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(54) **Process and apparatus for producing hydrogen**

(57) A process for producing hydrogen and apparatus therefore comprising the following steps:
(a) converting a hydrocarbonaceous feed (e.g. natural gas) in a reaction zone at elevated temperature and pressure at least partly into a gas mixture containing hydrogen and carbon monoxide,
(b) removing hydrogen (e.g. by means of pressure swing adsorption) from product gas obtained from step (a), and
(c) combusting hydrogen-depleted off gas obtained from step (b) with an oxygen-containing gas in a combustion zone and employing energy thus produced in at least one step of the process (e.g. for convective heating of the reaction zone or gas compression).

The drawing(s) originally filed was (were) informal and the print here reproduced is taken from a later filed formal copy.

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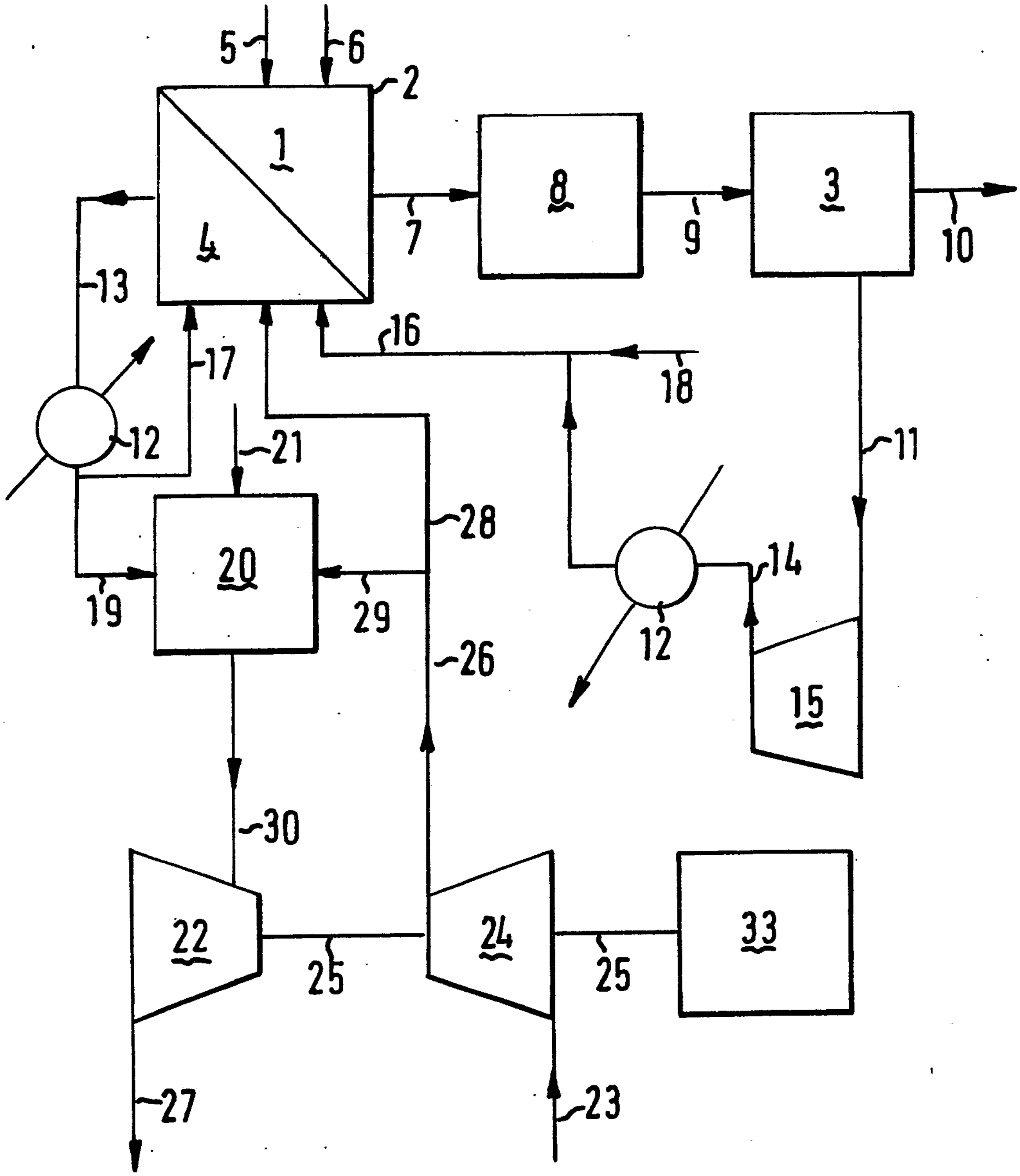
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FIG.1

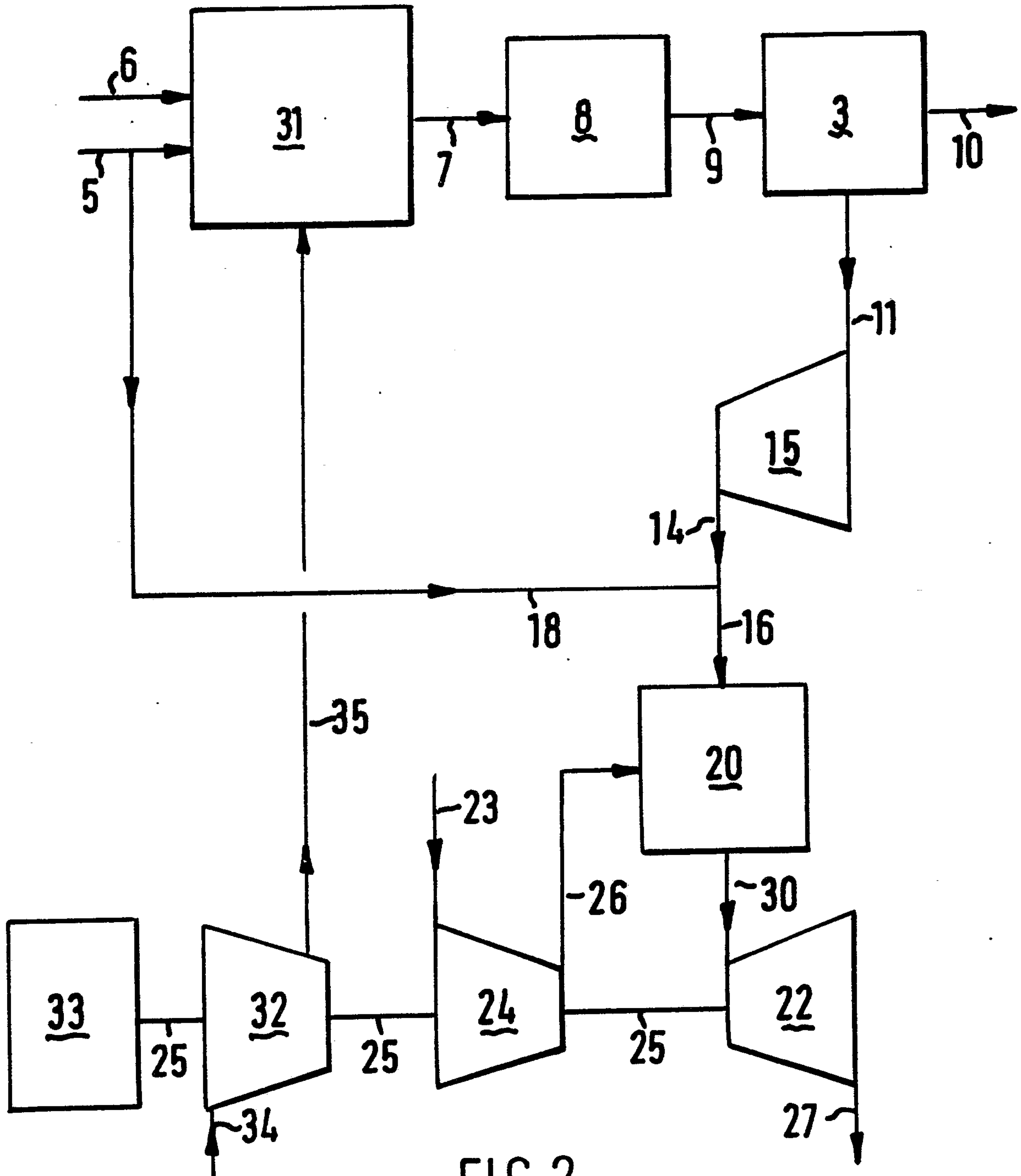

FIG. 2

PROCESS AND APPARATUS FOR PRODUCING HYDROGEN

The invention relates to a process for producing hydrogen and to an apparatus suitable for carrying out such a process.

It is well known to prepare a hydrogen-containing gas such as synthesis gas (which mainly contains hydrogen and carbon monoxide, and in addition carbon dioxide, nitrogen and (unconverted) hydrocarbons and steam) by means of steam reforming or (non) catalytic partial oxidation of a hydrocarbonaceous feed.

It is furthermore known to remove hydrogen from a hydrogen-containing product gas e.g. by means of pressure swing adsorption, thus obtaining substantially pure hydrogen and in addition hydrogen-depleted off gas.

It has now been found that said hydrogen-preparation and -separation steps can be efficiently integrated by employing energy produced by combusting in a combustion zone hydrogen-depleted off gas obtained from the latter step in at least one of the steps of the integrated process itself, e.g. for the compression of oxygen-containing gas required in at least the former step of the process.

The invention therefore relates to a process for producing hydrogen which comprises the following steps:

(a) converting a hydrocarbonaceous feed in a reaction zone at elevated temperature and pressure at least partly into a gas mixture containing hydrogen and carbon monoxide,

(b) removing hydrogen from product gas obtained from step (a), and

(c) combusting hydrogen-depleted off gas obtained from step (b) with an oxygen-containing gas in a combustion zone and employing energy thus produced in at least one step of the process.

The process according to the present invention will be elucidated hereinafter with the use of the Figures in which various preferred options of the process have been incorporated without having the intent of limiting said process to those particular embodiments as depicted in the Figures.

Figure 1 relates to a preferred embodiment of the present process wherein hydrogen-depleted off gas is heat-exchanged with flue gas, before use as fuel gas in a convective reforming zone.

Figure 2 relates to another preferred embodiment of the process according to the invention in which off gas is used as fuel gas in a gas turbine.

Reference numerals relating to similar process steps and/or equipment are the same in the two Figures.

In Figure 1 the essential process steps (a), (b) and (c) are carried out in reforming zone (1) of convective reformer (2), in pressure swing adsorption unit (3), and in combustion zone (4), respectively.

A hydrocarbonaceous feed, preferably containing normally liquid and/or gaseous hydrocarbons, in particular C_1-C_4 hydrocarbons such as those present in natural gas, is introduced via line (5) into reforming zone (1) together with steam introduced via line (6). In zone (1) step (a) of the present process is suitably carried out at a temperature from 600 to 1600 °C and a pressure from 2 to 200 bar. The reforming zone preferably comprises catalyst in order to operate said zone at a relatively low temperature from 600 to 1100 °C and at a pressure from 5-50 bar.

The reactor which contains said reforming zone (1) and optionally combustion zone (4) (which may also be spaced apart from the reforming zone and be located outside the reactor) preferably contains internals in order to improve heat exchange between said zones and ensure optimal use of catalyst, if any.

The reactor internals suitably comprise double concentric tubes with catalyst in the annular space between the tubes. The outer tubes are suitably mounted substantially vertically in a horizontal inlet manifold for hydrocarbon/steam feed distribution. The lower ends of the outer tubes are preferably closed in order to reverse the flow of gas having passed downwardly through the annular catalyst bed. The inner tubes into which the hydrogen-containing product gas is subsequently passed, are suitably connected to a product outlet manifold. Advantageously, the combustion gas (having a temperature of e.g. 900-1200 °C) enters the reforming reactor below or near the lower ends of the tubular reaction zone and leaves the reactor below the horizontal inlet manifold, situated at the relatively cold (e.g. 500-800 °C) upper part of the reactor. When the concentric tubes are mounted in the above-described manner, their hot lower ends can expand freely and thermal expansion in the manifolds is kept to a minimum.

A gas mixture containing hydrogen and carbon monoxide is removed from reforming zone (1) through line (7). In order to produce additional hydrogen, at least part and preferably all of said gas mixture is preferably directed to carbon monoxide conversion zone (8) in which at least part of the carbon monoxide present in the gas mixture is catalytically converted in the presence of steam at the appropriate carbonmonoxide conversion conditions in one or more steps into carbon dioxide. Conversion zone (8) is suitably maintained at a temperature from 180 to 450 °C and a pressure from 2 to 200 bar.

Hydrogen-containing product gas obtained from conversion zone (8) and/or reforming zone (1) is directed via line (9) to pressure swing adsorption unit (3) from which a substantially pure hydrogen gas stream is withdrawn via line (10). Unit (3) preferably comprises a plurality of vessels containing molecular sieve beds which are sequentially in the adsorption-, desorption- and purge-stage. However, it is also possible to substitute a liquid absorption unit (wherein carbon monoxide and/or carbon dioxide are selectively absorbed by a liquid which is subsequently regenerated) or a hydrogen-permeable membrane unit for pressure swing adsorption unit (3) in order to recover hydrogen from the product gas obtained via line (9).

Hydrogen-depleted off gas (which may still contain up to 5 or even up to 30% by volume of hydrogen, depending on the type of adsorption unit and pressure employed) obtained from unit (3) is preferably directed via line (11) to compressor (15) and subsequently via line (14) to heat exchanger (12) wherein heat is exchanged with the effluent gas stream (13) from combustion zone (4) which gas stream generally has a higher temperature (e.g. from 150 to 1000 °C) than the off gas. Accordingly, the energy efficiency of the process according to the invention is substantially improved, thus enabling optimal use of the hydrogen-depleted off-gas in one or more process steps.

The heat exchanged off-gas is directed via line (16) to combustion zone (4). As the energy-content of the off-gas is in many cases not sufficient to employ said gas as the only fuel source for a combustion zone, additional fuel is preferably provided via line (18).

In a preferred embodiment of the process according to the invention as depicted in Figure 1 the combustion zone (4) as applied in step (c) provides thermal energy for the reforming reaction zone (1) of step (a) by means of convective heat transfer. A main advantage of such an arrangement is that the reaction zone will as a result be heated substantially uniformly instead of risking local overheating by a number of burners located in the reaction zone, as in previous reforming processes.

Effluent gas from combustion zone (4) applied in steps (a) and (c) as discussed hereinbefore is suitably (after heat exchange) directed via line (19) to a separate combustion zone (20) to be used as moderator gas together with fuel gas supplied via line (21). Optionally, part of the heat-exchanged effluent gas is recycled via line (17) to combustion zone (4). Effluent gas emanating from the latter combustion zone (20) is preferably directed via line (30) to turbo-expander (22) wherein the gas is expanded to provide mechanical energy to compress oxygen-containing gas (e.g. air) supplied via line (23) to compressor (24). In some cases sufficient oxygen is present in the expanded effluent gas obtained via line (27) from turbo-expander (22) to enable the use of said gas as oxygen-containing gas for the combustion zone (not depicted in Figure 1).

Turbo-expander (22), compressor (24) and generator (33) are preferably coupled (e.g. by means of axis (25)) and optionally combined with one or more other compressors (15).

Compressed oxygen-containing gas (e.g. the gas provided via line (26)) is preferably employed in at least one of the steps (a) and (c) of the present process, in particular in combustion zone (4) (via line (28)) and via line (29) in combustion zone (20). The use of compressed, and thereby preheated, oxygen-containing gas is preferred in the process according to the invention in order to improve the thermal efficiency of the combustion zone(s) and thus of the entire process.

The process and apparatus which are schematically depicted in Figure 2 will be described hereinafter only in so far as features different from those depicted in Figure 1 are included.

A significant difference is the use of a catalytic or non-catalytic partial oxidation zone (31) in the embodiment depicted in Figure 2. Such a zone is generally operated at a temperature from 600 to 1600 °C and preferably at a temperature from 1000 to 1500 °C, whereas the pressure in said zone is generally from 1 to 250 bar and preferably from 10 to 100 bar. Zone (31) constitutes the reaction zone employed in step (a) as well as a combustion zone as employed in step (c) of the process according to the invention.

A further difference with the process and apparatus as depicted in Figure 1 is that in Figure 2 the hydrogen-depleted off gas obtained from hydrogen separation unit (3) through line (11) is used as fuel gas in combustion zone (20) of a gas turbine instead of in a combustion zone (4) of a reforming apparatus. Expanded effluent gas from turbo-expander (22) is optionally at least partly used in a combustion zone (not depicted in Figure 2). Oxygen-containing gas is advantageously provided by compressor (24) via line (26) to combustion zone (20). Substantially pure oxygen gas is supplied via line (34) to compressor (32) and subsequently directed via line (35) to partial oxidation zone (31).

The invention further relates to an apparatus suitable for producing hydrogen which comprises a reactor having feed inlet means and product outlet means communicating with heat exchanger reactor internals, a combustor which is in heat exchange relation with said internals, a pressure swing adsorption unit communicating with the product outlet means and having separate hydrogen- and off-gas outlet means, and a gasturbine which is in communication with the combustor and/or the off-gas outlet means.

The process according to the invention is illustrated by way of the following Example.

EXAMPLE

The process substantially as depicted in Figure 2 is carried out by introducing 872 tons/day of feed gas (containing substantially methane) at a temperature of 50 °C and a pressure of 51 bar in catalytic partial oxidation zone (31) and reacting the feed gas with 2490 tons/day of substantially pure oxygen gas introduced via line (35) at a temperature of 100 °C and a pressure of 48 bar.

The hydrogen-containing synthesis gas obtained via line (7) at 380 °C and 30 bar is subjected in carbon monoxide conversion zone (8) to a catalytic steam shift together with steam having a temperature of 380 °C and a pressure of 61 bar. 2160 tons/day of mainly hydrogen- and carbon dioxide-containing product gas from zone (8) is led to Pressure Swing Adsorption unit (3) at a temperature of 40 °C and a pressure of 26 bar; from unit (3) 200 tons/day of substantially pure hydrogen is obtained at 40 °C and 25 bar in addition to 1960 tons/day offgas containing carbon dioxide and hydrogen as major components at 40 °C and 1.6 bar. Said offgas is led via line (11) to compressor (15) from which an outlet gas stream (14) is obtained at a temperature of 310 °C and a pressure of 17 bar and combined with 344 tons/day of methane-containing gas at a pressure of 51 bar and a temperature of 50 °C having a similar composition as the feed gas to zone (31).

The combined gas stream (16) is directed to a gas turbine comprising combustion zone (20), compressor (24) and turbo expander (22). In said gas turbine 76 Megawatt electric power is generated by generator (33) of which 18 Megawatt is required for operating compressors (15) and (32), leaving 58 Megawatt nett power export, excluding additional electricity generation by means of waste heat recovery from the expanded effluent gas stream (27).

CLAIMS

1. A process for producing hydrogen which comprises the following steps:

(a) converting a hydrocarbonaceous feed in a reaction zone at elevated temperature and pressure at least partly into a gas mixture containing hydrogen and carbon monoxide,

(b) removing hydrogen from product gas obtained from step (a), and

(c) combusting hydrogen-depleted off gas obtained from step (b) with an oxygen-containing gas in a combustion zone and employing energy thus produced in at least one step of the process.

2. A process according to claim 1 wherein energy produced in step (c) is employed to compress oxygen-containing gas.

3. A process according to claim 2 wherein compressed oxygen-containing gas is employed in at least one of steps (a) and (c).

4. A process according to any one of the preceding claims wherein step (a) is carried out in the presence of steam at a temperature from 600 to 1600 °C and a pressure from 2 to 200 bar.

5. A process according to any one of the preceding claims wherein at least part of the carbon monoxide present in the gas mixture obtained from step (a) is catalytically converted in the presence of steam at carbon monoxide conversion conditions into carbon dioxide and hydrogen.

6. A process according to any one of the preceding claims wherein step b) is carried out by passing hydrogen-containing gas to a pressure swing adsorption zone.

7. A process according to claim 6 wherein hydrogen-depleted gas obtained from the pressure swing adsorption zone is heat exchanged with effluent gas from a combustion zone.

8. A process according to any one of the preceding claims wherein effluent gas from the combustion zone applied in step (c) is used as moderator gas for the combustion zone employed in step (a).

9. A process according to claim 1 wherein the combustion zone applied in step (c) provides thermal energy for the reaction zone of step (a) by means of convective heat transfer.

10. A process according to claim 9 wherein effluent gas from the combustion zone applied in steps (a) and (c) is used as moderator gas for a different combustion zone and effluent gas emanating from the latter zone is expanded to provide mechanical energy.

11. An apparatus suitable for producing hydrogen which comprises a reactor having feed inlet means and product outlet means communicating with heat exchanger reactor internals, a combustor which is in heat exchange relation with said internals, a pressure swing adsorption unit communicating with the product outlet means and having separate hydrogen- and off-gas outlet means, and a gasturbine which is in communication with the combustor and/or the off-gas outlet means.

12. A process for producing hydrogen according to claim 1 substantially as hereinbefore described with reference to the accompanying drawings.

13. An apparatus according to claim 11 substantially as hereinbefore described with reference to the accompanying drawings.

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