



(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2005/0257566 A1**

**De Sousa** (43) **Pub. Date: Nov. 24, 2005**

(54) **METHOD AND UNIT FOR THE PRODUCTION OF HYDROGEN FROM A HYDROGEN-RICH FEED GAS**

(52) **U.S. Cl. .... 62/607**

(57) **ABSTRACT**

(76) **Inventor: Guillaume De Sousa, Issy les Moulineaux (FR)**

The invention relates to a method and unit for the production of hydrogen from a hydrogen-rich feed gas. According to the invention, N adsorbers are used and, at intervals, each of said adsorbers follows a cycle comprising: an adsorption phase at a high cycle pressure (PH); and a regeneration phase, consisting of a depressurization step, an elution step at a low cycle pressure (PB) and a repressurization step. During the depressurization step: partial pressure balancing is performed between an adsorber at the start of the cocurrent depressurization and an adsorber in the repressurization step until the pressure of the adsorber at the start of the cocurrent depressurization reaches a partial balancing pressure ( $P_{\text{partial}}$ ); and the flow exiting the adsorber undergoing cocurrent depressurization, which has a pressure lower than the partial balancing pressure ( $P_{\text{partial}}$ ), is sent to the adsorbers in the elution step. In addition, at least one part of the flows exiting the adsorbers in the regeneration phase is recycled by compressing said part until the high cycle pressure (PH) is reached and supplying the adsorbers in adsorption with said recycled part. The invention is suitable for purifying hydrogen and for recovering hydrogen from a low-pressure fuel network.

Correspondence Address:  
**Air Liquide**  
**Intellectual Property Department**  
**Suite 1800**  
**2700 Post Oak Boulevard**  
**Houston, TX 77056 (US)**

(21) **Appl. No.: 10/504,810**

(22) **PCT Filed: Feb. 7, 2003**

(86) **PCT No.: PCT/FR03/00400**

(30) **Foreign Application Priority Data**

Feb. 15, 2002 (FR)..... 02/01914

**Publication Classification**

(51) **Int. Cl.<sup>7</sup> ..... F25J 1/00**

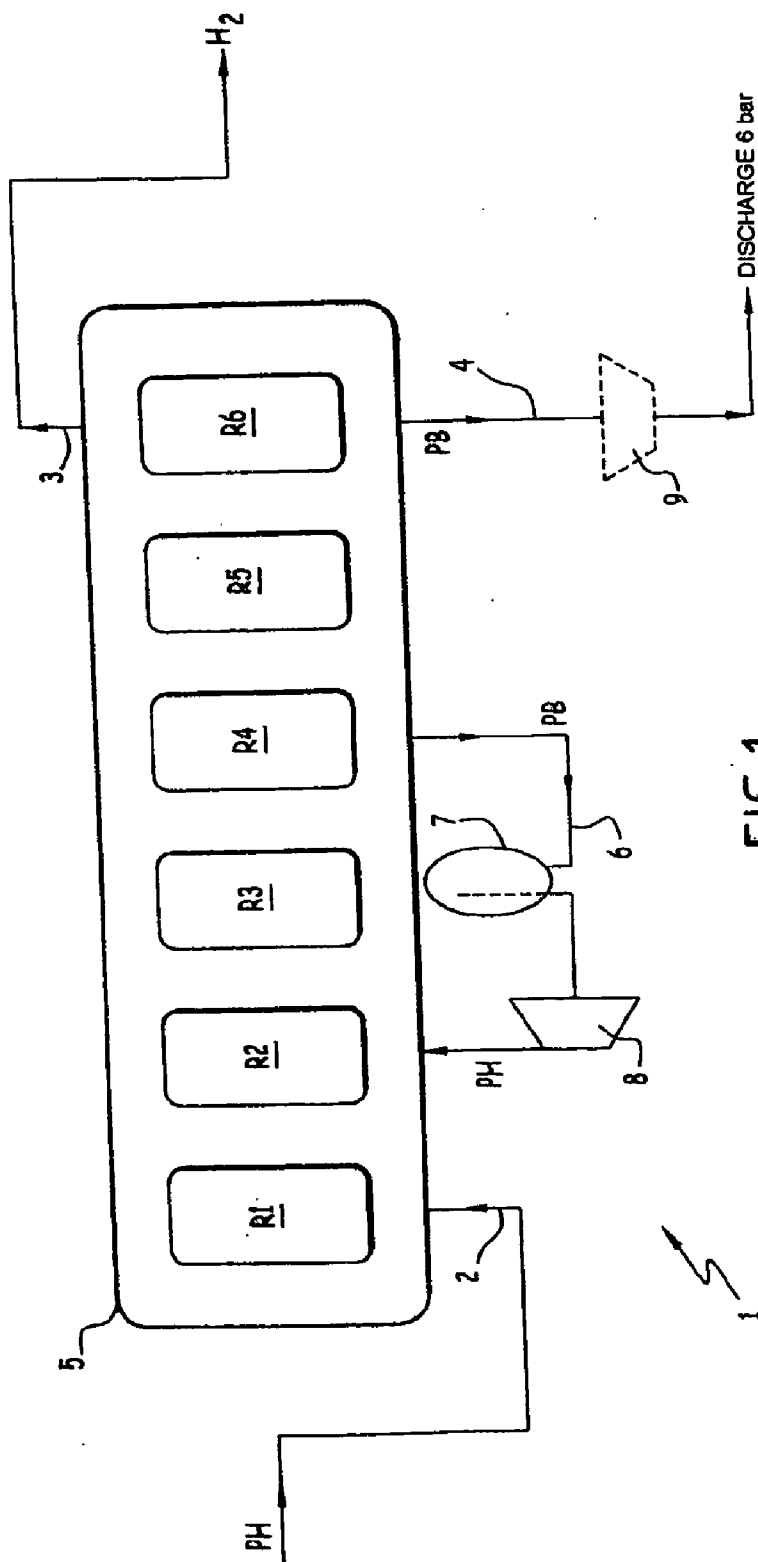
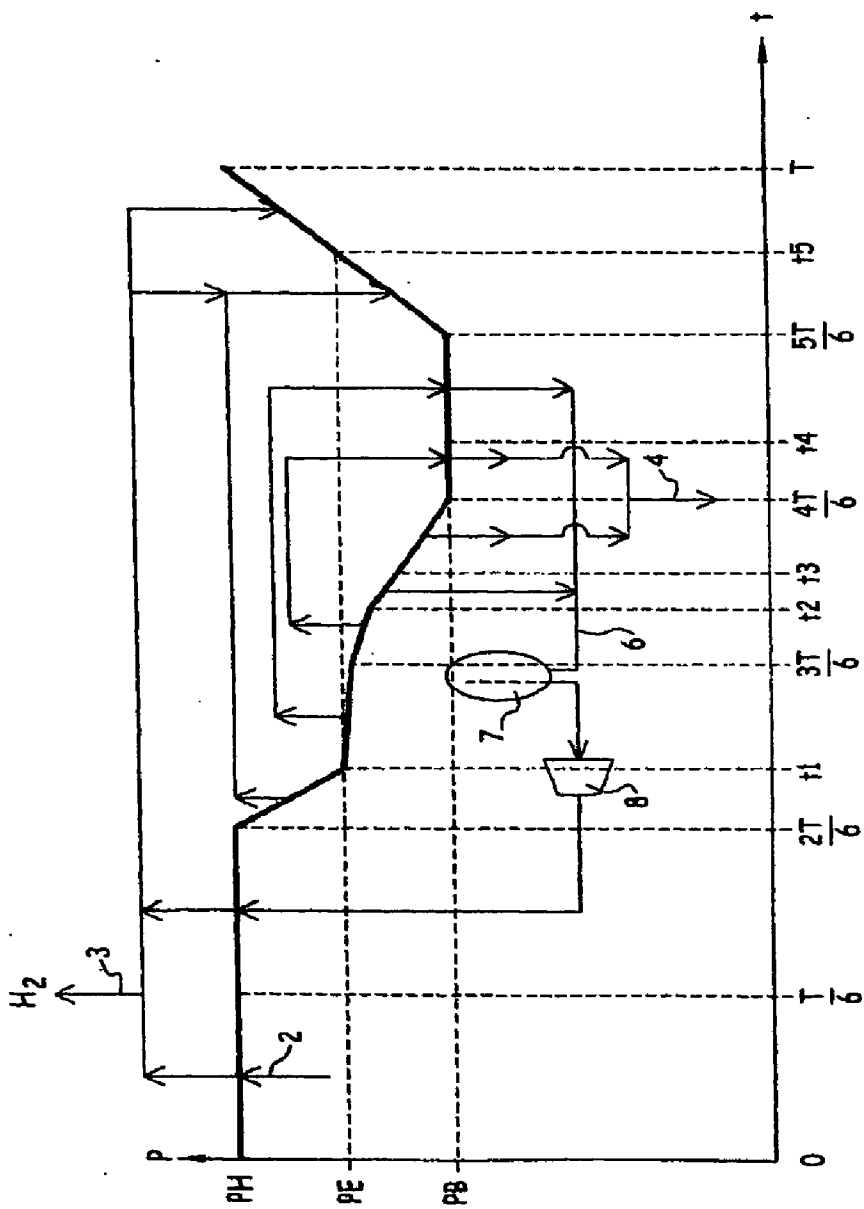


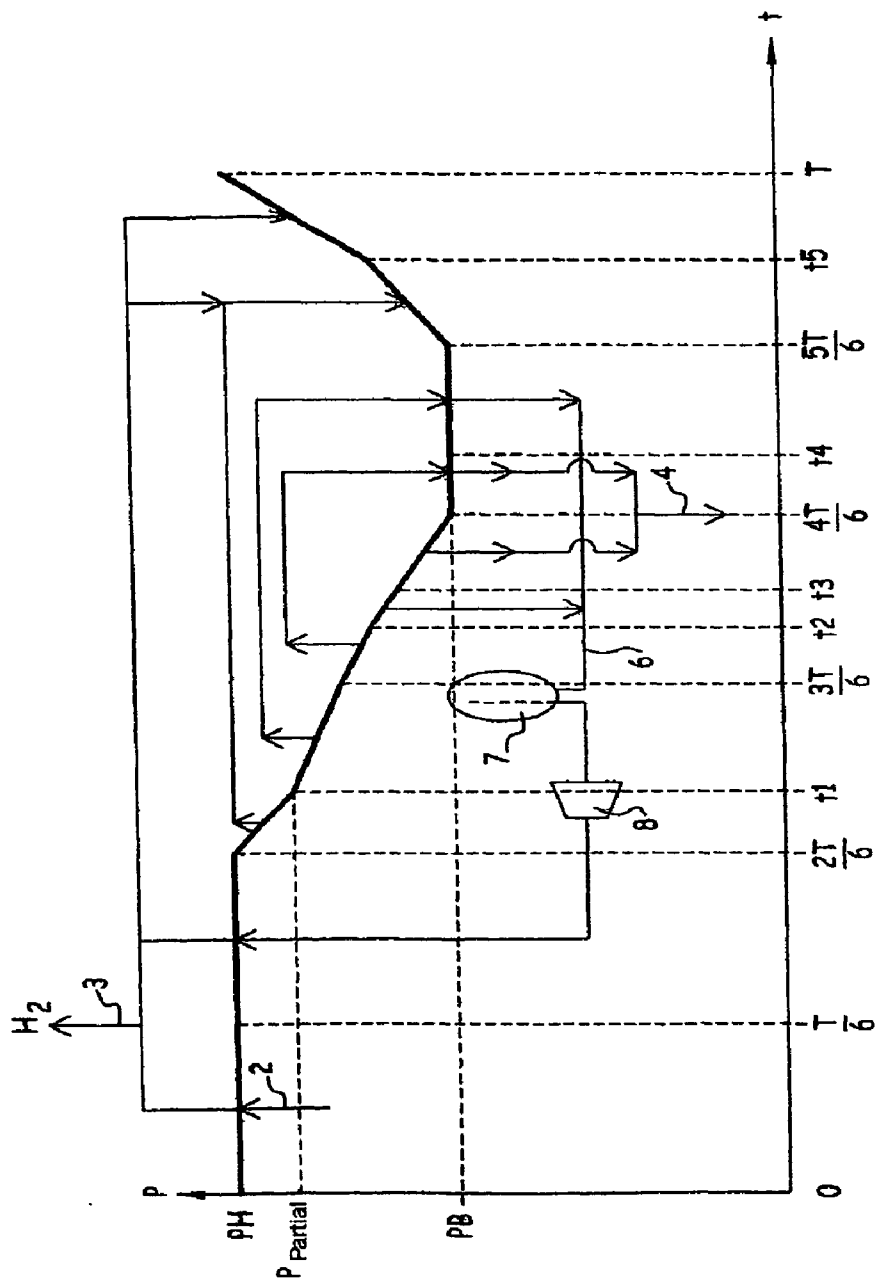
FIG. 1

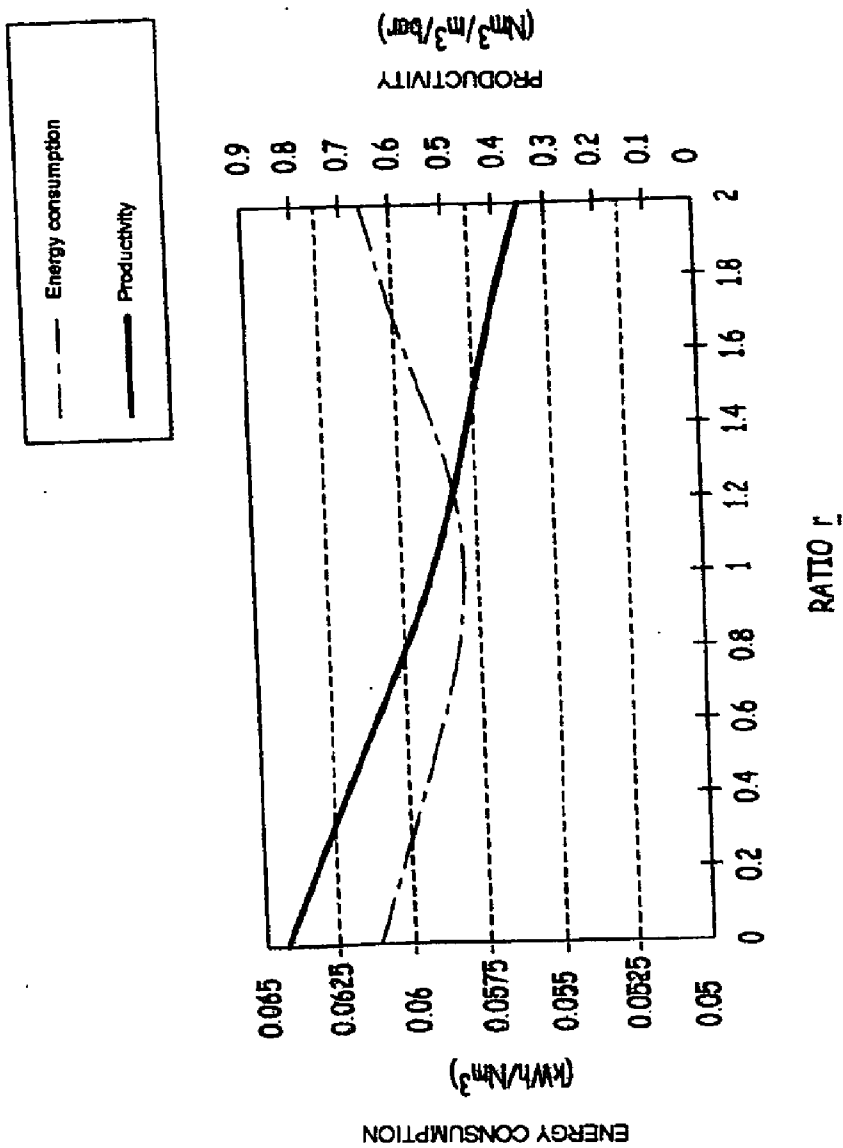


**FIG.2**

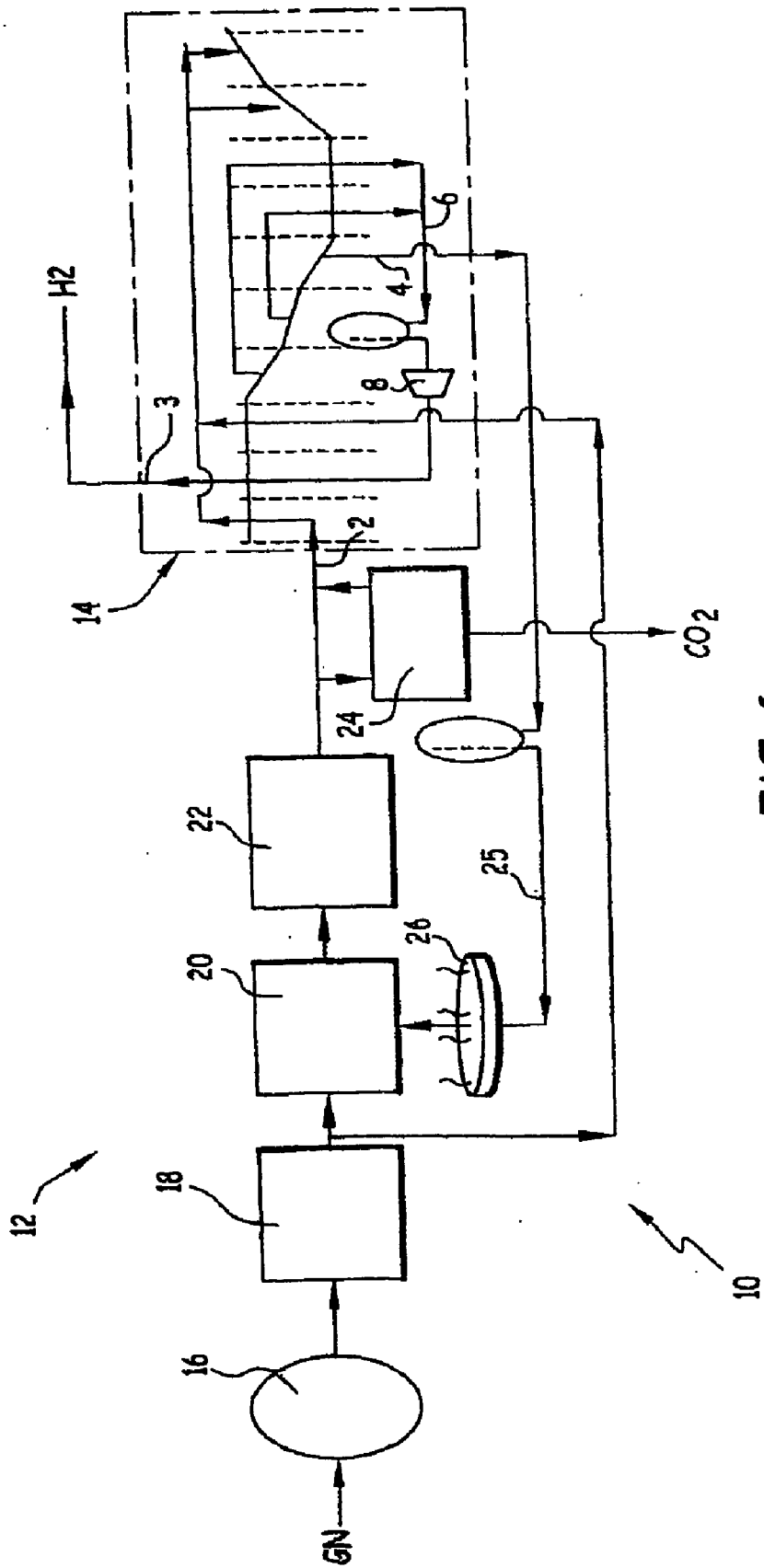
	I		II		III			IV	IV'
	613	613	613R	612R	622R	621R	620R	620R2	620R2
Name of cycle	613	613	613R	612R	622R	621R	620R	620R2	620R2
Value of low pressure PB (bar)	1.6	6	6	6	6	6	6	6	6
% H <sub>2</sub> produced	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5
H <sub>2</sub> yield	89%	64%	89%	89%	89%	89%	89%	120%	120%
Power (KW)	31	0	90.9	84.1	60.7	58	60.7	110.4	89.4
m <sup>3</sup> of adsorbent	152	7.12	9.73	7.22	5.45	3.55	2.31	3.55	2.54
Productivity (Nm <sup>3</sup> /m <sup>3</sup> /bar)	1.27	0.27	0.2	0.27	0.35	0.54	0.85	0.54	0.75
Energy consumption	0.031	0	0.091	0.084	0.061	0.058	0.061	0.110	0.089

**FIG.3**

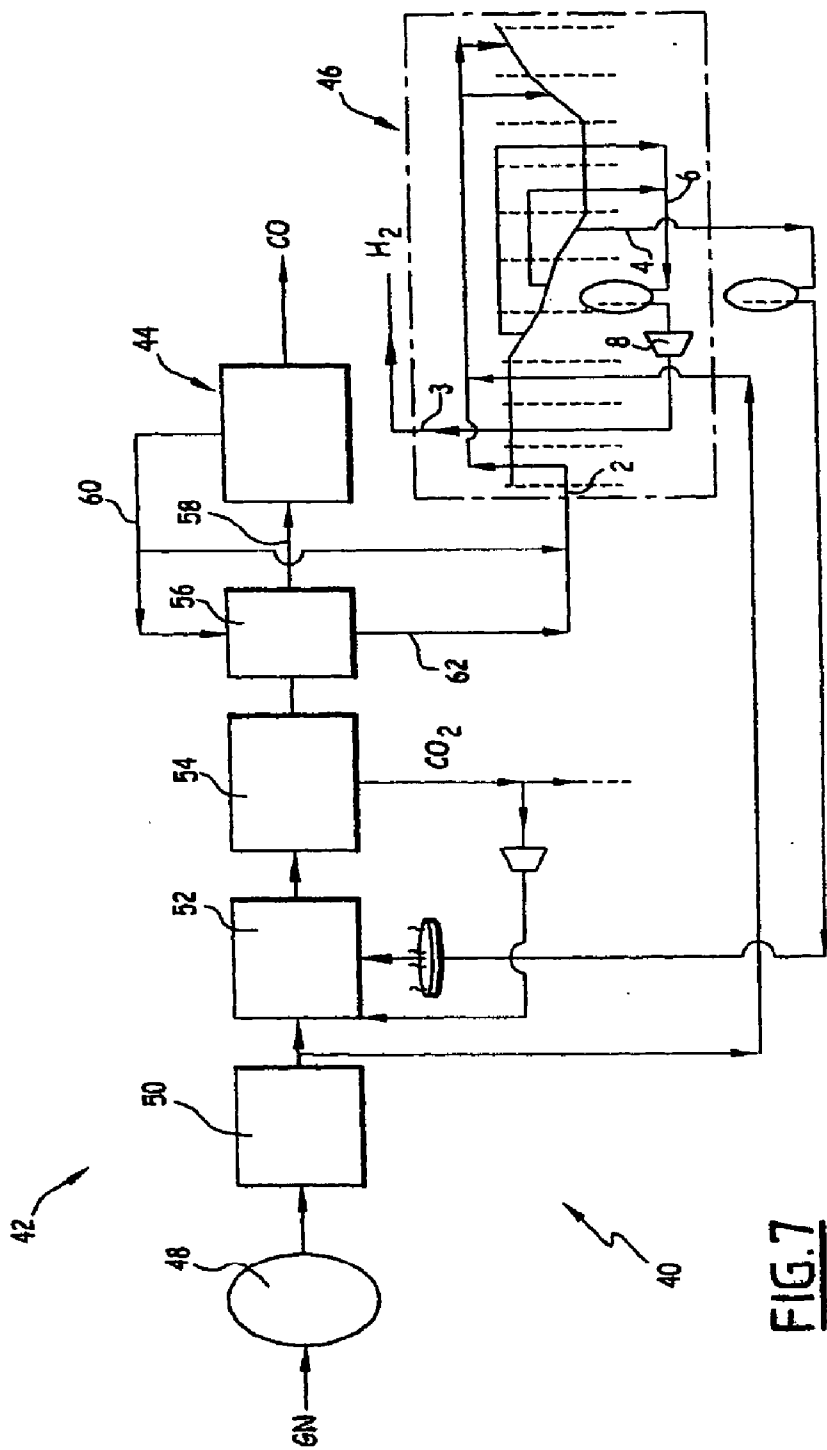




**FIG.5**

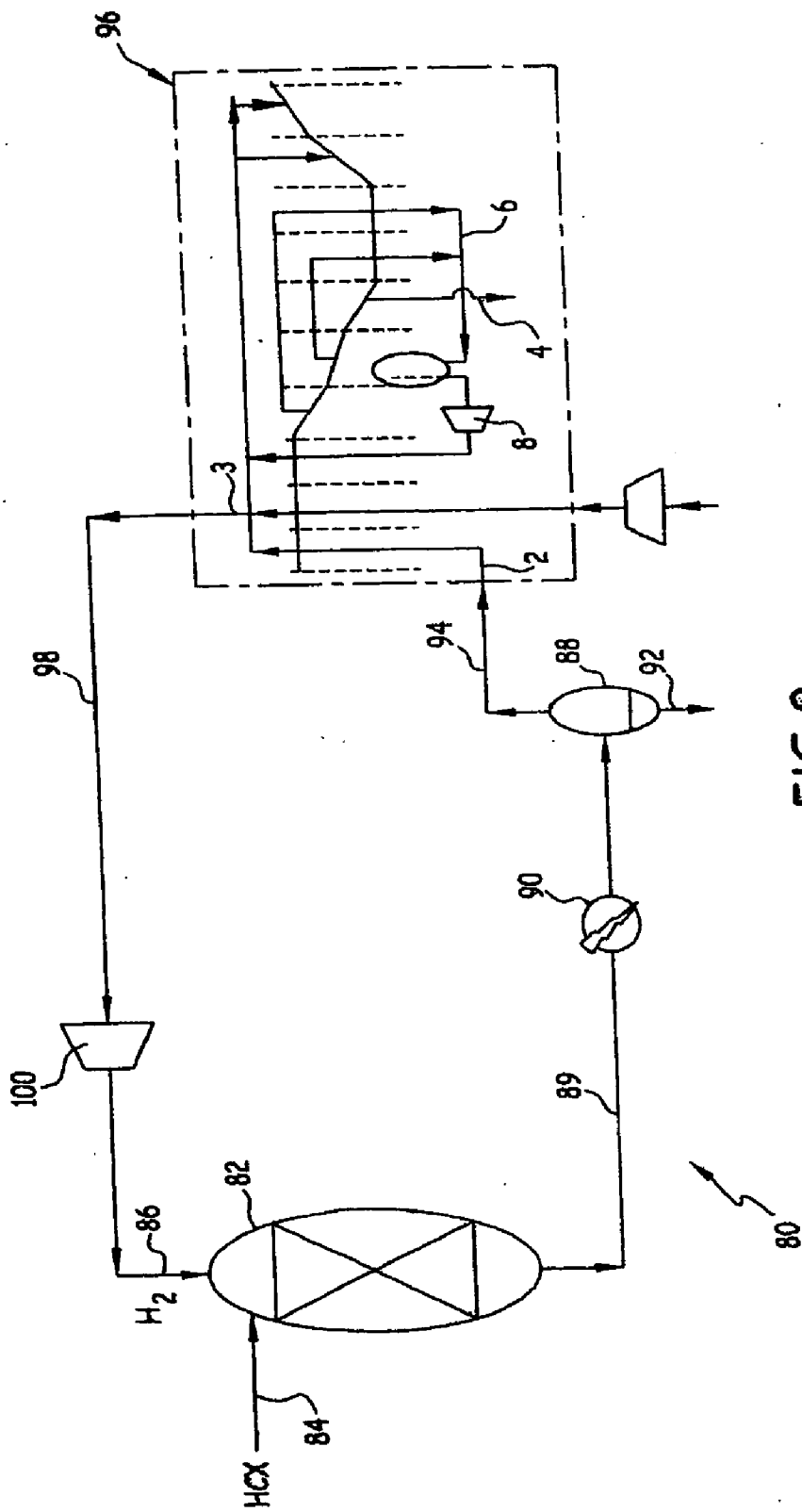


**FIG. 6**

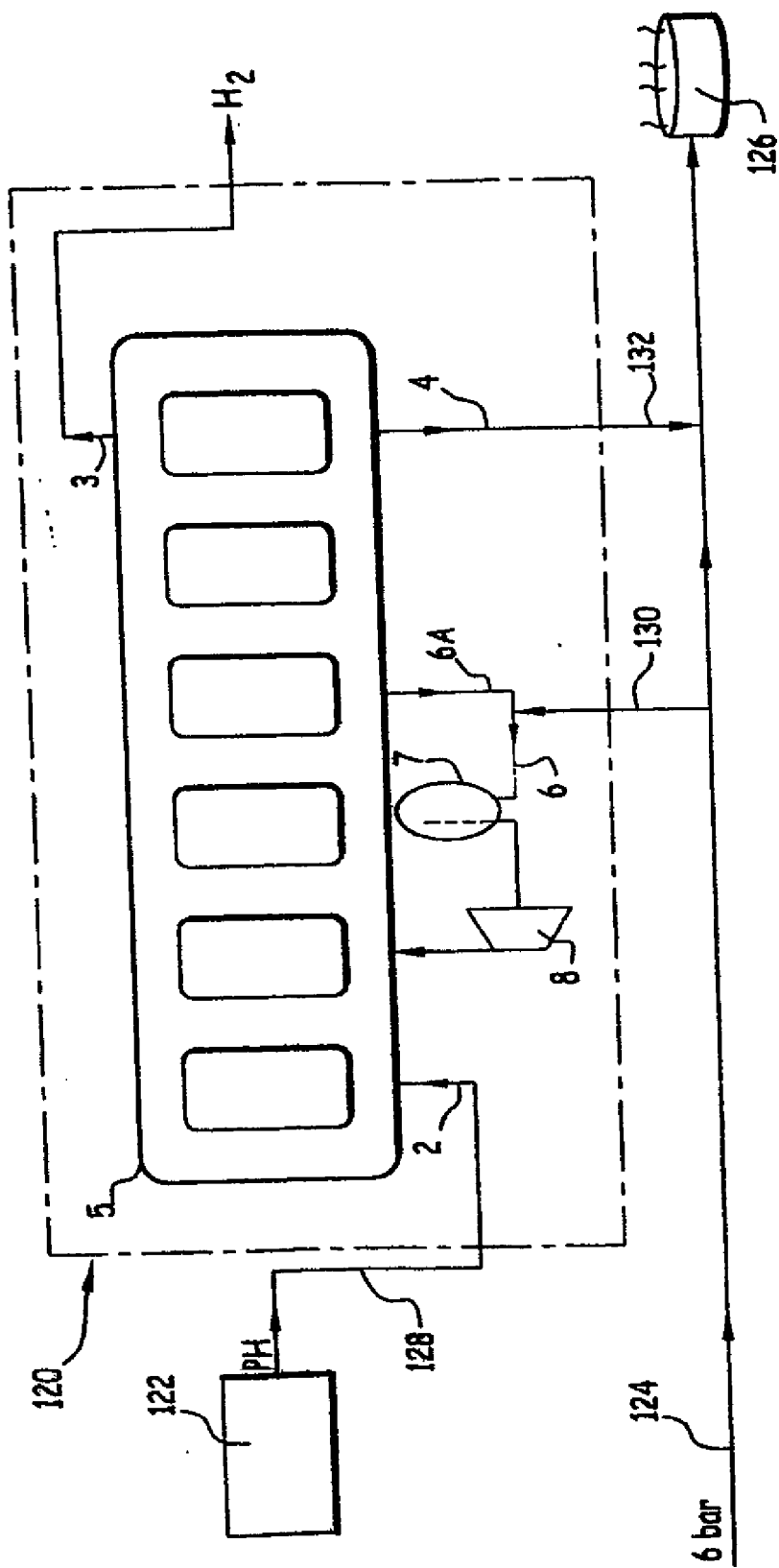


**FIG. 7**

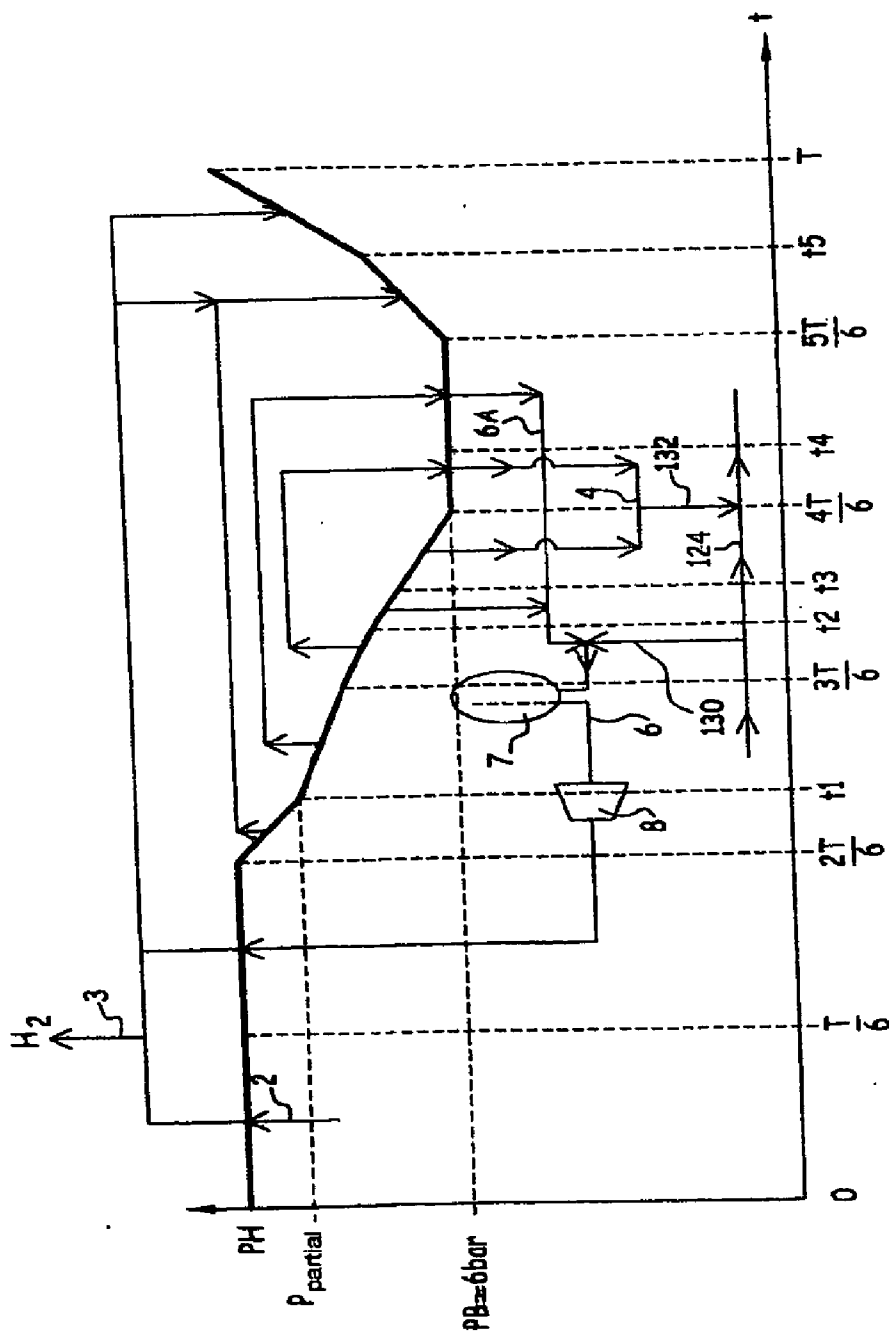




**FIG. 8**



**FIG. 9**



**FIG.10**

### METHOD AND UNIT FOR THE PRODUCTION OF HYDROGEN FROM A HYDROGEN-RICH FEED GAS

[0001] The present invention concerns a method for producing hydrogen from a hydrogen-rich feed mixture.

[0002] At the present time the recovery of hydrogen from such a feed mixture is generally achieved by means of an adsorption treatment unit of the PSA (Pressure Swing Adsorption) type. Such a unit employs a method in which at least one adsorber is used which follows a cycle where there are, successively, an adsorption phase substantially at a high cycle pressure and a regeneration phase comprising at least one depressurization step to a low cycle pressure and a repressurization step to the high cycle pressure.

[0003] Pressures will be subsequently indicated in bar absolute.

[0004] According to the composition of the feed gas, a conventional PSA unit has the ability to produce a flow of substantially pure hydrogen (with a hydrogen content above 95%) at a high pressure, but exhibits the defect of being limited to a hydrogen yield of around 90%, even in the case of a feed mixture that is very rich in hydrogen (for example with a hydrogen content between 90 and 98%).

[0005] In the case of a feed gas coming from a steam reforming unit, the hydrogen yield reached by a PSA unit is generally of the order of 90%. In order to exceed such a yield it is necessary to bring the hydrogen content in waste gases discharged from the PSA unit to below 20%, which at the present time only seems achievable by the use of selective adsorbents that are better suited to the feed gas to be treated and that are therefore costly.

[0006] Moreover, an improved hydrogen recovery method is known from document EP-A-1 023 934 that consists of recycling, within a PSA unit, a variable part of the waste gases coming from the PSA unit, into the feed gas. More precisely, in this document, the regeneration phase commences with a first cocurrent depressurization substep by completely balancing the pressure with an adsorber during repressurization, followed by a second cocurrent depressurization substep during which the gas coming from the adsorber in the second cocurrent depressurization substep is used as a gas for eluting the adsorbent material of another adsorber. The flow leaving this last adsorber during elution is then compressed to the high cycle pressure in order to be mixed with the gas feeding the PSA unit.

[0007] Such an arrangement for the operating cycle of a PSA unit ensures recycling of part of the waste gases that are hydrogen-rich to a varying degree. However, such recycling can prove to be detrimental to the productivity of the PSA unit.

[0008] The object of the present invention is to provide a method of the type described above, that improves the recovery of hydrogen from a given feed gas, while keeping constant, or even improving, the productivity of the PSA unit implementing this method and/or while reducing the overall investment in this unit.

[0009] To this end, the invention concerns a method for producing hydrogen from a main hydrogen-rich feed mixture in which N adsorbers are used, with N being greater than or equal to one, each following with a time lag a cycle

where there are, successively, an adsorption phase substantially at a high cycle pressure and a regeneration phase, this regeneration phase comprising a depressurization step to a low cycle pressure including a cocurrent depressurization substep, an elution step at the low cycle pressure, and a repressurization step to the high cycle pressure, wherein all of the flow or flows leaving the adsorber or adsorbers during cocurrent depressurization are sent to the adsorber or adsorbers during the elution step, and wherein at least part of the flow or flows leaving the adsorber or adsorbers in the regeneration phase is or are recycled, by compressing said recycled part to the high cycle pressure and by feeding the adsorber or adsorbers in the adsorption phase with said recycled part.

[0010] The invention also concerns a method for the production of hydrogen from a main hydrogen-rich feed mixture, wherein N adsorbers are used, with N being greater than or equal to one, each following with a time lag a cycle where there are, successively, an adsorption phase substantially at a high cycle pressure and a regeneration phase, this regeneration phase comprising a depressurization substep to a low cycle pressure including a cocurrent depressurization substep, an elution step at the low cycle pressure, and a repressurization step to the high cycle pressure wherein, during the depressurization step, a partial balancing of the pressures is carried out between at least one adsorber at the start of cocurrent depressurization and at least one adsorber in the repressurization step, until the pressure of said adsorber at the start of cocurrent depressurization is brought to a partial balancing pressure, strictly below the high cycle pressure, and the flow or flows leaving the adsorber or adsorbers in cocurrent depressurization of which the pressure is below said partial balancing pressure is or are sent to the adsorber or adsorbers in the elution step, and wherein at least part of the flow or flows leaving the adsorber or adsorbers in the regeneration phase is or are recycled, by compressing said recycled part to the high cycle pressure and by feeding the adsorber or adsorbers in the adsorption phase with said recycled part.

[0011] According to other features of these methods, taken in isolation or according to all technically possible combinations:

[0012] during the adsorption phase, there are, successively, a step, substantially at the high cycle pressure, for treating by adsorption the main feed mixture and a step, substantially at the same high cycle pressure, for treating by adsorption the compressed recycled part of the flow or flows leaving the adsorber or adsorbers during the regeneration phase;

[0013] the depressurization step includes, after the cocurrent depressurization substep, a countercurrent depressurization substep and the flow or flows leaving the adsorber or adsorbers at the start of the countercurrent depressurization substep is or are at least partially recycled;

[0014] the flow or flows leaving the adsorber or adsorbers at the end of the elution step is or are at least partially recycled;

[0015] the flow or flows leaving the adsorber or adsorbers in countercurrent depressurization during the first third of the countercurrent depressurization

substep, and/or the flow or flows leaving the adsorber or adsorbers in elution during the last two thirds of the elution step is or are at least partially recycled;

[0016] the adsorption phase comprises, after the step for treating the feed mixture, a step at the high cycle pressure, for the treatment by adsorption of at least one supplementary feed gas with a hydrogen content lower than that of said feed mixture, the step for treating said supplementary gas being placed after the step for treating the recycled part of the flow or flows leaving the adsorber or adsorbers in the regeneration phase when the hydrogen content of said supplementary gas is below that of said recycled part, or placed before the step for treating the second feed gas when the hydrogen content of said supplementary gas is above that of said recycled part; and

[0017] a fuel gas with a hydrogen content below that of the feed mixture is mixed with the recycled part of the flow or flows leaving the adsorber or adsorbers in the regeneration phase.

[0018] The invention also concerns a unit for producing hydrogen from a main hydrogen-rich mixture, which comprises N adsorbers, with N being greater than or equal to one, each following with a time lag a cycle where there are, successively, an adsorption phase substantially at a high cycle pressure and a regeneration phase, this regeneration phase comprising a depressurization step to a low cycle pressure, including a countercurrent depressurization substep, an elution step at the low cycle pressure, and a repressurization step to the high cycle pressure, said unit being associated with a fuel gas network, this unit including a line for recycling at least one of the flows leaving the adsorber or adsorbers in the regeneration phase, provided with a recycling compressor, and a branch adapted so as to convey part of the fuel gas from the fuel gas network to said recycling line.

[0019] The invention will be better understood on reading the following description, given solely by way of example with reference to the drawings in which:

[0020] FIG. 1 is a schematic view of a PSA unit;

[0021] FIG. 2 is a diagram of an operating cycle of the unit of FIG. 1 according to one aspect of the invention;

[0022] FIG. 3 is a table of data corresponding to the performance of units for producing hydrogen according to the prior art and according to the invention;

[0023] FIG. 4 is an operational diagram similar to that of FIG. 2, of a variant of the method according to the invention;

[0024] FIG. 5 is a diagram illustrating the influence of a parameter of the cycle of FIG. 4 on the energy consumption and productivity of a PSA unit for performing the cycle of FIG. 4;

[0025] FIG. 6 is a schematic view of an installation for producing hydrogen, including a unit for performing a cycle according to the invention;

[0026] FIG. 7 is a schematic view of an installation for the combined production of hydrogen and carbon monoxide, including a unit for performing a cycle according to the invention;

[0027] FIG. 8 is a schematic view of a hydrocarbon hydrodesulfuration installation, including a unit for the production of hydrogen for performing a cycle according to the invention;

[0028] FIG. 9 is a similar view to FIG. 1, of a variant of the unit according to the invention; and

[0029] FIG. 10 is a diagram of the operating cycle of the unit of FIG. 9 with conveyance of a secondary low pressure feed.

[0030] In FIG. 1, a unit 1 is shown for producing hydrogen from a hydrogen-rich gas, for example installed in an oil refinery. As an example, this feed gas contains 75% by volume of hydrogen and impurities, namely 11% methane, 7% ethane, 4% propane, 2.9% butane and 0.1% hydrogen sulfide ( $H_2S$ ). Such a feed gas comes from a catalytic reforming unit and is available at a pressure of around 26 bar. Various examples of types of this gas will be expanded on later on, in particular with regard to FIGS. 6 to 8.

[0031] Unit 1 is adapted so as to produce, from the feed gas led through a line 2, a flow of high-purity hydrogen (with a hydrogen content above 99% by volume) via an output line 3, while discharging therefrom a flow of waste gas through a discharge line 4 designed to be connected to an evacuation network at around 6 bar, at present installed in oil refineries.

[0032] Unit 1 includes an adsorption purification apparatus 5, provided with a recycling line 6. This recycling line is provided, from upstream to downstream, with a mixing tank 7 and a compression apparatus 8, for example a compressor.

[0033] Referring to the prior art, the unit 1 includes an optional compressor 9, drawn in dotted lines, on the waste line 4. This compressor 9 is typically dedicated to bringing the flow through the line 4 to the pressure of around 6 bar in the evacuation network, if this is at an insufficient pressure. One of the features of the invention is to dispense with this compressor 9, with compressor 8 in preference, as will be explained below.

[0034] The purification apparatus 5 comprises six adsorbers R1 to R6, each containing an adsorbent material adapted so as to fix impurities by adsorption (hydrocarbons and hydrogen sulfide) contained in the feed mixture. Different types of adsorbent materials can be envisaged, such as activated carbons, silica gels and/or molecular sieves.

[0035] The purification apparatus 5 is of the PSA type. It comprises to this end lines, valves and control means, not shown, adapted so as to cause each adsorber R1 to R6 to follow a cycle of period T, which consists of six phase times of substantially the same duration, and of which a first example is shown in FIG. 2. Considering that the cycle shown applies from instant  $t=0$  to  $t=T$  in the adsorber R6, the operation of the adsorber R5 is deduced from this by a time lag  $T/6$ , that of the adsorber R4 by a time lag of  $2T/6$  and so on until that of the adsorber R1 obtained by a time lag of  $5T/6$ . By a phase time/adsorber duality, this amounts to considering that, in FIG. 2, the adsorber R6 follows the first phase time shown between the instants  $t=0$  and  $t=T/6$ , the adsorber R5 follows the second phase time shown between the instants  $t=T/6$  and  $t=2T/6$ , and so on to the adsorber R1 which follows the sixth phase time shown between the instants  $t=5T/6$  and  $t=T$ .

[0036] In FIG. 2, where the times  $t$  are given as abscissae and the absolute pressures  $P$  as ordinates, the lines pointing along the arrows indicate the movements and destinations of the gas streams, and, in addition the direction of circulation in the adsorbers R1 to R6: when an arrow is in the direction of increasing ordinates (toward the top of the diagram) the stream is said to be cocurrent in the adsorber. If the arrow pointing upward is situated below the line indicating the pressure in the adsorber, the stream enters the adsorber through the entry end of this adsorber; if the arrow, pointing upward, is situated above the line indicating the pressure, the stream leaves the adsorber through the outlet end of the adsorber, the inlet and outlet ends being respectively those of the gas to be treated and the gas withdrawn as an output; when an arrow is in the direction of decreasing ordinates (toward the bottom of the diagram), the stream is said to be countercurrent in the adsorber. If the arrow pointing downward is situated below the line indicating the pressure of the adsorber, the stream leaves the adsorber through the inlet end of this adsorber; if the arrow pointing downward is situated above the line indicating the pressure, the stream enters the adsorber through the outlet end of this adsorber, the inlet and outlet ends being still those of the gas to be treated and the gas withdrawn as an output. The inlet end of the adsorbers is their lower end.

[0037] Accordingly, for example for the adsorber R6, the cycle includes an adsorption phase from  $t=0$  to  $t=2T/6$  and a regeneration phase from  $t=2T/6$  to  $t=T$ . More precisely, the adsorption phase includes:

[0038] from  $t=0$  to  $t=T/6$ , a first step for treating the feed gas during which impure hydrogen to be treated arrives at the inlet of the adsorber through the line 2 at a high adsorption pressure, referenced PH on the cycle, of around 26 bar. A substantially pure flow of hydrogen is then withdrawn at the head, at the same pressure, and partially feeds the output line 3, the remainder being conveyed to another adsorber during a repressurization step subsequently described;

[0039] from  $t=T/6$  to  $t=2T/6$ , a second step for treating a gas coming from the recycling line 6, formed by the discharge from the compressor 8 which brings this gas to the adsorption pressure PH. In the same way as in the previous step, part of the flow of substantially pure hydrogen withdrawn at the head constitutes the output flow at 3, the remainder being conveyed to the adsorber during the repressurization step referred to above.

[0040] The regeneration phase includes, from  $t=2T/6$  to  $t=4T/6$ , a depressurization step comprising:

[0041] from  $t=2T/6$  to  $t=t_2$ ,  $t_2$  being greater than  $3T/6$  and less than  $4T/6$ , a cocurrent depressurization substep. More precisely, from  $t=2T/6$  to  $t=t_1$ ,  $t_1$  being less than  $3T/6$ , the outlet from the adsorber R6 is connected to that of another adsorber at the start of the repressurization step, subsequently described, until the pressures of the two adsorbers are balanced at a balancing pressure referenced PE. Then, from  $t_1$  to  $t_2$ , the flow leaving the adsorber R6 cocurrently is decompressed and conveyed to the outlet from an adsorber in the elution step, subsequently described;

[0042] from  $t_2$  to  $t=4T/6$ , a countercurrent depressurization substep during which, from  $t_2$  to  $t_3$ , the flow

leaving the adsorber R6 is conveyed to the inlet of the recycling line 6, and from  $t_3$  to  $t=4T/6$ , the flow leaving the adsorber is conveyed to the waste line 4. This substep is continued to the low cycle pressure, referenced PB, and can take a value of between 1.6 bar and 10 bar, preferably 6 bar.

[0043] The regeneration phase then includes, from  $t=4T/6$  to  $t=5T/6$ , an elution step during which the adsorbent material is purged by an elution gas in order to desorb nearly all the previously adsorbed impurities. This elution step comprises:

[0044] from  $t=4T/6$  to  $t=t_4$ , an elution substep to waste, during which the adsorber is purged in countercurrent, by evacuating a waste gas at the low pressure PB through the line 4; and

[0045] from  $t_4$  to  $t=5T/6$ , an elution substep toward recycling, during which the adsorber is also countercurrently purged, this time forming a recycling gas at the low pressure PB, conveyed to the inlet of line 6.

[0046] Thus, during the start, that is to say from  $t_2$  to  $t_3$ , from the countercurrent depressurization substep and during the elution substep toward recycling, the line 6 receives a gas richer in hydrogen than the gas conveyed to the waste line 4, which amounts to only recycling the flows, coming in countercurrent from the adsorbers in the regeneration phase that are richest in hydrogen, the impurities having been mainly desorbed at the end of countercurrent depressurization and at the start of elution. The duration of the intervals  $[t_2;t_3]$  and  $[t_4;5T/6]$  can be modified according to the desired gas volume entering the recycling line 6. A valuable choice for the cycle with 6 adsorbers of FIG. 2 consists of choosing  $t_2$  and  $t_3$  so that the duration of the interval  $[t_2;t_3]$  is substantially equal to one third of the countercurrent depressurization substep (namely the step extending from  $t_2$  to  $4T/6$ ), and of choosing  $t_4$  so that the duration of the interval  $[t_4;5T/6]$  is substantially equal to two thirds of the elution step (namely the step extending from  $4T/6$  to  $5T/6$ ).

[0047] As a variant, not shown,  $t_3$  can be chosen equal to  $t_2$ , which amounts to only having available the flow leaving the adsorber in the elution substep toward recycling in order to feed line 6. Similarly,  $t_4$  can be chosen equal to  $4T/6$  which makes it possible to recycle to line 6 all the flows coming from the adsorbers in the elution step.

[0048] Once the gas from line 6 has been homogenized in the mixing tank 7 and compressed from the low pressure PB to the high pressure PH of the cycle by the compressor 8, it forms the gas feeding the adsorber in the second treatment step (from  $T/6$  to  $2T/6$  as described above).

[0049] Again taking up the description of the cycle of FIG. 2, the regeneration phase finally includes, from  $t=5T/6$  to  $t=T$ , a countercurrent repressurization step, during which the adsorber receives part of the flows coming from the adsorbers in the adsorption phase. In addition, from  $t=5T/6$  to  $t=t_5$ , the adsorber also receives the flow coming from the adsorber at the start of the cocurrent depressurization substep, until the pressure of the adsorber reaches the total balancing pressure PE which has a value for example of around  $(PH+PB)/2$ .

[0050] The secondary feed gas conveyed through the line 6 is more depleted in hydrogen than the main feed gas

conveyed through the line 2, and these two feed gases are asymmetrical in terms of the hydrogen content, when successively feeding each adsorber in the adsorption phase. This asymmetry makes it possible to achieve higher productivity than that of a PSA apparatus with a single feed flow. Moreover, this gain is even greater as there is an increase in the recycled flow, coming from adsorbers of the apparatus 5, on account of the fact that this asymmetry is increased by lowering the hydrogen content of the second feed gas. Thus, instead of having in the case of the prior art a deterioration in productivity when the quantity of recycled gas is increased in order to increase the hydrogen yield of a PSA apparatus, it is observed that this productivity is maintained.

[0051] Another feature of the invention will now be described, still with reference to the elements of the unit shown in FIG. 1, but while considering that this unit follows various operating cycles progressively detailed, some of these cycles being derived from the prior art and others being according to the invention.

[0052] To this end, the results of the operation of PSA units are given together in FIG. 3, with or without recycling of flow coming from adsorbers during regeneration, this recycling flow being mixed with or dissociated from the main feed flow, as will be progressively detailed in the description below. The units considered operate with the feed mixture having a composition detailed above, and all produce a substantially pure hydrogen flow (with a hydrogen content of around 99.5% by volume) and with an output rate of the order of 1000 Nm<sup>3</sup>/h (normal cubic meters an hour). Their low regeneration pressure PB is indicated in the table, according to whether these units follow a low pressure cycle PB of 1.6 or 6 bar, as previously explained.

[0053] In the table of FIG. 3 the following are successively indicated:

[0054] the % by volume of hydrogen in the output flow from the PSA unit considered;

[0055] the high pressure extraction yield in hydrogen, namely the quantity of hydrogen contained in the output flow over the quantity of hydrogen contained in the main feed gas (line 2);

[0056] the compressive power, in kW, necessary to operate the PSA unit considered;

[0057] the adsorbent volume, in m<sup>3</sup>, per adsorber, necessary to operate the PSA unit considered;

[0058] the productivity, in Nm<sup>3</sup>/m<sup>3</sup>/bar, which corresponds to the actual number of normal cubic meters of hydrogen produced per cubic meter of adsorbent used; and

[0059] the energy consumption, in kW/(Nm<sup>3</sup>/h), which corresponds to the compressive power per normal cubic meter of gas produced per hour.

[0060] Column I of the table of FIG. 3 corresponds to a standard PSA unit, not shown, with six adsorbers that follow a known cycle without recycling (this PSA unit does not therefore include a recycling compressor like the compressor 8 for unit 1 of FIG. 1), which is awkward to put into operation by reason of its complexity although recognized for its good performance. This is the case, for example, for

a cycle commonly called "613 cycle", with an adsorber in the adsorption phase and three total pressure balancing operations between adsorbers during cocurrent depressurization and adsorbers during repressurization. In the case of a cycle at a low pressure PB of 1.6 bar, a compressor is necessary placed at the outlet from the waste line, such as the compressor 9 for unit 1.

[0061] Column II corresponds to unit 1 of FIG. 1 which follows PSA cycles for which the recycling compressor 8 returns a recycling gas at a high pressure PH that is mixed with the main feed of line 2 before being conveyed to the adsorber. These cycles, called 613R and 612R ("R" for recycling) correspond to a cycle on six adsorbers with an adsorber during the adsorption phase and with respectively three and two total pressure balancing operations between adsorbers during cocurrent depressurization and adsorbers during repressurization.

[0062] On reading the two examples of column I individually, it will be noted that for a small low pressure PB, the hydrogen yield and productivity are much higher than those for a greater low pressure PB. It is indeed well known that hydrogen purification by adsorption is favored by a high PH/PB differential on the cycle of the PSA unit and that a high value for the low pressure is very unfavorable for standard cycles.

[0063] On the other hand, on comparing columns I and II, operating with a cycle at a low pressure PB equal to that of the discharge network (6 bar) makes it possible to dispense with the compressor 9, the latter being replaced by the recycling compressor 8. This compressor 8 makes it possible to regain good hydrogen yields while limiting the energy consumption of this compressor that pressurizes a gas to the high pressure PH from a pressure that is already around 6 bar. Comparing the cycles called 613 at 6 bar and 613R of column II makes it possible in point of fact to pass from 64 to 89% HP yield at the expense of purchasing a compressor and losing productivity.

[0064] It will be noted moreover that for the cycle called 612R, a productivity of 0.27 Nm<sup>3</sup>/m<sup>3</sup>/bar is regained for a hydrogen yield maintained at 89%, while also reducing the power of the compressor 8.

[0065] A variant of the operating cycle of the PSA unit 5 of FIG. 1 is shown in FIG. 4. The cycle of FIG. 4 is identical to that of FIG. 2, except that the total pressure balancing of the cycle of FIG. 2 between the adsorber at the start of the cocurrent depressurization step and the adsorber at the start of the repressurization substep is replaced by partial pressure balancing between these adsorbers. More precisely, FIG. 4 no longer shows the total balancing pressure PE, but a partial balancing pressure, referenced P<sub>partial</sub>, that corresponds to the pressure to which the adsorber is lowered at the start of the cocurrent depressurization substep (that is to say the pressure of the adsorber at the instant t=t1). The value of this pressure P<sub>partial</sub> is a parameter that can be selected from the cycle of FIG. 4. It makes it possible to define a partial balancing pressure ratio, referenced r, from the following formula:

$$r = \frac{PH - P_{\text{partial}}}{P_{\text{partial}} - PB}$$

[0066] It will be noted that for a ratio with a value of 1,  $P_{\text{partial}}$  has a value  $(PH+PB)/2$ , that is to say the value PE of the cycle of FIG. 2. For  $r=0$ ,  $P_{\text{partial}}=PH$ , which amounts to having a cycle not having a pressure balancing step between the adsorbers mentioned above. Conversely, a cycle with two balancing steps will have a ratio with a value of 2, corresponding to  $P_{\text{partial}}=(PH+2PB)/3$ , less than  $(PH+PB)/2$ .

[0067] The cycle of FIG. 4 makes it possible to have a greater eluting power available than in the cycle of FIG. 2. Indeed, for a ratio  $r$  strictly less than 1, the volume of the flows coming from the adsorbers during cocurrent depressurization and used for eluting the adsorber in the elution step is greater than that of flows of the same nature of the cycle of FIG. 2. Accordingly, the elution step is reinforced, which promotes regeneration of the adsorber and therefore the productivity of the PSA. Moreover, this gain in productivity compensates to a large extent for the increase in the quantity of hydrogen recycled through line 6, there being no deterioration in energy consumption.

[0068] As a comparison, column III of the table of FIG. 3 gives the performance of the PSA unit 5 of FIG. 1 which follows:

[0069] either the cycle of FIG. 4 with  $r=0$  (no pressure balancing), called 620R;

[0070] or the cycle of FIG. 2 with  $r=1$  (one total pressure balancing step), called 621R;

[0071] or a cycle with  $r=2$  (two total pressure balancing steps), called 622R.

[0072] Moreover, FIG. 5 shows the influence of the ratio  $r$  on the energy consumption and productivity of the PSA unit 5, with a constant yield and constant hydrogen purity of the output flow. It will be noted that the nearer the ratio  $r$  approaches 0, the greater the increase in productivity of the PSA unit, without any significant increase in energy consumption (less than 5%). This is confirmed both by the examples of column II and column III of FIG. 3.

[0073] It will be understood that the example enlarged on above does not limit the invention to improving a cycle with total pressure balancing (FIG. 2) by changing to a cycle with partial or "zero" balancing. In the case of a more complex cycle, with three total balancing steps for example, it can be envisaged, without departing from the scope of the invention, to convert this cycle by replacing one or more of these total balancing steps in favor of partial balancing steps, or even by dispensing with one or more of these total balancing steps. A very large volume of regenerating gas is then available, ensuring excellent elution of the adsorbent material and forming, at least partially, a hydrogen-rich recycling flow.

[0074] FIGS. 6 to 8 show several examples of installations incorporating a hydrogen production unit similar to the unit of FIG. 1. These different applications will be described below as non-limiting examples of fields for implementing the method according to the invention.

[0075] FIG. 6 shows an installation 10 for producing hydrogen from a feed gas consisting of natural gas GN. The installation includes a line 12 for treating natural gas, the outlet from which being connected to a PSA unit 14 for producing hydrogen. This unit 14 is similar to unit 1 of FIG. 1: firstly it includes the same elements denoted by the same references, except that its adsorption purification apparatus has ten absorbers and not six and, secondly, it operates substantially in the same way, except that it follows a cycle with ten phase periods, which will be detailed subsequently.

[0076] The treatment line 12 has, from upstream to downstream:

[0077] a desulfuration unit 16 adapted so as to reduce the sulfur content of the feed gas, by removing hydrogen sulfide ( $H_2S$ );

[0078] a prereforming unit 18 adapted so as to decompose  $C_nH_m$  into methane and carbon dioxide;

[0079] a steam reforming unit 20 adapted so as to catalytically convert methane in the feed gas into a synthesis gas rich in hydrogen (between 70 and 75% by volume) and containing carbon monoxide (around 10%) and carbon dioxide (between 10 and 15%);

[0080] a unit 22 for converting carbon monoxide into carbon dioxide, for example using steam; and

[0081] an amine scrubbing unit 24 for strongly reducing the carbon dioxide content of the feed gas, while producing a flow of carbon dioxide that can be profitably used.

[0082] As a variant, unit 24 can be replaced by a unit with selective membranes which promotes the permeation of carbon dioxide with respect to hydrogen.

[0083] The adsorption phase of the operating cycle of the PSA unit 14 extends over three phase periods and includes successively a first step for treating the synthesis gas leaving the line 12, a second step for treating the recycling gas leaving the recycling line 6 of the unit 14, and a third optional step for treating part of the prereformed natural gas withdrawn at the outlet from the prereforming unit 18. The hydrogen content of these three successive feed gases is decreasing, whereas the carbon dioxide content of these three gases is on the other hand increasing. A dissymmetry effect will thus be found here, in terms of hydrogen content, for the feed gases of the PSA unit, with the previously mentioned advantages on hydrogen production.

[0084] The regeneration phase of the cycle of PSA unit 14 extends over seven phase periods and comprises successively:

[0085] a cocurrent depressurization substep (over two phase periods) without pressure balancing;

[0086] a countercurrent depressurization substep (over one phase period) during which the discharge flow formed in the line 4 is conveyed by a line 25 to burners 26 responsible for providing heat to the endothermic steam reforming reaction of the reforming unit 20;



- [0087] an elution step toward recycling (over two phase periods) during which the adsorbent material is strongly purged by flows coming from the adsorb-ers in a cocurrent depressurization substep described above, while forming a low pressure recycling flow which feeds line 6; and
- [0088] a repressurization step (over two phase peri-ods).
- [0089] Since the waste gas from the line 4 is intended to provide combustion energy for the burners 26, the extent of its calorific value is arranged so as not to exceed the requirements of the burners. The cycle of the unit 14 makes it possible to optimize the distribution of flows leaving the unit 14 in the regeneration phase: part of these flows, which forms the waste gas depleted in hydrogen is put to use to the best extent in the burners 26, and the remaining part, that is richest in hydrogen, is recycled to feed the PSA unit of which the performance (hydrogen yield, productivity, etc.) is increased, as previously explained.
- [0090] FIG. 7 shows an installation 40 for the combined production of hydrogen and carbon monoxide from a feed gas consisting of natural gas GN. The installation includes a line 42 for treating natural gas, downstream from which are connected simultaneously a cryogenic unit 44 for producing carbon monoxide (CO) and a PSA unit 46 for producing hydrogen of which the cycle does not include pressure balancing. This unit 46 is identical to the unit 14 of the installation 10 and will not be detailed above.
- [0091] The treatment line 42 includes, from upstream to downstream:
- [0092] a desulfuration unit 48 adapted so as to reduce the sulfur content of the feed gas;
- [0093] a prereforming unit 50 adapted so as to decompose  $C_nH_m$  into methane and carbon dioxide;
- [0094] a steam reforming unit 52 adapted so as to catalytically convert methane in the feed gas into hydrogen-rich synthesis gas containing carbon mon-oxide and carbon dioxide;
- [0095] an amine scrubbing unit 54 from which the residual flow rich in carbon dioxide is compressed, at least partially, so as to be recycled to the inlet of the reforming unit 52; and
- [0096] a drying unit 56 for retaining water and for reducing the carbon dioxide content to approxi-mately one ppm (parts per million).
- [0097] A first outlet 58 from the drying unit 56 is con-nected to the cryogenic unit 44, which includes a return line 60 to the drying unit.
- [0098] A second outlet 62 from the drying unit 56 is connected to the PSA unit 46 so as to form, with part of the flow from the return line 60, the first feed mixture used by this unit.
- [0099] The second feed mixture is withdrawn from the recycling line 6 of the unit 46.
- [0100] The third optional feed mixture is formed in the same way as for installation 10 of FIG. 6, namely by part of the natural prereformed gas, withdrawn at the outlet from the prereforming unit 50.
- [0101] The installation 40 ensures a good hydrogen yield (for the same reasons as those set out with respect to FIG. 6) and, at the same time, a good carbon monoxide yield, accompanied by production of waste gas at the outlet from the PSA unit 46 rich in methane, that can be employed as a fuel gas for the burners for the reforming unit 52. As a variant, not shown, the waste gas can be partly recycled to the feed flow of the reforming unit 52 while profiting from the compressor for recycling carbon dioxide.
- [0102] FIG. 8 shows an installation 80 for reforming heavy hydrocarbons HCX, for example crude oil, the instal-lation 80 forming part of an oil refinery. The object of this installation is to hydrogenate and desulfurize a crude oil feed so as to produce a ready-to-use petroleum fuel, for example diesel fuel.
- [0103] This type of installation is a very high consumer of hydrogen, which is the basis of the majority of chemical reactions put into practice. These catalyzed reactions are moreover more efficient the higher the partial pressure of hydrogen consumed, so that a hydrogen flow with a purity greater than 99% is used. Conventional means for purifying hydrogen, such as a standard PSA unit, can be envisaged, but remain economically unprofitable by reason of large hydro-gen losses brought about by these closed cycle reactions.
- [0104] The hydrogen production method proposed with respect to FIGS. 1, 2 and 4, is here directly applicable to the treatment of these heavy hydrocarbon feeds, that are more or less rich in hydrogen, the hydrogen yield of the method according to the invention being able to exceed the limita-tions in yield of standard PSA units.
- [0105] The installation 80 includes to this end:
- [0106] a hydrodesulfuration reactor 82 connected to a feed line 84 and a hydrogen feed line 86;
- [0107] a separator pot 88 connected to the reactor 82 via a line 89 provided with a cooler 90;
- [0108] a line 92 for producing a liquid product such as diesel fuel in the vessel of the separator pot 88;
- [0109] a draw-off line 94 at the head of the pot 88, connected to a PSA unit 96 substantially analogous to the PSA unit 14 of the installation 10 of FIG. 6; and
- [0110] a line 98 for returning hydrogen to the reactor 82, which connects the hydrogen production outlet of the PSA unit 96 to the hydrogen feed line 86, and which is provided with a compressor 100 making it possible to compensate for pressure losses and to ensure recycling of the hydrogen-rich gas phase.

[0111] The operating cycle of the PSA unit **96** is very close to that of the unit **14** of FIG. 6. The adsorption phase includes successively a first step for treating a first feed gas leaving the line **94**, a second step for treating a second feed gas formed of a compressed top-up gas, for example coming from a catalytic reforming unit, not shown, and a third step for treating a third feed gas leaving the recycling line **6**. The regeneration phase, without pressure balancing, is substantially identical to that of the cycle of the unit **14** of FIG. 6, the discharge flow from the line **4** (formed of hydrogen sulfide, hydrocarbons and traces of hydrogen) being for example conveyed to a fuel gas network, that can be profitably used within the refinery.

[0112] As an example, this “closed loop cycle on the reactor **82**” operates with a flow rate of 40,000 Nm<sup>3</sup>/h of a flow of 95% pure hydrogen by volume in the main feed line **94** of the PSA unit, and with a flow rate of 8,000 Nm<sup>3</sup>/h of top-up gas with a hydrogen content equal to around 75% by volume, for a recycling gas in **6** with a hydrogen content equal to around 45% by volume.

[0113] FIG. 9 shows a unit **120** for producing hydrogen, a variant of the unit **1** of FIG. 1. Elements common to these two units carry the same references and will not be detailed again.

[0114] The unit **120** is associated with a high pressure source of synthesis gas and with a fuel gas network **124**, provided at the downstream end of burners **126**. Within the context of an oil refinery, the high pressure source is for example a catalytic reformer and the network **124** is the so-called fuel gas network that collects, typically at a pressure of around 6 bar, waste gases discharged from reforming and chemical treatment units currently installed in the refinery, and from which the burners **126** produce heat, profitably utilized in the refinery.

[0115] As an example, the flow of synthesis gas leaving the catalytic reforming unit **122** is at a pressure of 26 bar, has a hydrogen content of 75% by volume and possesses a flow

rate of the order of 1,100 Nm<sup>3</sup>/h. The fuel gas network **124** at around 6 bar, has a hydrogen content of between 30 and 60% for a flow rate of around 4,000 Nm<sup>3</sup>/h. An example of the composition of the flow of network **124** is: 50.3% hydrogen, 14.5% methane, 25.2% ethane, 7.8% butane, 2.1% propane and 0.1% hydrogen sulfide.

[0116] The unit **120** is fed with a charge from the source **122** through a line **128** delivering, in our example, a flow of around 1,100 Nm<sup>3</sup>/h. It is also connected to the medium pressure network **124**: firstly, part of the fuel gas is conveyed, via a branch **130**, to the recycling line **6**, the upstream part of the line **6** (namely the part collecting the recycled flows coming from the adsorbers in the regeneration phase) being referenced **6A**; and secondly, the outlet from the waste line **4** is connected by a discharge line **132** to the fuel gas network, downstream of the branch **130**.

[0117] The operating cycle of the PSA unit **120** is shown in FIG. 12, with the same notational conventions as for the cycle of FIG. 4, its low pressure PB having a value of around 6 bar. It is identical to the cycle of FIG. 4, except for the connection of the branch **130** to the recycling line **6**. The point of connection of the branch **130** to the line **6** is, as shown in FIG. 12, situated upstream of the mixing tank **7**.

[0118] As a variant, a high-pressure source of fuel gas can be directly mixed with the delivery from the compressor **8**.

[0119] Reinforcement of the recycling gas with part of the fuel gas, available on the refinery, appreciably increases the hydrogen production of unit **120**, the performance of which is given in column IV of the table of FIG. 3. The yield of this unit **120**, indicated as 120%, is explained by the profitable use of hydrogen by the fuel network **124**, the calculated yield in the table being the ratio between the quantity of hydrogen produced in **3** and the quantity of hydrogen introduced in **2**. The overall hydrogen yield (quantity of hydrogen added/quantity of hydrogen withdrawn as an output) has a value of 89%. As an example, for the composition of the flow of fuel gas detailed above, the material balance (in % by volume) of the installation of FIG. 11 is as follows:

	Gas of line 128	Gas of line 6	Gas of line 130	Gas of line 132	Gas of line 3	Gas of part of line 6A
Hydrogen	75%	44.5%	50.3%	19.2%	99.5%	41.1%
Methane	11%	24.3%	14.5%	29.3%	0.5%	29.9%
Ethane	7%	20.4%	25.2%	32.2%	0.0%	17.6%
Butane	4%	7.6%	7.8%	12.9%	0.0%	7.4%
Propane	3%	3.2%	2.1%	6.3%	0.0%	3.9%
Hydrogen sulfide	0.1%	0.1%	0.1%	0.2%	0.0%	0.1%
Total	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
Pressure (bar)	26	26	6	6	25	6
Flow rate (Nm <sup>3</sup> /h)	1103	1594	585	711	1000	1009

[0120] In the case where a lower energy consumption is sought, it is possible to reduce the part of the recycling gas coming from the adsorbers during regeneration (flow of part of line 6A) and therefore to reduce the compressive power necessary, the overall hydrogen yield being reduced from 89 to 76%. Such a situation corresponds to column IV' of the table of FIG. 3. The corresponding material balance is as follows:

	Gas of line 128	Gas of line 6	Gas of line 130	Gas of line 132	Gas of line 3	Gas of part of line 6A
Hydrogen	75%	50.3%	50.3%	29.8%	99.5%	50.2%
Methane	11%	16.7%	14.5%	24.1%	0.5%	23.3%
Ethane	7%	23.0%	25.2%	29.9%	0.0%	16.6%
Butane	4%	7.5%	7.8%	11.2%	0.0%	6.7%
Propane	3%	2.3%	2.1%	4.9%	0.0%	3.1%
Hydrogen sulfide	0.1%	0.1%	0.1%	0.2%	0.0%	0.1%
Total	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
Pressure (bar)	26	26	6	6	25	6
Flow rate (Nm <sup>3</sup> /h)	1106	1277	955	1066	1000	322

[0121] Various layouts for the PSA unit according to the invention are available to a person skilled in the art, without departing from the scope of the invention. Thus, in the case of PSA apparatuses with a smaller number of adsorbers, or even a single adsorber, one or more buffer tanks can be provided so as to permit temporary storage and deferred use of the flow leaving the adsorber or adsorbers.

#### 1-8. (canceled)

9. A method for producing hydrogen comprising producing said hydrogen from a main hydrogen rich feed mixture with at least one adsorber, wherein said adsorbers each follow, with a time lag, a cycle, wherein said cycle comprises:

- a) an adsorption phase operating substantially at a high cycle pressure;
- b) a regeneration phase, wherein said regeneration phase comprises:
  - 1) a depressurization step to a low cycle pressure, wherein said depressurization step comprises a cocurrent depressurization substep;
  - 2) an elution step at said low cycle pressure, wherein said elution step comprises receiving in said adsorber all flows exiting said adsorber during said depressurization substep; and
  - 3) a repressurization step to said high cycle pressure; and
- c) a recycle phase comprising:
  - 1) forming a recycled gas part by compressing at least part of the flow leaving said adsorber during said regeneration phase to said high cycle pressure; and

2) feeding said adsorber in said adsorption phase with said recycled part.

10. The method of claim 9, wherein said adsorption phase further comprises:

- a) treating by adsorption said main feed mixture at substantially said high cycle pressure; and
- b) treating by adsorption said recycled part at substantially said high cycle pressure.

11. The method of claim 9, wherein said depressurization step further comprises a countercurrent depressurization substep, wherein:

- a) said countercurrent substep occurs after said cocurrent substep; and
- b) the flow leaving said adsorber at the start of said countercurrent substep is at least partially recycled.

12. The method of claim 9, wherein the flow leaving said adsorber at the end of said elution step is at least partially recycled.

13. The method of claim 11, wherein:

- a) the flow leaving said adsorber during the first third of said countercurrent substep is at least partially recycled; and
- b) the flow leaving said adsorber during the last two thirds of said elution step is at least partially recycled.

14. The method of claim 10, wherein said adsorption phase further comprises treating by adsorption, at said high cycle pressure, at least one supplementary feed gas, wherein said supplementary feed gas treating occurs after the treating of said recycled part in said regeneration phase and wherein said supplementary feed gas comprises a hydrogen content less than that of said feed mixture and said recycled part.

15. The method of claim 10, wherein said adsorption phase further comprises treating by adsorption, at said high cycle pressure, at least one supplementary feed gas, wherein said supplementary feed gas treating occurs prior to the treatment of the second feed gas and wherein said supplementary feed gas comprises:

- a) a hydrogen content less than that of said feed mixture; and
- b) a hydrogen content greater than that of said recycled part.

16. The method of claim 9, further comprising mixing a fuel gas with said recycled part leaving said adsorber during

said regeneration phase, wherein said fuel gas comprises a hydrogen content less than that of said feed mixture.

**17.** An apparatus for producing hydrogen from a main hydrogen-rich feed mixture comprising:

- a) a line for recycling at least one of the flows leaving at least one adsorber during the regeneration phase;
- b) a recycling compressor;
- c) a line for providing part of said feed mixture to said recycling line; and
- d) wherein, said hydrogen is produced with a least one said adsorber wherein said adsorbers each follow, with a time lag, a cycle, wherein said cycle comprises:
  - 1) an adsorption phase operating substantially at a high cycle pressure;
  - 2) said regeneration phase, wherein said regeneration phase comprises:
    - i) a depressurization step to a low cycle pressure, wherein said depressurization step comprises a cocurrent depressurization substep;
    - ii) an elution step at said low cycle pressure, wherein said elution step comprises receiving in said adsorber all flows exiting said adsorber during said depressurization substep; and
    - iii) a repressurization step to said high cycle pressure; and
  - 3) a recycle phase comprising:
    - i) forming a recycled gas part by compressing at least part of the flow leaving said adsorber during said regeneration phase to said high cycle pressure; and
    - ii) feeding said adsorber in said adsorption phase with said recycled part.

**18.** The apparatus of claim 17, wherein said adsorption phase further comprises:

- a) treating by adsorption said main feed mixture at substantially said high cycle pressure; and
- b) treating by adsorption said recycled part at substantially said high cycle pressure.

**19.** The apparatus of claim 17, wherein said depressurization step further comprises a countercurrent depressurization substep, wherein:

- a) said countercurrent substep occurs after said cocurrent substep; and
- b) the flow leaving said adsorber at the start of said countercurrent substep is at least partially recycled.

**20.** The apparatus of claim 17, wherein the flow leaving said adsorber at the end of said elution step is at least partially recycled.

**21.** The apparatus of claim 19, wherein:

- a) the flow leaving said adsorber during the first third of said countercurrent substep is at least partially recycled; and
- b) the flow leaving said adsorber during the last two thirds of said elution step is at least partially recycled.

**22.** The apparatus of claim 18, wherein said adsorption phase further comprises treating by adsorption, at said high cycle pressure, at least one supplementary feed gas, wherein said supplementary feed gas treating occurs after the treating of said recycled part in said regeneration phase and wherein said supplementary feed gas comprises a hydrogen content less than that of said feed mixture and said recycled part.

**23.** The apparatus of claim 18, wherein said adsorption phase further comprises treating by adsorption, at said high cycle pressure, at least one supplementary feed gas, wherein said supplementary feed gas treating occurs prior to the treatment of the second feed gas and wherein said supplementary feed gas comprises:

- a) a hydrogen content less than that of said feed mixture; and
- b) a hydrogen content greater than that of said recycled part.

**24.** The apparatus of claim 17, further comprising mixing a fuel gas with said recycled part leaving said adsorber during said regeneration phase, wherein said fuel gas comprises a hydrogen content less than that of said feed mixture.

\* \* \* \* \*