METHOD FOR PRODUCING A HYDROGEN-ENRICHED GAS STREAM FROM HYDROGENATED GAS STREAMS COMPRISING HYDROCARBONS

Inventors: Francois-Xavier Haulle, Chatou (FR); Sylvain Gerard, Suresnes (FR); Bruno Alban, Massy (FR); Vincent Pudys, Paris (FR)

Correspondence Address:
AIR LIQUEIDE
Intellectual Property
2700 POST OAK BOULEVARD, SUITE 1800
HOUSTON, TX 77056 (US)

Assignee: L’Air Liquide Societe Anonyme Pour L’Etude Et L’Exloitation Des Procedes Georges Claude, Paris ,Cedex 7 (FR)

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ABSTRACT
The invention concerns a method for producing a hydrogen-enriched gas stream from at least one gas stream comprising for the major part hydrogen and a gas stream comprising hydrogen and hydrocarbons, using a pressure-modulated gas adsorption unit, the temperature of the gas stream comprising hydrogen and hydrocarbons being first lowered so as to condense the hydrocarbons.
METHOD FOR PRODUCING A HYDROGEN-ENRICHED GAS STREAM FROM HYDROGENATED GAS STREAMS COMPRISING HYDROCARBONS

[0001] The present invention relates to a process for enhancing various streams based on hydrogen and on hydrocarbons so as to produce a high-purity hydrogen stream.

[0002] Refineries or petrochemical plants use large amounts of hydrogenated streams, preferably of high purity. In many industrial cases, the performances of the units, and especially the grades of the products produced, are limited by the purity of the supplied hydrogen. Furthermore, in these units, it is sometimes necessary to eliminate gases that are still rich in hydrogen under the effect of the recycle gas purges. This results in a cost premium for the operation of the unit. In order to avoid these problems, processes for recovering the hydrogen from streams of relatively low purity in order to produce high-purity hydrogenated streams have been proposed, especially in Application WO 2005/042640 which proposes using a pressure swing adsorption unit to treat these various hydrogenated streams and to obtain a high-purity stream. This type of pressure swing adsorption unit may represent a significant investment in terms of adsorbent cost and compressor cost.

[0003] The objective of the present invention is to propose a process for enhancing various streams based on hydrogen and hydrocarbons so as to produce a high-purity hydrogen stream, a liquefied petroleum gas and a waste gas, the investment cost of which is reduced by increasing the high-purity hydrogen production yield.

[0004] Another objective of the present invention is to propose a process for enhancing various streams based on hydrogen and hydrocarbons so as to produce a high-purity hydrogen stream, a liquefied petroleum gas and a waste gas, of which the energy consumption is optimized.

[0005] For this purpose, the invention relates to a process for producing a hydrogen-enriched gas stream and a liquefied petroleum gas from at least one gas stream mainly comprising hydrogen at pressure P and a gas stream comprising hydrogen and hydrocarbons, in which the following steps are carried out:

[0006] during step a), the gas stream comprising hydrogen and hydrocarbons is adjusted to the pressure P;
[0007] during step b), the gas stream comprising hydrogen and hydrocarbons and adjusted to the pressure P is treated in a pressure swing gas adsorption unit (U) fed with the gas stream mainly comprising hydrogen and having a pressure P so as to supply:
[0008] at a first outlet, the hydrogen-enriched gas stream having a hydrogen concentration greater than that of the gas stream mainly comprising hydrogen; and
[0009] at a second outlet, a waste stream, characterized in that between step a) and step b), the temperature of the gas stream comprising hydrogen and hydrocarbons and adjusted to the pressure P is lowered so as to condense the hydrocarbons and form the liquid petroleum gas.

[0010] The process according to the invention allows the treatment of two gas streams comprising hydrogen at various concentrations so as to produce a hydrogen-enriched gas stream, a liquefied petroleum gas (or LPG) and a waste gas. The first gas stream treated is a gas stream that mainly comprises hydrogen, that is to say having a hydrogen concentration between 50 and 99 vol %. This stream also comprises hydrocarbons having from 1 to 8 carbon atoms and compounds such as CO, CO₂, H₂S, etc. The second stream treated is a gas stream comprising hydrogen and hydrocarbons having a hydrogen concentration at least 10% lower, preferably at least 15% lower and more preferably still 15 to 50% lower, relative to the value of the hydrogen concentration of the gas stream mainly comprising hydrogen. This second stream also comprises hydrocarbons having 1 to 18 carbon atoms, and also compounds such as H₂O, H₂S, etc. Generally, this second gas stream has a hydrogen concentration between 10 and 50 vol %. According to the invention, the pressure of this second gas stream comprising hydrogen and hydrocarbons is adjusted so that it is close to 2, either by compression, or by pressure drop depending on the origin of this stream. It is also possible that this stream already has a pressure P, in this case it is used as is without a pressure adjustment. These various streams may be derived from the purge of the gas loop of a hydro treatment unit such as a hydrodesulfurization or hydrocracking unit of a refinery, or else such as a hydrodealkylation or isomerization unit of a petrochemical site. The first and second gas streams treated in the present invention may be derived from mixtures of various purges of such units. These mixtures may make it possible to attain the pressure P desired by combining the streams having a pressure below P with streams having a pressure above P.

[0011] By treatment of these various streams, the invention makes it possible to enrich the gas stream mainly comprising hydrogen. This enrichment is obtained by hydrogen depletion of the second gas stream comprising hydrogen and hydrocarbons. The unit thus produces the hydrogen-enriched gas stream generally having a hydrogen purity greater than 99 vol %, and the unit also produces a waste stream of low hydrogen purity and of low pressure which may be conveyed to the fuel gas network. The pressure and hydrogen concentration of the waste stream are respectively below the pressure and hydrogen concentration values of all the effluents going into the unit (U). This waste stream also comprises hydrocarbons (C₃ to C₇) and compounds such as H₂O, H₂S, CO, CO₂, etc.

[0012] Preferably, the gas separation unit (U) is a pressure swing adsorption (PSA) unit combined with an integrated compressor, in which, for each adsorber of the unit, a pressure swing cycle is carried out comprising a succession of phases which define the phases of adsorption, decompression, purge and pressure rise, such that:

[0013] during the adsorption phase:
[0014] during a first step, the gas stream mainly comprising hydrogen and having a pressure P is brought into contact with the bed of the adsorber; and
[0015] during a second step, introduced into contact with the bed of the adsorber is the mixture of pressure P whose temperature has been lowered so as to condense the hydrocarbons and that is composed of:
[0016] on the one hand, the gas stream comprising hydrogen and hydrocarbons; and
[0017] on the other hand, the PSA recycle gas, so as to adsorb the compounds other than hydrogen and to produce, at the top of the adsorber bed, the enriched stream having a hydrogen concentration greater than that of the gas stream mainly comprising hydrogen;
[0018] during the decompression phase, the PSA waste stream is produced;
during the purge phase, a purge gas is produced; and

where the PSA recycle gas is either the waste stream compressed to the pressure P, or the purge gas compressed to the pressure P. According to this PSA process, in a first adsorption phase, the gas stream mainly comprising hydrogen is brought into contact with a first PSA adsorbent bed and in a second phase, it is the mixture of streams comprising hydrogen and hydrocarbons and of the PSA recycle gas which are brought into contact with this first adsorbent assembly. The recycle gas may be composed of two gases, alone or as a mixture: the waste gas resulting from the PSA which has been compressed, and the purge gas resulting from the PSA which has been compressed. Preferably, it is the purge gas and not the waste gas. The waste gas is derived from the final step of the PSA decompression phase and is partly compressed by the compressor integrated into the PSA unit of the gas separation unit (U) whereas the purge gas is derived from the purge phase of the PSA and is partly compressed by this same compressor integrated into the PSA unit before being used as a recyle gas. These two gases both comprise hydrogen and mainly impurities. Once compressed, they are mixed with a stream comprising hydrogen and hydrocarbons. This mixing may be carried out in various ways depending on the pressure value of the stream comprising hydrogen and hydrocarbons. This stream comprising hydrogen and hydrocarbons may be mixed with the waste gas or with the purge gas, then this mixture may be compressed by the compressor integrated into the PSA unit to the pressure P. When the stream comprising hydrogen and hydrocarbons has a pressure above P, its compression may be avoided; in this case, only the waste gas or the purge gas is compressed to form the recyle gas. Before its introduction into the PSA unit, the mixture at pressure P of the stream comprising hydrogen and hydrocarbons and the recyle gas is treated so as to lower its temperature and condense the hydrocarbons. It may be envisioned then to reheat the stream comprising hydrogen and hydrocarbons by heat exchange with at least one other gas stream of the process in order to avoid conveying a cold gas to the PSA unit. Next, the introduction of these mixed gases at pressure P into the adsorbent bed allows them to be retreated. During the adsorption phase, the gas streams are introduced into the bottom part of the bed in the direction known as the co-current direction. During this contacting step, the most adsorbable compounds other than H₂, are adsorbed on the adsorbent and a gas mainly comprising hydrogen is produced at the pressure P reduced by around 1 bar of pressure drop. During this step, the hydrogen produced generally has a purity greater than at least 99 mol %, preferably greater than at least 99.5 mol %.

So as to obtain an effective purification, the adsorbent of the PSA beds should, in particular, allow the adsorption and desorption of impurities. The adsorbent bed is generally composed of a mixture of several adsorbents, said mixture comprising, for example, at least two adsorbents chosen from: activated carbons, silica gels, alumina or molecular sieves. Preferably, the silica gels should have a pore volume between 0.4 and 0.8 cm³/g and a specific surface area greater than 600 m²/g. Preferably, the alumina has a pore volume greater than 0.2 cm³/g and a specific surface area greater than 220 m²/g. The zeolites preferably have a pore size below 4.2 Å, an Si/Al molar ratio below 5 and contain Na and K. The activated carbons preferably have a specific surface area greater than 800 m²/g and a micropore size between 8 and 20 Å. According to one preferred embodiment, each PSA adsorbent bed is composed of at least three layers of adsorbents of different natures. Each PSA adsorbent bed may comprise: in the bottom part, a protective layer composed of alumina and/or silica gel surrounded by a layer of activated carbon and/or of carbon-based molecular sieves and optionally in the upper part a molecular sieve layer. The proportions vary as a function of the nature of the gas mixture to be treated (especially as a function of its percentages of CH₄ and of Cₓᵧ hydrocarbons). For example, a water-free gas mixture comprising 75 mol % of H₂, 5% of Cₓᵧ and 20% of light (C₁₋C₂) hydrocarbons, CO and N₂ may be treated by an adsorption unit whose beds comprise at least 10 vol % of alumina and 15 vol % of silica gel in the bottom bed, the remainder being obtained from activated carbon.

During the decompression phase of the PSA, the waste gas is produced. This production of the waste gas may be obtained by countercurrent decompression initiated at a pressure below P. This waste gas comprises impurities and has a hydrogen content lower than all the streams introduced into the PSA unit. This waste gas may be discharged from the process and burnt or reused as a recyle gas in the PSA unit as indicated previously.

The low pressure of the cycle being attained, a purge phase is carried out to finalize the regeneration of the adsorber. During the purge phase, a gas is introduced countercurrently into the adsorber and a purge gas is produced. The gas introduced countercurrently into the adsorber during the purge phase is a gas stream derived from one of the steps of the decompression phase. The purge gas is generally used as a recyle gas after recompression.

During the pressure rise phase, the pressure of the adsorber is increased by countercurrent introduction of a gas stream comprising hydrogen such as the gas produced during the various steps of the decompression phase.

According to the main feature of the invention, between step a) of adjusting the pressure of the gas stream comprising hydrogen and hydrocarbons and step b) of treating this stream via the gas separation unit (U), the temperature of the gas stream comprising hydrogen and hydrocarbons is lowered so as to condense the hydrocarbons, preferably to less than 0° C, more preferably still to less than –20° C. Preferably, this temperature drop is carried out by means of a cryogenic device, such as cryogenic (compression/expansion) loops using liquid ammonia or propane.

FIG. 1 illustrates the process according to the invention. The stream 2 comprising hydrogen and hydrocarbons is compressed by the compressor 3 to have a pressure P equal to that of the stream 1 that mainly comprises hydrogen. The stream 21 comprising hydrogen and hydrocarbons and that is compressed is then treated by a device 4 that makes it possible to lower its temperature and to condense the hydrocarbons. The device 4 produces:

- on the one hand, a liquid stream 10 of hydrocarbons (LPG); and
- on the other hand, a gas stream 22 comprising hydrogen and still some hydrocarbons having a pressure P and a lowered temperature.

This stream 22 and the stream 1 are treated by the gas separation unit 5 so as to produce: a hydrogen-enriched...
stream 6, a waste gas 7 and a purge gas 8 which is mixed with the stream 2 comprising hydrogen and hydrocarbons before compression of the latter. The process also makes it possible to treat another stream 9 comprising hydrogen and hydrocarbons that is equivalent to the stream 2 but originates from another purge. This stream 9 already has a pressure P or a pressure that is slightly greater than P; it is therefore directly treated by the device 4 with the mixture 21 resulting from the compressor.

[0030] By implementation of the process as described above, it is possible to reduce the size of the pressure swing adsorption unit and to reduce the compression costs of the unit (U) while increasing the hydrogen yield. The process additionally makes it possible to produce, at the outlet of the temperature-lowering device, a liquefied petroleum gas, which may be a stream of high added value, that can be recovered as a fuel.

[0031] The process of the invention also has the advantage of allowing a natural energy integration between the cryogenic device enabling the temperature to be reduced and the compressor of the pressure swing adsorption unit.

EXAMPLE

[0032] Two gas streams comprising hydrogen were treated by means of a pressure swing adsorption unit. These two streams had the following concentrations:

<table>
<thead>
<tr>
<th>Composition (vol %)</th>
<th>Gas stream comprising hydrogen</th>
<th>Gas stream comprising hydrogen and hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flow rate $5 \text{m}^3$/h</td>
<td>10 000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 200</td>
</tr>
<tr>
<td>H$_2$</td>
<td>81.4</td>
<td>57</td>
</tr>
<tr>
<td>C$_1$</td>
<td>9.3</td>
<td>23.7</td>
</tr>
<tr>
<td>C$_2$</td>
<td>5.1</td>
<td>2.2</td>
</tr>
<tr>
<td>C$_3$</td>
<td>2.6</td>
<td>5.35</td>
</tr>
<tr>
<td>C$_4$</td>
<td>1.1</td>
<td>8.2</td>
</tr>
<tr>
<td>C$_5$</td>
<td>0.6</td>
<td>2.9</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

[0033] These streams were treated by a pressure swing adsorption unit according to the invention as illustrated in FIG. 1 and by a CPSA pressure swing adsorption unit according to the prior art corresponding to the CPSA according to the invention but not comprising means for lowering the temperature of the gas stream comprising hydrogen and hydrocarbons so as to condense the hydrocarbons. The features of the process according to the prior art and of the process according to the invention are described in table 2.

<table>
<thead>
<tr>
<th>Process according to the prior art</th>
<th>Process according to the invention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen yield</td>
<td>82.3%</td>
</tr>
<tr>
<td>Volume of adsorbent (relative)</td>
<td>100</td>
</tr>
<tr>
<td>Hydrocarbon recovery (t/h)</td>
<td>2.02</td>
</tr>
<tr>
<td>mol % C3</td>
<td>21.2</td>
</tr>
<tr>
<td>mol % C4</td>
<td>51.4</td>
</tr>
<tr>
<td>mol % C5</td>
<td>27.4</td>
</tr>
<tr>
<td>Energy used by the compressor (kW)</td>
<td>564</td>
</tr>
<tr>
<td>Energy used by the cryogenic device (kW)</td>
<td>541</td>
</tr>
</tbody>
</table>

[0034] It is observed that by the implementation of the invention, it is possible:

[0035] to reduce the volume of the adsorbents of the PSA unit by 10 vol %; and

[0036] to decrease the power of the compressor by 5%;

[0037] to increase the hydrogen yield by 0.3 points.

[0038] Furthermore, the stream of liquefied hydrocarbons may be recovered as a commercial product within the plant.

[0039] The liquefied petroleum gas resulting from the cryogenic device is a product of high added value which compensates for the additional energy used by the cryogenic device of the process according to the invention relative to the process of the prior art.

1-7. (canceled)

8. A process for producing a hydrogen-enriched gas stream and a liquefied petroleum gas from at least one gas stream mainly comprising hydrogen at pressure P and a gas stream comprising hydrogen and hydrocarbons, in which the following steps are carried out:

 during step a), the gas stream comprising hydrogen and hydrocarbons is adjusted to the pressure $P$;

during step b), the gas stream comprising hydrogen and hydrocarbons and adjusted to the pressure $P$ is treated in a pressure swing adsorption unit fed with the gas stream mainly comprising hydrogen and having a pressure $P$ so as to supply:

 at a first outlet, the hydrogen-enriched gas stream having a hydrogen concentration greater than that of the gas stream mainly comprising hydrogen; and

 at a second outlet, a waste stream.

characterized in that between step a) and step b), the temperature of the gas stream comprising hydrogen and hydrocarbons and adjusted to the pressure $P$ is lowered so as to condense the hydrocarbons and form the liquid petroleum gas.

9. The process of claim 8, wherein the gas stream mainly comprising hydrogen has a hydrogen concentration between 50 and 99 vol %.

10. The process of claim 8, wherein the gas stream comprising hydrogen and hydrocarbons has a hydrogen concentration at least 10% lower relative to the value of the hydrogen concentration of the gas stream mainly comprising hydrogen.

11. The process of claim 8, wherein the gas stream comprising hydrogen and hydrocarbons has a hydrocarbon concentration between 10 and 50 vol %.

12. The process of claim 8, wherein the gas separation unit is a pressure swing adsorption (PSA) unit combined with an integrated compressor, in which, for each adsorber of the unit,
a pressure swing cycle is carried out comprising a succession of phases which define the phases of adsorption, decompression, purge and pressure rise, such that:

during the adsorption phase:

during a first step, the gas stream mainly comprising hydrogen and having a pressure $P$ is brought into contact with the bed of the adsorber; and

during a second step, introduced into contact with the bed of the adsorber is the mixture of pressure $P$ whose temperature has been lowered so as to condense the hydrocarbons and that is composed of:

on the one hand, the gas stream comprising hydrogen and hydrocarbons; and

on the other hand, the PSA recycle gas, so as to adsorb the compounds other than hydrogen and to produce, at the top of the adsorber bed, the enriched stream having a hydrogen concentration greater than that of the gas stream mainly comprising hydrogen;

during the decompression phase, the PSA waste stream is produced;

during the purge phase, a purge gas is produced; and

where the PSA recycle gas is either the waste stream compressed to the pressure $P$; or the purge gas compressed to the pressure $P$.

13. The process of claim 8, wherein between step a) and step b), the temperature of the gas stream comprising hydrogen and hydrocarbons is lowered to at least 0°C.

14. The of claim 8, wherein between step a) and step b), the temperature of the gas stream comprising hydrogen and hydrocarbons is lowered by means of a cryogenic device.

15. The process of claim 9, wherein the gas stream comprising hydrogen and hydrocarbons has a hydrogen concentration at least 10% lower relative to the value of the hydrogen concentration of the gas stream mainly comprising hydrogen.

16. The process of claim 15, wherein the gas stream comprising hydrogen and hydrocarbons has a hydrocarbon concentration between 10 and 50 vol %.

17. The process of claim 16, wherein the gas separation unit is a pressure swing adsorption (PSA) unit combined with an integrated compressor, in which, for each adsorber of the unit, a pressure swing cycle is carried out comprising a succession of phases which define the phases of adsorption, decompression, purge and pressure rise, such that:

during the adsorption phase:

during a first step, the gas stream mainly comprising hydrogen and having a pressure $P$ is brought into contact with the bed of the adsorber; and

during a second step, introduced into contact with the bed of the adsorber is the mixture of pressure $P$ whose temperature has been lowered so as to condense the hydrocarbons and that is composed of:

on the one hand, the gas stream comprising hydrogen and hydrocarbons; and

on the other hand, the PSA recycle gas, so as to adsorb the compounds other than hydrogen and to produce, at the top of the adsorber bed, the enriched stream having a hydrogen concentration greater than that of the gas stream mainly comprising hydrogen;

during the decompression phase, the PSA waste stream is produced;

during the purge phase, a purge gas is produced; and

where the PSA recycle gas is either the waste stream compressed to the pressure $P$, or the purge gas compressed to the pressure $P$.

18. The process of claim 17, wherein between step a) and step b), the temperature of the gas stream comprising hydrogen and hydrocarbons is lowered to at least 0°C.

19. The of claim 18, wherein between step a) and step b), the temperature of the gas stream comprising hydrogen and hydrocarbons is lowered by means of a cryogenic device.

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