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(54) Title: BIOMASS ACTIVATED CARBON AS CO2 AND CO ABSORBENT, METHOD AND APPARATUS FOR SEPARATING CO AND CO2 FROM A GAS SUCH AS BLAST FURNACE GAS

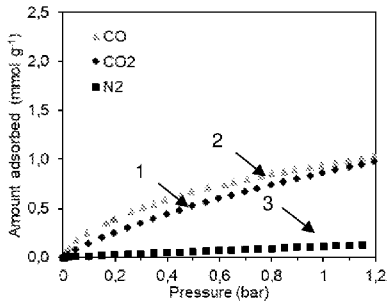

FIG. 10

(57) Abstract: The invention mainly relates to a biomass activated carbon as adsorbent for the separation of carbon dioxide and carbon monoxide from a gas containing at least carbon dioxide, carbon monoxide and inert components such as nitrogen and hydrogen, said biomass activated carbon having a porous structure prepared from fruit stones such as olive stones and impregnated with copper chloride. The invention also relates to a method of separation of carbon dioxide and carbon monoxide from a gas containing at least carbon dioxide, carbon monoxide, and inert components such as nitrogen and hydrogen, wherein said gas is subjected to flow through a CO2 and CO adsorbent layer comprising said biomass activated.

Biomass activated carbon as CO2 and CO adsorbent, method and apparatus for separating CO and CO2 from a gas such as blast furnace gas

The invention relates to a biomass activated carbon used as adsorbent for the separation of carbon dioxide and carbon monoxide from a gas.

The invention also relates to a method for preparing such biomass activated carbon.

The invention further relates to a method and an apparatus for separating both carbon monoxide and carbon dioxide from a gas containing at least carbon dioxide, carbon monoxide and inert components such as nitrogen and hydrogen.

Reduction of carbon dioxide and carbon monoxide emission is strongly desired to protect global environment. In a blast furnace ironmaking process, blast furnace top gas mainly contains carbon monoxide, carbon dioxide and inert components such as nitrogen and hydrogen. It is expected to separate carbon monoxide and carbon dioxide from the inert components to take advantages of them and to reduce the carbon dioxide and carbon monoxide emissions. It is therefore desired to carry out a selective separation of the two gases, carbon monoxide and carbon dioxide, from the rest of components, especially inert components such as nitrogen and hydrogen, in a gas, especially but not limited to blast furnace gas.

For recovering carbon dioxide, activated carbons are one of the widely used adsorbent in many industries involving separation, purification, water treatment, or energy storage because of their high surface area and pore volumes. They can be easily regenerated, and unlike other physical adsorbents such as zeolites or Metal Organic Framework adsorbents, they are hydrophobic and show high stability in humid conditions.

For this purpose, the use of activated carbon made from vegetable materials such as coconut shells, bamboo and olive stones is known but they are all only selective

towards carbon dioxide and are therefore only able to separate carbon dioxide from carbon monoxide.

An objective of the invention is to provide an activated adsorbent able to efficiently recovering both carbon monoxide and carbon dioxide from gas, especially from blast furnace gas.

Another objective of the invention is to provide an activated adsorbent prepared from vegetable material which is cheap, easily accessible and widely available.

Another objective of the invention is to provide a method and an apparatus for the separation of carbon dioxide and carbon monoxide from a gas which has high CO_2 and CO adsorption capacities and which is easy to implement.

To this end, the invention relates to a biomass activated carbon as adsorbent for the separation of carbon dioxide and carbon monoxide from a gas containing at least carbon dioxide, carbon monoxide and inert components such as nitrogen and hydrogen, said biomass activated carbon having a porous structure prepared from fruit stones and impregnated with copper chloride. Preferably, fruit stones comprise or are olive stones.

The invention also relates to a method for preparing such biomass activated carbon wherein said method comprises at least the following steps:

- supplying particles of fruit stones
- activating said particles to obtain activated particles of fruit stones
- mixing said activated particles of fruit stones with dissolved copper chloride, and
- drying and heat treating said mixing to obtain a biomass activated carbon having a porous structure prepared from fruit stones and impregnated with copper chloride.

The preparation method of the invention may also comprise the following optional characteristics considered separately or according to all possible technical combinations:

- the particles of fruit stones have a size between 1 and 3 millimeters,
- the activation step is carried out in a single activation procedure,
- wherein the activation step is carried out under carbon dioxide flow,
- fruit stones comprise or are olive stones

The invention further relates to a method of separation of carbon dioxide and carbon monoxide from a gas containing at least carbon dioxide, carbon monoxide, and inert components such as nitrogen and hydrogen, wherein said gas is subjected to flow through a CO_2 and CO adsorbent layer comprising the biomass activated carbon having a porous structure prepared from fruit stones and impregnated with copper chloride. Preferably, fruit stones comprise or are olive stones.

The separation method of the invention may also comprise the following optional characteristics considered separately or according to all possible technical combinations:

- the gas is further subjected to flow through a CO_2 adsorbent layer comprising a biomass activated carbon having a porous structure prepared from fruit stones,
- the gas is first subjected to flow through the CO_2 adsorbent layer and then subjected to flow through the CO_2 and CO adsorbent layer,
- the CO_2 and CO adsorbent layer and the CO_2 adsorbent layer are arranged in a single layered bed,
- the height of the CO_2 and CO adsorbent layer and the height of the CO_2 adsorbent layer in the single layered bad are substantially equal,

- the gas is subjected to flow through the CO_2 and CO adsorbent layer, or the CO_2 and CO, and CO_2 adsorbent layers, under a Vacuum Swing Separation method,

- the Vacuum Swing Separation method is a three-step Vacuum Swing Separation method comprising the steps of pressurization with feed, adsorption and evacuation,

- the Vacuum Swing Separation method is a four-step Vacuum Swing Separation method comprising the steps of pressurization with feed, adsorption, rinse and evacuation, or a five-step Vacuum Swing Separation method comprising the steps of pressurization with feed, adsorption, rinse, evacuation and purge,

- the step of rinse is carried out with a mixture of carbon dioxide and carbon monoxide,

- the duration of the step of rinse is less than the duration of the step of evacuation.

- the gas is a blast furnace gas

The invention finally relates to an apparatus for separating carbon dioxide and carbon monoxide from gas containing at least carbon dioxide, carbon monoxide, and inert components such as nitrogen and hydrogen, comprising at least one adsorption unit wherein at least a CO_2 and CO adsorbent layer comprising the biomass activated carbon having a porous structure prepared from fruit stones and impregnated with copper chloride is arranged in a single layered bed.

The apparatus of the invention may also comprise the following optional characteristics considered separately or according to all possible technical combinations:

- the CO_2 and CO adsorbent layer and a CO_2 adsorbent layer comprising a biomass activated carbon having a porous structure prepared from fruit stones, are arranged in the single layered bed,

- the CO_2 adsorbent layer is arranged before the CO_2 and CO adsorbent layer according to the direction of the gas flow,

- the height of the CO_2 and CO adsorbent layer and the height of the CO_2 adsorbent layer in the single layered bad are substantially equal.

Other characteristics and advantages of the invention will emerge clearly from the description of it that is given below by way of an indication and which is in no way restrictive, with reference to the appended figures in which :

- figure 1 is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with 3% of oxygen,
- figure 2 is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with hydrochloric acid,
- figure 3 is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with potassium chloride,
- figure 4a is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with carbon dioxide,
- figure 4b is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from cherry stones activated with carbon dioxide,
- figure 5 is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper acetate,

- figure 6 is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper nitrate,
- figure 7 is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper nitrate following by washing with distilled water at neutral pH,
- figure 8 is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper sulfate,
- figure 9 is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper chloride following by washing with distilled water at neutral pH,
- figure 10 is a graph showing adsorption isotherms of CO_2, CO and N_2 for a biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper sulfate without further washing with distilled water,
- figure 11 illustrates schematically a breakthrough curve for the sorption process in fixed beds,
- figure 12 illustrates the CO_2 and CO breakthrough curves obtained for a biomass activated carbon prepared from olive stones activated with carbon dioxide without further impregnation,
- figure 13 illustrates the CO_2 and CO breakthrough curves obtained for a biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper sulfate without further washing with distilled water,
- figure 14 illustrates the CO_2 and CO breakthrough curves obtained for a layered bed composed of a CO_2 adsorbent layer comprising the biomass activated carbon prepared from olive stones (without further impregnation), and the CO_2 and CO adsorbent layer comprising the biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper chloride (without further washing with distilled water), wherein the height of the CO_2 adsorbent layer

is of 25% and the height of the CO_2 and CO adsorbent layer is of 75%, and wherein the gas is first subjected to flow through the CO_2 adsorbent layer,

- figure 15 illustrates the CO_2 and CO breakthrough curves obtained for a layered bed composed a CO_2 and CO adsorbent layer comprising the biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper sulfate (without further washing with distilled water) and of the CO_2 adsorbent layer comprising the biomass activated carbon prepared from olive stones (without further impregnation), wherein the height of the CO_2 adsorbent layer and the height of the CO_2 and CO adsorbent layer are substantially equal, and wherein the gas is first subjected to flow through the CO_2 and CO adsorbent layer,

- figure 16 illustrates the CO_2 and CO breakthrough curves obtained for a layered bed composed a CO_2 and CO adsorbent layer comprising the biomass activated carbon prepared from olive stones activated with carbon dioxide and impregnated with copper sulfate (without further washing with distilled water) and of a CO_2 adsorbent layer comprising the biomass activated carbon prepared from olive stones (without further impregnation), wherein the height of the CO_2 adsorbent layer and the height of the CO_2 and CO adsorbent layer are substantially equal, and wherein the gas is first subjected to flow through the CO_2 adsorbent layer,

- figure 17 illustrates a cycle schedule for a 2 bed 3-step Vacuum Swing Separation cycle in an adsorption unit wherein a CO_2 adsorbent layer is arranged,

- figure 18 illustrates a cycle schedule for a 3 bed 4-step Vacuum Swing Separation cycle in an adsorption unit wherein a CO_2 adsorbent layer is arranged, and wherein the duration of the step of rinse and the duration of the step of evacuation are equal,

- figure 19 illustrates a cycle schedule for a 3 bed 4-step Vacuum Swing Separation cycle in an adsorption unit wherein a CO_2 adsorbent layer is arranged, and wherein the duration of the step of rinse is less than the duration of the step of evacuation, and

- figure 20 illustrates a cycle schedule for a 3 bed 5-step Vacuum Swing Separation cycle in an adsorption unit wherein a CO_2 adsorbent layer is arranged.

The inventors has discovered that a biomass activated carbon prepared from fruit stones such as olive stones and impregnated with copper chloride (without further washing) is highly suitable to carry out the separation of CO and CO_2 from a gas containing at least carbon dioxide, carbon monoxide and inert components such as nitrogen and hydrogen.

They have also discovered that the use of a second biomass activated carbon as adsorbent prepared from fruit stones as such olive stones without any further impregnation in combination with the CO and CO_2 biomass activated carbon involves a very high adsorption ability to CO and CO_2 and could therefore be use as adsorbents to carry out the separation of CO and CO2 from gas, as blast furnace gas.

They have also discovered that Vacuum Swing Separation is a suitable technology to achieve the separation of CO and CO_2 from the other components of the blast furnace gas with these both adsorbents. Moreover, it has been identified that applying the two selected adsorbents in layers in a bed of solids enhances the individual performance of the adsorbents to separate CO and CO_2 from the blast furnace gas.

A biomass activated carbon prepared from olive stones has been identified as the best candidate for the preparation of both adsorbents (CO_2 adsorbent, and CO_2 and CO adsorbent). Olive stones is an agricultural by-product which is abundant in many countries from the production of olive oil. The olive stones can be recycled by means of the production of activated carbons, since they constitute a source of renewable carbon with a low cost. In addition, they are suitable for preparing microporous activated carbons due to their low ash content.

The development of the porous structure is attained by an activation procedure. The production of carbon adsorbents from biomass precursors can involve chemical or physical activation to develop the porosity. Chemical activation involves the pyrolysis of the precursor with a chemical activating agent: hydroxides, carbonates, H_3PO_4 or $ZnCl_2$. Its main drawbacks are the price and the

environmental impact of the chemicals, which need to be eliminated after the treatment by thorough washing of the resulting carbon. Physical activation is considered to be more environmentally friendly. Such activation is commonly carried out in a two-step process. In a preferred embodiment a physical activation in a single-step activation procedure is chosen mainly because the single-step procedure is competitive to the conventional two-step procedure since it offers the possibility of carrying out the activation directly, avoiding the carbonisation or pyrolysis step.

Regarding the activating agent, although the use of steam as an activating agent is more widespread in the industry, the inventors has, in a preferred embodiment, chosen to use carbon dioxide which has been identified as more appropriate when precise control of porosity is needed. The activation with CO_2 generates, fundamentally, microposity, because CO_2 is an activating agent less oxidant than steam, which also generates meso and macropores. This microporosity is critical for defining the adsorption capacity at atmospheric pressure.

The results shown on figures 1 to 4 indicate the capacity at equilibrium of activated carbons prepared from olive stones and submitted to physical activation with different gases (3% of oxygen for figure 1, hydrochloric acid for figure 2, potassium chloride for figure 3 and carbon dioxide for figure 4) to adsorb CO_2 (reference 1), CO (reference 2) and N_2 (reference 3), the main components of the blast furnace gas. The physical adsorption of CO_2, CO, and N_2 at 50°C and up to 1.2 bar is determined in a volumetric device, TriStar 3000 from Micromeritics. The temperature is controlled by a Thermo Haake thermostatic bath. Prior to adsorption, the samples are outgassed at 100°C under vacuum overnight. It is observed that the physical activation with carbon dioxide involves the best absorption ability to CO_2, while it exhibits a very low absorption ability to CO. Figure 4b indicates the capacity at equilibrium of activated carbons prepared from cherry stones and submitted to physical activation carbon dioxide. It is observed that a biomass activated carbon prepared from cherry stones is also a candidate for the preparation of both adsorbents (CO_2 adsorbent, and CO_2 and CO adsorbent).

The preparation of the CO_2 adsorbent (and of the CO_2 and CO adsorbent of the invention) involve the following steps. Olive stones are ground and sieved, and particles with a size between 1 and 3 mm are selected for further processing. These particle sizes have been identified as the most suitable ones according to the dimensions of the adsorption column in order to avoid pressure drop through the system and channeling effects.

The development of the porous structure is attained by the activation procedure. The physical activation in a single-step activation procedure has been chosen, using a double-jacketed quartz reactor in a vertical furnace under gas flow. The activation of the adsorbent is obtained by loading approximately 70 g of raw biomass in a quartz reactor (I.D. 3.8 cm) and running an activation in CO_2 with a flow rate of 370 cm3 min-1. The heating rate used is 5°C min-1 and the temperature of activation and holding time are set at 800°C-360 min, respectively. Then a biomass activated carbon as adsorbent for the separation of CO_2 is obtained. Such biomass activated carbon is named the CO_2 adsorbent in the followings.

Concerning the preparation of the CO_2 and CO adsorbent of the invention, it has been identified that the best method to enhance the CO adsorption capacity of an activated carbon is by promoting copper chloride on the surface of the activated carbon through chemical impregnation. In order to do so, a carbon with substantial wider microporosity and/or mesoporosity is required to provide rapid internal mass transfer as well as to accommodate the reactive impregnates. Based on the textural characterization (showed below), the most promising material has been identified as the CO_2 adsorbent from olive stones activated with a carbon dioxide flow as obtained under the operating conditions as previously described.

Regarding the impregnation agent, the results showed on figures 5 to 10 indicate the capacity at equilibrium of activated carbons prepared from olive stones, submitted to physical activation in the single-step procedure with carbon dioxide, and impregnated with several agents (copper acetate for figure 5, copper nitrate for

figure 6, copper nitrate following by washing with distilled water at neutral pH for figure 7, copper sulfate not followed by washing with distilled water for figure 8, copper chloride following by washing with distilled water at neutral pH for figure 9, and copper chloride not followed by washing with distilled water for figure 10) to adsorb CO_2 (reference 1), CO (reference 2) and N_2 (reference 3).

It has been surprisingly observed that the only one activated carbon which is able to both adsorb CO and CO_2 is the sample impregnated with copper chloride not followed by washing with distilled water. Even if its CO_2 adsorption capacity is reduced compared to that of the CO_2 absorbent (figure 4), this double adsorption of CO and CO_2 allows to consider the use of a single activated carbon adsorbent for the reduction of CO and CO_2 from gas.

Then, the preparation of the CO_2 and CO adsorbent of the invention first involves the steps of preparation of particles of olives stones and physical activation, preferablywith carbon dioxide, as previously described for the preparation of the CO_2 adsorbent.

For the preparation of the impregnated CO_2 and CO adsorbent, 5 g of the copper chloride are dissolved in 50 mL distilled water and stirred magnetically for 5 minutes. Then, 10 g of the CO_2 adsorbent is poured into the solution and keep under stirring at room temperature and atmospheric pressure for 15 h. The sample is then dried at 100°C for 1 h. Finally, the prepared sample is heat-treated under N_2 (100 cm3 min-1) at 300°C for 2 h to produce the CO2 and CO adsorbent of the invention. As copper chloride is particular sensitive to air and water, all operations including preparation and storage must be performed in a dry inert atmosphere to prevent oxidation and hydrolysis.

The textural characterization of the CO_2 adsorbent and of the CO_2 and CO adsorbent of the invention is carried out by means of physical adsorption of N_2 at -196°C in a Micromeritics ASAP 2010 and adsorption of CO_2 at 0°C in a Micromeritics TriStar 3000. The adsorbents are outgassed at 100°C under vacuum overnight prior to adsorption measurements. The use of both adsorbates, N_2 and

CO_2, provides complementary information about the porous texture of the samples: the adsorption of CO_2 at 0°C and up to 1 bar is restricted to pores narrower than 1 nm, whereas N_2 adsorption at -196°C covers wider pore sizes but presents diffusion limitations in the narrower pores. The total pore volume is calculated from the amount of N_2 adsorbed at a relative pressure of 0.99, and the BET surface area from the Brunauer-Emmett-Teller equation (Brunauer, Emmett et al. 1938). The micropore volume is determined from the Dubinin- Radushkevich (DR) (Stoeckli 2001) and Dubinin-Astakhov (DA) (Stoeckli 1981) equations assuming a density of the adsorbed phase of 0.808 $cm^3\ g^{-1}$ for N_2 and 1.023 $cm^3\ g^{-1}$ for CO_2, a cross sectional area of 0.162 nm^2 for N_2 and 0.187 nm^2 for CO_2 and finally an affinity coefficient of 0.34 for N_2 and 0.36 for CO_2. The average micropore width (L0) is calculated through the Stoeckli-Ballerini equation (Stoeckli and Ballerini 1991).

Table 1 summarizes the textural parameters obtained from the analysis of the N_2 and CO_2 adsorption isotherms.

	CO2 adsorbent	CO2 and CO adsorbent
BET surface area ($m^2\ g^{-1}$)	1248	501
Total pore volume ($cm^3\ g^{-1}$)	0.53	0.24
Micropore volume ($cm^3\ g^{-1}$)[a]	0.48	0.19
Average micropore width (nm)[c]	1.09	1.12
Narrow Micropore colume ($cm^3\ g^{-1}$)[a]	0.44[b]	0.13[a]
Average narrow micropore width (nm)[c]	0.8	0.68

[a] Evaluted with the Dubinin-Radushkevich equation (n=2).

[b] Evaluted with the Dubinin-Astakhov equation (n=1.70).

[c] Determined with the Stoeckli-Ballerini relation.

Table 1 : Textural properties of the CO_2 adsorbent and of the CO2 and CO adsorbent of the invention

The CO and CO_2 adsorption capacities of the CO_2 adsorbent and of the CO_2 and CO adsorbent of the invention considered independently and also together in a single adsorption unit are submitted to dynamic tests in adsorption-desorption

cycles. From the knowledge of the inventors, all CO and CO_2 separation was previously carried out in two different adsorption unit.

The following five adsorbents are tested:

- adsorbent 1 is the CO_2 adsorbent as previously described,
- adsorbent 2 is the CO_2 and CO adsorbent of the invention as previously described,
- adsorbent 3 forms a layered bed of 25% height basis of CO_2 adsorbent and 75% height basis of CO_2 and CO adsorbent wherein the gas to be treated is first submitted to flow through the CO_2 adsorbent,
- adsorbent 4 forms a layered bed of 50% height basis of CO_2 adsorbent and 50% height basis of CO_2 and CO adsorbent wherein the gas to be treated is first submitted to flow through the CO_2 adsorbent,
- adsorbent 5 forms a layered bed of 50% height basis of CO_2 and CO adsorbent and 50% height basis of CO_2 adsorbent wherein the gas to be treated is first submitted to flow through the CO_2 and CO adsorbent.

Concerning the tests carried out with only adsorbent 1 or 2, the main characteristics of the adsorbent beds are summarized in Table 2 below. Because of their differences of density, the amount of adsorbent 2 (7.7 g) required for the experimental runs almost doubled that used for adsorbent 1 (4.5 g), as a consequence of targeting a similar bed height in all the experiments.

	Adsorbent 1	**Adsorbent 2**
Mass of adsorbent (g)	4.5	7.7
Particle size (mm)	1 to 3	1 to 3
Total porosity, ε_T	0.87	0.77
Helium density (g cm-3)[a]	2.14	2.26
Apparent density (g cm-3)[b]	0.50	0.85
Bed diameter (cm)	1.30	1.30
Bed height (cm)	12.15	11.00
Bed density (g cm^{-3})	0.28	0.53

[a] Determined by He pycnometry

[b] Determined with Hg porosimetry at 100 kPa.

Table 2 : Characteristics of the adsorbent 1 bed and of the adsorbent 2 bed.

For the adsorbents 3, 4 et 5, the total height of adsorbents used in the layered bed configurations is similar to that of the single bed of adsorbent 1 and adsorbent 2.

The tests are performed in a stainless steel fixed-bed reactor which is 13.3 cm in height, 1.3 cm in diameter and which is equipped with a porous plate located 4.7 cm from the base of the column. The gas manifold system consists of three lines fitted with mass flow controllers with flows ranging between 1 and 200 mL min^{-1} STP (Standard Temperature and Pression conditions).

The bed is packed with the activated carbon adsorbents 1, 2, 3, 4 and 5 in order to measure the dynamics of the CO_2 and CO in the column. A simulated blast furnace gas $CO_2/CO/N_2$ mixture (25/25/50 vol. %) is fed (40 mL.min^{-1} STP) to the adsorption unit and the adsorption performance of the samples is evaluated at a temperature of 45°C under isothermal conditions and at atmospheric pressure. For each adsorbent, six consecutive adsorption-desorption cycles are conducted to test the reproducibility of the system, where adsorption proceeded until saturation and desorption is extended to full regeneration of the activated carbon samples.

Each experimental run involved the following steps:

- (i) drying of the adsorbent before each experiment by flowing N_2 (40 mL min^{-1} STP) for 60 min at 180°C in the case of adsorbent 1 and under vacuum for 60 min at 100°C for adsorbents 2, 3, 4, and 5,
- (ii) after the drying step, the bed temperature and pressure are adjusted to the adsorption values in a pre-conditioning step of 30 min, where 40 mL min^{-1} (STP) of N_2 are allowed to flow through the system,
- (iii) this is followed by the adsorption step in which a $CO_2/CO/N_2$ gas mixture (25/25/50 vol. %) is fed to the pre-cleaned and pre-conditioned column for 60 min. The feed gas inlet flowrate is kept constant (40 mL min^{-1} (STP)),

- (iv) the adsorbed CO_2 and CO are completely desorbed by activating the vacuum pump for 60 min at a constant temperature of 45°C. The minimum pressure of the vacuum line is set to 0.005 bar to ensure dynamic vacuum during the evacuation step.

During the adsorption stage the CO_2 and CO concentrations in the column effluent gas are continuously monitored as a function of time-breakthrough curve (Figures 12, 13, 14, 15 and 16) and maximum or equilibrium dynamic adsorption capacity of the adsorbents are calculated after the outlet CO_2 concentration equaled that of the inlet stream. However, in a typical operation, the flow would be stopped or diverted to a fresh adsorbent bed once the CO_2 concentration reached that limit.

An example of breakthrough curve is illustrated in figure 11 where the C/C_0 (outlet adsorbate concentration/adsorbate feed concentration) is plotted versus time, and wherein C_0 is the initial feed concentration, t_b is the breakthrough time corresponding to the breakthrough concentration (C_b) and t_s is the saturation time.

At first, most of the mass transfer takes place near the bed inlet where the fluid first contacts the sorbent. As the experiment progresses, the solid near the inlet becomes saturated and the mass-transfer zone (which is S-shaped) where most of the change in concentration occurs moves down the bed further away from the inlet. At the break point, the solid between the bed inlet and the start of the mass-transfer zone is completely saturated (at equilibrium with the feed). In the case of no mass-transfer this zone would be of infinitesimal width, and the breakthrough curve would exhibit a perfect step with a vertical line from 0 to 1.0 when the solid reaches saturation. The limits of the breakthrough curve are often taken as C/C_0 values from 0.05 to 0.95, unless any other recommendation prevails. They are related to the break point (t_b, C_b) and saturation point (t_s, C_s), respectively.

Figures 12, 13, 14, 15 and 16 show the breakthrough curves respectively obtained for the adsorbent 1, 2, 3, 4 and 5 as previously described. In these figures, the breakthrough curves for CO are referenced by 4 and the breakthrough curves for CO_2 are referenced by 5.

The equilibrium CO_2 adsorption capacity and breakthrough time, t_b, or time it takes for CO_2 and CO to be detected at the adsorption column outlet, are calculated as an average of the values obtained from six consecutive adsorption-desorption cycles. Moreover, as adsorbents are fully regenerated, the repeatability of breakthrough curves could be assessed. Equilibrium adsorption capacities are determined by applying a mass balance to the bed as well as accounting for the gas accumulated in the intra-particle voids and dead volume of the bed.

The mass balance applied to the bed in each adsorption-desorption cycle is illustrated in Equation (1):

$$q_i = \frac{1}{m_{adsorbent}}\left[\underbrace{\int_0^{t_s}\left(F_{i,feed} - F_{i,out}\right)dt}_{(A)} - \underbrace{\frac{y_{i,feed}P_b\varepsilon_T V_b}{ZRT_b}}_{(B)} - \underbrace{\frac{y_{i,feed}P_b V_d}{ZRT_b}}_{(C)}\right] \quad (1)$$

where q_i is the specific adsorption capacity of the adsorbent for the component i; $m_{adsorbent}$ is the mass of adsorbent in the bed; $F_{i,feed}$ and $F_{i,out}$ are the molar flow rates of the component *i* at the inlet and outlet of the bed, respectively; t_s is the time required to reach saturation; $y_{i,feed}$ is the molar fraction of the component *i* in the feed stream; P_b and T_b are the pressure and temperature of the bed at equilibrium; ε_T is the total porosity of the bed; V_b is the bed volume; V_d is the dead volume in the system (tubing + column); *Z* is the compressibility factor of the component *i* at P_b and T_b; and *R* is the universal gas constant. In the present work, t_s is the time at which the bed is completely saturated, which means that the concentration of the component *i* at the bed outlet equals the feed concentration ($y_{i,out} = y_{i,feed}$).

The total porosity of the bed, ε_T, is calculated by means of the following equation:

$$\varepsilon_T = \varepsilon_b + (1 - \varepsilon_b)\varepsilon_p \qquad (2)$$

where ε_b is the packed bed porosity and ε_p is the particle porosity.

In Equation (1), the term (A) is the total number of moles of the component *i* retained in the system over the cycle time and it can be calculated by a graphical method that makes use of the outlet concentration of the component *i* and the total molar flow rate at each time *t* between 0 and t_s. Terms (B) and (C) are correction factors to account for the gas component *i* which has accumulated in the interstitial voids and dead space of the system, respectively.

Blank experiments are also conducted at 45°C and at atmospheric pressure in a bed packed with glass beads of approximately 3 mm diameter. With these experiments extra-column effects (e.g., gas holdup) during the breakthrough tests could be accounted for.

The adsorbed amounts of CO_2 and CO calculated from the breakthrough experiments are tabulated in Table 3.

Adsorbent N°	Description	CO_2 adsorption capacity		t_b, min	CO adsorption capacity		t_b, min
		(mmol g^{-1})	(g CO_2)		(mmol g^{-1})	(g CO)	
1	CO2 adsorbent	1.28	0.23	12.8	0.14	0.01	3.9
2	CO2 + CO adsorbent	0.26	0.07	4.8	0.37	0.07	5.1
3	25% ads 1 + 75% ads 2	0.40	0.10	4.6	0.43	0.07	4.5
4	50% ads 1 + 50% ads 2	0.45	0.10	6.0	0.31	0.04	4.3
5	50% ads 2 + 50% ads 1	0.62	0.13	6.2	0.28	0.03	2.7

Table 3 : Adsorbed amounts of CO and CO_2 estimated from breakthrough experiments with simulated blast furnace gas $CO_2/CO/N_2$ (25/25/50 vol. %) at 45°C and at atmospheric pressure on adsorbents 1, 2, 3, 4, and 5.

The values reported in Table 3 firstly confirm that the CO_2 adsorbent (adsorbent 1) is the best candidate for CO_2 separation. These values also confirm that the CO_2 and CO adsorbent of the invention (adsorbent 2) is able to adsorb CO_2 and CO at the same time even if its adsorption capacity to CO_2 is reduced compared to the CO_2 adsorbent (adsorbent 1).

These values also show that the combination of CO_2 adsorbent and CO_2 and CO adsorbent in a single layered bed allows to reach of very good adsorption capacity of both gases. This combination is then preferred to the sole CO_2 and CO adsorbent.

If we compare absorbent 4 (50% of CO_2 adsorbent and 50% of CO_2 and CO adsorbent wherein the gas is first submitted to flow through the CO_2 adsorbent) and adsorbent 5 (50% of CO_2 and CO adsorbent and 50% of CO_2 adsorbent wherein the gas is first submitted to flow through the CO_2 and CO adsorbent), it is observed that the values of CO and CO_2 are coherent while the CO breakthrough time t_b of adsorbent 5 is shorter than the breakthrough time t_b of adsorbents 3 and 4 and even than the breakthrough time t_b of absorbent 1 (CO_2 adsorbent) despite the fact that the CO absorption is higher. A combination of CO_2 adsorbent and CO_2 and CO adsorbent in a single layered bed wherein the gas containing CO, CO_2 and inert components as nitrogen and hydrogen is first submitted to flow through the CO_2 adsorbent is then preferred.

In terms of regeneration strategy, a Vacuum Swing Separation (VSA) based method has been selected to potentiate the performance of the adsorbents for the separation of CO and CO_2 containing CO, CO_2 and inert components as nitrogen and hydrogen, for example from the blast furnace gas.

A series of VSA cycles are tested in the one-column adsorption unit used to carry out the breakthrough curves previously described. The feed consisted of a mixture of CO_2/CO/N_2 (25/25/50 vol. %) with a flow rate of 40 mL min−1 (STP). The pressure and temperature during the adsorption step are fixed at atmospheric pressure and 45°C, and the minimum pressure of the vacuum line is set to 0.005 bar during regeneration. All the VSA steps are carried out co-currently with the feed.

The simplest VSA cycle that can be carried out consists of three steps: pressurization, adsorption and evacuation. In the 3-step VSA carried out experimentally, pressurization is carried out with the outlet of the column closed and using the feed. The duration of the pressurization and adsorption steps is set to 9 min for adsorbent 1 and 4 min for adsorbents 2, 3 and 4; this is near the breakthrough time of CO_2 under the aforementioned conditions. To simulate an operation with two columns and constant feed consumption, the time of the evacuation step is set equal to the sum of the adsorption and pressurization steps. As an example, the cycle schedule for the adsorbent 1 is presented in Figure 17 wherein the 2 bed 3-step VSA cycle is carried out at 45°C in the one column adsorption unit, wherein P is the pressurization with feed, A is adsorption and E is evacuation.

When the desired product is the component that is preferentially adsorbed, it is common practice to recycle part of the product to carry out a rinse step between the adsorption and evacuation steps that may improve the purity. To explore this possibility, a 4-step VSA cycle has been carried out consisting of: pressurization with feed, adsorption, rinse and evacuation. The rinse step has been carried out with pure CO_2 in the case of the bed with CO_2 adsorbent (adsorbent 1) and with a mixture of CO and CO_2 when adsorbents 2, 3 and 4 have been evaluated. The duration of the feed and evacuation steps are kept equal to those of the previous cycle for comparison purposes, and the rinse step duration is set equal to that of the feed to simulate and operation with three columns and constant feed consumption. As an example, the cycle schedule for the absorbent 1 is presented in figure 18 wherein P is the pressurization with feed, A is adsorption, R is rinse

with CO_2 and E is evacuation. The flow rate of CO_2 during the rinse step is set to give a molar rinse-to-feed (R/F) ratio of 0.7 (wherein R is the quantity of CO_2 fed during the rinse step expressed in mol and F is the quantity of CO_2 fed during both pressurization and adsorption steps also expressed in mol), whereas the flow rate of the mixture of CO/CO_2 is set to give a molar rinse-to-feed ratio of 0.9.

To improve the recovery of CO_2 and CO_2/CO, the evacuation step of the 4-step cycle is extended. The duration of the feed step (pressurization and adsorption steps) is kept equal to that of the previous cycles, and the duration of the rinse step is shortened to account for the extension of the evacuation step. The cycle schedule for the absorbent 1 is presented in figure 19 wherein as for the cycle of figure 18 P is the pressurization with feed, A is adsorption, R is rinse with CO_2 and E is evacuation. The rinse-to-feed ratio is kept at 0.7 and 0.9 for CO_2 and CO/CO_2, respectively, as in the previous configuration.

In order to try to improve further the recovery of the desired product a purge step at low pressure after the evacuation step is carried out by recycling part of the raffinate product. To carry out this 5-step cycle configuration in the separation unit, a small flow rate (10 mL min−1 (STP)) of pure N_2 is used. The feed and rinse step times and flow rates are kept equal to those used in the previous cycle configuration, but the last stage of the evacuation step is replaced with a purge step at low pressure The cycle schedule for the absorbent 1 is presented in figure 20 wherein P is the pressurization with feed, A is adsorption, R is rinse with CO_2, E is evacuation and N is light purge with N_2.

Three parameters are evaluated to compare different cycle configurations and adsorbent performances: the purity of the product stream (CO and CO_2 concentration in the product gas), the recovery of the components of interest (CO_2 and CO) and the throughput per mass of adsorbent and cycle time. These parameters are calculated as follows:

$$CO_2(CO)\ purity\ (\%) = \frac{mol\ CO_2(CO)\ out\ production\ stage}{total\ mol\ out\ production\ stage}$$

$$= \frac{\int_{t_{R_0}}^{t_{R_f}} F_{CO_2/CO,out}\,dt}{\int_{t_{R_0}}^{t_{R_f}} F_{CO_2,out}\,dt + \int_{t_{R_0}}^{t_{R_f}} F_{CO,out}\,dt + \int_{t_{R_0}}^{t_{R_f}} F_{N_2,out}\,dt} \times 100 \quad (3)$$

$$CO_2(CO)\ recovery\ (\%) = \frac{mol\ CO_2(CO)\ out\ production\ stage}{total\ mol\ CO_2(CO)\ fed\ in\ cycle\ time}$$

$$= \frac{\int_{t_{R_0}}^{t_{R_f}} F_{CO_2/CO,out}\,dt}{\int_0^{t_{Feed}} F_{CO_2/CO,in}\,dt} \times 100 \quad (4)$$

$$Throughput\ (mol\ kg^{-1}h^{-1}) = \frac{mol\ CO_2(CO)\ out\ production\ stage}{cycle\ time\ \times mass\ of\ adsorbent}$$

$$= \frac{\int_{t_{R_0}}^{t_{R_f}} F_{CO_2/CO,out}\,dt}{t_{cycle} \times m_{adsorbent}} \quad (5)$$

where t_{R0} refers to the time of the cycle at which the production step begins, t_{Rf} refers to the cycle time at which the production step is finalized, and t_{cycle} to the full cycle time. To reduce the calculation error in the integration of the outlet flow rate due to the limited number of data points, only the data corresponding to cyclic steady state are used (CSS). CSS is attained when the molar flow rates at any time in the cycle remain the same in all subsequent cycles.

Alternatively, when the VSA cycle configuration includes a step with product recycle (rinse) the recovery and productivity of CO_2 and CO are calculated as follows:

$$CO_2(CO)\ recovery\ (\%)$$

$$= \frac{mol\ CO_2(CO)\ out\ production\ stage - mol\ CO_2(CO)\ in\ rinse}{mol\ CO_2(CO)\ fed\ in\ pressurization\ and\ adsorption\ steps} \quad (6)$$

$$= \frac{\int_{t_{R_0}}^{t_{R_f}} F_{CO_2/CO,out}\,dt - \int_{t_{0,Rinse}}^{t_{f,Rinse}} F_{CO_2/CO,in}\,dt}{\int_0^{t_{Feed}} F_{CO_2/CO,in}\,dt} \times 100$$

$$Throughput\ (mol\ kg^{-1}h^{-1})$$

$$= \frac{mol\ CO_2(CO)\ out\ production\ stage - mol\ CO_2(CO)\ in\ rinse}{cycle\ time\ \times mass\ of\ adsorbent} \quad (7)$$

$$= \frac{\int_{t_{R_0}}^{t_{R_f}} F_{CO_2/CO,out}\,dt - \int_{t_{0,Rinse}}^{t_{f,Rinse}} F_{CO_2/CO,in}\,dt}{t_{cycle} \times m_{adsorbent}}$$

where $t_{0,Rinse}$ refers to the cycle time at which the rinse step begins, and $t_{f,Rinse}$ to the cycle time at which the rinse step finishes.

Table 4 summarizes the operating conditions of the VSA experiments conducted.

Total flow : 40 ml.min^{-1} at 45°C CO_2/CO/N_2 (25/25/50% vol.)						
		P	A	R	E	N
Adsorbent 1	3 Step cycle	2 min	7 min	No	9 min	No
	4-step cycle	2 min	7 min	9min 70% CO_2	9 min	No
	4-step cycle	2 min	7 min	5min 70% CO_2	13 min	No
	5-step cycle	2 min	7 min	5min 70% CO_2	5 min	4 min 10mL/min N_2
Adsorbent 2, 3 and 4	3-step cycle	2 min	2 min	No	4 min	No
	4-step cycle	2 min	2 min	4 min (90% CO+CO_2)	4 min	No
	4-step cycle	2 min	2 min	2 min	6 min	No

				(90% $CO+CO_2$)		
	5-step cycle	2 min	2 min	4 min (90% $CO+CO_2$)	2 min	2 min 10mL/min N_2
	5-step cycle	2 min	2 min	2 min (90% $CO+CO_2$)	4 min	2 min 10mL/min N_2

Table 4. Operating conditions and parameters of the VSA adsorption-desorption cycles for adsorbent 1, and adsorbents 2, 3 and 4 submitted to a 3-step VSA cycle, to a 4-step VSA cycle wherein the rinse step duration is set equal to that of the feed, to a 4-step VSA cycle wherein the rinse step is shortened, to a 5-step VSA cycle wherein the rinse step duration is set equal to that of the feed, and to a 5-step VSA cycle wherein the rinse step is shortened. P= pressurization step, A = adsorption step, R = Rinse step, E = evacuation step and N = purge step with N2

During the pressurization step, the adsorber outlet is closed, and neither CO_2, CO nor N_2 leave the adsorber. When the adsorber outlet is opened, during the first moments part of the CO_2 fed leaves the column in the raffinate. During the adsorption step, a partially decarbonized raffinate is produced due to the preferential adsorption of CO_2 over CO and N_2 on the CO_2 adsorbent. At the beginning of the evacuation step, the pressure in the bed decreases very fast and the molar flow rates of CO_2, CO and N_2 leaving the adsorber reach their maximum values but drop down afterwards.

Tables 5, 6, 7 and 8 summary of the results for the different VSA configurations evaluated on adsorbents 1, 2, 3 and 4 for the five cycles, the 4-step previously described.

VSA configurations		CO_2 Purity (%)	CO_2 Recovery (%)	Throughput (mol CO_2 kg^{-1} h^{-1})	qCO_2 (mmol CO_2 g $adsorbent^{-1}$)
3-step		61.3	>100	3.03	0.74
4-step	**9 min R**	82.3	44.3	1.56	1.42
	5 min R	67.2	79.3	2.17	1.11
5-step	**9 min R**	73.3	53.3	1.78	1.43

R = rinse with pure CO_2

Table 5 : Results of the VSA configurations evaluated on adsorbent 1.

VSA configurations		CO_2+ CO Purity (%)	CO_2+CO Recovery (%)	Throughput (mol CO_2+CO kg^{-1} h^{-1})	QCO_2+CO (mmol CO_2+CO g $adsorbent^{-1}$)
3-step		79.5	>100	4.15	0.44
4-step	**4 min R**	95.3	59.4	2.77	0.83
	2 min R	93.5	78.2	2.80	0.64
5-step	**4 min R**	90.9	57.7	2.78	0.90
	2 min R	89.3	84.3	3.07	0.68

R = rinse with à mixture CO_2-CO

Table 6 : Results of the VSA configurations evaluated on adsorbent 2.

VSA configurations		CO_2+CO Purity (%)	CO_2+CO Recovery (%)	Throughput (mol CO_2+CO kg^{-1} h^{-1})	QCO_2+CO (mmol CO_2+CO g $adsorbent^{-1}$)
3-step		78.5	>100	5.07	0.50
4-step	**4 min R**	94.6	58.1	3.14	0.95
	2 min R	92.9	84.3	3.53	0.74
5-step	**4 min R**	90.2	58.0	3.17	1.02
	2 min R	88.4	88.2	3.86	0.81

R = rinse with à mixture CO_2-CO

Table 7 : Results on the VSA configurations evaluated on adsorbent 3

VSA configurations		CO_2+CO Purity (%)	CO_2+CO Recovery (%)	Throughput (mol CO_2+CO kg^{-1} h^{-1})	QCO_2+CO (mmol CO_2+CO g $adsorbent^{-1}$)
3-step		72.9	>100	6.14	0.55
4-step	**4 min R**	94.6	70.1	4.31	1.03
	2 min R	92.8	95.8	4.46	0.82
5-step	**4 min R**	91.1	75.3	4.56	1.13
	2 min R	89.0	81.2	3.81	0.84

R = rinse with à mixture CO_2-CO

Table 8 : Results on the VSA configurations evaluated on adsorbent 4

From the analysis of the VSA cycles parameters it is clearly deduced that there is a trade-off between the purity and the recovery whereas the throughput is linked to the adsorption capacity of the adsorbent bed. The performance of the beds with a single adsorbent to separate CO and CO_2 from the simulated blast furnace gas stream seems discrete in all the tested configurations particularly for adsorbent 1 that shows greater selectivity to adsorb CO_2. Adsorbent 2 shows good performance, in terms of purity and recovery, in some of the tested VSA configurations but this is at the expense of the reduction in capacity and productivity. However, when these both adsorbents 1 and 2 are layered in the same bed the performance to separate CO and CO_2 is significantly enhanced: purity and recovery can be as high as 95% and the throughput is significantly enhanced compared to the single adsorbent 2 bed due to the improvement obtained in the adsorption capacity to CO and CO_2. Finally, it is observed that the reduction of the rinse step duration allow to reach the best results. Such configuration is then preferred.

Although the above results have been conducted with a simulated blast furnace gas, the biomass activated carbon as adsorbent of the invention and the method and the apparatus of separation of the invention apply to all gas containing at least carbon dioxide, carbon monoxide and inert components such as nitrogen and hydrogen.

CLAIMS

1. Biomass activated carbon as adsorbent for the separation of carbon dioxide and carbon monoxide from a gas containing at least carbon dioxide, carbon monoxide and inert components such as nitrogen and hydrogen, said biomass activated carbon having a porous structure prepared from fruit stones and impregnated with copper chloride.

2. Biomass activated carbon of claim 1, wherein said fruit stones comprise olive stones.

3. Method of preparation of the biomass activated carbon of claims 1 or 2, wherein said method comprises at least the following steps:

    - supplying particles of fruit stones
    - activating said particles to obtain activated particles of fruit stones
    - mixing said activated particles of fruit stones with dissolved copper chloride, and
    - drying and heat treating said mixing to obtain a biomass activated carbon having a porous structure prepared from fruit stones and impregnated with copper chloride.

4. Method according to the preceding claim wherein said particles of fruit stones have a size between 1 and 3 millimeters.

5. Method according to one of claims 3 and 4, wherein the activation step is carried out in a single activation procedure.

6. Method according to the preceding claim wherein the activation step is carried out under carbon dioxide flow.

7. Method according to one of claims 3 to 6, wherein said fruit stones comprise olive stones.

8. Method of separation of carbon dioxide and carbon monoxide from a gas containing at least carbon dioxide, carbon monoxide, and inert components such as nitrogen and hydrogen, wherein said gas is subjected to flow through a CO_2 and CO adsorbent layer comprising the biomass activated carbon of claims 1 or 2.

9. Method according to the preceding claim, wherein said gas is further subjected to flow through a CO_2 adsorbent layer comprising a biomass activated carbon having a porous structure prepared from fruit stones.

10. Method according to the preceding claim, wherein said gas is first subjected to flow through the CO_2 adsorbent layer and then subjected to flow through the CO_2 and CO adsorbent layer.

11. Method according to one of claims 8 and 9, wherein the CO_2 and CO adsorbent layer and the CO_2 adsorbent layer are arranged in a single layered bed.

12. Method according to the preceding claim, wherein the height of the CO_2 and CO adsorbent layer and the height of the CO_2 adsorbent layer in the single layered bad are substantially equal.

13. Method according to one of claims 8 to 12, wherein said gas is subjected to flow through the CO_2 and CO adsorbent layer, or the CO_2 and CO, and CO_2 adsorbent layers, under a Vacuum Swing Separation method.

14. Method according to the preceding claim, wherein said Vacuum Swing Separation method is a three-step Vacuum Swing Separation method comprising the steps of pressurization with feed, adsorption and evacuation.

15. Method according to claim 11, wherein Vacuum Swing Separation method is a four-step Vacuum Swing Separation method comprising the steps of pressurization with feed, adsorption, rinse and evacuation, or a five-step

Vacuum Swing Separation method comprising the steps of pressurization with feed, adsorption, rinse, evacuation and purge.

16. Method according to the preceding claim, wherein the step of rinse is carried out with a mixture of carbon dioxide and carbon monoxide.

17. Method according to one of the claims 13 and 14, wherein the duration of the step of rinse is less than the duration of the step of evacuation.

18. Method according to one of claims 6 to 15 wherein said gas is a blast furnace gas.

19. Apparatus for separating carbon dioxide and carbon monoxide from gas containing at least carbon dioxide, carbon monoxide, and inert components such as nitrogen and hydrogen, comprising at least one adsorption unit wherein at least a CO_2 and CO adsorbent layer comprising the biomass activated carbon of claims 1 or 2 is arranged in a single layered bed.

20. Apparatus according to the preceding claim, wherein the CO_2 and CO adsorbent layer and a CO_2 adsorbent layer comprising a biomass activated carbon having a porous structure prepared from fruit stones, are arranged in the single layered bed.

21. Apparatus according to the preceding claim, wherein the CO_2 adsorbent layer is arranged before the CO_2 and CO adsorbent layer according to the direction of the gas flow.

22. Apparatus according to one of claims 18 and 19, wherein the height of the CO_2 and CO adsorbent layer and the height of the CO_2 adsorbent layer in the single layered bad are substantially equal.

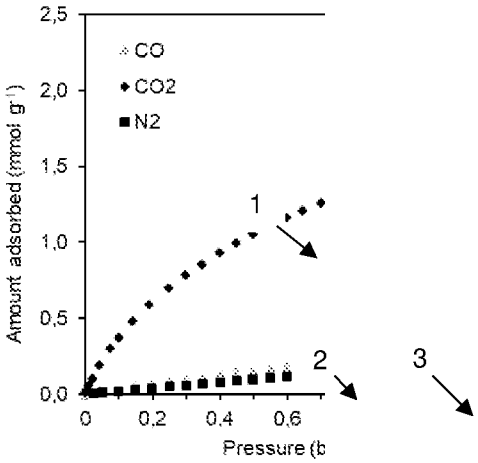

FIG. 1

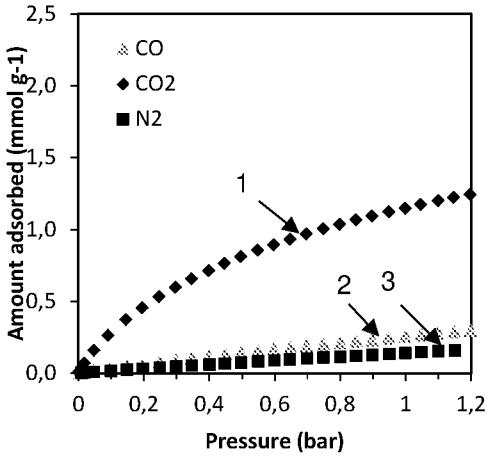

FIG. 2

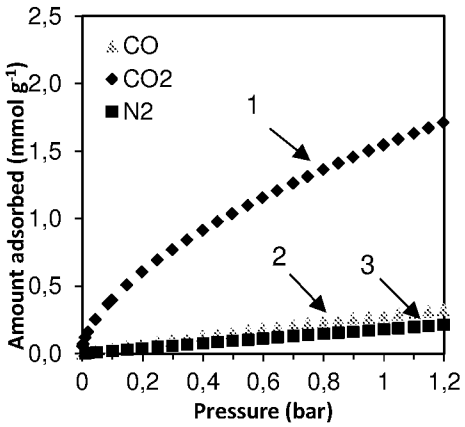

FIG. 3

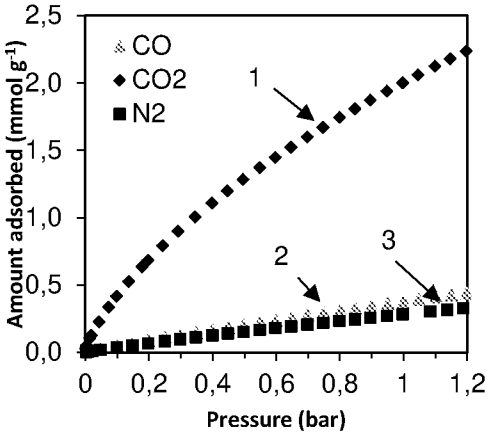

FIG. 4a

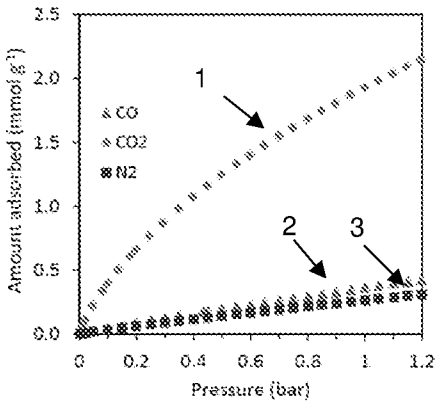

FIG. 4b

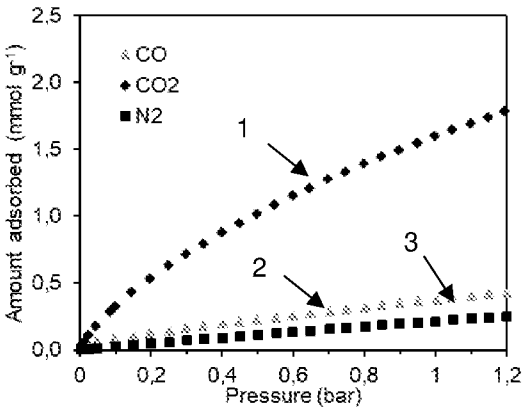

FIG. 5

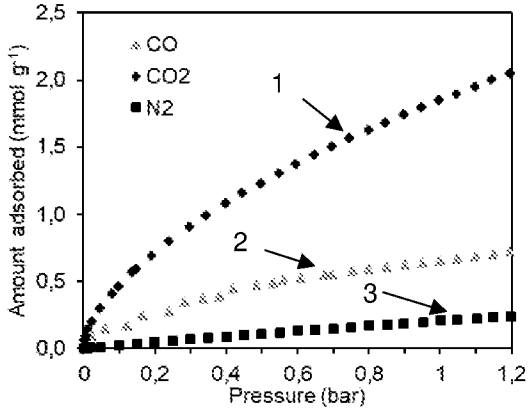

FIG. 6

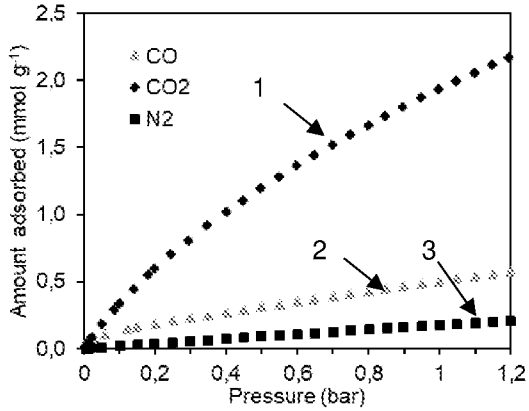

FIG. 7

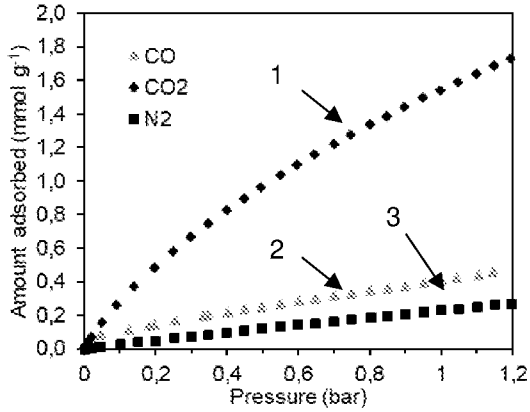

FIG. 8

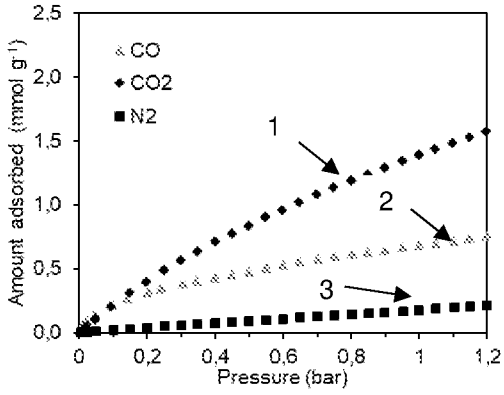

FIG. 9

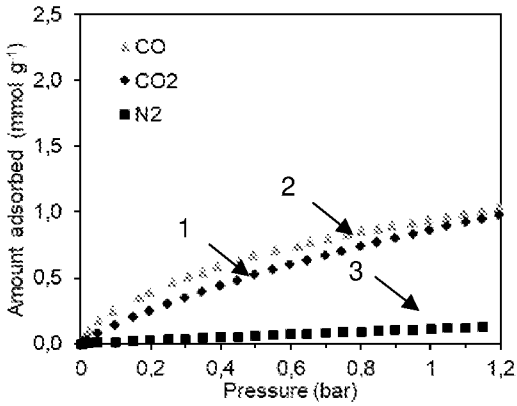

FIG. 10

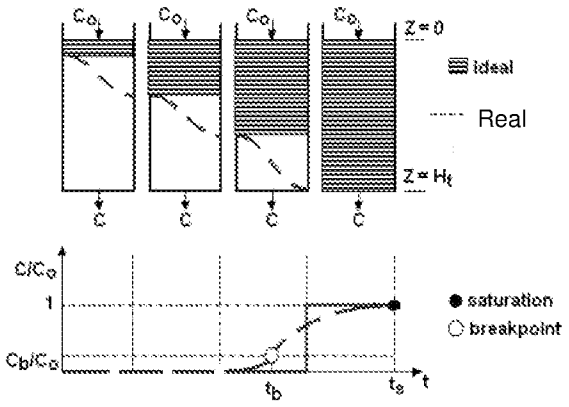

FIG. 11

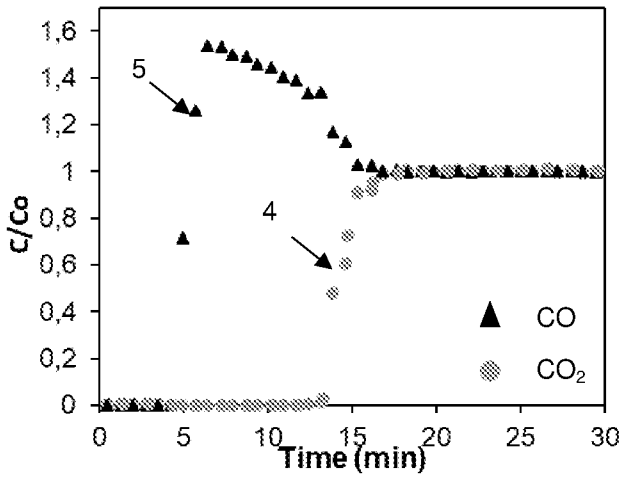

FIG. 12

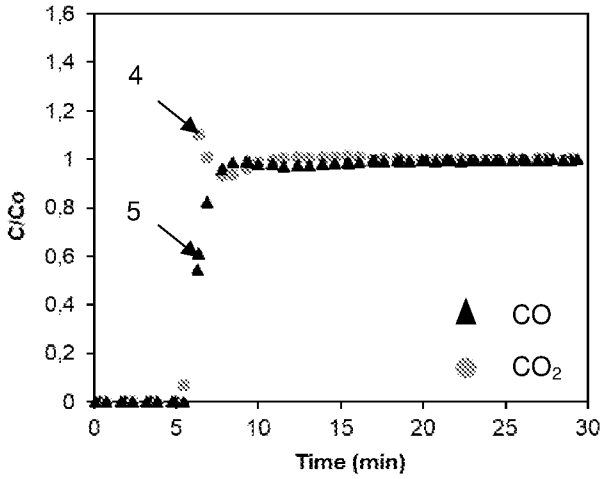

FIG. 13

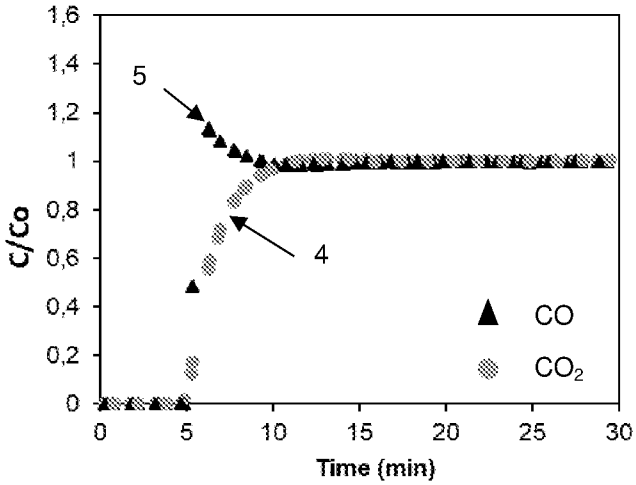

FIG. 14

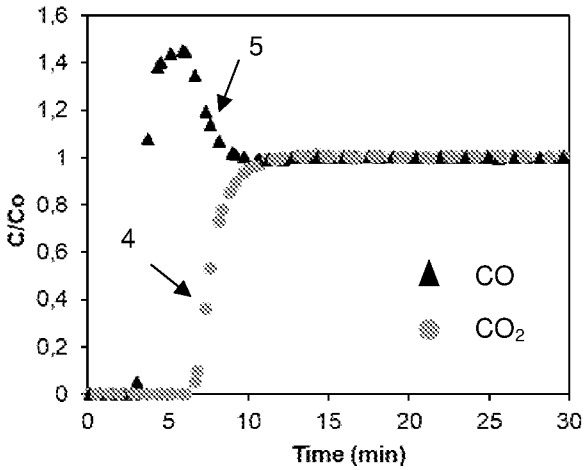

FIG. 15

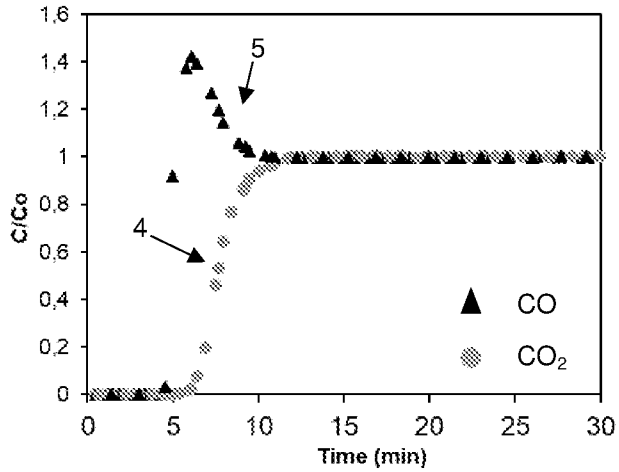

FIG. 16

FIG. 17

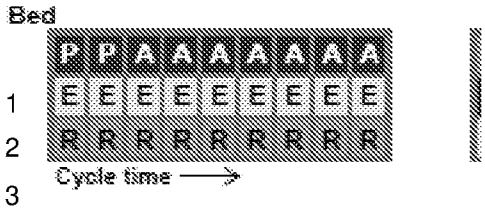

FIG. 18

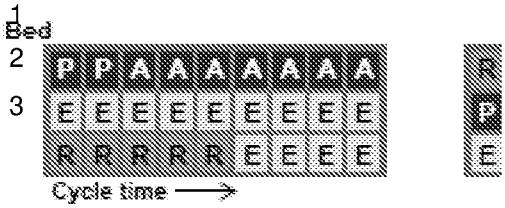

FIG. 19

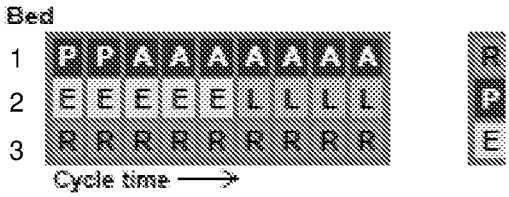

FIG.20

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/056878

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/32 B01J20/20 B01J20/02 B01D53/02 B01D53/047
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)
B01J B01D C01B

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.
X	US 5 482 915 A (GOLDEN TIMOTHY C [US] ET AL) 9 January 1996 (1996-01-09) column 3, line 47 column 3, lines 33-34 column 6, lines 33-34,62 column 7; table 1 column 8, lines 31-34 column 3, lines 15-22 column 4, lines 14-28 column 6, lines 24-31 column 5, lines 63-64 ----- -/--	1,19

[X] Further documents are listed in the continuation of Box C.

[X] 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

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 March 2019	03/04/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Hilgenga, Jan

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/056878

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	NAUSIKA QUEREJETA ET AL: "Standing out the key role of ultramicroporosity to tailor biomass-derived carbons for CO 2 capture", JOURNAL OF CO2 UTILIZATION, vol. 26, 1 July 2018 (2018-07-01), pages 1-7, XP055569148, ISSN: 2212-9820, DOI: 10.1016/j.jcou.2018.04.016 the whole document	1-22
A	US 4 587 114 A (HIRAI HIDEFUMI [JP] ET AL) 6 May 1986 (1986-05-06) the whole document	1-22

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/056878

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/259729 A1 (KAISER MARK [US] ET AL) 23 December 2004 (2004-12-23) page 3, paragraphs 32,33,35 -----	1,2,19
A	WO 02/085498 A1 (MERCK & CO INC [US]; EL-SHOUBARY YOUSSEF [US]; MAES RUDY [US]) 31 October 2002 (2002-10-31) page 3, lines 17-18 page 4, line 28 -----	1,19

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Information on patent family members

International application No
PCT/IB2018/056878

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