 15 m^ 2/g.

3. Fremgangsmåde ifølge krav 1 eller 2, **kendetegnet ved, at** hovedkatalysatoren (7) har et aktivt metal, som i det væsentlige svarer til det aktive metal i forkatalysatoren (5), foretrukket, at hovedkatalysatoren har et bæremateriale, som i det væsentlige svarer til bærematerialet i forkatalysatoren (5), særligt, at hovedkatalysatorens (7) materialeegenskaber i det væsentlige svarer til forkatalysatorens (5).

4. Fremgangsmåde ifølge et af kravene 1 til 3, **kendetegnet ved, at** dampreformeringen katalyseret af forkatalysatoren (5) finder sted ved en temperatur mellem 400° C og 550° C, foretrukket, at dampreformeringen katalyseret af hovedkatalysatoren (7) finder sted ved en temperatur, som i det væsentlige svarer til temperaturen på dampreformeringen katalyseret af forkatalysatoren (5).

5. Fremgangsmåde ifølge et af kravene 1 til 4, **kendetegnet ved, at** forkatalysatorbeholderen (6) har et i det væsentlige lukket forreaktionskammer til optag af forkatalysatoren (5), og/eller at hovedkatalysatorbeholderen (8) har et i det væsentlige lukket hovedreaktionskammer til optag af hovedkatalysatoren (7), foretrukket, hvor hovedreaktionskammeret befinder sig med afstand til forreaktionskammeret.

6. Fremgangsmåde ifølge et af kravene 1 til 5, **kendetegnet ved, at** forkatalysatorbeholderen (6) er adskilt fra hovedkatalysatorbeholderen (8) af mindst en væg, foretrukket, at pre-reformeren (2) har en særligt rørlignende ledningsstrækning (12) til at føre energibærestrømmen (1) fra forkatalysatorbeholderen (6) til hovedkatalysatorbeholderen (8).

7. Fremgangsmåde ifølge et af kravene 1 til 6, **kendetegnet ved, at** katalysatorindretningen (4) har en yderligere forkatalysator (13) til katalysering af dampreformeringen i en yderligere forkatalysatorbeholder (14), særligt af pre-reformeren (2), hvilken yderligere forkatalysatorbeholder (14) er anbragt med afstand til forkatalysatorbeholderen (6), og at energibærestrømmen (1) via en omstillelig ventilindretning (15) føres skiftevis gennem forkatalysatorbeholderen (6) og den yderligere forkatalysatorbeholder (14) før hovedkatalysatorbeholderen (7), foretrukket, at den yderligere forkatalysators (13) materialeegenskaber i det væsentlige svarer til forkatalysatorens (5).

8. Fremgangsmåde ifølge et af kravene 1 til 7, **kendetegnet ved, at**, efter isolering af forkatalysatorbeholderen (6) fra energibærestrømmen (1), forkatalysatoren (5) i forkatalysatorbeholderen (6) erstattes af en frisk forkatalysator (5).

9. Fremgangsmåde ifølge krav 8, **kendetegnet ved, at** forkatalysatorbeholderen (6) isoleres fra energibærestrømmen (1), sådan at ved omstilling af ventilindretningen (15) energibærestrømmen (1) føres gennem den yderligere forkatalysatorbeholder (14), foretrukket, at ved omstilling af ventilindretningen (15) en dampreformering i forkatalysatorbeholderen (6) afsluttes.

10. Fremgangsmåde ifølge krav 8 eller 9, **kendetegnet ved, at** målingen af degradationsgraden af forkatalysatoren (5) omfatter en måling af en temperaturgradient langs en strømningssti i forkatalysatoren (5), foretrukket, at degradationstærsklen overskrides, hvis den målte temperaturgradient hvad angår sin maksimale værdi ligger under en gradienttærskel.

11. Fremgangsmåde ifølge et af kravene 1 til 10, **kendetegnet ved, at** forkatalysatoren (5) har en mindre masse og/eller en mindre volumen end hovedkatalysatoren (7).

12. Fremgangsmåde ifølge et af kravene 1 til 11, **kendetegnet ved, at** den metanholdige strøm (3) tilføres til en syntesegasreaktorindretning til spaltning af metanen i den metanholdige strøm (3) og opnåelse af en syntesegasstrøm (17) med hydrogen og carbonoxider.

13. Fremgangsmåde ifølge et af kravene 1 til 12, **kendetegnet ved, at** den carbonholdige energibærestrøm (19) tilføres til en mætningsanordning (18), som procesteknisk er placeret før pre-reformeren (2), til berigelse med vanddamp, foretrukket, at den carbonholdige energibærestrøm (1) tilføres til en varmeindretning (19), som procesteknisk er placeret før pre-reformeren (2), til opvarmning af energibærestrømmen (1), særligt, at den metanholdige strøm (3) tilføres til en yderligere varmeindretning (20), som procesteknisk er placeret før syntesegasreaktorindretningen (16), til opvarmning af den metanholdige strøm (3).

14. Anlæg til afsvovling af en carbonholdig energibærestrøm (1) med en pre-reformer (2) til pre-reforming af den carbonholdige energibærestrøm (1) og til opnåelse af en afsvovlet metanholdig strøm (3), hvor i pre-reformeren (2) kulbrinter i energibærestrømmen (1) med mindst to carbonatomer, via en dampreformering spaltes i metan, hydrogen og carbonoxider, hvor pre-reformeren (2) har en katalysatorindretning (4) til katalysering af dampreformeringen, hvor katalysatorindretningen (4) har en forkatalysator (5) til katalysering af dampreformeringen i en forkatalysatorbeholder (6) i pre-reformeren (2) og en hovedkatalysator (7) til katalysering af dampreformeringen i en hovedkatalysatorbeholder (8) i pre-reformeren (2), hvor forkatalysatorbeholderen (6) er anbragt med afstand til hovedkatalysatorbeholderen (8), og hvor energibærestrømmen (1) passerer forkatalysatorbeholderen (6) før hovedkatalysatorbeholderen (8), **kendetegnet ved, at** der måles en degradationsgrad af forkatalysatoren (5), og at hvis den målte degrationsgrad overskrider en degradationstærskel, forkatalysatorbeholderen (6) isoleres fra energibærestrømmen (1).

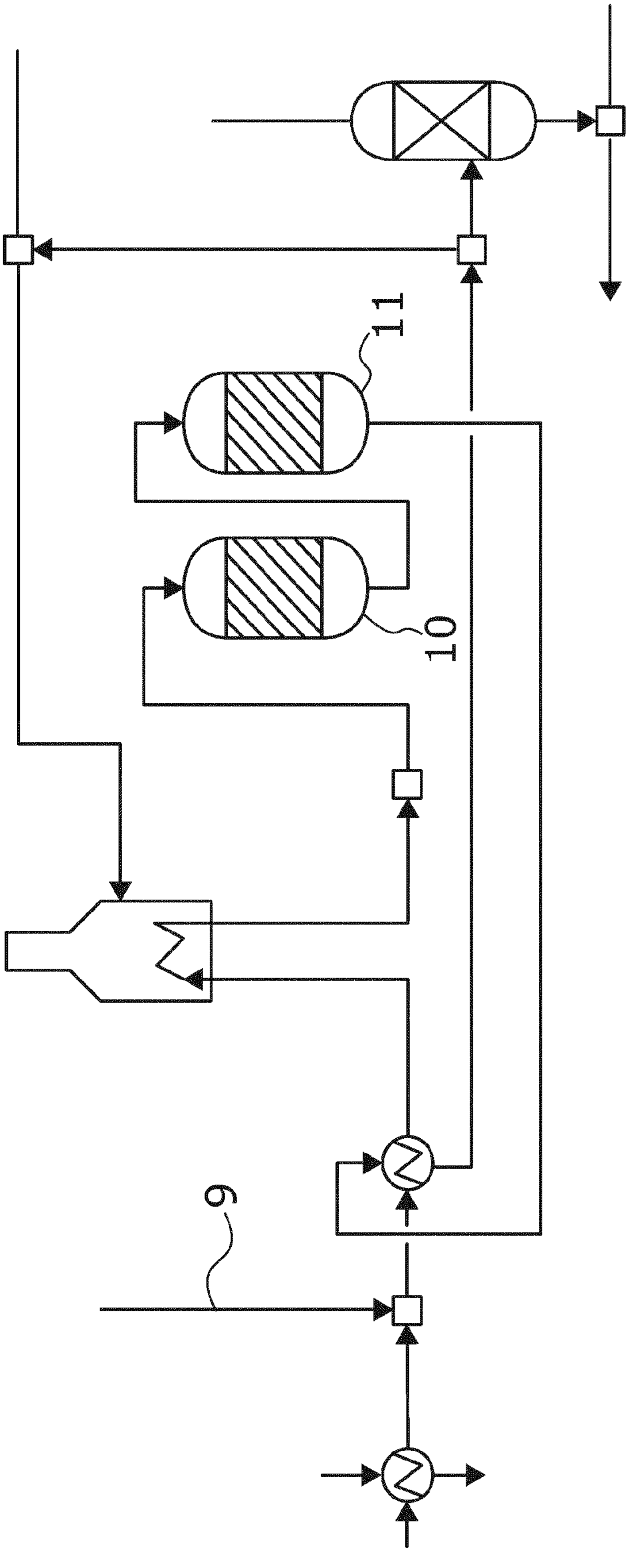

Fig. 1

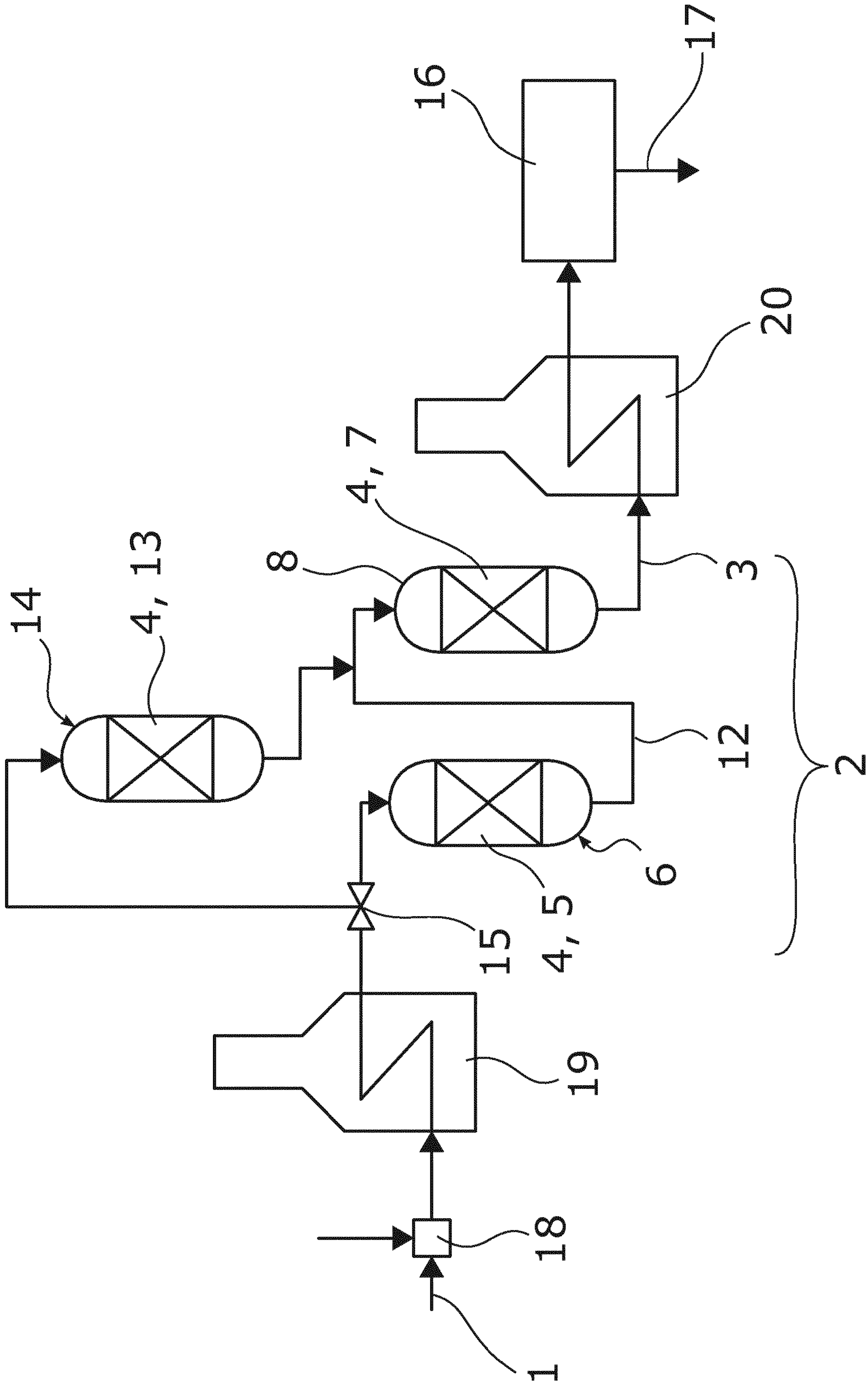

Fig. 2