(54) Title: A SORPTION DEVICE
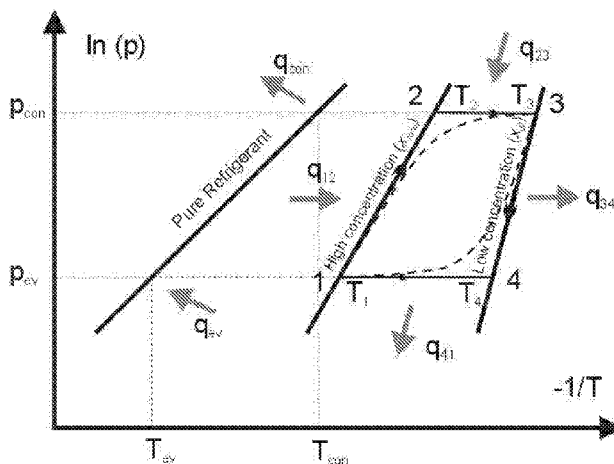
Figure 2

(57) Abstract: A sorption device comprising a heat exchanger, wherein the heat exchanger comprises: a sorbate chamber containing
a porous sorbent material, a thermal fluid conduit that is fluidly isolated from the sorbate chamber, and solid heat transfer means for
providing thermal communication between a thermal fluid in the thermal fluid conduit and the porous sorbent material, characterised
in that the porous sorbent material has a thermal conductivity of $>0.3 Wm^{-1}K^{-1}$, preferably $>0.4 Wm^{-1}$, and the porous sorbent material
is selected such that the ratio Hi/H_2 is 0.7 or less, wherein H_2 is the heat energy used to heat the porous sorbent material and sorbate
from a first temperature at which the porous sorbent material contains a maximum cyclic concentration of adsorbed sorbate to a
second temperature at which the porous sorbent material has a minimum cyclic concentration of adsorbed sorbate, and Hi is the heat
energy that is used to heat the heat transfer means and thermal fluid during the course of heating the porous sorbent material and
sorbate from the first temperature to the second temperature.

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A Sorption Device

The present invention relates to a sorption device and a method of heat exchange using such a sorption device.

Heat pumps, thermal transformers and cooling systems are generally based on the thermodynamics of condensation and evaporation of a refrigerant gas. On condensation of a gas to a liquid, heat is rejected to the environment and on evaporation of a liquid, heat is absorbed. The evaporation / condensation cycle is driven by compression. If a selected environment is brought into thermal contact with the gas / liquid only during the evaporation phase, for example, then that environment experiences an overall cooling effect.

In conventional air conditioning units, the necessary compression is driven by mechanical work that is normally provided by an electric motor. By way of contrast, sorption devices (whether operated as heat pumps or cooling systems) are driven by the adsorption or absorption of the refrigerant (or sorbate), such as ammonia, by a solid or liquid sorbent. The sorbent therefore acts as a chemical compressor.

In its simplest form a sorption device comprises a linked generator and receiver enclosing a sorbate gas. The receiver acts either as an evaporator or a condenser at different times. A sorbent is present in the generator. Operation of the device is performed by cycling the temperature of a thermal fluid that is pumped through the generator.

When the generator is at essentially ambient temperature, a relatively large amount of refrigerant is adsorbed in the sorbent. On heating the generator, the refrigerant desorbs from the sorbent, raising the internal pressure of the generator, which forms a closed system with the receiver. Under pressure, the refrigerant condenses in the receiver and rejects heat to the environment.

The generator is then cooled back to ambient temperature, leading to resorption of the refrigerant, reducing the system pressure. The reduced pressure in the receiver causes the liquid therein to boil. In this phase of the cycle heat is thereby extracted from the environment to the receiver, producing an external cooling / refrigeration effect. If cooling is desired, two such systems operating out of phase may be used to provide continuous cooling.

Various sorbent materials may be used in the generator. Suitable examples include active carbons, zeolites, metal organic frameworks, metal halide salts and silica gels. Ideally, the sorbent

should be capable of absorbing or adsorbing a large amount of refrigerant when cooled, and desorbing substantially all the absorbed/adsorbed refrigerant when heated. In other words, during a heating/cooling cycle, it is desirable for the difference between the maximum concentration of refrigerant in the sorbent and the minimum concentration of refrigerant in the sorbent to be maximised. The porosity of the sorbent, therefore, is important. At the same time, however, the sorbent should be capable of responding to changes in temperature effectively, so that the refrigerant can be absorbed/adsorbed or released within an acceptable timeframe. The latter is dependent on the heat transfer properties of the sorbent.

Many sorbent materials, however, exhibit poor heat transfer properties, mainly due to a high permeability required to allow the sorbate to permeate the sorbent and the high porosity needed to adsorb large amounts of refrigerant. In particular, the discontinuity of these materials, which are typically in granular or powder form, can lead to poor thermal conductivity. Attempts have been made to improve thermal conductivity by mixing the sorbent material with highly conductive additives, such as graphite or metallic foam. However, as well as increasing the overall production costs of the device, such additives can increase the resistance to the mass transfer of sorbate through the absorbent bed. The present inventors have also found that highly conductive additives reduce the thermal efficiency of the sorption device, since energy used to heat and cool such additives does not contribute to the absorption and desorption of the sorbate.

The present inventors have developed a sorption device which relies on the use of a porous sorbent material that is developed to maximise the thermal efficiency of the overall device.

According to the present invention, there is provided a sorption device comprising a heat exchanger, wherein the heat exchanger comprises:

a sorbate chamber containing a porous sorbent material,

a thermal fluid conduit that is fluidly isolated from the sorbate chamber, and

solid heat transfer means for providing thermal communication between a thermal fluid in the thermal fluid conduit and the porous sorbent material, characterised in that

the porous sorbent material has a thermal conductivity of >0.3 $Wm^{-1}V^{-1}$, preferably 0.4 $Wm^{-1}K^{-1}$, and

the porous sorbent material is selected such that the ratio H_1/H_2 is 0.7 or less,

wherein H_2 is the heat energy used to heat the porous sorbent material and sorbate from a first temperature at which the porous sorbent material contains a maximum concentration of

adsorbed sorbate to a second temperature at which the porous sorbent material has a minimum concentration of adsorbed sorbate, and

Hi is the heat energy that is used to heat the heat transfer means and contained thermal fluid during the course of heating the porous sorbent material and sorbate from the first
5   temperature to the second temperature.

In the present invention, the thermal conductivity of the porous sorbent material and the ratio of Hi/H_2 provide a compromise between efficiency and size for a given duty (output). In the prior art, relatively large quantities of thermally conductive additives, such as graphite and metal,
10   have been used to improve the thermal conductivity and, hence, power output for a given size. However, the present inventors have recognised that the improvement in thermal conductivity can be offset by a decrease in thermal efficiency, since such additives are thermally massive and the heat required to heat such additives does not contribute to the sorption and desorption of the sorbate. The present inventors have identified the need to achieve desirable thermal conductivities without
15   undesirable increases in the thermal mass. Indeed, the present inventors have developed a porous sorbent material that has the characteristics necessary for achieving a desirable balance between efficiency and output.

In one embodiment, the porous sorbent material may be densified to improve thermal
20   contact between the grains of the porous sorbent material. This densification can be used to improve the thermal conductivity of the porous sorbent material, reducing the need for conductive additives, such as graphite and metal. This, in turn, allows a sorbent device to be configured in which the ratio of H_1/H_2 is reduced, such that the desirable thermal efficiencies can be achieved.

25   The ratio of H_1/H_2 may be less than **0.7.** Preferably, the ratio H_1/H_2 is less than **0.6,** more preferably, less than **0.5** and, even more preferably, less than **0.4.** In a preferred embodiment, the ratio of H_1/H_2 is less than **0.35.** The ratio H_1/H_2 may be greater than **0,** for instance, greater than **0.1,** greater than **0.2** or greater than **0.3.**

30   For the avoidance of doubt, H_2 can be calculated from knowledge of the thermodynamic properties of the porous sorbent material and sorbate and their equilibrium porosity data using well-known literature methods. A suitable method is described in Chapter **10** entitled 'Adsorption Refrigerators and Heat Pumps' of 'Carbon Materials for Advanced Technologies', **[38** pages] ed. T.D. Burchell **(1**999), Elsevier ISBN **0-08-042683-2.** In particular, the necessary calculations are described
35   in detail in section **3.1** of that Chapter.

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The porous sorbent material may be selected from carbon, zeolite, silica gel, alumina, a halide salt and a metal organic framework. The porous sorbent material may be a monolithic, particulate, granular or powder material. Preferably, the porous sorbent material is carbon. Any

5   suitable form of carbon may be used. Active carbon is preferred. Examples include monolithic active carbon, granular active carbon and active carbon powder.

The porous sorbent material (preferably carbon, more preferably active carbon) may have a bulk density of at least 500 kg/m^3. Preferably, the porous sorbent material has a bulk density of 700

10   to 1000 kg/m^3, more preferably 800 to 950 kg/m^3, yet more preferably 850 to 900 kg/m^3. The porous sorbent material may be densified by mixing particles having different average particle sizes together. The resulting mixture, therefore, may have a multimodal (e.g. a bimodal) particle size distribution. The multimodal particle size distribution desirably results in an increased bulk density, since differently sized particles can pack into a smaller volume.

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In one embodiment, the porous sorbent material (preferably carbon, more preferably active carbon) may comprise at least in part a granular material. The grains may have a particle size distribution, whereby at least 90%, preferably at least 95%, more preferably at least 98% of the grains have a particle size of 150 microns or greater. The grains may additionally or alternatively

20   have a particle size distribution whereby at least 90%, preferably at least 95%, more preferably at least 98% of the grains have a particle size of 4 mm (e.g. 2 mm) or smaller. In one embodiment, the grains may have a particle size distribution, whereby at least 90%, preferably at least 95%, more preferably at least 98% of the grains have a particle size of 212 microns or greater. Preferably, the grains have a particle size distribution whereby at least 90%, preferably at least 95%, more

25   preferably at least 98% of the grains have a particle size of 850 microns (e.g. 600 microns) or smaller. In one embodiment, the grains have a particle size distribution whereby at least 90%, preferably at least 95%, more preferably at least 98% of the grains have a particle size of 425 microns or smaller. Suitable grains sizes are 12 x 30, 20 x 40, 30 x 70, and 50 x 100 (ASTM USA standard mesh number).

30   Preferably, the porous sorbent material has a bimodal or multi-modal particle size distribution. In a preferred embodiment, the material (preferably carbon, most preferably activated carbon) comprises a mixture of grains and powder. Suitable grains for forming the mixture are described above. In one example, the material comprises 30 x 70 grains and powder. The powder may have a particle size range of 0.1 to 150 microns. Preferably, the powder has a particle size

distribution whereby 95 to 100% of the particles have a particle size of less than 150 microns, preferably less than 125 microns, more preferably less than 112 microns, even more preferably 106 microns, for example, 100 microns. Additionally or alternatively, 85 to 92% of the particles have a particle size of less than 75 microns and/or 45 to 55% of the particles have a particle size of less than 20 microns. The ratio of grains to powder may be 0.3 - 10:1; preferably 0.5 - 5 : 1; more preferably 1 - 3: 1 . Suitable ratios include 2:1, 1:1 and 1:2.

Where the porous sorbent material has a monomodal size distribution, the porous sorbent material may be such that 95 to 100% of the particles have a particle size greater than 180 microns, preferably greater than 250 microns, more preferably greater than 300 microns. In other words, it is preferred that the porous sorbent material does not consist exclusively of powder. Although it may be possible to achieve relatively high bulk densities using a porous sorbent material that consists exclusively of a powder, the thermal conductivity of the resulting material may be compromised . Without wishing to be bound by any theory, this is believed to be because of the increased number of grain boundaries compromising thermal contact between the particles in the powder.

In one embodiment, the porous sorbent material does not have a monomodal distribution.

Whether the porous sorbent material is monomodal or multimodal (but particularly where the material is multimodal), it is preferable for a significant proportion of the particles to have particle sizes greater than 180 microns, preferably greater than 250 microns, more preferably greater than 300 microns. For example, at least 10%, preferably at least 20%, more preferably at least 30%, even more preferably at least 50%, yet more preferably at least 60% of the particles have a particle size of greater than 180 microns, preferably greater than 200 microns, more preferably 300 microns.

An increase in bulk density may be achieved by using particles that are shaped to improve their packing density. For example, porous sorbent particles of a substantially ellipsoidal and/or flake-like shape may be used.

An increase in bulk density may also/additionally be achieved by vibration and/or compression. Compression may be carried out under constant pressure or using a "hammer" effect. Vibration is preferred as this reduces the risk of damage to the particles and/or the sorption device itself. Densification (e.g. compression) may also be carried out in the presence or absence of a

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binder and/or lubricant. The densified (e.g. compressed) material may subsequently be heat-treated.

In one embodiment, grains of the porous sorbent material are mixed with a solvent (e.g. water or an organic solvent) to form a slurry. The slurry may then be dried to remove the solvent. In an alternative embodiment, a powder or granular form of the porous sorbent material may be mixed with a liquid and/or binder(s) and the mixture moulded to produce the resulting porous sorbent material.

The thermal conductivity of the porous sorbent material (e.g. carbon) in the direction of required heat flux may be ≥ 0.3 WrrfV [1], preferably ≥ 0.4 WrrfV [1], more preferably ≥ 1 WrrfV [1], yet more preferably ≥ 2 WrrfV [1]. In one embodiment, the thermal conductivity may be 0.4 to 4 WrrfV [1], for example, 2 to 3 $Wm^{-}V$ [1]. Thermal conductivity is measured by ASTM E1530. The porous sorbent material may exhibit anisotropic thermal conductivities where the thermal conductivity in one direction is different from the thermal conductivity in another. This may arise, for example, if the porous sorbent material is densified by compression. In this instance, the thermal conductivity may be higher in a direction normal to the direction of compression. Where anisotropic behaviour arises, the maximum thermal conductivity may be ≥ 0.3 WrrfV [1], preferably ≥ 0.4 $Wm^{-}V$ [1], more preferably ≥ 1 WrrfV [1], yet more preferably ≥ 2 WrrfV [1]. The minimum thermal conductivity may also be ≥ 0.3 WrrfV [1], preferably ≥ 0.4 WrrfV [1], more preferably ≥ 1 WrrfV [1], yet more preferably ≥ 2 WrrfV [1]. For avoidance of doubt, it is noted that the units WrrfV [1] can also be denoted W/m/K.

If desired, a thermally conductive additive may be placed in thermal communication with the porous sorbent material. Such additives form part of the heat transfer means. The thermally conductive additive may be a solid material having a thermal conductivity of at least 5 WrrfV [1], preferably at least 10 WrrfV [1], more preferably at least 16 WrrfV [1], yet more preferably, at least 30 WrrfV [1], even more preferably at least 100 WrrfV [1] and most preferably at least 120 WrrfV [1]. In some embodiments, for example, when pure graphite is used as the thermal conductive additive, the thermal conductive additive may have a thermal conductivity of up to 500 WrrfV [1]. The thermally conductive additive may be mixed or otherwise placed in thermal contact with the porous sorbent material. Examples of suitable thermally conductive additives include metal or graphite. For example, metal or graphite particles may be mixed with particles of the porous sorbent material. Alternatively, a metal scaffold (e.g. honeycomb structure) may be used to support the porous sorbent material. Suitable metals include aluminium and copper.

The solid heat transfer means includes any suitable solid means for transferring heat to and from the porous sorbent material. Such means would typically include the walls of the fluid sorbate chamber and/or the walls of the thermal fluid conduit. The walls of the fluid sorbate chamber and/or the walls of the thermal fluid conduit may be formed of any suitable material, including metals, such as steels, copper and aluminium. Where a thermally conductive additive is used as described above, this would also form part of the solid heat transfer means. The solid heat transfer means, therefore, may be any solid material having a thermal conductivity of at least 5 $Wm^{-1}V^{-1}$ that is in thermal communication with the porous sorbent material. The solid heat transfer means may have a thermal conductivity of at least 5 $Wm^{-1}V^{-1}$, preferably at least 10 $Wm^{-1}V^{-1}$, more preferably at least 16 $Wm^{-1}V^{-1}$, yet more preferably, at least 30 $Wm^{-1}V^{-1}$, and even more preferably at least 100 $Wm^{-1}V^{-1}$ and most preferably at least 120 $Wm^{-1}V^{-1}$. In some embodiments, for example, when the solid heat transfer means is aluminium, the thermal conductivity of the solid heat transfer means may be 200 $Wm^{-1}V^{-1}$ or more. The heat transfer means may be in thermal contact with the porous sorbent material to allow the heat to be transferred to the porous sorbent material by conduction (e.g. through solid or gas).

The porous sorbent material may have a permeability such that the pressure drop of gaseous sorbate in the fluid sorbate chamber does not typically exceed 5% of the total pressure the sorbate when the flow rate is at design levels. Preferably, the porous sorbent material may have permeability in the direction of sorbate flow such that the pressure drop of fluid sorbate in the fluid sorbate chamber does not typically exceed 5% of the total pressure in the direction of sorbate flow. Permeability may be measured using the technique described in International Journal of Heat and Mass Transfer 43 (2000) 2053 - 2058. The porous sorbent material may exhibit anisotropic permeability where the permeability in one direction is different from the permeability in another. This may arise, for example, if the porous sorbent material is densified by compression. In this instance, the permeability may be higher in a direction normal to the direction of compression. Where anisotropic behaviour arises, at least the minimum pressure drop should not exceed 5% of the total pressure when the sorbate flow rate is at design levels. The minimum pressure drop may also not exceed 5% of the total pressure when the sorbate flow rate is at design levels.

The porous sorbent material may have a permeability such that the pressure drop of fluid sorbate in the fluid sorbate chamber does not typically exceed 3% and preferably does not exceed 1% of the total pressure the sorbate flow rate is at design levels. Preferably, the porous sorbent

material may have a permeability in the direction of sorbate flow such that the pressure drop of fluid sorbate in the fluid sorbate chamber does not typically exceed 3%, and preferably does not exceed 1% of the total pressure in the direction of sorbate flow. Where anisotropic behaviour arises, at least the minimum pressure drop should not exceed 3% and preferably does not exceed 1% of the total pressure when the sorbate flow rate is at design levels. The minimum pressure drop may also not exceed 3% and preferably does not exceed 1% of the total pressure when the sorbate flow rate is at design levels.

In the device of the present invention, the ratio of the thermal mass of the solid heat transfer means and thermal fluid to the thermal mass of the porous sorbent material containing the refrigerant may be ≤ 2. Preferably, this ratio is ≤ 1, more preferably ≤ 0.7 .

Any suitable sorbate (refrigerant) may be used in the fluid sorbate chamber. Examples include ammonia, methanol and water. Ammonia is preferred, particularly when the porous sorbent material comprises carbon. In this regard, the present inventors have found that for a given cooling or heating power the pressure drop across the porous sorbent material is lower when ammonia is used as a sorbate. As a consequence, the porous sorbent material may be densified to a greater extent to improve thermal contact between the particles of the porous sorbent material while, at the same time, maintaining desirable levels of permeability. This advantage is less pronounced with sorbate materials, such as methanol and water, because these sorbate materials result in greater decreases in relative pressure across the absorbent bed. As a result, decreases in permeability are less well tolerated when sorbate material, such as water and methanol are used.

Any suitable heat exchanger may be used in the sorbent device of the present invention. Typically, therefore, the heat exchanger will comprise a plurality of thermal fluid conduits. A plurality of fluid sorbate chambers may also be present. Examples of suitable heat exchangers include shell-and-tube, plate or plate-and-fin heat exchanges. Where a shell-and-tube heat exchanger is used, the shell may be used as the fluid sorbate chamber containing the porous sorbent material. The tubes positioned within the shell may be the thermal fluid conduits. The heat transfer means for providing thermal communication between a thermal fluid in the thermal fluid conduit and the porous sorbent material may include the tube walls and any metal or graphite mixed with the porous sorbent material in the fluid sorbate chamber. Where a plate heat exchanger is used, the heat transfer means for providing thermal communication between a thermal fluid in the thermal

fluid conduit and the porous sorbent material may include the plates and any metal or graphite mixed with the porous sorbent material in the fluid sorbate chamber.

Suitable heat exchanger designs are described in WO 2008/029185 and WO 2011/007166.

The sorption device may be used as or as part of an air-conditioning apparatus, refrigerator, heat pump and/or thermal transformer.

According to a further aspect, there is provided a sorption device comprising a heat exchanger, wherein the heat exchanger comprises:

a sorbate chamber containing a porous sorbent material,

a thermal fluid conduit that is fluidly isolated from the sorbate chamber, and

solid heat transfer means for providing thermal communication between a thermal fluid in the thermal fluid conduit and the porous sorbent material, characterised in that

the porous sorbent material has a thermal conductivity of >0.3W/m ^{2}/K, and

wherein the porous sorbent material is a particulate material having a bimodal or multi-modal particle size distribution, and

optionally has a bulk density of at least 600 kg/m^3.

According to a further aspect of the invention, there is provided a method of exchanging heat using a sorption device as described above, the method comprising:

introducing sorbate into the sorbate chamber to cause the sorbate to be absorbed or adsorbed by the porous sorbent material,

passing thermal fluid at a higher temperature than the porous sorbent material to heat the porous sorbent material and desorb the sorbate therefrom, whereby the desorption of sorbate results in an increase in pressure which causes desorbed sorbate to be condensed in a condenser, and

passing thermal fluid at a lower temperature than the porous sorbent material to cool the porous sorbent material and re-absorb or re-adsorb sorbate, whereby the re-absorption or re-adsorption of sorbate results in a decrease in pressure which causes the sorbate to be evaporated in an evaporator.

The temperature of the thermal fluid may be cycled. For example, in one heating/cooling cycle, the thermal fluid may be heated, subsequently cooled to ambient temperature and then re-heated.

5   When the sorbate chamber is at essentially ambient temperature, a relative large amount of sorbate is adsorbed or absorbed by the porous sorbent material. On heating, the sorbate desorbs from the sorbent material, raising the internal pressure of the sorbate chamber. Under pressure, the sorbate condenses in a separate vessel (the condenser) at lower temperature and releases heat to the environment.

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The sorbate chamber may then be cooled back to ambient temperature, leading to re-absorption or re-adsorption of the sorbate, reducing the system pressure. The reduced pressure causes the sorbate which is in the liquid phase within another vessel (an evaporator) at lower temperature to boil. In this phase of the cycle, the heat is extracted from the environment to the

15   other vessel producing a cooling effect.

If cooling is desired, two devices may be operated out of phase to produce continuous cooling.

20   In the method of the present invention, the porous sorbate material is selected and/or treated such that it has a thermal conductivity of $>0.3 \mathrm{Wm}^{-1}\mathrm{K}^{-1}$, preferably $\geq Q4 \mathrm{Wm}^{-i}\mathrm{K}^{-i}$, and a ratio of $\mathbf{Hi/H_2}$ is less than 0.7. As discussed above, $\mathbf{H_2}$ is the heat energy used to heat the porous sorbent material and sorbate from a first temperature at which the porous sorbent material contains a maximum concentration of adsorbed sorbate to a second temperature at which the porous sorbent

25   material has a minimum concentration of adsorbed sorbate. H_1 is the heat energy that is used to heat the heat transfer means and thermal fluid contained by the walls of the thermal fluid conduit during the course of heating the porous sorbent material and sorbate from the first temperature to the second temperature. The maximum concentration achieved at the first temperature is the maximum concentration achieved in the heating/cooling cycle of the thermal fluid, while the

30   minimum concentration achieved at the second temperature is the minimum concentration achieved in the heating/cooling cycle of the thermal fluid.

Figure 1 is a plot showing the reduction in the coefficient of performance (COP) of a heat pump against increasing $\mathbf{Hi/H_2}$. COP is equal to the heating output power of the device divided by

the high temperature   input power and the abscissa shows the COP normalised with respect to the COP when Hi is zero. The data are derived from a sorbent system consisting of two beds of a particular active carbon sorbent material operating with heat recovery and mass recovery and with particular   characteristic   temperatures: evaporating   7°C, condensing   50°C, final adsorption temperature   50°C and driving temperature   200°C. As can be seen from the Figure, the higher the value of Hi/H_2, the poorer the COP. Other sorbents and temperatures   would give slightly different plots but with similar trend.

Example 1

In this Example, the method of determining the values of H_1 and H_2 is outlined by way of example in relation to carbon as a porous sorbent material (adsorbent).   The method is also described in Chapter 10 entitled 'Adsorption Refrigerators and Heat Pumps' of 'Carbon Materials for Advanced Technologies',   [38 pages] ed. T.D. Burchell (1999), Elsevier ISBN 0-08-042683-2.

Fig. 2 (Clapeyron diagram) shows both the actual cycle (shown in dashed lines) and the idealised cycle, which consists of two isosteres and two isobars. Heat flows in J/kg adsorbent *(q)* are shown as shaded arrows. For most purposes, analysis of the ideal cycle gives an adequate estimate of the COP and cooling or heating per kg of adsorbent. An accurate calculation of the path of the actual cycle needs information   on the dead volume of the whole system and of the heat transfer characteristics of the condenser and evaporator. General trends are more apparent from an analysis of the idealised cycle.

The COP in cooling *(COP$_C$)* or heating *(COP$_H$)* is defined by:

$$COP_C = \frac{q_{ev}}{q_{12} + q_{23}} \quad , \quad COP_H = \frac{q_{con} + q_{34} + q_{41}}{q_{12} + q_{23}}$$

Considering the processes occurring in Fig. 2 in sequence:

Process 1-2

The heat input per unit mass of adsorbent in the isosteric heating phase when the concentration   is x_{conc} is given by:

$$q_n = \int_{T_1}^{T_2} (c_{pc} + x_{conc}\, c_{va})\, dT$$

where:

c_{pc} = Specific heat of adsorbent (carbon), possibly a function of temperature.

x_{conc} = maximum concentration, obtained at point 1 by using the evaporating pressure and bed temperature $_{J1}$ in the Dubinin-Astakhov equation.

c_{va} = Specific heat of adsorbed phase at constant volume.

Ti = minimum cycle temperature (K).

T_2 = temperature at start of desorption (K).

The integrated term is simply the combined specific heat of the unit mass of adsorbent and its associated adsorbate. The specific heat at constant volume has been used for the adsorbate since, theoretically, there is no expansion of the adsorbate volume and the heat required to raise the temperature is the change in internal energy. In practice there will be some expansion and a pessimistically high estimate could use the specific heat at constant pressure c_{pa}.

The specific heat of the adsorbed phase is in any case difficult to estimate and it is common to approximate it to that of saturated liquid adsorbate at the same temperature.

T_2 is easily calculated, since the ratio of T/T_{sat} is constant along an isostere, giving:

$$\frac{T_1}{T_{ev}} = \frac{T_2}{T_{con}}$$

Process 2-3

The heat input per unit mass of adsorbent in the isobaric heating phase where the concentration varies is given by:

$$q_{23} = \int_{T_2}^{T_3} (C_{pc} + x\, c_{pa})dT + \int_{x_{dil}}^{x_{conc}} Hm\,dx$$

where x_{dil} is the minimum concentration and *Hm* is the heat of desorption per unit mass of adsorbate. *Hm* at any point on 2-3 or 4-1 can be derived from the slope of the isostere on the Clapeyron diagram *(A)*:

$$Hm = RA$$

where:

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$$A = \left(\frac{\partial \left(ln[p] \right)}{\partial \left(1/T \right)} \right)_x$$

$R =$ The gas constant at the system pressure and temperature.

Assuming the form of the Dubinin equation to be correct, or more generally that the ratio T/T_{sat} is constant along an isostere then H can be expressed as a multiple of the latent heat L of the refrigerant at the system pressure:

$$Hm = L \frac{T}{T_{sat}}$$

From the above, we can determined **H_2** and H_1 as follows:

$H2 = q_{12} + q_{23}$ (**J/kg** adsorbent)

and

$H_1 = C_{HTM}(T_3 - T_1)$

where:

$C_{HTM} =$ thermal capacity of heat transfer means and fluid per unit mass of adsorbent

$= m_{HTM}C_{pHTM} + m_{TF}C_{pTF}$

where:

$m_{HTM} =$ mass of heat transfer means/mass of adsorbent

$C_{pHTM} =$ specific heat of heat transfer means (J/kgK)

$m_{TF} =$ mass of thermal fluid in generator/mass of adsorbent

$C_{pTF} =$ specific heat of thermal fluid (J/kgK)

Example 2

In this Example, the thermal conductivities of various granular carbon materials were determined. The samples were obtained from Chemviron Carbon Ltd (laboratory samples of Chemviron 208C) with the following grain sizes: 12 x 30, 20 x 40, 30 x 70 and 50 x 100 (US standard mesh). The samples were densified by vibration and the thermal conductivities at various densities were determined. The results are shown in Figure 3.

Example 3

The following bimodal mixtures were prepared in a grain to powder weight ratio of 2:1:

  a) 12 x 30 and powder

  b) 20 x 40 and powder

5 c) 30 x 70 and powder

The powder employed was obtained from Chemviron Carbon Ltd (Pulsorb 208CP).

The bimodal samples were densified by vibration and their thermal conductivities

10 determined. The results are shown in Figure 4.

Example 4

The following bimodal mixtures were prepared in a grain to powder weight ratio of 1:1:

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  a) 12 x 30 and powder

  b) 30 x 70 and powder

The powder employed was obtained from Chemviron Carbon Ltd (Pulsorb 208CP).

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The bimodal samples were densified by vibration and their thermal conductivities

determined. The results are shown in Figure 5.

Discussion

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For a good bimodal mixture, high conductivity implies high density. From Figures 4 and 5, it

can be seen that the best mixture corresponds to point 770 kg/m^3 and 0.35 W m^{-1} K^1 of 30x70 grains

and powder mixture.

$$\rho_1 = 770 \ \frac{kg}{m^3} \quad \text{(from Figure 4,5)} \qquad \rightarrow \qquad K_{c1} = 0.35$$

30 The mixture can be used in a sorption device configured to achieve H_1/H_2 of 0.7.

$$\frac{H_1}{H_2} = 0.7 \qquad \text{(from Figure 1)} \rightarrow \qquad COP_1 \, (normalised) = 0.93$$

Let us normalise the heating power to 1 for this mixture.

Now the COP and the SHP (Specific heating power) can be calculated knowing that for an only grains mixture the density is 520 kg/m3 and corresponds a conductivity of 0.25 Wm⁻V¹. It can be assumed, for approximate comparison, that the heating power into the generator is proportional to the carbon conductivity and that *this* multiplied by the COP gives the output power

$$p_2 \approx 520 \frac{kg}{m^3} \quad \text{(from Figure 3)} \rightarrow \quad K_{c2} \approx 0.25$$

$$\frac{H_1}{H_{22}} = \frac{H_1}{H_{21}} \cdot \frac{\rho_1}{\rho_4} = 0.7 \cdot \frac{770}{520} = 1.04 \quad \text{(from Figure 1)} \rightarrow \quad COP_2 \approx 0.9$$

$$SHP_2 = SHP_1 \cdot \frac{K_{c2}}{K_{c1}} \cdot \frac{COP_2}{COP_1} \approx 1 \cdot \frac{0.25}{0.35} \cdot \frac{0.9}{0.93} = 0.69$$

	Carbon density (kg/m3)	Conductivity (Wm⁻¹K¹)	H1/H2	Normalised COP	Normalised power (W/kg)
Grains	520	0.25	1.04	0.9	0.69
Bimodal mixture	770	0.35	0.7	0.93	1

The calculation shows that, if we were to substitute the best bimodal mixture with a grains-only mixture having a density of 520 kg/m³, the COP would drop by 3% and the power by 31%. However, any given machine is designed to deliver a certain power. The options available to deliver the same power from grains only are either to make the sorption containers 30% larger(increasing capital cost) or to run the machine in a less efficient way (shorter cycle times with larger temperature differences) that might reduce COP by a further 10%.

Claims

1.   A sorption device comprising a heat exchanger, wherein the heat exchanger

5   comprises:

        a sorbate chamber containing a porous sorbent material,

        a thermal fluid conduit that is fluidly isolated from the sorbate chamber, and

        solid heat transfer means for providing thermal communication between a thermal fluid in

the thermal fluid conduit and the porous sorbent material, characterised in that

10   the porous sorbent material has a thermal conductivity of $>0.3 Wm^{-1}K^{-1}$, preferably $>0.4Wm^{-1}K^{-1}$, and

        the porous sorbent material is selected such that the ratio H_1/H_2 is 0.7 or less,

        wherein H_2 is the heat energy used to heat the porous sorbent material and sorbate from a

first temperature at which the porous sorbent material contains a maximum cyclic concentration of

15   adsorbed sorbate to a second temperature at which the porous sorbent material has a minimum

cyclic concentration of adsorbed sorbate, and

        Hi is the heat energy that is used to heat the heat transfer means and thermal fluid during

the course of heating the porous sorbent material and sorbate from the first temperature to the

second temperature.

20

2.   A sorption device comprising a heat exchanger, wherein the heat exchanger comprises:

        a sorbate chamber containing a porous sorbent material,

        a thermal fluid conduit that is fluidly isolated from the sorbate chamber, and

        solid heat transfer means for providing thermal communication between a thermal fluid in

25   the thermal fluid conduit and the porous sorbent material, characterised in that

        the porous sorbent material has a thermal conductivity of $>0.3 Wm^{-}V^{-1}$, and

        wherein the porous sorbent material is a particulate material having a bimodal or multi-

modal particle size distribution, and

        optionally has a bulk density of at least 600 kg/m^3.

30

3.   A device as claimed in claim 1 or 2, wherein the porous sorbent material is selected from

carbon, zeolite, silica gel, alumina, a halide salt and a metal organic framework.

4.   A device as claimed in claim 3 wherein the porous sorbent material is carbon.

5.   A device as claimed in claim 1, wherein the porous sorbent material has a bulk density of at least 500 kg/m^3.

6.   A device as claimed in any one of the preceding claims, wherein the porous sorbent material has a bulk density of 700 to 950 kg/m^3.

7.   A device as claimed in claim 1, wherein the porous sorbent material comprises particles having a multi-modal particle size distribution.

8.   A device as claimed in any one of the preceding claims, wherein the porous sorbent material comprises particles that are substantially ellipsoidal or flake-like in shape.

9   A device as claimed in any one of the preceding claims, wherein the porous sorbent material is densified by vibration and/or compression.

10.   A device as claimed in any one of the preceding claims, wherein the porous sorbent material is mixed with a binder or lubricant.

11.   A device as claimed in any one of the preceding claims, wherein the porous sorbent material by forming a slurry of particles of the porous sorbent material in a solvent and subsequently removing the solvent.

12.   A device as claimed in any one of the preceding claims, wherein the heat transfer means comprises the walls of the fluid sorbate chamber and/or the walls of the thermal fluid conduit.

13.   A device as claimed in any one of the preceding claims, wherein the heat transfer means comprises any solid material having a thermal conductivity of at least 5 $Wm^{-}V$ [1] that is in thermal communication with the porous sorbent material.

14.   A device as claimed in claim 13, wherein the heat transfer means comprises metal and/or graphite.

15.   A device as claimed in any one of the preceding claims, wherein the porous sorbent material has a permeability such that the pressure drop of fluid sorbate in the fluid sorbate chamber does not exceed 5% of the total pressure when the sorbate flow rate is at design level.

16.   A device as claimed in any one of the preceding claims, wherein the fluid sorbate chamber comprises a fluid sorbate selected from ammonia, methanol and water.

17.   A device as claimed in claim 16, wherein the fluid sorbate is ammonia.

18.   A device as claimed in any one of the preceding claims, wherein Hi/H_2 is less than 0.5.

19.   A method of exchanging heat using a sorption device as claimed in any one of the preceding claims, the method comprising:

introducing sorbate into the fluid sorbate chamber to cause the sorbate to be absorbed or adsorbed by the porous sorbent material,

passing thermal fluid at a higher temperature than the porous sorbent material to heat the porous sorbent material and desorb the sorbate therefrom, whereby the desorption of sorbate results in an increase in pressure which causes desorbed sorbate to be condensed in a condenser, and

passing thermal fluid at a lower temperature than the porous sorbent material to cool the porous sorbent material and re-absorb or re-adsorb sorbate, whereby the re-absorption or re-adsorption of sorbate results in a decrease in pressure which causes the sorbate to be evaporated in an evaporator.
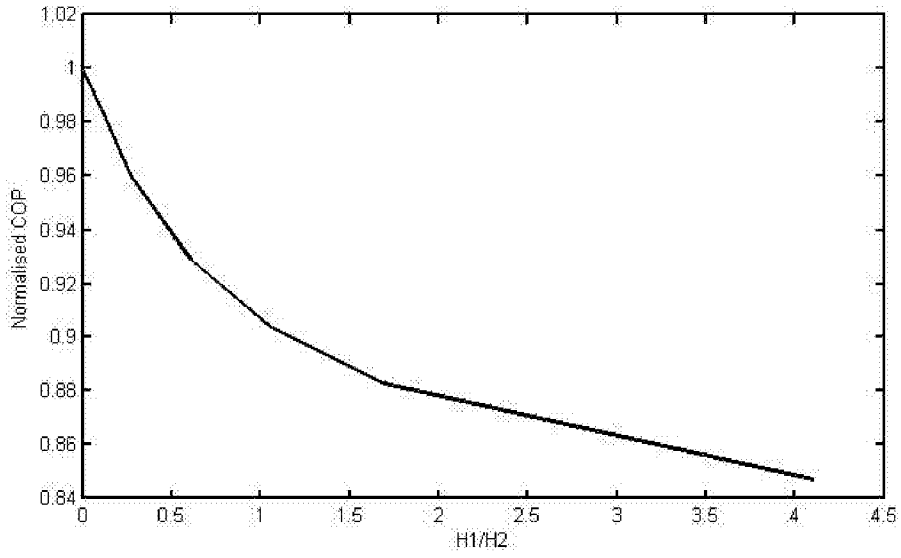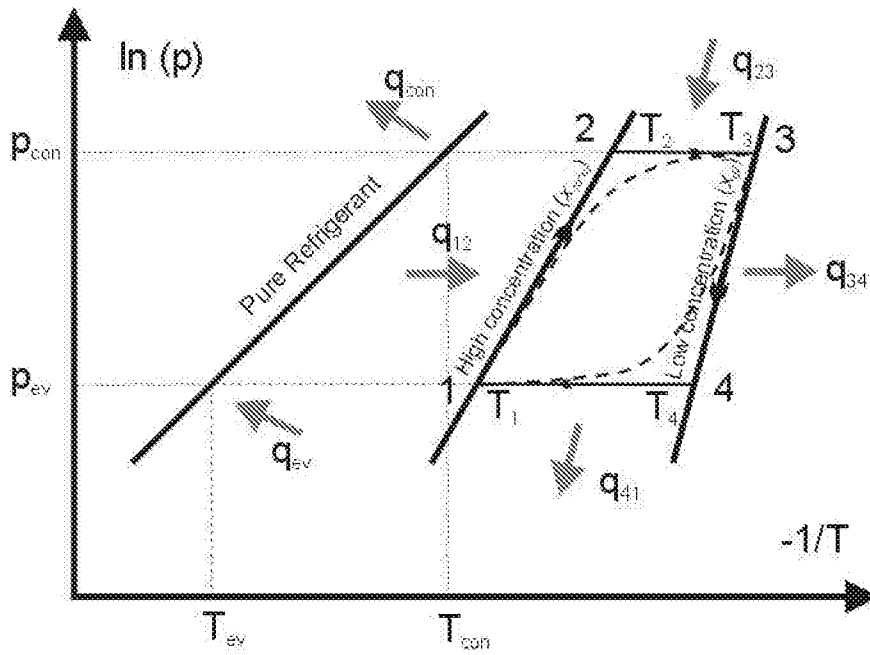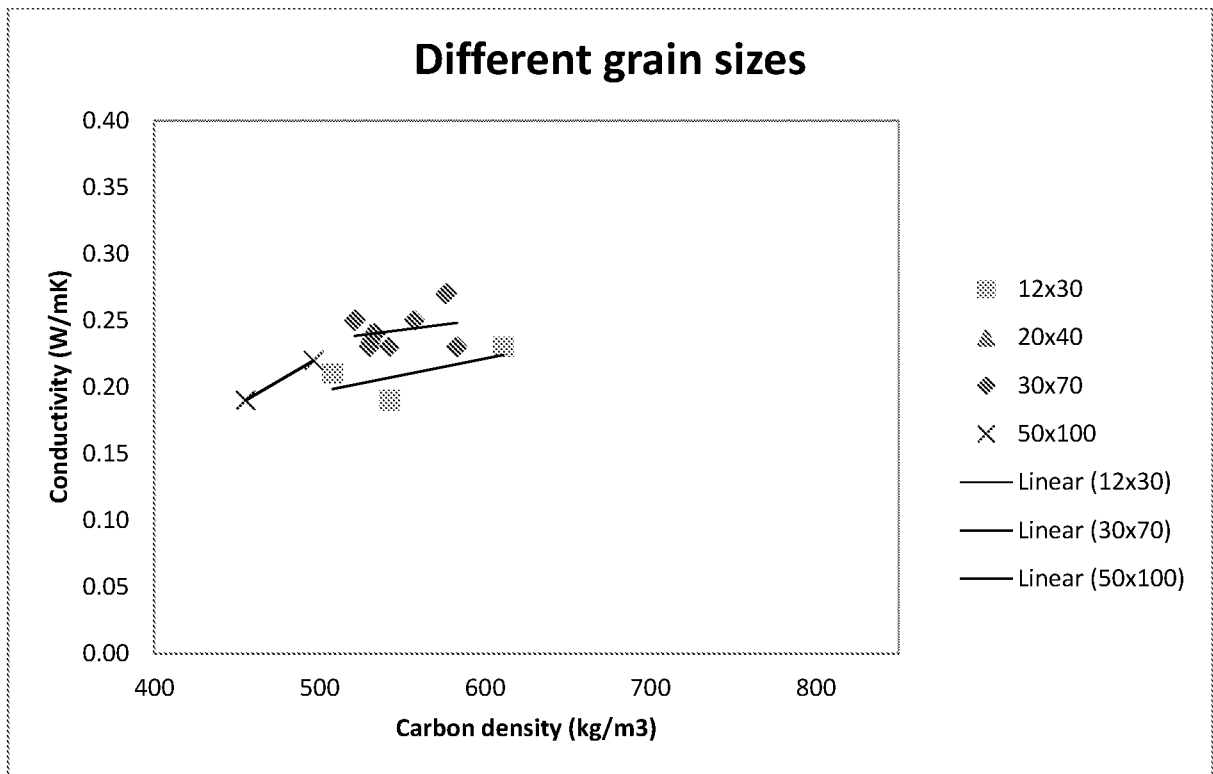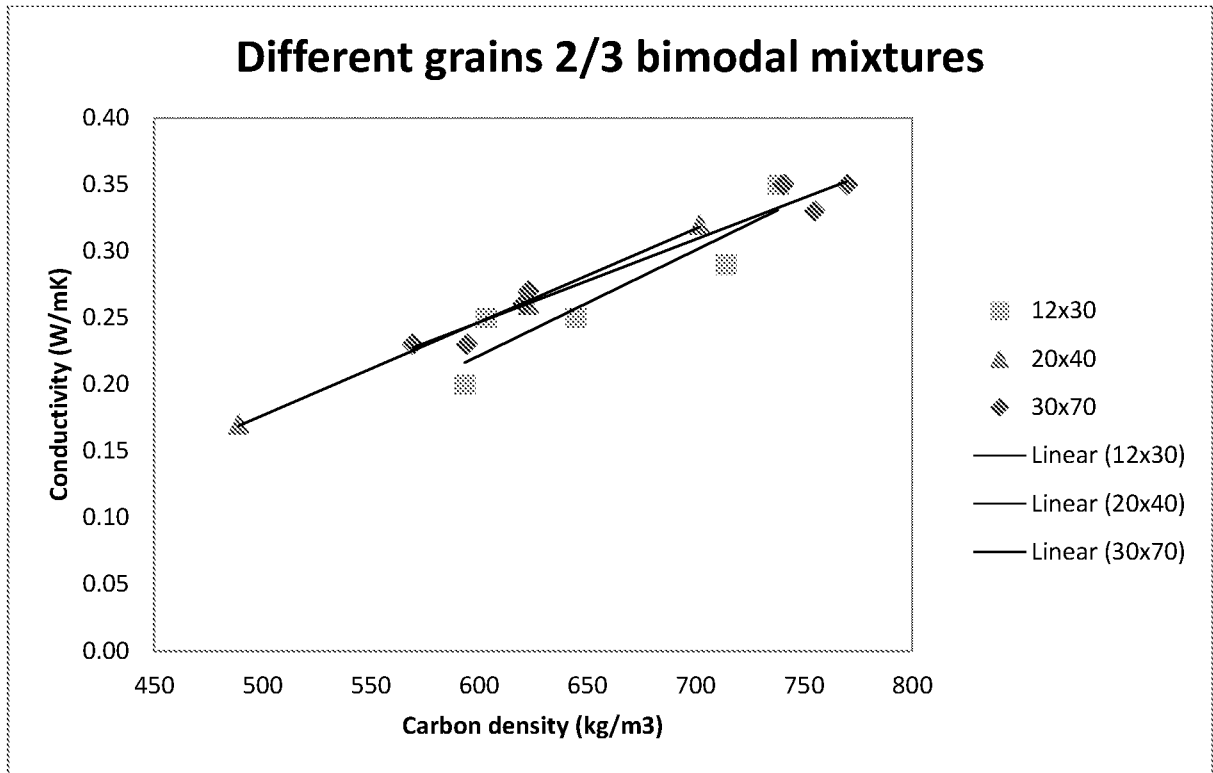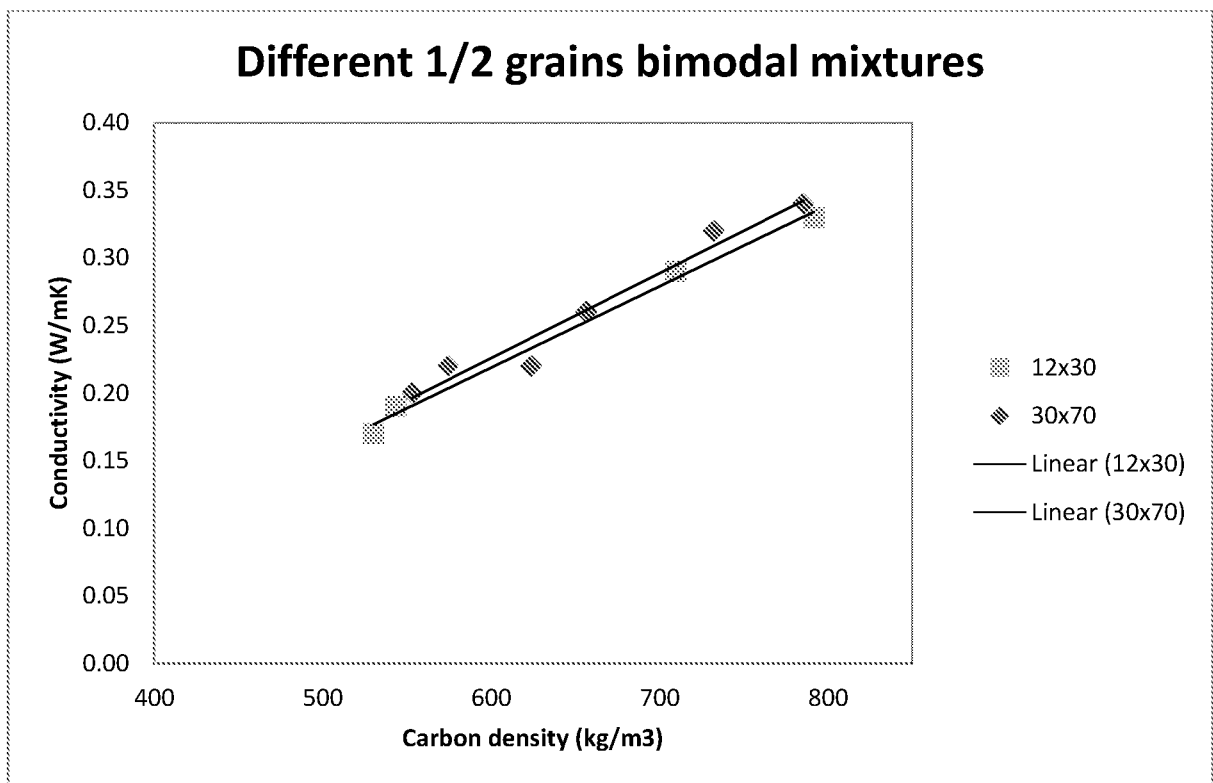
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. F25B17/08   B01J20/28
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)

F25B   B01J

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	GB 2 441 657 A (UNIV WARWICK [GB]) 12 March 2008 (2008-03-12) cited in the application	1,3,4, 10-19
Y	page 10 - page 29; figures 1-23 -----	2,5-9
X	WO 2008/155543 A2 (THERMAL ENERGY SYSTEMS LTD [GB]; POWELL RICHARD [GB]; EDWARDS DEREK WI) 24 December 2008 (2008-12-24) page 5, line 24 - page 41, line 32; figures 1-22 -----	1,3,4, 12-14, 16,17,19
X	US 2008/023181 A1 (DUNNE STEPHEN R [US] ET AL) 31 January 2008 (2008-01-31) paragraph [0029] - paragraph [0061]; figures 1-10 -----	1,3,4, 12,14,16

-/- ·

[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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 May 2013	21/05/2013

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

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

C(Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2010/025948 AI (AMMINEX AS [DK] ; QUAADE ULRICH [DK] ; SVAGIN JAKOB [DK] ; JOHANSEN JOHNN) 11 March 2010 (2010-03-11) page 2, line 29 - page 9, line 12; figures 1,2 -----	5,6,9
Y	US 6 221 492 BI (M0REAU SERGE [FR] ET AL) 24 April 2001 (2001-04-24) column 1, line 13 - column 8, line 50; figures 1-5 -----	8
A	US 2002/192155 AI (STERTE PER J0HAN [SE] ET AL) 19 December 2002 (2002-12-19) paragraph [0003] - paragraph [0085] ; figures 1-5 paragraph [0046] -----	8
Y	WO 2011/063370 A2 (3M INNOVATIVE PROPERTIES CO [US] ; BADRI BRINDA B [US] ; DAVID MOSES M [) 26 May 2011 (2011-05-26) page 9, line 5 - page 78, line 5; figures 1-5 page 71, line 3 - page 78, line 5 -----	2,7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2012/053042

Box No. II	Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III	Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos. :

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

Form PCT/ISA/21 0 (continuation of first sheet (2)) (April 2005)

FURTHER INFORMATION CONTINUED FROM   PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1, 3-6, 9, 12-19

    Sorption device wherein the porous sorbent material has a bulk density of at least 500 kg/m3
    ---

2. claims: 1, 3, 4, 8, 10, 11

    Sorption device, wherein the porous sorbent material comprises particles that are substantially ellipsoidal or flake-like in shape.
    ---

3. claims: 1, 2, 7

    Sorption device, wherein the porous sorbent material has a bimodal or multimodal particle size distribution.

INTERNATIONAL SEARCH REPORT

Information on patent family members

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