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- (54) **Title:** ALTERNATING POTENTIAL GAS SEPARATION PROCESS WITH CAPACITIVE MEMBRANES, AND RELEVANT PLANT

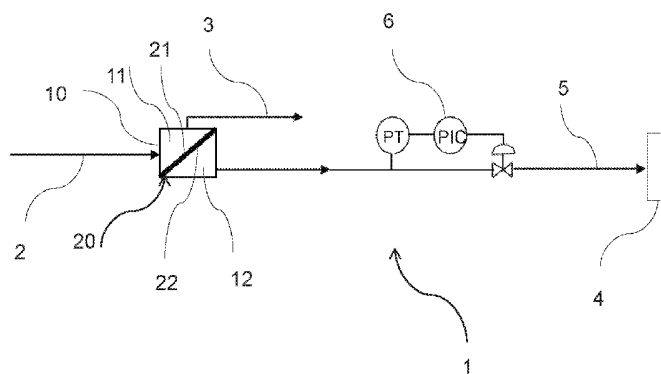


Fig. 2

- (57) **Abstract:** The present invention relates to a process, and relevant plant (1), for separating at least one key component (KC) from a multicomponent gas stream (GS) that is caused to flow on a composite membrane (20) comprising dense domains (21) permeable to the key component (KC) and porous domains (22) intended to adsorb preferentially the key component (KC). A permeate stream (PS), separated from the multicomponent gas stream (GS) and containing the key component (KC), is extracted through a discharge line (5) depending on the measured value of the pressure (P) downstream the membrane (20). Upon reaching a predetermined maximum value ( $p^{\max}$ ) of such pressure (P), the permeate stream (PS) is extracted until reaching a predetermined minimum value ( $p^{\min}$ ) of such pressure (P) downstream the membrane (20), and upon reaching such predetermined minimum value ( $p^{\min}$ ), the extraction of the permeate stream (PS) is stopped. Thus by repeating such operations extracting and stopping the extraction downstream the membrane (20), alternated cycles are generated and a pseudo-steady state condition is accomplished, where the plant (1) receives the feed stream (GS) in the continuous mode and releases the permeate stream (PS) in an intermittent manner, while a retentate stream (RS), containing the components of the feed stream (GS) that have not been collected in the permeate stream (PS) is discharged with continuity. By handling the predetermined maximum value (p

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ALTERNATING POTENTIAL GAS SEPARATION PROCESS WITH CAPACITIVE  
MEMBRANES, AND RELEVANT PLANT

DESCRIPTION

**TECHNICAL FIELD**

The present invention relates to the field of processes and plants for treating gas streams.

- 5 The present invention particularly relates to a membrane process, and relevant plant, for separating a mixture of gas phase species into two streams with the same phase and different composition.

More particularly the present invention relates to a continuous process, where the multicomponent gas mixture is fed in a continuous manner to a separation chamber

- 10 wherein the separation into two output streams is carried out.

The invention particularly relates to membrane processes using composite membranes, composed of dense domains and porous domains that together guarantee resistive and capacitive characteristics with respect to the flow of the different gaseous components.

- 15 The invention is preferably and advantageously applied, but not exclusively, for separating gas streams containing contaminants to be removed or components to be recovered, for example for removing nitrogen, carbon dioxide, water or liquefiable components from natural gas streams; for recovering hydrogen from off-gas streams in refinery processes; for separating carbon dioxide in steam-reforming or coal
- 20 gasification streams; for removing carbon dioxide from power station flue gases; for separating olefins/ paraffins mixtures; for separating oxygen from air streams for preparing enriched oxygen streams or inert gas streams; for separating hydrogen from nitrogen in drain streams in ammonia production processes; for separating hydrogen sulphide from acid streams; for dehumidifying air streams and for
- 25 removing volatile organic compounds from gaseous effluents of different nature.

## PRIOR ART

Current processes for membrane separation of vapor/gas streams are run in steady-state condition, in a continuous manner and at constant potential, and provide to divide the feed stream of gas or vapor phase into two output streams of equal phase, a retentate collected upstream the membrane and a permeate collected downstream the membrane respectively; particularly the steady-state condition of currently used processes is obtained by employing dense and composite membranes, whose properties of permeability and selectivity by permeability are exploited, which correspond to only the resistive characteristics of the membranes, regardless of their nature.

In literature the limits in developing processes of this type for reaching contemporaneously high permeability and selectivity with one key component are known and well pointed out, such as disclosed in publications W.J. Koros and G.K. Fleming, "Membrane-based gas separation" *Journal of Membrane Science*, vol. 83, 1993, p. 1-80, e L.M. Robeson et al., "Contribution of diffusion and solubility selectivity to the upper bound analysis for glassy gas separation membranes" *Journal of Membrane Science*, v. 453, 2014, p. 71-83.

Moreover due to the fact that the current membrane processes are run under steady-state conditions, it results that the recovery factor of the key component and the purity therein of the permeate stream are only determined by the resistive characteristics of the membrane, when process load (flow rate and composition of the feed stream) and volume (area of the membrane) of the plant are fixed. This means that in gas separation processes with membrane apparatuses currently used it is not possible to regulate performances (recovery factor and degree of permeate purity) to different values unless changing the plant (membrane) and/or load.

In comparison with other types of separation processes (for example adsorption in discontinuous/cyclic condition) the membrane separation technology provides the possibility of working in a modular manner within a wide range of flow rates of the streams, with more simple and more compact apparatuses; on the contrary limits about selectivity performances restrict their use to the case of separation of compounds massively present in the stream to be treated, while the same process is

little competitive in the field of treatments removing components present in the diluted form.

In addition to the incremental improvement of performances of membrane separation processes pursued by the synthesis and formulation of new materials for the membranes, also variants for the process have been suggested that involve the modes for running it, that can use characteristics of the membrane different from the resistive ones, that is permeability and selectivity by permeability.

A first attempt with reference to the above, about the fact of running the process in a non-steady-state condition, is disclosed in publication by D.R. Paul "Membrane Separation of Gases Using Steady Cyclic Operation", I&E.C. Proc.Des.Dev., vol. 10, 1971, p. 375, whose basic idea starts from the consideration that permeability of the membrane to the individual components is the result of the contribution of solubility coefficient and diffusion coefficient and that, while when running the process in steady-state condition the real selectivity is determined only by the permeability contribution, in processes where pressure or feed flow are managed by cyclic modes, the preferential permeation of the components can be obtained with a higher diffusion coefficient in the dense material composing the dense membrane used; the mechanism identified for separating components in the gas mixture of this type of processes however does not consider the separation factor in favor of components preferably adsorbed in porous elements and it only exploits the higher diffusivity of the quickest component (thus to the detriment of the slowest component) that, however, does not allow an efficacious separation due to the very short time in crossing the membrane and for this reason it is almost operatively impracticable.

For the implementation of these membrane separation processes run in a semi-continuous mode, different technical solutions have been studied and suggested, some examples of which are found in the US patents n. US 3,818,679, n. US 4,955,998 and n. US 5,354,474.

The US patent n. US 3,818,679 describes the use of the preferential transient permeation mechanism of the key component in the membrane to organize the absorption of the key component in an area of the apparatus where the membrane is put in contact with the feed mixture and the desorption in a different area of the

apparatus where the membrane is moved prior to reaching a steady state condition and where the permeate is collected.

The US patent n. US 4,955,998 discloses the use of dense membranes according to the mechanism disclosed in the above mentioned document by D.R. Paul "Membrane  
5 Separation of Gases Using Steady Cyclic Operation", I&E.C. Proc.Des.Dev., vol. 10, 1971, p. 375 and considered in the above patent US 3,818,679, but supposing cyclic changes of the feed pressure.

The US patent n. US 5,354,474 provides to use synchronized cycles to collect permeate and to introduce the feed mixture into the membrane module to exploit the  
10 preferential permeation of components with the highest diffusion coefficient in the transient permeation through the membrane.

The solutions described in the above patents, although allowing a discontinuous/cyclic condition by changing the flow and/or pressure of the feed mixture and/or retentate, however have the drawbacks of operating on very short  
15 cycle times, due to the very small value of the characteristic diffusion time of the components in the system, in turn due to the need of guaranteeing sufficiently high permeance values for the components. In such conditions, the control of the process for carrying out the cycles feeding the gas stream and collecting the permeate particularly affects productivity of the system, expressed by its efficacious  
20 permeability.

Other, more recent, patent documents exploit the characteristics of the transient phenomenon of the transport in the membrane of the components of the gas mixture to be treated; for example such solutions are found in the US patent n. US 5,928,409 and in International Patent application under n. WO 2013/076652 A1.

25 The US patent n. US 5,928,409 provides to use a composite membrane in a process run through the sequence of two different steps; in the first step of the process the feed mixture is put in contact with membrane domains having adsorbing characteristics with respect to key components and a permeate stream is collected, while in the second step of the process the collection of the retentate, as well as the  
30 feeding, is stopped and the components adsorbed in the membrane domains in direct contact with the feed mixture move towards the permeate stream passing through

dense domains of the membrane that are placed on the downstream side thereof; such solution provide the feeding to be provided till saturating the dense layers of the membrane. In the process described in US 5,928,409, inherently discontinuous due to the feed being intermittent, the productivity is considerably penalized due to the fact that the membrane works in all the steps of the process under minimum potential difference conditions with respect to the case of the equivalent process using the same membrane under steady-state operating conditions.

The International patent application published under n. WO 2013/076652 A1 relates to a batch process, wherein the components of the gas mixture fed into the upstream compartment of the apparatus permeate through a membrane and are collected in the downstream compartment; the handling of the process time allows the different speed in storing the components in the two compartments to be exploited, which results from the different permeance thereof through the membrane. By the process described in this patent it is possible to vary the real separation factor for the gas stream to be treated, by changing the time in which the permeate is stored before being extracted, however the values of efficacious permeability and separation factor remain both lower than values that can be obtained by using the same membrane under steady-state operating conditions with a minimum downstream pressure, at any selected characteristic time. This is essentially determined by the non-selective nature of the upstream and downstream environments of the membrane on whose storage the process suggested in the patent is handled.

Therefore currently there is the unsatisfied need of providing a continuous process wherein the feed mixture and the retentate are in steady-state conditions, wherein the permeate is managed under non-steady state conditions and wherein a composite membrane is used with dense domains in contact with the feed/retentate environment and porous domains in contact with the permeate.

There is also the unsatisfied need of providing a process where the limit separation factor is driven by specific capacity characteristics of the porous domains of the membrane.

There is also the unsatisfied need of providing a process where the separation factor is controlled by regulating the width of the range in permeate pressure cycles, or

another considerable variable thereof, such as for example the partial pressure of the key component in the permeate stream inside the separation module.

Briefly all the technical solutions known until now have a performance limitation in the dependence between absolute permeability and permeability ratio between  
5 compounds to be separated that characterizes dense or composite materials used for producing membranes; that is to say all the currently known technical solutions have the drawback of limiting the separation factor in membrane separation process relative to the specific productivity (permeate flow per unit of area of the membrane) and determined by the relations between permeability and selectivity that  
10 characterize dense membranes whose resistive properties are used in the current continuous processes performed under steady-state conditions, a drawback intended to be solved by the present invention.

#### OBJECTS AND SUMMARY OF THE INVENTION

It is the object of the present invention to overcome the limits and solve the  
15 drawbacks of prior art processes and plants, specifically those using the membrane technology for separating gas/vapor streams.

Particularly it is an object of the present invention to provide a process and a relevant plant, allowing an efficacious separation of gas or vapor phase streams to be accomplished by using the capacitive characteristics of the membranes and by acting  
20 only on the permeate stream by handling, under non-steady state conditions, the variables determining the driving potential of the separation.

Still more particularly it is the object of the present invention to provide a process and a relevant plant, that is clearly different and improved with respect to those described in prior art, and in particularly overcoming the performance limits of  
25 processes and plants using only the resistive characteristics of the materials used for separating the components by the separation membranes.

These and other objects of the present invention are achieved by a process and a plant embodying the characteristics of the annexed claims.

The idea at the base of the present invention is to use the capacitive characteristics of  
30 composite membranes to be used in a process separating gas or vapor phase streams and also in handling in a non-steady state condition the variables determining the



driving potential, that is the thrusting force, of the separation.

It has to be intended that all the annexed claims form an integral part of the present description and each one of the technical characteristics claimed therein is possibly independent and usable autonomously from the other aspects of the invention.

- 5 It is immediately clear that it is possible to make many changes to what described (for example about shape, dimensions, arrangements and parts with equivalent functionalities) without departing from the scope of protection of the invention as claimed in the annexed claims.

The present invention advantageously allows:

- 10 - get much higher selectivity for the same overall permeance;  
- considerably improve the separation factors without reduction in productivity;  
- operate with continuous mode of operation;  
- set to different values the performances of the process (recovery factor and purity of the permeate) within a wide range, by acting on the internal parameters of the  
15 process, with no changes in plant and with load unchanged (flow rate, condition and composition of the feed stream);  
- preserve the characteristics of modularity, simplicity and compactness of the apparatuses, resulting in lower investment costs; and  
- avoid the presence of moving parts, and alternation of streams on the same path,  
20 with a positive impact on reliability, potentiality, operating costs and maintenance costs.

In comparison with currently used processes separating gases by membranes, the adoption of the solution according to the present invention is further particularly convenient in cases of separation of components present in a diluted form and for  
25 producing high purity streams in the key component.

The solution according to the present invention is preferably applied in the industrial field for example for producing gas (purification of process streams and capture/recovery of components from gas process streams/off-gas streams) and energy (capture of CO<sub>2</sub> from fossil sources).

- 30 Further advantageous characteristics will be more clear from the following description of preferred but not exclusive embodiments, provided by way of

example and not as a limitation.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be described below with reference to non-limitative examples provided by way of example and not as a limitation in the annexed  
5 drawings.

These drawings show different aspects and embodiments of the present invention and, where appropriate, like structures, components, materials and/or elements in different figures are denoted by like reference numerals.

Fig. 1 is a block diagram of a process for separating multi-component gas streams according to the invention; and  
10

Fig. 2 is the simplified process diagram of a plant for separating multi-component gas streams according to the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

While the invention is susceptible of various modifications and alternative forms, some preferred embodiments are shown in the drawings and are described below in details. It should be understood, however, that there is no intention to limit the invention to the specific embodiments disclosed, but, on the contrary, the intention of the invention is to cover all modifications, alternative constructions and equivalents falling within the scope of protection of the invention as defined in the annexed  
15  
20 claims.

The use of "for example", "etc", "or" indicates non-exclusive alternatives without limitation unless otherwise defined; the use of "include/comprise" means "include/comprise, but not limited to," unless otherwise defined.

As mentioned above the present invention relates to a new process and relevant  
25 plant for separating components in gas streams, for being applied in purifying gases or capturing specific components in gas streams.

The process and relevant plant according to the present invention exploit the properties of composite membranes comprising dense domains and porous domains, and specifically exploit both resistive characteristics of the membranes (resistance to  
30 the flow of components of the gas stream) and capacitive characteristics (adsorption capacities of the components of the gas phase).

In particular by the process and relevant plant according to the present invention the use of capacitive characteristics of the composite membrane occurs by running the process in a pseudo-steady state condition with regulation by cycles of the pressure downstream the membrane.

5 In the present description, the term "upstream the membrane" means the position on a face of the membrane facing the flow direction of an incident multi-component gas stream, while the term "downstream the membrane" means the position of the opposite face of the membrane with respect to the one facing the flow direction of an incident multi-component gas stream.

10 In the present description, the term "alternating potential" means the handling under non-steady state condition of the variables, with respect to the flow direction of a multi-component gas stream, downstream the membrane that determine the driving potential of the separation, or that is to say, the regulation by cycles of the pressure of the permeate stream or of another important variable thereof.

15 In the present description the term "membrane" means the solid component present in the plant (comprising dense domains and porous domains) interposed, without interruption, between the bed of the feed and retentate streams and the bed of the permeate stream; the membrane can have different shapes and dimensions, it remaining unchanged the condition for which the status of the membrane, as regards  
20 composition, pressure, temperature and flow of the components, possibly variable in time, substantially changes as a function of the distance from the "upstream" face (boundary of the membrane with the bed of the feed/retentate stream) and from the "downstream" face (boundary of the membrane with the bed of the permeate stream), while it changes in a comparatively negligible manner as a function of other  
25 coordinates.

In the present description the term "capacitive membrane" means a composite membrane comprising dense domains and porous domains wherein the porous domain are enhanced such to use above all the capacitive characteristics (absorption capacity of components of the gas phase) than the resistive characteristics (resistance  
30 to the flow of the components of the gas stream).

In the present description the term "dense domains" means a continuous, steady

liquid or solid, homogeneous or not homogeneous area that can be of different nature, for example polymer, ceramic, composite, and that is provided with an overall permeance near to that of the whole membrane.

In the present description the term "porous domains" means a solid, coherent or not-coherent (particulate) or mixed area, with an overall adsorption/absorption capacity of the key component near to that of the whole membrane.

In the present description the term "key component" means a component present in the feed gas stream that is desired to be removed or recovered from said stream; preferred key components are selected, for example, between nitrogen, carbon dioxide, sulphur dioxide, water, hydrogen, oxygen, hydrogen sulphide, methane, ethane, liquefiable components of natural gas and volatile organic compounds.

With reference to Fig. 2 it shows a plant that allows a method to be implemented (described below with reference to fig.1) for separating at least one key component KC from a multi-component gas stream GS according to the present invention.

Such process comprises the steps of:

a. providing a module 10 comprising at least one composite membrane 20, in turn comprising dense domains 21 permeable to the key component KC and porous domains 22 intended to adsorb the key component KC, wherein the dense domains 21 will be preferably and prevalently placed in the membrane 20 near the "upstream" face, while the porous domains 22 will be preferably and prevalently placed in the membrane 20 near the "downstream" face or, that is to say, wherein the porous domains 22 will be placed in series to the dense domains 21 with respect to the direction going from a first chamber 11 of the module 10 positioned upstream the composite membrane 20, or bed of feed stream GS/retentate RS, to a second chamber 12 of the module 10 placed downstream the composite membrane 20, or bed of the permeate stream (step 100);

b. feeding a multi-component gas stream GS to said module 10 and causing it to flow on the composite membrane 20 to divide it into a retentate stream RS (residual on the upstream side of the membrane) and a permeate stream PS (produced on the downstream side of the membrane), the permeate stream PS containing the key component KC in a preferential manner (step 101);

c. measuring the pressure  $P$  downstream the composite membrane 20 (or, as an alternative, measuring the partial pressure  $PP$  of the key component  $KC$  downstream the composite membrane 20) (step 102);

d. controlling the extraction of said permeate stream  $PS$  depending on the measured value of the pressure  $P$  downstream the composite membrane 20, such that

- upon reaching a predetermined maximum value  $p^{\max}$  of the pressure downstream the membrane, the permeate stream  $PS$  is extracted (or the extraction of the same stream  $PS$  is increased) until reaching a predetermined minimum value  $p^{\min}$  of the pressure  $P$  downstream the membrane, and

- upon reaching said predetermined minimum value  $p^{\min}$  of the pressure downstream the membrane, the extraction of the permeate stream  $PS$  is stopped (or the extraction of the same stream is reduced),

thus generating alternating cycles of partial pressure of the (potential) key component in the area downstream the membrane and performing a pseudo-steady state (step 103).

It is specified that, in comparison with continuous processes, strictly steady and with a constant potential for membrane separation of gas streams according to prior art, the process according to the present invention is run in a continuous, pseudo-steady state condition and with alternating potential through the regulation by cycles of the pressure  $P$  downstream the membrane 20, or of the partial pressure  $PP$  of the key component  $KC$  downstream the membrane 20.

The measurement of the pressure  $P$ , or of the partial pressure  $PP$  of the key component  $KC$ , downstream the composite membrane 20 preferably occurs in the second chamber 12 of the module 10 placed downstream the composite material 20, but it can occur in any point between the surface downstream the composite membrane 20 and the extraction of the permeate stream  $PS$ .

The process according to the present invention provides the pressure  $P$  downstream the membrane to be regulated by cycles between a maximum value  $p^{\max}$  and a minimum value  $p^{\min}$ ; as an alternative such regulation can be carried out between a maximum value  $pp^{\max}$  and a minimum value  $pp^{\min}$  of the partial pressure  $PP$  of the key component  $KC$  downstream the membrane.

The regulation by cycles of the pressure downstream the membrane occurs by subjugating to the latter variable to the extraction of permeate PS, which extraction is subjected to a cyclic change.

Cycles are determined by the maximum and minimum values set for the pressure P  
5 of the downstream permeate stream PS.

In the embodiment of the plant according to the present invention, that will be disclosed below in details with reference to figure 2, the regulation by cycles is performed by defining the opening/closing condition of a valve placed on the discharge line of the permeate stream.

10 In the embodiment of the plant according to the present invention therefore the measurement of the pressure P, or of the partial pressure PP of the key component KC, downstream the composite membrane 20 preferably occurs in the second chamber 12 of the module 10 placed downstream the composite membrane 20, but it can occur in any point between the face immediately downstream the membrane 20  
15 and the valve placed on the discharge line of the permeate stream.

The maximum and minimum values set for pressure P downstream the membrane or for the partial pressure PP of the key component KC downstream the membrane are defined by the permeance/separation factor combination desired for the process.

Generally the alternating conditions of the cycles of the extraction of the permeate  
20 stream are defined as a function of the combined target of recovery factor/permeate purity defined for the process. Particularly the maximum and minimum values of pressure or partial pressure of the key component downstream the membrane – or as an alternative such alternating frequency– can be optimized for achieving specific targets of real permeance  $n^E$  and of real selectivity  $\alpha^E$  to the key component KC of the  
25 membrane 20, from which the results of separation and purity factor of the permeate in the key component depend.

To this end the inventors have developed a suitable mathematical model that relates the partial pressure values to the characteristics of the membrane on the basis of some boundary conditions, shown below.

30 The model, simplified in the terms expressed below, describes the expected performances for separating the components A and B depending on characteristics of

permeance to gas species of dense domains of the membrane (denoted by  $\Pi_A$  and  $\Pi_B$ , respectively) and capacity of the porous domains of the membrane for the same components (denoted by  $C_A$  and  $C_B$ , respectively and by the symbols  $C_A''$  and  $C_B''$  with reference to the same properties evaluated per unit of area of the membrane).

- 5 The model relates the real performances of permeance to the key component A (denoted by  $\Pi_A^E$ ) and of the separation factor or selectivity of the membrane (denoted by the symbol  $\alpha_{A/B}^E$ ) to the cycle parameter of the pressure represented by the ratio (denoted below by  $x$ ) of maximum pressure in the cycle of the key component downstream the membrane ( $P_A^{PM}$ ) to the pressure of the same component in the feed flow ( $P_A^F$ ).

10 The discussion developed below makes reference to the simple case in which the opening degree of the valve collecting the permeate is subjugated to the pressure downstream the membrane by a simple scheme "all or nothing", between the lowermost limit (in this example, for simplicity reason, taken as equal to the null value,  $p^{\min} = 0$ ) and the uppermost limit ( $p^{\max}$ ) set such to guarantee the selected ratio ( $x$ ) of maximum pressure of the key component downstream the membrane to the pressure thereof in the feed flow ( $P_A^{PM}/P_A^F$ ).

The simplifying hypotheses formulated for developing the model are listed below:

- 20 a) the absorption capacity of dense domains in the membrane is negligible with respect to that of porous domains;
- b) the resistance to flow of gases in porous domains of the membrane is negligible with respect to that in dense domains;
- c) the absorption coefficient for gases A and B in porous domains is constant within the considered range of pressure;
- 25 d) the permeability to gases A and B in dense domains of the membrane is constant within the considered range of pressure;
- e) dead volumes between membrane and permeate collecting valve, downstream the membrane, are negligible.

30 Considering the hypotheses (a) and (b) it is possible to indicate that in all instants of the cycle, for times  $t$  ranging from time  $t = 0$ , where the pressure on the permeate side is minimum (null, in this example) to time  $t = t_C$ , where the pressure on the

permeate side reaches the maximum value (overall pressure  $p(t_c) = p^{\max}$ , pressure of the key component  $P_A^F(t_c) = P_A^{PM}$ , pressure of the second component  $P_B^F(t_c) = P_B^{PM}$ ), the flow of the key component through the membrane can be calculated by assuming the partial pressure profile of the component in dense domains of the membrane to correspond to the “pseudo-steady” state condition and that the partial pressure profile in porous domains of the membrane is substantially uniform and equal to the value of the same variable downstream the membrane (permeate side).

The flow density of each one of the components ( $J_A$  and  $J_B$ ) through the membrane at the generic time instant can therefore be expressed as the product of the corresponding permeance of dense domains of the membrane by the (instantaneous) difference in partial pressure of the component through the membrane, between the feed side and the permeate side:

$$J_A(t) = \Pi^A [P_A^F - P_A^{PM}(t)] \quad (\text{I-a})$$

$$J_B(t) = \Pi^B [P_B^F - P_B^{PM}(t)] \quad (\text{I-b})$$

Still considering the hypothesis (b), it is possible to ignore, with respect to  $t_c$ , the duration of the extraction of the permeate from dense domains of the membrane in the condition when the corresponding valve is opened and therefore to assume the whole cycle time to correspond to the interval  $t_c$ .

Considering the hypotheses (a) and (e), the number of moles stored at the generic time  $t$  in porous domains of the membrane per unit of area thereof ( $N_A''(t)$  and  $N_B''(t)$  for components A and B respectively) can be expressed as it follows, by the mass balance to the membrane (for times  $t \leq t_c$ ):

$$N_A''(t) = C_A'' P_A^P(t) = \int_0^t J_A(t') dt' \quad (\text{II-a})$$

$$N_B''(t) = C_B'' P_B^P(t) = \int_0^t J_B(t') dt' \quad (\text{II-b})$$

clearly resulting that:

$$\frac{dP_A^P}{dt} = \frac{J_A(t)}{C_A''} = \frac{\Pi_A}{C_A''} [P_A^F - P_A^P(t)] \quad (\text{III-a})$$



$$\frac{dP_B^P}{dt} = \frac{J_B(t)}{C_B''} = \frac{\Pi_B}{C_B''} [P_B^F - P_B^P(t)] \quad \text{(III-b)}$$

and, consequently, due to the constant value of the partial pressure of the feed components:

$$\frac{d(P_A^P - P_A^F)}{dt} = -\frac{\Pi_A}{C_A''} (P_A^P - P_A^F) \quad \text{(IV-a)}$$

$$5 \quad \frac{d(P_B^P - P_B^F)}{dt} = -\frac{\Pi_B}{C_B''} (P_B^P - P_B^F) \quad \text{(IV-b)}$$

By integrating the ordinary differential equations (IV) between the initial moment (null partial pressure on permeate side for both the components) and the time corresponding to cycle time  $t_C$  (partial pressure in the permeate equal to the corresponding maximum value for both the components), the following relations are  
10 obtained:

$$P_A^{PM} = P_A^F \left[ 1 - \exp\left(-\frac{\Pi_A}{C_A''} t_C\right) \right] \quad \text{(V-a)}$$

$$P_B^{PM} = P_B^F \left[ 1 - \exp\left(-\frac{\Pi_B}{C_B''} t_C\right) \right] \quad \text{(V-b)}$$

Therefore the cycle time can be evaluated as a function of the set ratio  $x$  ( $0 \leq x \leq 1$ ) of maximum pressure downstream the membrane (permeate side) to the feed pressure  
15 for the key component:

$$t_C = \frac{\Pi_A}{C_A''} \ln\left(\frac{1}{1-x}\right) = -\ln\left[(1-x)^{\Pi_A/C_A''}\right] \quad \text{(VI)}$$

The real permeance of the membrane therefore now can be evaluated as the ratio of number of moles of the key component collected to the permeate to the cycle time, per unit of nominal driving force (feed partial pressure). From (II-a) and from (VI)  
20 therefore it follows that

$$\Pi_A^E = \frac{N_A''(t_C)}{t_C} \frac{1}{P_A^F} = \frac{C_A''}{t_C} \frac{P_A^{PM}}{P_A^F} = \Pi_A \frac{x}{\ln\left(\frac{1}{1-x}\right)} \quad \text{(VII)}$$

Moles of the component B stored in the membrane per unit of area, in the time

corresponding to the closing interval of the valve, can be calculated by evaluating the maximum pressure of the component downstream the membrane (equations V-b and VI):

$$P_B^{PM} = P_B^F \left[ 1 - \exp\left(-\frac{\Pi_B}{C_B''} t_C\right) \right] \tag{VIII}$$

$$N_B''(t_C) = C_B'' P_B^{PM} = C_B'' P_B^F \left\{ 1 - \left[ \exp(-t_C) \right]^{\frac{\Pi_B}{C_B''}} \right\} = C_B'' P_B^F \left[ 1 - (1-x)^{\frac{C_A/C_B}{\Pi_A/\Pi_B}} \right] \tag{IX}$$

As regards the separation factor (corresponding to the efficacious selectivity of the membrane) it is possible to calculate such ratio between the moles of the components stored in the membrane during the cycle (and permeated through the membrane at the end of the cycle), with reference to the ratio between moles of the same components in the feed mixture:

$$\alpha_{A/B}^E = \frac{N_A''(t_C)/N_B''(t_C)}{P_A^F/P_B^F} = \frac{C_A'' P_A^{PM} P_B^F}{N_B''(t_C) P_A^F} = \left( \frac{C^A}{C^B} \right) \frac{x}{1 - (1-x)^{(C^A/C^B)/(\Pi^A/\Pi^B)}} \tag{X}$$

In order to manage the cycles it is finally useful to bring back the maximum value  $p^{\max}$  reached by the pressure of the permeate in the cycle, at which value the control system will operate the opening of the permeate collecting valve:

$$p^{\max} = P_A^{PM} + P_B^{PM} = P_A^F \left\{ x + \left[ 1 - (1-x)^{\frac{C_A/C_B}{\Pi_A/\Pi_B}} \right] \frac{P_B^F}{P_A^F} \right\} \tag{XI}$$

Below conclusions are summarized about the relations between membrane performances (efficacious permeance to the key component and separation factor), the capacity and permeability characteristics of the membrane components and the operating variable  $x$ , related to the maximum pressure of the cycle, that can be set to the optimal value within the range [0,1] as a function of specific targets, value of recovery of the key component or purity value of the permeate in the same component:

$$\Pi_A^E = \Pi^A \frac{x}{\ln\left(\frac{1}{1-x}\right)} \quad \text{Eq. (A)}$$

$$\alpha_{A/B}^E = \left(\frac{C^A}{C^B}\right) \frac{x}{1 - (1-x)^{(C^A/C^B)/(\Pi^A/\Pi^B)}} \quad \text{Eq. (B)}$$

$$\frac{P^{\max}}{P_A^F} = x + \left(\frac{P_B^F}{P_A^F}\right) \left[1 - (1-x)^{\frac{C_A/C_B}{\Pi_A/\Pi_B}}\right] \quad \text{Eq. (C)}$$

5

The fluctuation between  $p^{\min}$  and  $p^{\max}$  of the pressure downstream the membrane (permeate side) (or the fluctuation between  $pp^{\min}$  and  $pp^{\max}$  of the partial pressure of the key component KC downstream the membrane (permeate side) causes alternated phases of absorption and desorption of the chemical species, specifically of the key component KC, in porous domains 22 of adsorbent material, overlapping the flow of the same species, specifically of the key component KC, constantly directed from the retentate side to the permeate side of the membrane 20.

The process according to the present invention guarantees better separation efficiency conditions with respect to conventional membrane processes, in terms of productivity and selectivity for the key component KC to be separated (combination of real permeance  $\pi^E$  and real selectivity  $\alpha^E$ ), that can be optimized in the management of the process by selecting the maximum value  $p^{\max}$  in pressure fluctuation on the permeate side of the membrane (or by selecting the maximum value  $pp^{\max}$  in the fluctuation of the partial pressure of the key component on the permeate side of the membrane); in particular, by using selectivity characteristics of the porous domains 22 of the membrane 20, the membrane separation process according to the present invention allows values of separation factors to be obtained that are much higher than those that can be obtained in conventional processes.

The process according to the present invention provides to use a composite membrane 20 where dense domains 21, provided with a good permeability to the key component KC to be separated and placed in areas near the upstream surface of the membrane 20, and porous domains 22, characterized by high permeability (open

porosity and good void fraction) and a good selectivity in adsorption capacity for the key component KC to be separated and placed in areas near the downstream surface of the membrane are organized in series, with respect to the flow of the stream GS through the membrane itself.

- 5 The different dense domains 21 and porous domains 22 of the composite membrane 20 give thereto resistive and capacity characteristics, that are used for accomplishing the pseudo-steady state condition, with alternating potential, of the process according to the present invention; in particular the capacitive characteristics of the membrane 20 are those used in the transient state use condition, specific of the process according to the present invention, such capacitive characteristics being
- 10 substantially the capacity of storing the key component in the membrane, that is used in "loading" stages (that is adsorption ones) and "discharging" stages (that is desorption) provided by the process.

The composite membrane 20 may be made by putting near to each other a dense layer (resistive one) and a porous layer (capacitive one); or it can be a asymmetric composite membrane, that is a membrane with dense and porous layers made of the same material but with different structures; or according to a preferred embodiment of the present invention it can comprise new adsorbent materials whose porosity characteristics can be controlled.

- 15 As said above, the resistive characteristics of the membrane 20 are guaranteed by the dense domains 21, for example dense layers of a suitable thickness, placed on the upstream side of the membrane; such dense domains can be composed of polymeric rubbery or glassy material such as for instance polydimethylsiloxane (PDMS), polytrimethylsilylpropyne (PTMSP), ceramic matrices (for example the case of high
- 25 temperature applications) or other known matrices for gas separation membranes and whose permeability to the key component to be separated is such to allow layers to be obtained with permeance values suitable for the process by selecting values of the thickness of the layer within an acceptable range (typically, from some units to some tens of micrometers).

- 30 The porous domains 22 of the membrane 20 for example porous layers with a suitable thickness, are placed on the downstream side of the membrane such to

guarantee, as said above, the capacitive characteristics necessary for the process; such porous domains can be composed for instance of zeolites, metal-organic adsorbent materials (Metal-Organic Frameworks, MOFs), active carbons or other known materials applied in discontinuous adsorption separation processes, such as PSA (Pressure Swing Adsorption) or TSA (Temperature Swing Adsorption) wherein the capacitive properties of the materials are used to obtain high purity streams in the key component. The thickness of the porous layer of the membrane is limited, on one hand, by the condition of acceptable value for the characteristic cycle time in the regulation of the fluctuations of the pressure of the downstream environment of the membrane and, on the other side, by the need of maintaining sufficiently low the overall resistance of the porous layer to the permeation of gas components, such that it is considerably lower than the corresponding value for the set of the dense domains of the membrane.

Preferably the key component KC is selected among nitrogen, carbon dioxide, sulphur dioxide, water, hydrogen, oxygen, hydrogen sulphide, methane, ethane, liquefiable components of natural gas and volatile organic compounds.

Preferably the multi-component gas stream GS is selected among natural gas streams from which nitrogen, carbon dioxide, water or liquefiable components have to be removed; off-gas streams in refinery processes from which hydrogen has to be removed; steam-reforming streams or coal gasification streams for separating carbon dioxide from hydrogen; power station flue gases from which carbon dioxide has to be removed; olefins/ paraffins mixtures to be separated; air streams for preparing enriched oxygen streams or inert gas streams from which oxygen has to be separated; drain streams in ammonia production processes where hydrogen has to be separated from nitrogen; acid streams from which hydrogen sulphide has to be separated; air streams to be dehumidified; gaseous effluents of different nature to be purified from volatile organic compounds.

With reference to figure 2 the alternating potential plant 1 for separating at least one key component KC from a multi-component gas stream GS by capacitive membranes according to the present invention comprises:

- a module 10 comprising a first chamber 11, a second chamber 12 and at least one

composite membrane 20, wherein the first chamber 11 is positioned upstream the composite membrane 20 and the second chamber is positioned downstream the composite membrane 20;

- a feeding line 2 for the multi-component gas stream GS;

5 - a first discharge line 3 connected to the first chamber 11 and positioned also upstream the composite membrane 20, for a retentate stream RS separated from the multi-component gas stream GS;

- a second discharge line 5 connected to the second chamber 12 also placed downstream the composite membrane 20, for a permeate stream PS, separated from  
10 the multi-component gas stream GS and containing the key component KC;

- a storage unit 4; and

- means 6 for measuring and controlling the pressure P downstream the composite membrane 20; such means comprise for example a pressure transducer PT and a pressure controller (for example a microcontroller PIC).

15 In the suggested process, the composite membrane 20 comprises dense domains 21 permeable to the key component KC and porous domains 22 intended to adsorb the key component and wherein the means 6 are intended, upon reaching a predetermined maximum value  $p^{\max}$  of the pressure P downstream the composite membrane 20, to extract the permeate stream PS conveying it to the storage unit 4  
20 and, upon reaching a predetermined minimum value  $p^{\min}$  of said pressure P downstream the composite membrane 20, to stop the extraction of the permeate stream PS.

Preferably said means 6 comprise at least one pressure gauge, transmitter and regulator and a valve subjugated to said pressure gauge, transmitter and regulator.

25 It is specified that while the application of the process describe above can be considered for any value of the volumes of the upstream areas (first chamber 11) and downstream area (second chamber 12) of the membrane 20, the best performances as regards the separation factor of the key component are obtained for the case where the volume of the downstream area of the membrane (second chamber 12) is reduced  
30 to minimum values, consistently with the need of guaranteeing a good uniformity in pressure and composition on the whole downstream interface of the membrane 20, in

the different moments provided by the pressure cycle and by arranging the means intended to measure the pressure and to extract the permeate PS; this last consideration has a clear impact on operations adapting, for the use according to the process suggested in the present description, the current membrane separation modules, that can be considered for such type of use.

For clarity purposes, it is pointed out that the first chamber 11 and second chamber 12 have to be intended as environments, possibly also with very small volumes, wherein conditions different from each other are accomplished and are measurable for instance, according to the present process, pressure and composition conditions.

It is pointed out that, similarly to the process described above, the plant according to the present invention provides the possibility of performing a regulation by cycles between a maximum value  $p^{\max}$  and a minimum value  $p^{\min}$  of the pressure  $P$  downstream the composite membrane 20; as an alternative such regulation can be performed between a maximum value  $pp^{\max}$  and a minimum value  $pp^{\min}$  of the partial pressure  $PP$  of the key component  $KC$  downstream the composite membrane 20.

Such regulation can be performed by modulating the opening/closing degree of the valve collecting the permeate depending on the measurement of the pressure downstream the membrane or by modulating the purge gas flow that collects the permeate depending on the composition of the gas phase downstream the membrane.

The maximum and minimum values of the pressure can be optimized for achieving specific targets of real permeance  $\pi^E$  and real selectivity  $\alpha^E$  to the key component  $KC$  of the membrane 20.

The process and the plant according to the present invention are described below more in details and specifically with reference to the following Example, that has been developed on the basis of experimental data and as well as on the mathematical model disclosed above and that has to be intended for illustrative purposes and not as a limitation to the present invention.

**Example:** process for capturing carbon dioxide from flue gases

Performances obtainable by using the above process have been evaluated by

simulating it for the case of the separation of components of a binary mixture A/B, with key component A, specifically with  $A = \text{CO}_2$  and  $B = \text{N}_2$  for the process capturing carbon dioxide from flue gases.

5 The use of a simple two-layer membrane was assumed: a dense layer interfacing the retentate side of the separator and a porous layer interfacing the permeate side of the separator; the dense layer exhibits a permeance to components A and B equal to  $\pi^A$  and  $\pi^B$  respectively while the porous layer has adsorption capacity coefficients with respect to the two components equal to  $C^A$  and  $C^B$  respectively.

10 The relations for real permeance and selectivity are shown below for the case when the opening degree of the permeate collecting valve, as provided in the plant diagram shown in fig.2, is subjugated to the pressure downstream the membrane with a simple ON/OFF regulation between the lowermost null pressure limit ( $p^{\min} = 0$ ) and the uppermost limit set such that the ratio of maximum pressure of the key component downstream the membrane  $p^{\max}$  to the corresponding feed pressure  $P_A^F$  is equal to  $x$  ( $p^{\max} = x P_A^F$ ), when the following simplifying hypotheses are confirmed:

- a) absorption capacity of dense domains in the membrane is negligible with respect to that of dense domains;
- b) resistance to gas flow in porous domains in the membrane is negligible with respect to that in dense domains;
- c) absorption coefficient for gases A and B in porous domains is constant within the considered pressure range;
- d) permeability to gases A and B of the dense layer of the membrane is constant within the considered pressure range;
- 25 e) dead volumes between membrane and permeate collecting valve, downstream the membrane, are negligible.

Due to what mentioned above, the resulting relations for real permeance and selectivity to component A are:



$$\Pi_A^E = \Pi^A \frac{x}{\ln\left(\frac{1}{1-x}\right)} \tag{Eq. (A)}$$

$$\alpha_{A/B}^E = \left(\frac{C^A}{C^B}\right) \frac{x}{1-(1-x)^{(C^A/C^B)/(\Gamma^A/\Gamma^B)}} \tag{Eq. (B)}$$

The improvement in performances of the new process according to the present invention in comparison to the use of a conventional process using a membrane composed only of the dense layer according to prior art can be evaluated by the comparison with the corresponding permeance and selectivity values:  $\Pi^A$  and  $(\Pi^A / \Pi^B)$ .

The importance of the cycle regulation of the pressure downstream the membrane is essential for the process functionality, and in particular, for the actual influence of the contribution of porous domains on performances.

In the limit  $x \rightarrow 0$  (corresponding to the case  $p^{\max} = p^{\min} = 0$ , with strictly continuous process, without cycle regulation of the permeate pressure) from the above relations it results:

$$\lim_{x \rightarrow 0} \Pi_A^E = \Pi^A \tag{Eq. (D)}$$

$$\lim_{x \rightarrow 0} \alpha_{A/B}^E = \frac{\Pi^A}{\Pi^B} \tag{Eq. (E)}$$

Therefore in the case of a separation process using the considered membrane without the cycle regulation of the pressure downstream the membrane, the expected performances are the performances characteristic only of the dense layer.

As regards the actual performances of the process according to the present invention (see Eq.1), the comparison with reference values makes it possible to verify that the real permeability is influenced only by the permeability value of the membrane dense layer and by the value of the ratio  $x$ , decreasing as the latter increases up to the null real permeance limit for the limit condition  $x = 1$ , while the real selectivity value changes with continuity between value  $\Pi^A / \Pi^B$ , for the case of  $x = 0$ , finally

approaching the value  $C^A / C^B$ , the characteristic value for porous domains of the membrane, for the limit  $x = 1$ .

Considering the fact that for many pairs of low molecular weight species whose separation is of interest, the selectivity by adsorption of different adsorbent materials is much higher than the ratio between the permeance of the same components in conventional dense membranes, it is possible to appreciate the improvement of the performances thereof that can be obtained by modifying the membrane and by the contemporaneous regulation by cycles of the pressure downstream the membrane according to the present invention.

As regards the previous Example that makes reference to the case of the separation of  $\text{CO}_2/\text{N}_2$  mixture for which adsorbent materials with selectivity by adsorption in the order of several hundreds (order  $C^{\text{CO}_2} / C^{\text{N}_2} = 400$ ) are available, while the best high permeance dense membranes (order  $\pi^{\text{CO}_2} = 1.000$  GPU) are characterized by the permeability ratio  $\text{CO}_2/\text{N}_2$  lower than 10 (order  $\pi^{\text{CO}_2} / \pi^{\text{N}_2} = 10$ ).

Considering a possible coupling of a dense membrane of the above type with a good selectivity adsorbent material, on the basis of the relations expressed in Eq.1, in a process with regulation by cycles of the permeate pressure it is possible to raise to more than 10 times the real selectivity ( $\alpha_{\text{CO}_2/\text{N}_2}^E$  goes from 10 to 120) while reducing the real permeance only by about 16% ( $\pi^E$  from 1.000 GPU to 840 GPU) when the fraction  $x$  changes from 0 (steady continuous process) to 30% (pseudo-steady continuous process with regulation by cycles of the permeate pressure from  $p^{\text{min}} = 0$  to  $p^{\text{max}} = 0,3 P_{AF}$ ).

Real performances of the type calculated in the Example are actually higher than the limit currently found for conventional membrane separation processes.

Therefore as it results from the above Example the performances expected from the simplified analysis suggested above are actually better than those reached by the currently available technology.

Briefly, the main advantages of the process and plant according to the present invention are the fact of:

- getting much higher selectivity for the same overall permeance, thus considerably improving the separation factors without reduction in

productivity

- operating with continuous mode of operation, with strictly steady conditions for feed and retentate streams and with pseudo-steady cyclic conditions for the permeate stream;
- 5 - obtaining flexibility in running the process with the possibility of changing the performances of recovery factor/purity of the permeate through the handling of the level of the maximum pressure downstream the membrane in the used cycle;
- preserving the characteristics of modularity, simplicity and compactness of  
10 the apparatuses, resulting in lower investment costs; and
- avoiding the presence of moving parts, with positive impact on reliability, potentiality, operating costs and maintenance costs.

In the light of the above it is clear how the alternating potential process and plant with capacitive membranes described above allow the suggested objects to be  
15 achieved allowing a key component to be removed or recovered efficaciously from a multi-component gas stream.

Many variants can be made by the person skilled in the art to the process and plant described above, without for this reason departing from the scope of protection as it results from the annexed claims.

20

CLAIMS

1. A process for separating at least one key component (KC) from a multicomponent gas stream (GS) comprising the following steps:

- 5 a. providing a module (10) comprising at least one composite membrane (20), in turn comprising dense domains (21) permeable to said at least one key component (KC) and porous domains (22), placed in series to said dense domains (21) with respect to the direction going from a first chamber (11) of the module (10) positioned upstream the composite membrane (20) to a second chamber (12) of the module (10) positioned downstream the composite membrane (20), and suitable to adsorb said at least one key component (KC) (step 100);
- 10 b. feeding said multicomponent gas stream (GS) to said module (10) and causing it to flow on said at least one composite membrane (20) to divide it into a retentate stream (RS) and a permeate stream (PS), said permeate stream (PS) containing said at least one key component (KC) (step 101);
- 15 c. measuring the pressure (P) downstream the composite membrane (20) (step 102);
- d. controlling the extraction of said permeate stream (PS) depending on the measured value of the pressure (P) downstream the composite membrane (20), so that
- 20 - upon reaching a predetermined maximum value ( $p^{\max}$ ) of said pressure (P) downstream the composite membrane (20), said permeate stream (PS) is extracted until reaching a predetermined minimum value ( $p^{\min}$ ) of said pressure (P) downstream the composite membrane (20), and
- 25 - upon reaching said predetermined minimum value ( $p^{\min}$ ) of said pressure (P) downstream the composite membrane (20), the extraction of said permeate stream (PS) is stopped,

thus generating alternating cycles and performing a pseudo-steady state

condition (step 103).

2. A process according to claim 1, wherein said dense domains (21) are placed in the areas close to the upstream surface, with respect to the direction going from said first chamber (11) of the module (10) positioned upstream the composite membrane (20) to said second chamber (12) of the module (10) positioned downstream the composite membrane (20), and said porous domains (22) are placed in the areas close to the downstream surface, with respect to the direction going from said first chamber (11) of the module (10) positioned upstream the composite membrane (20) to said second chamber (12) of the module (10) positioned downstream the composite membrane (20).
3. A process according to claim 1 or 2, wherein the pressure (P) is measured at any point between the downstream surface of the composite membrane (20) and the extraction of the permeate stream (PS).
4. A process according to claim 3, wherein the pressure (P) is measured in said second chamber (12) of the module (10).
5. A process according to any of the preceding claims, wherein said predetermined maximum value ( $p^{\max}$ ) of said pressure (P) downstream the composite membrane (20) and said predetermined minimum value ( $p^{\min}$ ) of said pressure (P) downstream the composite membrane (20) are determined depending on the characteristics of real permeance ( $\Pi^E$ ) and real selectivity ( $\alpha^E$ ) to said at least one key component (KC), of said dense domains (21) and of said porous domains (22), respectively, of said composite membrane (20), according to the following equations:

$$\Pi_A^E = \Pi^A \frac{x}{\ln\left(\frac{1}{1-x}\right)} \quad (\text{VII})$$

$$\alpha_{A/B}^E = \left(\frac{C^A}{C^B}\right) \frac{x}{1 - (1-x)^{(C^A/C^B)/(\Pi^A/\Pi^B)}} \quad (\text{X})$$

$$\frac{P^{\max}}{P_A^F} = x + \left(\frac{P_B^F}{P_A^F}\right) \left[1 - (1-x)^{\frac{C_A/C_B}{\Pi_A/\Pi_B}}\right] \quad (\text{XI}).$$

wherein  $\pi^A$  and  $\pi^B$  denote the permeance of the dense domains of the composite membrane to key components A and B, respectively;  $C^A$  and  $C^B$  denote the solubility coefficients to key components A and B, respectively, in the porous domains of the composite membrane;  $P_A^F$  and  $P_B^F$  denote the partial pressure of components A and B, respectively, in the feed;  $x$  denotes the ratio between the cycle maximum value of the partial pressure of key component A downstream the composite membrane and  $p^{\max}$  denotes the corresponding maximum value of the total pressure downstream the composite membrane.

- 5  
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6. A process according to any of the preceding claims, wherein said at least one key component (KC) is nitrogen, carbon dioxide, sulfur dioxide, water, hydrogen, oxygen, hydrogen sulphide, methane, ethane, natural gas liquefiable components or volatile organic compounds, and wherein said multicomponent gas stream (GS) is selected from natural gas streams from which nitrogen, carbon dioxide, sulfur dioxide, water or liquefiable components have to be removed; off-gas streams of refinery processes from which hydrogen has to be recovered; steam-reforming or coal gasification streams in which carbon dioxide has to be separated from hydrogen; power plants flue gases from which carbon dioxide has to be removed; olefins/paraffins mixtures to be separated; air streams for preparing enriched oxygen or inert gas streams from which oxygen has to be separated; drain streams of ammonia production processes from which hydrogen has to be separated from nitrogen in streams; acid streams from which hydrogen sulphide has to be separated; air streams to be dehumidified; gaseous effluents of various origin to be purified from volatile organic compounds.
7. A process according to any of the preceding claims, further comprising the step of storing in a storage unit (4) said permeate stream (PS) separated from said multicomponent gas stream (GS) and containing said at least one key component (KC), said permeate stream (PS) being extracted upon reaching a predetermined maximum value ( $p^{\max}$ ) of the pressure (P) downstream the composite membrane (20) and until reaching a predetermined minimum value ( $p^{\min}$ ) of the pressure (P) downstream the composite membrane (20).
8. A plant (1) for the separation of at least one key component (KC) from a

multicomponent gas stream (GS) comprising:

- 5 - a module (10) comprising a first chamber (11), a second chamber (12) and at least one composite membrane (20), wherein said first chamber (11) is positioned upstream said at least one composite membrane (20) and said second chamber is positioned downstream said at least one composite membrane (20), with respect to the flow direction going from said first chamber (11) to said second chamber (12), and wherein said at least one composite membrane (20) in turn comprises dense domains (21) permeable to said at least one key component (KC) and porous domains (22) intended to adsorb said at least one key component (KC) and placed in series to said dense domains (21) with respect to the direction going from said first chamber (11) of the module (10) positioned upstream the composite membrane (20) to said second chamber (12) of the module (10) positioned downstream the composite membrane (20);
- 10 - a feeding line (2) for said multicomponent gas stream (GS);
- a first discharge line (3) for a retentate stream (RS), connected to said first chamber (11) and positioned upstream, with respect to the direction going from said first chamber (11) to said second chamber (12), said at least one composite membrane (20), said retentate stream (RS) being separated from said multicomponent gas stream (GS);
- 20 - a second discharge line (5) for a permeate stream (PS), connected to said second chamber (12) and positioned downstream, with respect to the direction going from said first chamber (11) to said second chamber (12), said at least one composite membrane (20), said permeate stream (PS) being separated from said multicomponent gas stream (GS) and containing said at least one key component (KC);
- 25 - a storage unit (4) connected to said second discharge line (5); and
- means (6) for measuring and controlling the pressure (P) downstream the

composite membrane (20),

characterized in that said means (6) are suitable, upon reaching a predetermined maximum value ( $p^{\max}$ ) of said pressure (P) downstream the composite membrane (20), to extract said permeate stream (PS) conveying it to said storage unit (4) and, upon reaching a predetermined minimum value ( $p^{\min}$ ) of said pressure (P) downstream the composite membrane (20), to stop the extraction of said permeate stream (PS).

9. A plant (1) according to claim 8, wherein said dense domains (21) and said porous domains (22) of said at least one composite membrane (20) are arranged in series with respect to the direction going from said first chamber (11) to said second chamber (12), said dense domains (21) being placed in the areas close to the upstream surface, with respect to the direction going from said first chamber (11) to said second chamber (12), of said composite membrane (20) and said porous domains (22) being placed in the areas close to the downstream surface, with respect to the direction going from said first chamber (11) to said second chamber (12), of said composite membrane (20).



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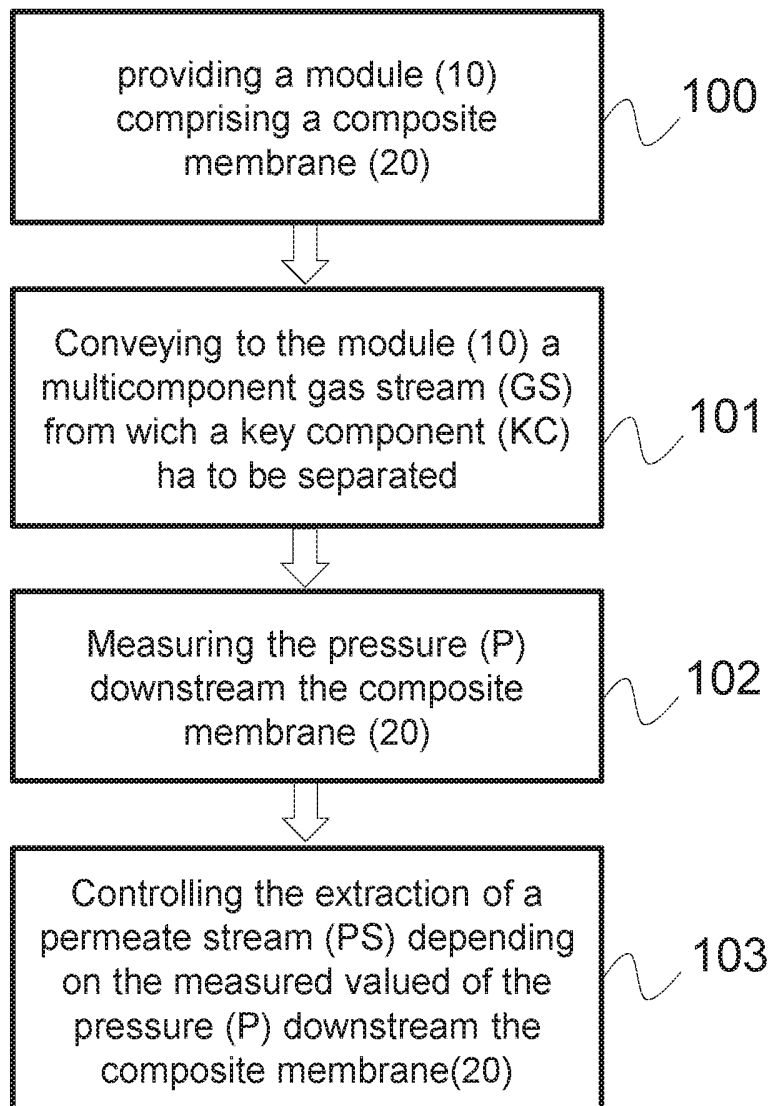


Fig. 1

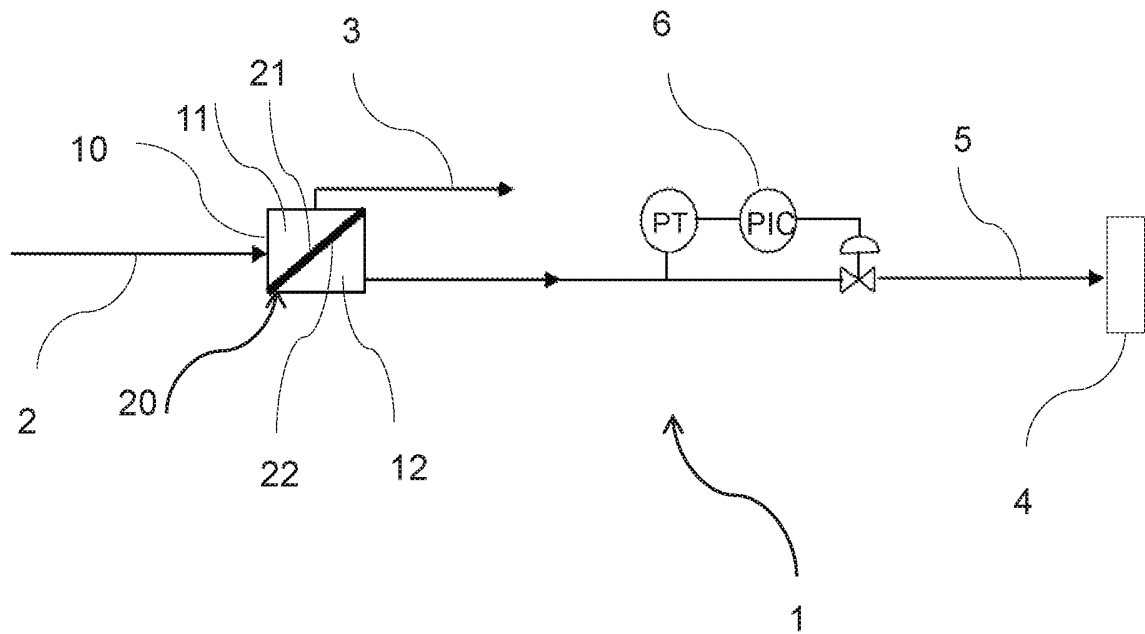


Fig. 2

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/IB2016/054285

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. B01D53/22 B01D71/00  
 ADD.  
 According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 B01D  
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/094377 A1 (NEL JOHANNES THEODORUS [ZA] ET AL) 28 April 2011 (2011-04-28) paragraphs [0010], [0050] - [0054]; figures 1, 2	1-9
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A	----- US 2006/107830 A1 (MILLER STEPHEN J [US] ET AL) 25 May 2006 (2006-05-25) paragraph [0064]; figure 1	1-9
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Further documents are listed in the continuation of Box C.  See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  27 October 2016	Date of mailing of the international search report  08/11/2016
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Focante, Francesca
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**INTERNATIONAL SEARCH REPORT**

International application No PCT/IB2016/054285
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