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(54) Title: ARTICLE FOR CO_2 CAPTURE HAVING HEAT EXCHANGE CAPABILITY

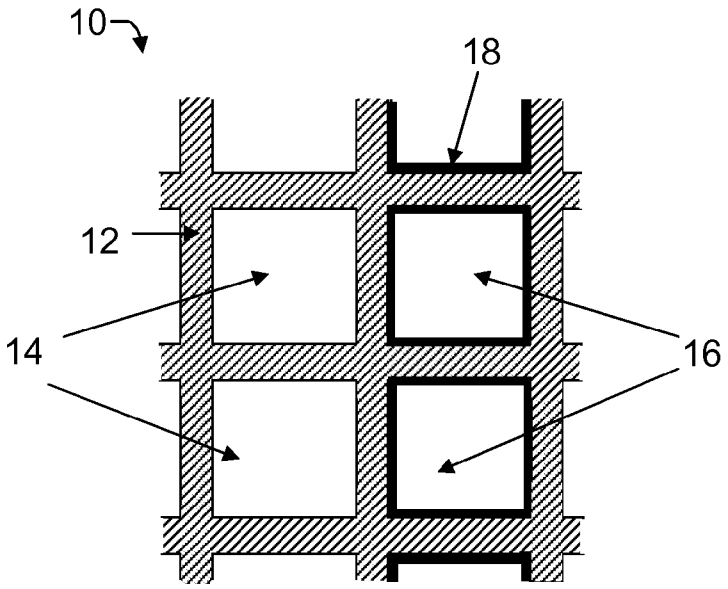

Figure 1

(57) Abstract: An article comprising a plurality of intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end, wherein the walls forming each cell in a first subset of cells are covered by a barrier layer to form a plurality of heat exchange flow channels, and wherein the walls forming each cell in a second subset of cells different from the first subset of cells, comprise a CO_2 sorbent and form reaction flow channels. Heat exchange flow channels allow quick and uniform heating and cooling of the sorbent body. The article may be useful, for example, for removing CO_2 from a gas stream.

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ARTICLE FOR CO_2 CAPTURE HAVING HEAT EXCHANGE CAPABILITY

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority under 35 U.S.C. §120 of U.S. Application Serial No. 13/097,495, filed on April 29, 2011, the content of which is relied upon and incorporated herein by reference in its entirety.

FIELD OF THE DISCLOSURE

[0002] This disclosure relates to an article comprising a first subset of cells forming a plurality of heat exchange flow channels and a second subset of cells forming reaction flow channels. The article may be useful, for example, for removing CO_2 from a gas stream.

BACKGROUND

[0003] CO_2 capture by solid sorbent can be realized by processes such as thermal swing, pressure swing, or vacuum swing. Due to the large quantity of CO_2 released from coal fire plants, a large amount of sorbent is generally needed for CO_2 capture. A honeycomb structure sorbent bed may solve the high pressure drop problem for fixed bed adsorption using a large amount of sorbent; but uniform and fast heating and cooling of the sorbent bed is still a challenge.

[0004] In CO_2 solid sorbent capture, known processes mentioned above involve two steps: adsorption and desorption (or regeneration); and known processes involve sorbent bed temperature change. In thermal swing adsorption (TSA) processes, the sorbent adsorbs at a lower temperature and is then heated for desorption; after the desorption, the sorbent needs to be cooled down to a lower temperature for adsorption again. For vacuum and pressure swing adsorption (VSA and PSA) processes, the adsorption, an exothermal process, is accompanied with an temperature increase of the sorbent bed, which eventually prohibits the adsorption, or in other words, decreases the sorbent CO_2 capacity; while the desorption, an endothermal process, is accompanied with a decrease of the sorbent bed temperature, and therefore, slows down the desorption process.

SUMMARY

[0005] Disclosed herein is an article for removing CO_2 from a gas stream, the article comprising a plurality of intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end, wherein the walls forming each cell in a first subset of cells are covered by a barrier layer to form a plurality of heat exchange flow channels, and wherein the walls forming each cell in a second subset of cells different from the first subset of cells, form reaction flow channels.

[0006] Also disclosed is a method of making an article for removing CO_2 from a gas stream, the method comprising providing a substrate comprising intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end, wherein the intersecting walls have a median pore size greater than 10 microns, wherein the porosity of the intersecting walls is greater than 50 percent, impregnating the intersecting walls with a solid sorbent capable of adsorbing CO_2, wherein the amount of solid sorbent in the intersecting walls is greater than 150 grams per liter of substrate, masking the ends of selected cells of the substrate, applying a barrier layer on the intersecting walls of the unmasked cells, removing the mask, and drying, and optionally firing, the article.

[0007] Also disclosed is a method of removing CO_2 from a gas stream, the method comprising passing through and contacting a gas stream comprising CO_2 with the reaction flow channels of the article disclosed above resulting in CO_2 adsorption on the article, and flowing a cooling fluid through the heat exchange flow channels of the article, wherein the cooling fluid acts to remove the heat resulting from the adsorption of the CO_2.

[0008] Honeycomb sorbent beds disclosed herein can be used to heat and cool the sorbent bed quickly and uniformly for the TSA process and to stabilize or optimize the operation temperatures for both adsorption and desorption in VSA and PSA processes.

[0009] Additional features and advantages will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the embodiments as described in the written description and claims hereof.

[0010] It is to be understood that both the foregoing general description and the following detailed description are merely exemplary, and are intended to provide an overview or framework to understand the nature and character of the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 is a partial view of one embodiment disclosed herein, showing reaction flow channels and heat exchange flow channels separated by barrier layer.

[0012] Figure 2 is a cross-sectional view of one embodiment of an article disclosed herein showing different configurations for reaction flow and heat exchange flow channels.

[0013] Figure 3a is a cross-sectional view of one embodiment of an article disclosed herein showing flow channels having different cross-sectional areas.

[0014] Figure 3b is a cross-sectional view of one embodiment of an article disclosed herein showing flow channels having different cross-sectional areas.

[0015] Figure 4 is one embodiment disclosed herein showing an inlet-outlet example for heat exchange flow and end sealing.

[0016] Figure 5 is a 2D schematic representation of a complex 3D honeycomb structure with heat exchange flow channels.

[0017] Figure 6 is a schematic representation of the modeling analysis domain.

[0018] Figure 7 is a graph showing the average temperature in degrees K (T_{avg}) plotted against time in seconds (T) which illustrates the effectiveness of the heat exchange flow channel on article temperature.

[0019] Figure 8 is a graph showing the CO_2 amount in the article in gmol of CO_2 per kg of sorbent (CO_2), plotted against time in seconds (T), which illustrates the effectiveness of the heat exchange flow channel on CO_2 capture capacity.

[0020] Figure 9 is a graph showing the average temperature in degrees K (T_{avg}) plotted against time in seconds (T) which illustrates the effect of sorbent thickness in maintaining the article temperature.

[0021] Figure 10 is a graph showing the CO_2 amount in the article in gmol of CO_2 per kg of sorbent (CO_2), plotted against time in seconds (T), which illustrates the effect of sorbent thickness on sorbent body CO_2 capture capacity.

[0022] Figure 11 is a graph showing the CO_2 amount in the article in gmol of CO_2 per kg of sorbent (CO_2), plotted against time in seconds (T), which illustrates the impact of sorbent thickness on amount of CO_2 adsorbed.

[0023] Figure 12 is a graph showing the average temperature in degrees K (T_{avg}) plotted against time in seconds (T) which illustrates the effect of glass (G) vs. polymer (P) barrier layer on heat conduction.

[0024] Figure 13 is a graph showing the CO_2 amount in the article in gmol of CO_2 per kg of sorbent (CO_2), plotted against time in seconds (T), which illustrates the effect of glass (G) vs. polymer (P) barrier layer on sorbent body CO_2 capture capacity.

[0025] Figure 14 is a graph showing the average temperature in degrees K (T_{avg}) plotted against time in seconds (T) which illustrates the effect of glass barrier layer thickness on heat conduction.

[0026] Figure 15 is a graph showing the CO_2 amount in the article in gmol of CO_2 per kg of sorbent (CO_2), plotted against time in seconds (T), which illustrates the effect of glass barrier layer thickness on sorbent body CO_2 capture capacity.

DETAILED DESCRIPTION

[0027] Disclosed herein is an article for removing CO_2 from a gas stream, the article comprising a plurality of intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end, wherein the walls forming each cell in a first subset of cells are covered by a barrier layer to form a plurality of heat exchange flow channels, and wherein the walls forming each cell in a second subset of cells different from the first subset of cells, comprise a CO_2 sorbent material and form reaction flow channels.

[0028] The article may comprise ceramic, glass, glass-ceramic, metal or combinations thereof. In some embodiments, the article comprises cordierite, mullite, alumina, zeolite, carbon/activated carbon, silicon carbide, stainless steel or combinations thereof. In some embodiments, the article may be formed from a sorbent material, for example, activated carbon or zeolite.

[0029] The surface of the intersecting walls forming each cell in the second subset of cells can be comprised of a porous material such as porous ceramics or carbon. In some

embodiments, at least a majority of the intersecting walls are comprised of a porous material throughout the entire thickness of the wall, except for the barrier layer.

[0030] In some embodiments, the article is in the form of a honeycomb, the honeycomb comprising an inlet end, an outlet end, and cells extending from the inlet end to the outlet end. In some embodiments, the honeycomb has a cell density of from 100 cells per square inch to 5000 cells per square inch.

[0031] The intersecting walls define the cells of the article. In some embodiments, the intersecting walls, without a barrier layer, have a thickness of from 35 microns to 500 microns. The intersecting walls of the article are porous. Porous walls allow sorbent loading on and/or within the intersecting walls. In some embodiments, the article has high porosity and pore volume. In some embodiments, the intersecting walls have a porosity greater than 50 percent. In some embodiments, the intersecting walls have a porosity from 55% to 75%. In some embodiments, the intersecting walls have a median pore size (D50) greater than 10 microns, for example, 15 microns to 30 microns. In some honeycomb embodiments, the cell geometry is such that the pore volume percentage is in the range of 20-35%. The cell geometry can be designed so that the pore volume percentage in the article is not less than 20, not less that 30%, or not less than 35%.

[0032] Embodiments of the article have a void fraction, also described as the total void or voidage of the article. The term "void fraction" is defined as the cell void (open frontal area) plus wall porosity and particle porosity. The term solid porosity may be used to represent wall porosity and particle porosity combined. An applicable void fraction can be selected for the gas separation or capture application. For CO_2 or gas separation from an industrial gas process such as H_2 and natural gas, a low void fraction is applicable, for example, less than 85%, 80%, 75%, or 70%. For separation of CO_2 from air or flue gas applications, greater than 50%, 55%, 60%, 65%, or 70% is applicable. In some embodiments, the article has a void fraction less than 70%. In other embodiments, the article has a void fraction greater than 70%.

[0033] In some embodiments, the reaction flow channels and heat exchange flow channels have different cross-sectional areas. For example, the reaction flow channels of the article may be of a larger cross section than the heat exchange flow channels, or vice versa. The

cross sectional shape of the reaction flow channels may also differ from the cross sectional shape of the heat exchange flow channels, for example, square, rectangle, triangular or circular cross sectional shapes may be present in the article.

[0034] Embodiments disclosed herein include a shaped body of sorbent material, a body impregnated with a solid sorbent, and a shaped body of sorbent material impregnated with a solid sorbent. In some embodiments, the solid sorbent impregnates the intersecting wall, for example, to a depth of at least 100 microns or more, 200 microns or more, or 300 microns or more. In some embodiments, the solid sorbent impregnates the entire thickness of the intersecting wall. In some embodiments, the amount of solid sorbent, or sorbent loading, is greater than 150 g/L, greater than 175 g/L, greater than 200 g/L, or greater than 250 g/L.

[0035] A barrier layer is used to create separate channels for heat exchange flow. The barrier layer is disposed on selected intersecting walls and prevents flow through the porous channel walls having the barrier layer disposed thereon. Intersecting walls having no barrier layer may allow flow through the intersecting walls. In some embodiments, the barrier layer comprises polymer, glass, wax, metal, ceramic, glass-ceramic, or combinations thereof. The barrier layer may be applied before or after sorbent loading.

[0036] In some embodiments, the barrier layer has a minimum thickness of 10 microns. In some embodiments, the barrier layer has a thickness from 10 microns to 100 microns, for example 10 microns to 90 microns, 20 microns to 80 microns, 30 microns to 70 microns , 40 microns to 50 microns, or 50 microns to 100 microns.

[0037] Reaction flow channels are defined herein as those cells not having a barrier layer on the intersecting walls defining the cell. Heat exchange flow channels are defined herein as those cells having a barrier layer on the intersecting walls defining the cell. The article may have one or multiple reaction flow channels. The article may have one or multiple heat exchange flow channels. **Figure 1** shows a partial view **10** of one embodiment of an article for removing CO_2 from a gas stream. Intersecting walls **12** define the cells. Intersecting walls **12** having a barrier layer **18** thereon define the heat exchange flow channels **16**. The reaction flow channels **14** are defined by intersecting walls **12** having no barrier layer.

[0038] **Figure 2** is an example showing a honeycomb embodiment having reaction flow channels **14** and heat exchange flow channels **16**. Embodiments of the article may have different configurations of reaction and heat exchange flow channels.

[0039] In some embodiments, the reaction flow channels and heat exchange flow channels have different cross-sectional areas. For example, the reaction flow channels of the article may be of a larger cross section than the heat exchange flow channels, or vice versa. **Figure 3a** is a cross sectional view of an embodiment of the article showing intersecting walls (light gray) defining cells (black) having different cross-sectional areas. **Figure 3b** shows a cross-sectional view of another embodiment of the article having larger cells among smaller cells. In the embodiment shown in **Figure 3b**, the larger cells may, for example, function as the heat exchange flow channels, and the smaller cells may, for example, function as the reaction flow channels. The cross sectional shape of the reaction flow channels may also differ from the cross sectional shape of the heat exchange flow channels, for example, square, rectangle, triangular or circular cross sectional shapes may be present in the article.

[0040] Disclosed herein is a method of making an article for removing CO_2 from a gas stream, the method comprising providing a substrate comprising intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end, wherein the intersecting walls have a median pore size greater than 10 microns, wherein the porosity of the intersecting walls is greater than 50 percent, impregnating the intersecting walls with a solid sorbent capable of adsorbing CO_2, wherein the amount of solid sorbent in the intersecting walls is greater than 150 grams per liter of substrate, masking the ends of selected cells of the substrate, applying a barrier layer on the intersecting walls of the unmasked cells, removing the mask, and drying, and optionally firing, the article.

[0041] The substrate may comprise ceramic, glass, glass-ceramic, metal or combinations thereof. In some embodiments, the substrate comprises cordierite, mullite, alumina, carbon/activated carbon, silicon carbide, stainless steel or combinations thereof. In some embodiments, the substrate may be formed from a sorbent material, for example, activated carbon or zeolite.

[0042] In some embodiments, the substrate is in the form of a honeycomb, the honeycomb comprising an inlet end, an outlet end, and open channels extending from the inlet end to the

outlet end. In some embodiments, the honeycomb has a channel or cell density of from 100 cells per square inch to 5000 cells per square inch.

[0043] Intersecting walls define a plurality of cells in the substrate. In some embodiments, the intersecting walls have a thickness of from 35 microns to 500 microns. Porous intersecting walls allow sorbent loading on and/or within the porous intersecting walls. In some embodiments, the substrates have high porosity and pore volume. In some embodiments, the intersecting walls have a porosity greater than 50 percent. In some embodiments, the intersecting walls have a porosity from 55% to 75%. In some embodiments, the intersecting walls have a median pore size (D50) greater than 10 microns, for example, 15 microns to 30 microns. In some honeycomb embodiments, the cell geometry is such that the pore volume percentage is in the range of 20-35%.

[0044] In some embodiments, the substrate may also be considered a sorbent body, for example when the substrate is made of a sorbent material such as activated carbon or zeolite. In other embodiments, the substrate becomes a sorbent body after impregnation with a solid sorbent.

[0045] In some embodiments, the intersecting walls are impregnated with a solid sorbent capable of adsorbing CO_2. The solid sorbent may be present on or in intersecting walls as well as inner pores of the intersecting walls. Impregnation may be accomplished, for example, via slurry coating. The viscosity of the slurry comprising the solid sorbent should be low enough to enable the slurry to easily flow into the pores of the walls. For example, slurry viscosities smaller than 1.5 Pc may be used. In some embodiments, more than one coating cycle may be used. In some embodiments, the solid sorbent impregnates the intersecting wall, for example, to a depth of at least 100 microns or more, 200 microns or more, or 300 microns or more. In some embodiments, the solid sorbent impregnates the entire thickness of the intersecting wall. In some embodiments, the amount of solid sorbent, or sorbent loading, is greater than 150 g/L, greater than 175 g/L, greater than 200 g/L, or greater than 250 g/L. For example, a honeycomb having a porosity of 65% with cell geometry of 300 cpsi (cells per square inch) and wall thickness of 13 mil (1.09 mm), the pore volume percentage of the honeycomb is 26%. If loading a sorbent with density of 1.5 g/cm^3, the honeycomb can load up to 390 g/L sorbent.

[0046] The solid sorbent capable of adsorbing CO_2 may be a porous solid with an affinity and high selectivity for CO_2. In some embodiments, the solid sorbent may be a molecular sieve such as a zeolite, or a molecular sieve that is occluded with a functionality that also has an affinity for CO_2. In some embodiments, the solid sorbent may be carbon or carbon material functionalized with an organic group that complexes CO_2. The solid sorbent may also be a mixture of a carbon/zeolite, metal-organic frameworks, and combinations thereof.

[0047] In embodiments, a barrier layer is applied to intersecting walls of the substrate. The barrier layer may be applied before or after sorbent impregnation. In some embodiments, the barrier layer comprises polymer, glass, wax, metal, ceramic, glass-ceramic, or combinations thereof.

[0048] A polymer barrier layer may be realized by monomer coating and then cross-linking at the surface of the intersecting wall, or a polymer particle coating and then melting polymer particle coating to form the barrier layer. A glass barrier layer may be a slip casting of glass frit slurry. This slurry may be made by glass frit of particle size of 0.1 microns to 10 microns in water, added with polymer binder and dispersant and deforming agent. Flow coating, vacuum coating, dip coating, or water fall coating may be used for slip casting of the glass frit on the intersecting walls.

[0049] For applications of a glass barrier layer after sorbent loading, low melting temperature glass should be chosen for the barrier layer to meet the sorbent thermal stable temperature range and prevent thermal degradation of the sorbent. For applications of a glass barrier layer before sorbent loading, the pores of the intersecting walls should be pre-filled or plugged, and then the glass frit applied. A glass barrier layer may also be applied to green bodies. In some embodiments, the slurry is not water based due to the solubility of polymer binder in green parts. Alcohol may be used to make the slurry in this case. In other embodiments, water base slurry can be using for glass frit barrier layer if the green part is treated with cross-linking agent and a polymer film formed on the surface of the green part.

[0050] In embodiments where a barrier layer is only applied to selected intersecting walls, a mask may be used to block the ends of cells not selected for application of the barrier layer, thereby preventing the barrier layer from being applied to the walls within the blocked cells. In some embodiments, a patterned mask may be glued at the two outer ends of the substrate

before the applying the barrier layer. After applying the barrier layer, the mask may be removed and the substrate may undergo drying, and optionally firing. In embodiments where glass frits are used, a firing temperature higher than the glass melting temperature allows the glass frits to melt and form an acceptable glass barrier layer.

[0051] Disclosed herein is a method of removing CO_2 from a gas stream, the method comprising passing through and contacting a gas comprising CO_2 with the reaction flow channels of an article comprising a plurality of intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end, wherein the walls forming each cell in a first subset of cells are covered by a barrier layer to form a plurality of heat exchange flow channels, and wherein the walls forming each cell in a second subset of cells different from the first subset of cells, form reaction channels, wherein the contacting step results in CO_2 adsorption on the article; and flowing a cooling fluid through the heat exchange flow channels of the article; wherein the cooling fluid acts to remove the heat resulting from the adsorption of the CO_2.

[0052] A gas may pass through and contact the reaction flow channels of the article from an inlet end to an outlet end. As used herein, the terms "sorb", "sorption", and "sorbed", refer to the adsorption, sorption, or other entrapment of CO_2 on the article, either chemically, physically, or both chemically and physically. During adsorption, at least a portion of CO_2 is removed from the gas stream, for example, some, or all of the CO_2. In some embodiments, the article removes at least 5%, at least 10%, at least 20%, at least 50%, at least 70%, or at least 90% of the CO_2 from the gas stream.

[0053] During CO_2 desorption, the method may further comprise flowing a heating fluid through the heat exchange flow channels of the article described above to increase the temperature of the article thereby releasing the adsorbed CO_2. One example of a heating fluid is steam. In one embodiment, the heating fluid raises the temperature of the article to a temperature sufficient to desorb the sorbed CO_2 from the article. It should be appreciated that a sufficient temperature to desorb the CO_2 will depend, in part, on the amount of CO_2 that is present. In one embodiment, a sufficient temperature can comprise heating the article to a temperature in the range of from 60°C to 150°C, including, for example, temperatures of 80°C, 100°C, 120°C, or 140°C or above. In another embodiment, the sufficient heating

temperature can be in the range derived from these values, including for example, a range from 100°C to 120°C, or 100°C to 140°C.

[0054] One embodiment of the disclosed article for CO_2 capture from a gas stream is shown in **Figure 4**. At the two ends of the article, slots **26**, **28** are cut at the heat exchange flow channels for interconnecting these heat exchange flow channels as well as for introducing heating/cooling fluid from the side of the article. Two caps **24** on which the channels matching the heat exchange flow channels are plugged **22**, for example, with cement and are then glued and sealed at the two ends of the article. The gas stream to be treated **20** can be introduced at one end of the article and the treated gas flow **30** exits from the other end. The heating/cooling fluid is introduced at the flow inlet slots **28** and exits at the flow outlet slots **26**, or vice versa.

[0055] After desorption the article may be cooled by flowing cooling fluid, such as cooling water, through the slots at the side of the article. By heating and cooling individual channels in the article, the heating and cooling can be very efficient. In some embodiments, the barrier layer can effectively conduct heat from one side/channel to the other/channel.

[0056] In an aspect (1), the disclosure provides an article for removing CO_2 from a gas stream, the article comprising: a plurality of intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end; wherein the walls forming each cell in a first subset of cells are covered by a barrier layer to form a plurality of heat exchange flow channels, and wherein the walls forming each cell in a second subset of cells different from the first subset of cells, comprise a CO_2 sorbent material and form reaction flow channels. In an aspect (2), the disclosure provides the article of aspect 1, wherein the intersecting walls have a porosity greater than 50 percent. In an aspect (3), the disclosure provides the article of any aspect 1 or 2, wherein the intersecting walls have a thickness of from 35 microns to 500 microns. In an aspect (4), the disclosure provides the article of any one of aspects 1-3 comprising a shaped body of sorbent material. In an aspect (5), the disclosure provides the article of any one of aspects 1-3, wherein the intersecting walls are impregnated with a solid sorbent. In an aspect (6), the disclosure provides the article of aspect 5, wherein the amount of solid sorbent in the intersecting walls is greater than 150 grams per liter of intersecting wall. In an aspect (7), the disclosure provides the article of aspect 5,

wherein the solid sorbent impregnates the entire thickness of the intersecting wall. In an aspect (8), the disclosure provides the article of aspect 5, wherein the solid sorbent impregnates the intersecting wall to a depth of at least 100 microns. In an aspect (9), the disclosure provides the article of aspect 1, wherein the barrier layer has a minimum thickness of 10 microns. In an aspect (10), the disclosure provides the article of aspect 1, wherein the barrier layer has a thickness from 10 microns to 100 microns. In an aspect (11), the disclosure provides the article of any one of aspects 1, 9 or 10, wherein the barrier layer comprises polymer, glass, metal, ceramic, glass-ceramic, or combinations thereof. In an aspect (12), the disclosure provides the article of any one of aspects 1-11, wherein the article is in the form of a honeycomb. In an aspect (13), the disclosure provides the article of aspect 1, wherein the intersecting walls comprises ceramic, glass, glass-ceramic, metal or combinations thereof. In an aspect (14), the disclosure provides the article of aspect 1, having a void fraction less than 70 percent. In an aspect (15), the disclosure provides the article of aspect 1, having a void fraction greater than 70 percent. In an aspect (16), the disclosure provides the article of aspect 1, having a cell density of from 100 cells per square inch to 5000 cells per square inch. In an aspect (17), the disclosure provides the article of aspect 1, wherein the reaction flow channels and heat exchange flow channels have different cross-sectional areas. In an aspect (18), the disclosure provides a method of making an article for removing CO_2 from a gas stream, the method comprising: providing a substrate comprising intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end; wherein the intersecting walls have a median pore size greater than 10 microns; wherein the porosity of the intersecting walls is greater than 50 percent; impregnating the intersecting walls with a solid sorbent capable of adsorbing CO2; wherein the amount of solid sorbent in the intersecting walls is greater than 150 grams per liter of substrate; masking the ends of selected cells of the substrate; applying a barrier layer on the intersecting walls of the unmasked cells; removing the mask, and drying, and optionally firing, the article. In an aspect (19), the disclosure provides a method of removing CO2 from a gas stream, the method comprising: contacting a gas stream comprising CO2 with the reaction flow channels of the article of claim 1 thereby adsorbing CO2 on the article; and flowing a cooling fluid through the heat exchange flow channels of the article; wherein the

cooling fluid acts to remove the heat resulting from the adsorption of the CO2. In an aspect (20), the disclosure provides the method of aspect 19, further comprising: flowing a heating fluid through the heat exchange flow channels of the article of claim 1 to increase the temperature of the article thereby releasing the adsorbed CO2.

[0057] Various embodiments will be further clarified by the following examples.

EXAMPLES

[0058] Advantages of the heat exchange flow channel functionality are illustrated through modeling the behavior of embodiments of the article. The results of the model may be used to provide guidance in sorbent and barrier material thickness selection.

[0059] A honeycomb structure can be thought of as a collection of isolated combinations of one reaction flow channel and one heat exchange flow channel. As shown in the embodiment of **Figure 2**, all the reaction flow channels **14** (with 4 sides) have only one side in contact with the heat exchange flow channels **16**, while the other three sides are in contact with the reaction flow channels **14**. If the interaction of one reaction flow channel with another reaction flow channel is assumed to be small, then for modeling purposes, a model for a single reaction flow channel with a heat exchange channel on one side would be representative of the whole honeycomb structure. Such an assumption would be valid when most of the heat flows from the reaction flow channel to the heat exchange flow channel, and an insignificant amount flows between reaction flow channels. If diffusion within the porous channel wall is small, then adsorption effects are limited within reaction flow channels and there are no interactions between the reaction flow channels in terms of adsorption. Therefore, **Figure 5**, illustrating one side of a reaction flow channel **14** in contact with one side of a heat exchange flow channel **16**, is a simple 2D analogy of a complex 3D honeycomb structure with heat exchange flow channels. **Figure 5** illustrates the gas stream to be treated **20** moving into a honeycomb through reaction flow channel **14**. CO_2, represented by the wiggly arrows, is absorbed in the bed at intersecting walls **12** define the cells, and heat is released. Heat is conducted in the barrier layer **18**. At **16**, heat is carried away by the flowing coolant in the heat exchange flow channels **16**.

[0060] **Figure 6** shows CO_2 entering the system, represented by wiggly arrows. CO2 is absorbed in the bed intersecting walls **12** and heat is released. Heat is conducted in the

barrier layer **18**. Heat is carried away by flowing coolant, as illustrated by the dashed arrow in **Figure 6**. **Figure 6** is a schematic representation of the analysis domain used for modeling purposes and is based on following assumptions:

- The CO_2 concentration of the gas stream in the reaction flow channels is not changing, and not solved for in the reaction flow channels. Therefore, the reaction flow channel domain is ignored from the analysis domain, replaced by constant CO_2 concentration boundary condition at the interface of reaction flow channel and sorbent.
- The cooling fluid takes away heat from the surface as convective heat transfer. Therefore, the heat exchange flow channel domain is ignored from the analysis domain, replaced by constant convective heat transfer boundary condition at the interface of barrier layer and sorbent.
- The barrier layer can only conduct away heat.
- CO_2 adsorption in the sorbent body is not diffusion limited. The sorbent at all thicknesses is equally accessible to CO_2.

Mathematical Model:

[0061] *Mass balance:* CO_2 adsorption is solved for in the sorbent body, Zeolite 13X in this example. Diffusion inside the sorbent body is ignored. The CO_2 adsorption capacity of the sorbent body is estimated from Langmuir isotherms. The capacity of the sorbent body is a function of temperature.

[0062] *Energy balance:* Conductive heat transfer equation is solved for in both the sorbent body layer and the barrier layer. In the sorbent body, there is an additional volumetric heat source term (due to energy released from adsorption reaction). The barrier layer can only conduct away heat. The model input data is shown in Table 1 and the results are presented in Figures 7, 8, 9, 10, 11, 12, 13, 14 and 15.

Table 1: Model Input data

Parameters	Value	Unit
Zeolite (sorbent body)		
Density	640	kg/m3
Thermal Conductivity	0.12	W/m/K
Specific Heat Capacity	920	J/kg/K
Glass (barrier layer)		
Density	2800	kg/m3
Thermal Conductivity	1.05	W/m/K
Specific Heat Capacity	840	J/kg/K
Polymer (barrier layer)		
Density	1000	kg/m3
Thermal Conductivity	0.17	W/m/K
Specific Heat Capacity	1200	J/kg/K
Dimensions		
Sorbent thickness	380	microns
Barrier layer thickness	100	microns

[0063] Figure 7 shows the effectiveness of using a heat exchange flow channel **1**, compared to no heat exchange flow channel **2**, to keep the sorbent body temperature close to the initial temperature. Increase in the CO_2 amount in the sorbent body with a heat exchange flow

channel **1**, compared to no heat exchange flow channel **2**, is shown in **Figure 8**. The CO_2 capture capacity of the sorbent body decreases with rise in sorbent body temperature; therefore a maximum capacity of the sorbent body is available when a heat exchange flow channel is used.

[0064] The effect of sorbent thickness in maintaining the temperature of the sorbent body closer to initial temperature is shown in **Figure 9**. When the sorbent thickness is 100 microns, the heat is removed faster and therefore the sorbent body temperature does not rise much, in comparison to 380 microns. The difference in temperature rise between 380 microns and 100 microns sorbent thickness, *do not* cause any significant change in sorbent body CO_2 capture (shown in **Figure 10**), but there is significant change observed in the total amount of CO_2 adsorbed (shown in **Figure 11**), as the amount of sorbent for 100 microns is less.

[0065] In embodiments where glass is used as a barrier material, heat is removed faster; therefore the sorbent body temperature does not rise by much (shown in **Figure 12**), when compared to polymer material barrier layer. The reason for above observation is that polymer is not as good a heat conductor as glass. The difference in temperature rise between embodiments with glass barrier layer and polymer barrier layer, do not cause any significant change in sorbent body CO_2 adsorbed by sorbent body (shown in **Figure 13**).

[0066] The effect of glass barrier layer thickness in removing heat from an embodiment is shown in **Figure 14**. There is a very small difference in the rate of removal with change in barrier layer thickness from 20 to 100 microns. The change in the amount of CO_2 adsorbed is insignificant (shown in **Figure 15**) as barrier layer thickness is increased from 20 to 100 microns. This concludes that barrier layer thickness between 20 and 100 microns is not a limiting variable in heat transfer for the present embodiment.

[0067] It should be understood that while the invention has been described in detail with respect to certain illustrative embodiments thereof, it should not be considered limited to such, as numerous modifications are possible without departing from the broad spirit and scope of the invention as defined in the appended claims.

[0068] Unless otherwise indicated, all numbers used on the specification and claims are to be understood as being modified in all instances by the term “about”, whether or not so stated.

It should also be understood that the precise numerical values used on the specification and claims form additional embodiments of the invention.

What is claimed is:

1. An article for removing CO_2 from a gas stream, the article comprising:

a plurality of intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end,

wherein the walls forming each cell in a first subset of cells are covered by a barrier layer to form a plurality of heat exchange flow channels, and

wherein the walls forming each cell in a second subset of cells different from the first subset of cells, comprise a CO_2 sorbent material and form reaction flow channels.

2. The article of claim 1, wherein the intersecting walls have a porosity greater than 50 percent.
3. The article of claim 1 or 2, wherein the intersecting walls have a thickness of from 35 microns to 500 microns.
4. The article of any one of claims 1-3 comprising a shaped body of sorbent material.
5. The article of any one of claims 1-3, wherein the intersecting walls are impregnated with a solid sorbent.
6. The article of claim 5, wherein the amount of solid sorbent in the intersecting walls is greater than 150 grams per liter of intersecting wall.
7. The article of claim 5, wherein the solid sorbent impregnates the entire thickness of the intersecting wall.
8. The article of claim 5, wherein the solid sorbent impregnates the intersecting wall to a depth of at least 100 microns.
9. The article of claim 1, wherein the barrier layer has a minimum thickness of 10 microns.
10. The article of claim 1, wherein the barrier layer has a thickness from 10 microns to 100 microns.
11. The article of any one of claims 1, 9 or 10, wherein the barrier layer comprises polymer, glass, metal, ceramic, glass-ceramic, or combinations thereof.
12. The article of any one of claims 1-11, wherein the article is in the form of a honeycomb.
13. The article of claim 1, wherein the intersecting walls comprises ceramic, glass, glass-ceramic, metal or combinations thereof.

14. The article of any one of claims 1, having a void fraction less than 70 percent.
15. The article of claim 1, having a void fraction greater than 70 percent.
16. The article of claim 12, having a cell density of from 100 cells per square inch to 5000 cells per square inch.
17. The article of claim 1, wherein the reaction flow channels and heat exchange flow channels have different cross-sectional areas.
18. A method of making an article for removing CO_2 from a gas stream, the method comprising:

providing a substrate comprising intersecting walls having outer surfaces that define a plurality of cells extending from one end to a second end;

wherein the intersecting walls have a median pore size greater than 10 microns;

wherein the porosity of the intersecting walls is greater than 50 percent;

impregnating the intersecting walls with a solid sorbent capable of adsorbing CO_2;

wherein the amount of solid sorbent in the intersecting walls is greater than 150 grams per liter of substrate;

masking the ends of selected cells of the substrate;

applying a barrier layer on the intersecting walls of the unmasked cells;

removing the mask, and

drying, and optionally firing, the article.

19. A method of removing CO_2 from a gas stream, the method comprising:

contacting a gas stream comprising CO_2 with the reaction flow channels of the article of claim 1 thereby adsorbing CO_2 on the article; and

flowing a cooling fluid through the heat exchange flow channels of the article;

wherein the cooling fluid acts to remove the heat resulting from the adsorption of the CO_2.

20. The method of claim 19, further comprising:

flowing a heating fluid through the heat exchange flow channels of the article of claim 1 to increase the temperature of the article thereby releasing the adsorbed CO_2.

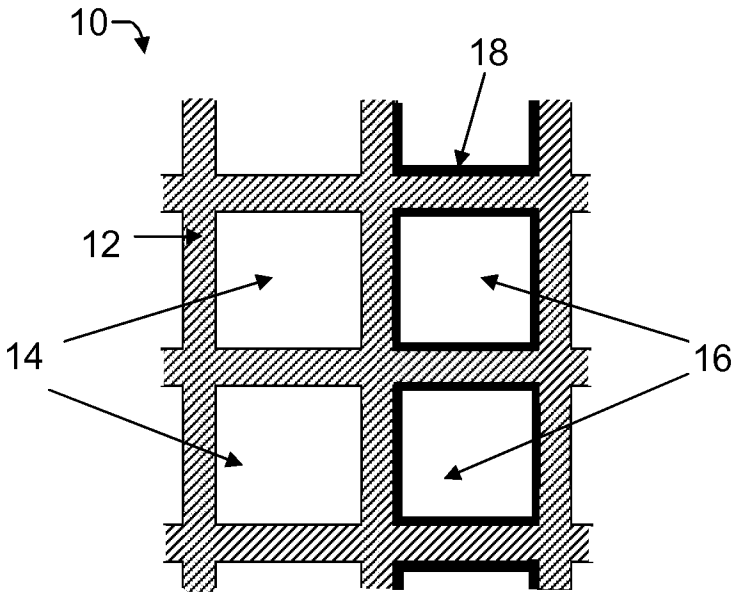

Figure 1

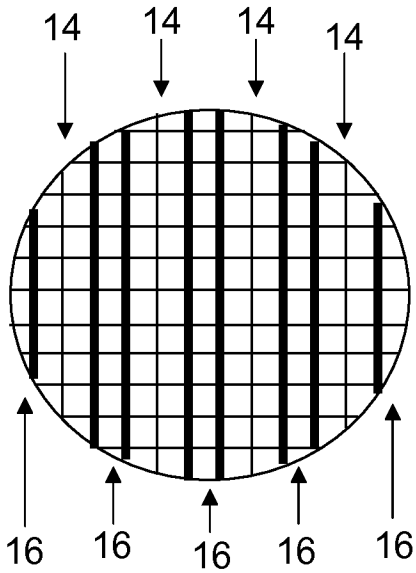

Figure 2

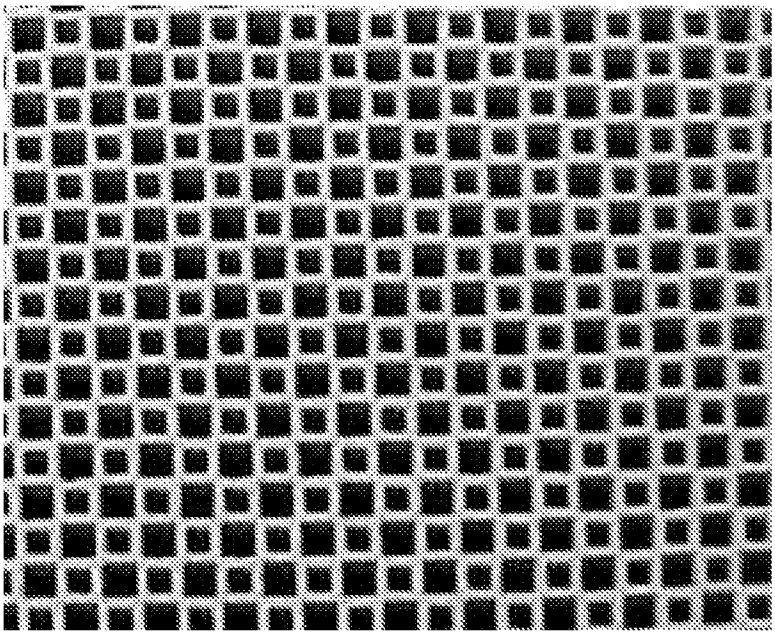

Figure 3a

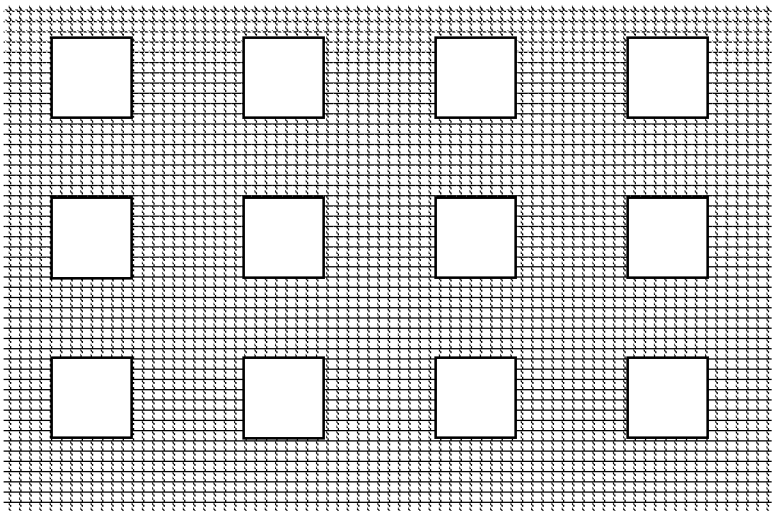

Figure 3b

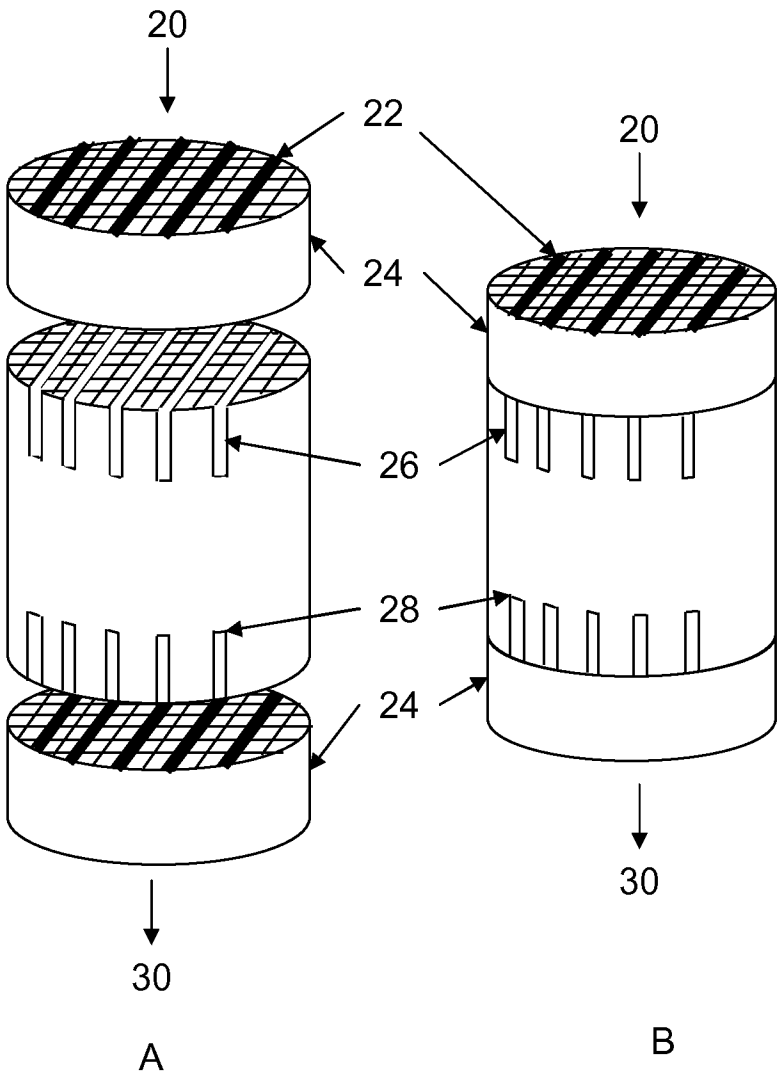

Figure 4

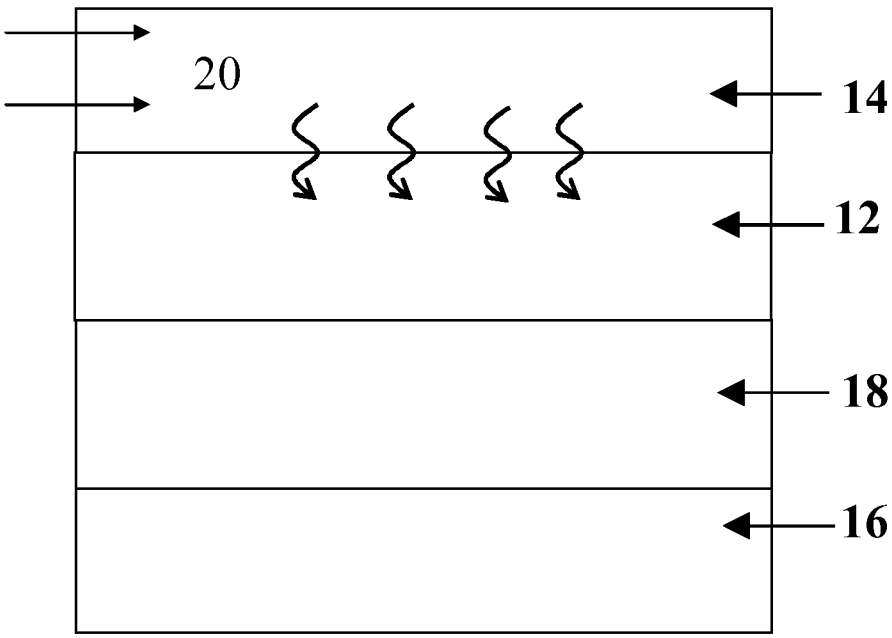

Figure 5

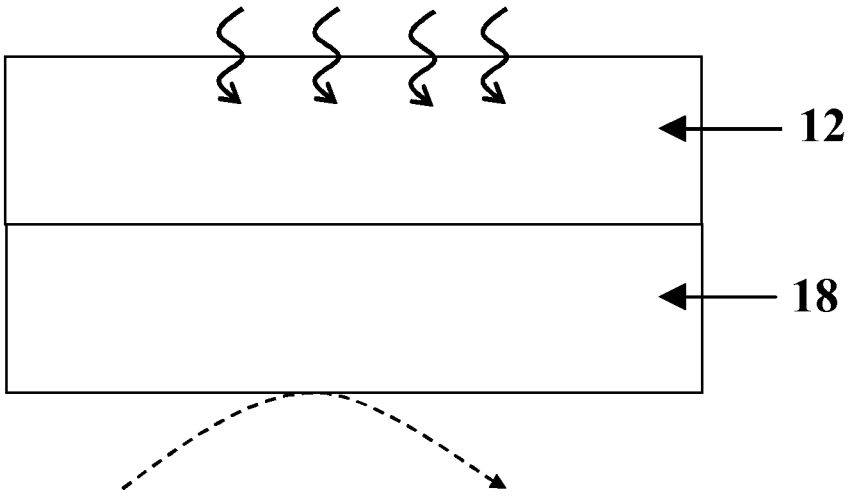

Figure 6

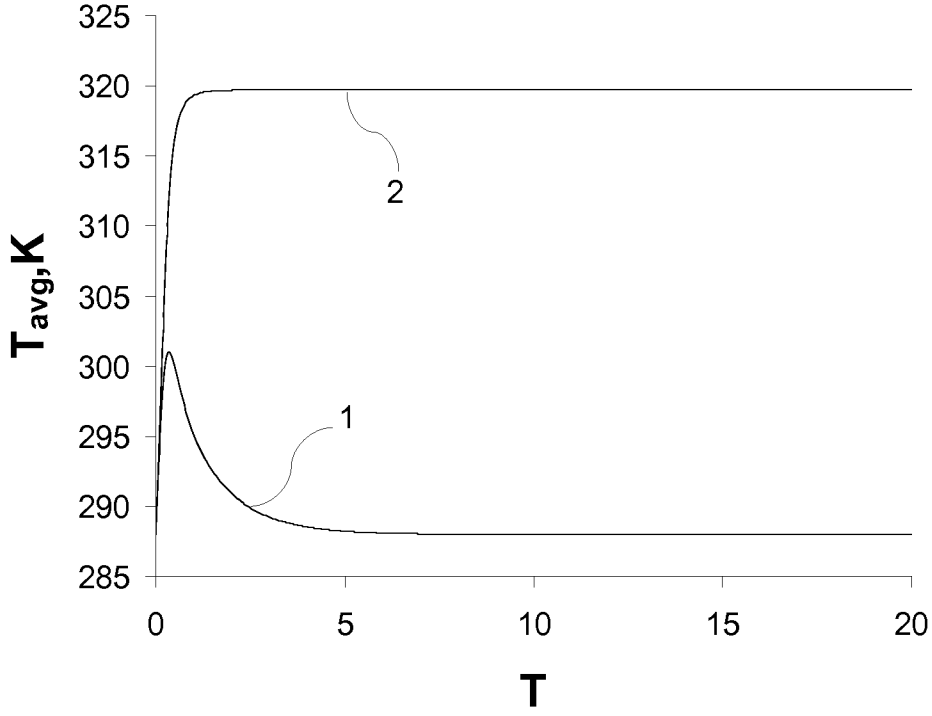

Figure 7

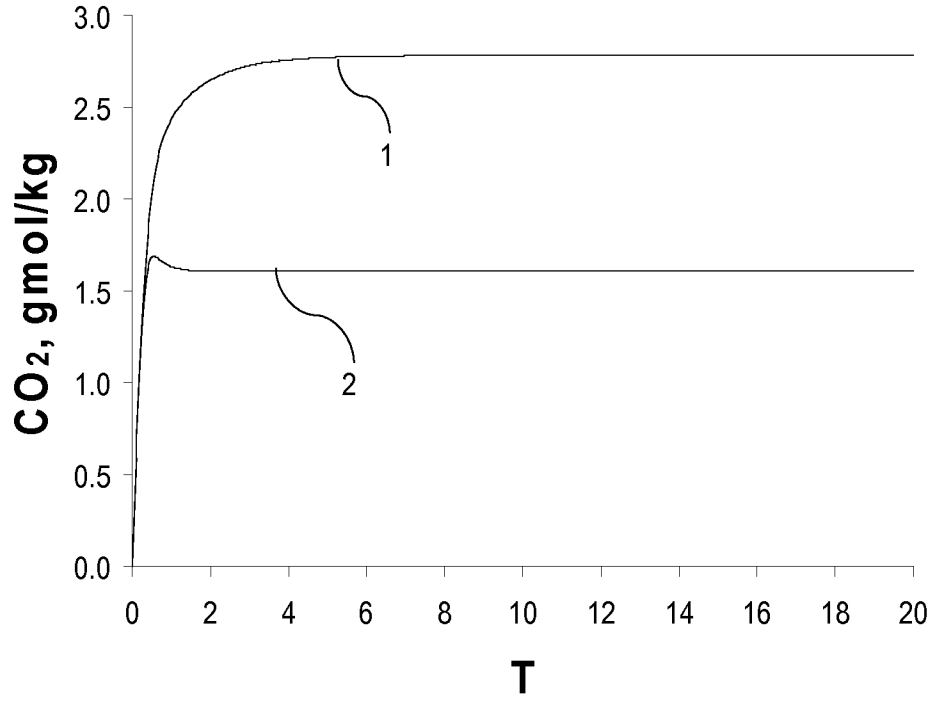

Figure 8

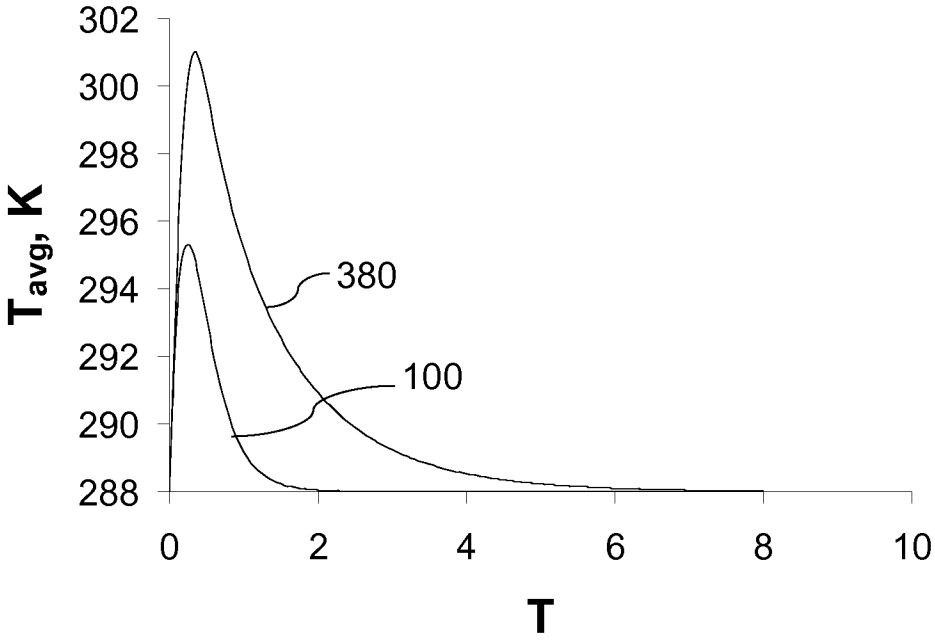

Figure 9

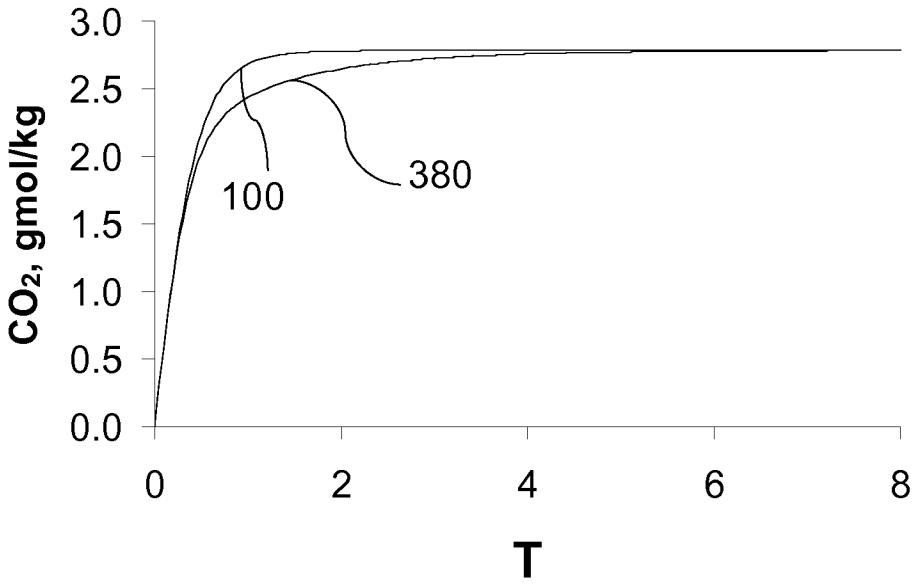

Figure 10

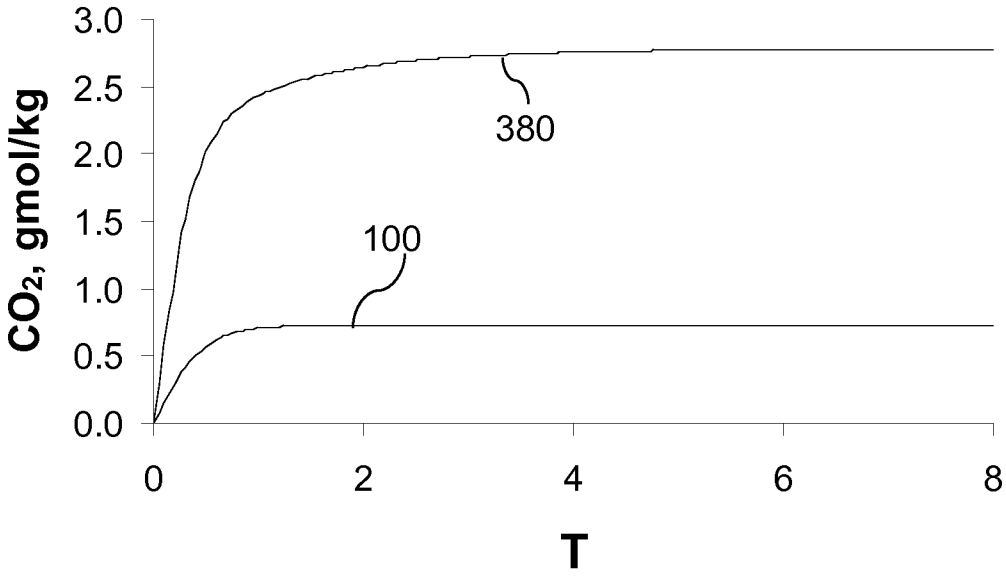

Figure 11

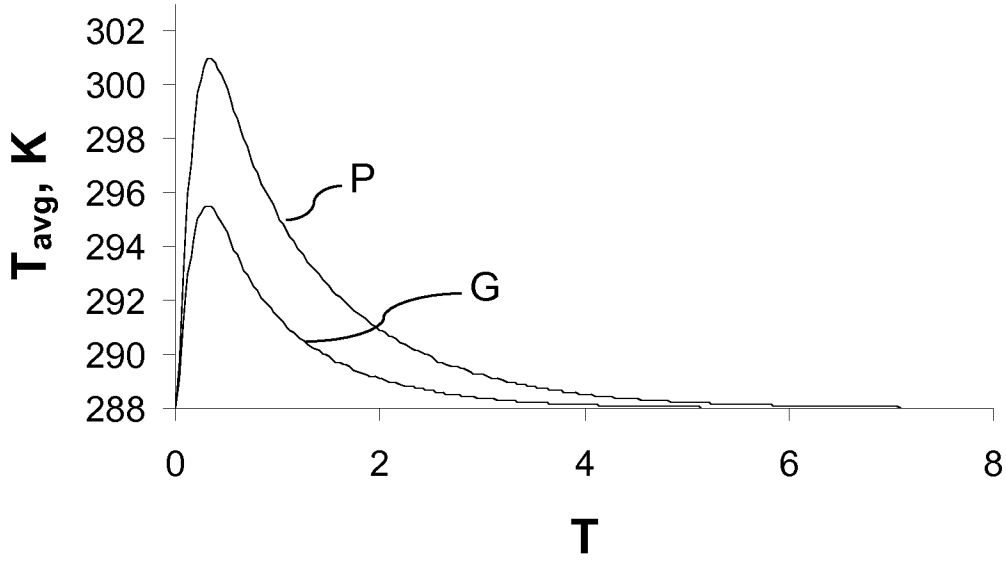

Figure 12

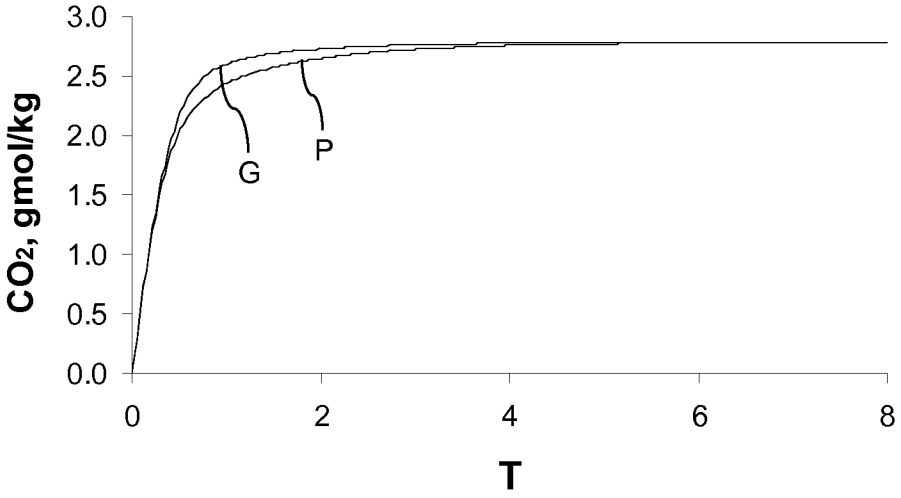

Figure 13

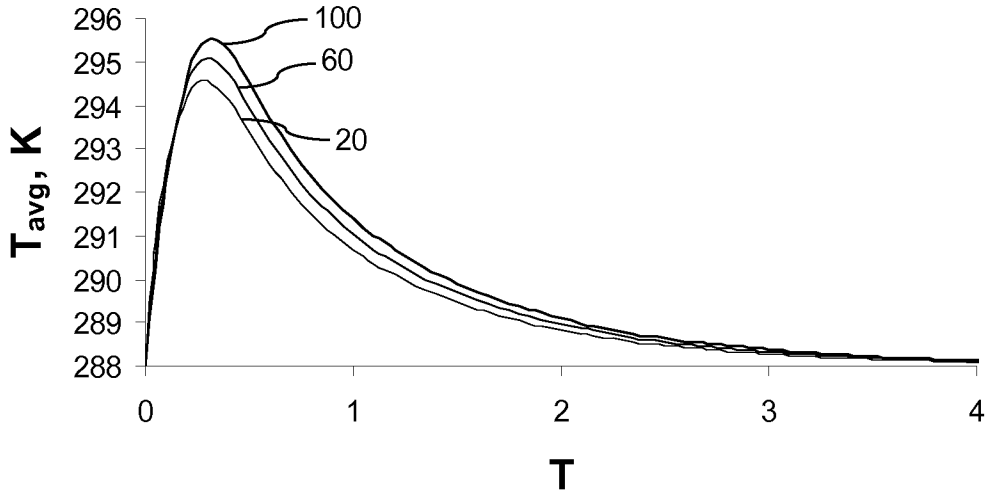

Figure 14

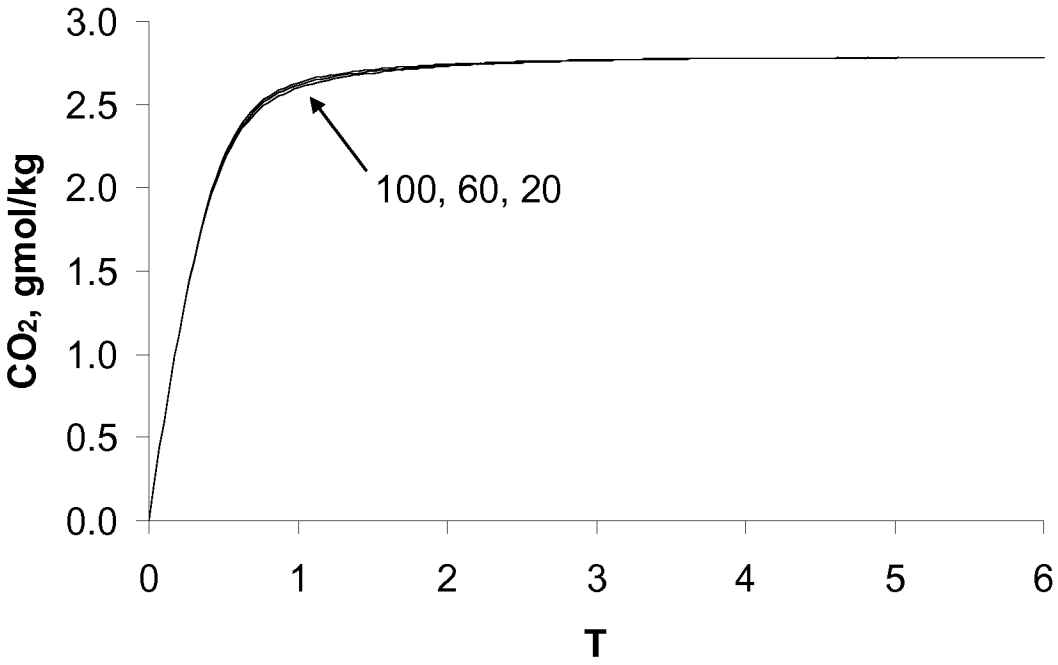

Figure 15