

UTILIZATION OF WASTE HEAT USING FIBER SORBENT SYSTEM AND METHOD OF USING SAME

FIELD OF THE DISCLOSED SUBJECT MATTER

[0001] The disclosed subject matter relates to a fiber sorbent system, and particularly a sorbent system for rapid heat transfer capable of being heated and cooled rapidly.

BACKGROUND OF THE DISCLOSED SUBJECT MATTER

[0002] Chemical processing operations, including petroleum refining and chemical processing operations, are energy intensive. It is often necessary to conduct these operations at high temperatures using high temperature heat sources including but not limited to steam and other hot streams present in refining and petrochemical processing facilities. After the steam and other hot streams have performed their intended functions, there remains “waste” or unutilized energy that can be further utilized. Refineries and petrochemical facilities typically utilize only about 70% of the input energy needed to conduct processing of crude oil to products.

[0003] In an effort to increase efficiency, it is desirable to recover and utilize the waste or unutilized heat. One method described in U.S. Patent No. 5,823,003 to Rosser et al. attempts to make use of waste heat and apply such heat to an adsorbent material in order to release an adsorbed gas at a higher pressure, which in turn can be used in a refrigeration cycle that contains an expansion valve. U.S. Patent No. 5,823,003, the entirety of which is incorporated herein, describes the use of a zeolite-water combination for a sorption refrigeration system.

[0004] Current methods to obtain refrigeration and work from sorbent materials in chemical process applications have limitations. For example, the temperature swings (ΔT) provided by lower grade heat sources, such as waste heat, are less than that which would be provided using primary heat sources. Such limitations render the recovery of useful energy from waste heat economically unsustainable, or impractical.

[0005] Accordingly, there remains a need to improve unutilized heat recovery efforts (e.g., waste heat recovery) and render such efforts more cost-effective by maximizing output from the temperature swings (ΔT) provided by lower grade sources. There is a need to provide sorption systems with improved heat transfer rate which are capable of being heated and cooled rapidly, thus rendering sorption systems driven by lower grade heat sources more economically sustainable.

SUMMARY OF THE DISCLOSED SUBJECT MATTER

[0006] The purpose and advantages of the disclosed subject matter will be set forth in and apparent from the description that follows, as well as will be learned by practice of the disclosed subject matter. Additional advantages of the disclosed subject matter will be realized and attained by the methods and systems particularly pointed out in the written description and claims hereof, as well as from the appended drawings.

[0007] To achieve these and other advantages and in accordance with the purpose of the disclosed subject matter, as embodied and broadly described, the disclosed subject matter includes a hollow fiber sorbent system and particularly a sorption system capable of being heated and cooled rapidly.

[0008] In accordance with one aspect of the present invention, a fiber sorption system is provided. The system includes at least one vessel, a working fluid, at least one thermal fluid and at least one hollow fiber located within the at least one vessel. Each hollow fiber includes a sorbent material and binder material that together form an elongated body. The elongated body has a hollow interior and an inner surface adjacent the hollow interior. One of the inner surface and the outer surface has a coating layer formed thereon. The coating layer being impermeable to both the working fluid and the thermal fluid.

[0009] The coating layer may be formed from a material selected from the group consisting of poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl fluoride), poly(vinylidene fluoride), ethylene vinyl alcohol copolymer, poly vinyl alcohol, polyamides, polyethylene (preferably high density), polypropylene (preferably high density), polyesters, polyimides, polyacrylonitrile, polysulfone, polyurethane, combinations thereof and derivatives thereof.

[0010] In accordance with one aspect of the present invention, the coating layer is formed on the inner surface. The thermal fluid passes the hollow interior, but does not pass through the coating layer to the sorbent material. The thermal fluid may include a heating fluid and a cooling fluid. The working fluid may include carbon dioxide. The carbon dioxide may be supplied from a process stream within a petrochemical or chemical processing operation. The working fluid is in fluid communication with the outer surface of the hollow fiber.

[0011] In accordance with another aspect of the present invention, the coating layer is formed on the outer surface. The working fluid passing through the hollow interior such that it is capable of being adsorbed and desorbed by the sorbent material in the elongated body.

[0012] In accordance with another aspect of the present invention, a fiber sorption system is disclosed comprising at least one vessel, a working fluid, at least one thermal fluid and at least one fiber located within the at least one vessel. Each fiber includes a sorbent material and binder material forming an elongated body having an outer surface. The working fluid flows past the outer surface and is capable of being adsorbed and desorbed by the sorbent material. The thermal fluid may flow past the outer surface and is capable of transferring heat without wetting the fiber surface. Thermal fluid contact angle with the fiber surface is more than 90 degrees. The fiber may further include an outer coating on the outer surface. The outer coating is permeable to the working fluid such that working fluid may pass through the outer coating for adsorption and desorption by the sorbent material. The outer coating is impermeable to the thermal fluid, whereby the thermal fluid is prevented from passing through the outer coating to the sorbent material. The outer coating may be formed from an organometallic compound.

[0013] In accordance with another aspect of the disclosed subject matter, a fiber sorption system is disclosed comprising at least one hollow fiber including an inner coating generally impermeable to a thermal fluid (i.e. heating fluid or a cooling fluid) as well as working fluid. The inner coating defines a channel adapted to receive a supply of the thermal fluid (e.g., steam). The hollow fiber further includes an outer surface that is permeable to a working fluid. A chamber is defined by and between the outer surface

and the inner coating, with a sorbent material contained within the chamber. The fiber sorption system further comprises a supply of the working fluid (e.g., carbon dioxide) in fluid communication with the outer surface of hollow fiber. Additionally, the inner coating can be, for example, poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl fluoride), Poly(vinylidene fluoride), Ethylene vinyl alcohol copolymer, poly vinyl alcohol, polyamides, polyethylene (preferably high density), polypropylene (preferably high density), polyesters, polyimides, polyacrylonitrile, polysulfone, polyurethane, etc. - their combinations or derivatives.

[0014] The disclosed subject matter also includes a method of creating work from a pressurized working fluid that includes providing a vessel containing a fiber sorption system as disclosed herein, and introducing a supply of the working fluid to an exterior surface of the outer coating; introducing the thermal fluid (e.g., heating fluid) to the inner channel to obtain a pressurized working fluid; and directing the pressurized working fluid to a work component. The work component can be an expansion valve to provide refrigeration, or a turboexpander to provide electricity.

[0015] In accordance with another aspect of the disclosed subject matter, a fiber sorption system is disclosed that includes at least one hollow fiber including an inner surface that is permeable to a working fluid, with the inner surface defining a channel adapted to receive a supply of the working fluid (e.g., carbon dioxide). The hollow fiber further includes an outer coating that is impermeable to the thermal fluid and working fluid, wherein the outer coating defines a chamber between the outer coating and the inner surface, with a sorbent material contained within the chamber. The fiber sorption system further includes a supply of the working fluid in fluid communication with the inner surface. Additionally, the outer coating can be, for example, poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl fluoride), Poly(vinylidene fluoride), Ethylene vinyl alcohol copolymer, poly vinyl alcohol, polyamides, polyethylene (preferably high density), polypropylene (preferably high density), polyesters, polyimides, polyacrylonitrile, polysulfone, polyurethane, etc. - their combinations or derivatives.

[0016] The disclosed subject matter also includes a method of creating a pressurized working fluid that includes providing a vessel containing a fiber absorption system as disclosed herein, and introducing a supply of the working fluid to the channel;

introducing the heating fluid to an exterior surface of the chamber to obtain a pressurized working fluid; and directing the pressurized working fluid to a work component. The work component can be an expansion valve to provide refrigeration, or a turboexpander to provide electricity.

[0017] In an exemplary embodiment, the channel and the chamber are each circular in cross-section and concentric with each other wherein the cross-section of the channel is about 50 microns to about 400 microns in diameter. Additionally, the linear distance from an interior surface of the outer membrane to an exterior surface of the inner membrane is from about 50 to about 400 microns. The sorbent material is a zeolite, such as zeolite 13X, and is about 10% to about 95% of the total weight of the chamber.

[0018] The fiber sorption system disclosed herein is suitable for use in applications in which the carbon dioxide is obtained from a process stream within a petrochemical or chemical processing operation, such as a combustion operation.

[0019] It is to be understood that both the foregoing general description and the following detailed description are exemplary and are intended to provide further explanation of the disclosed subject matter claimed.

[0020] The accompanying drawings, which are incorporated in and constitute part of this specification, are included to illustrate and provide a further understanding of the method and system of the disclosed subject matter. Together with the description, the drawings serve to explain the principles of the disclosed subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] Figure 1 is a schematic representation of a conventional adsorption system.

[0022] Figure 2 is a graphical illustration depicting the adsorptive properties of a working fluid in accordance with the disclosed subject matter.

[0023] Figure 3 is a sectional view of an uncoated fiber for use in the fiber sorbent system according to an embodiment of the present invention.

[0024] Figure 4 is a sectional view of a coated fiber for use in the fiber sorbent system according to another embodiment of the present invention.

[0025] Figure 5 is a cross-sectional view of a hollow fiber for use in the fiber sorbent system according to another embodiment of the present invention.

[0026] Figure 6 is a cross-sectional view of another hollow fiber for use in the fiber sorbent system according to a yet another embodiment of the present invention.

[0027] Figure 7 is a cross-section view of yet another hollow fiber for use in the fiber sorbent system according to the present invention.

DETAILED DESCRIPTION OF THE DISCLOSED SUBJECT MATTER

[0028] The presently disclosed subject matter will now be described in greater detail in connection with the Figures and the following terms.

[0029] As used herein, the term “sorbent material” refers to a material that reversibly binds to a working fluid. Sorbent materials include, but are not limited to, adsorbents.

[0030] As used herein, the term “working fluid” refers to a liquid or gas that can reversibly bind to the sorbent material, either in a chemical or physical sense. When the working fluid is introduced to an expansion valve, it can also be referred to as a refrigerant.

[0031] As used herein, the term “driver device” refers to a turbine, shaft or other mechanism driven by a working fluid to generate electricity or work.

[0032] As used herein, the term “vessel” refers to a container suitable for containing the fibers and a thermal fluid under suitable conditions to permit sorption and desorption.

[0033] As used herein, the term “thermal fluid” refers to a liquid or gas capable of introducing a temperature change to the sorbent material. Thermal fluid can be a heating fluid or a cooling fluid.

[0034] As used herein, the term “unutilized heat” or “unutilized heat source” refers to the residual or remaining heat (e.g., steam) following the processing operation after

the heat sources has been used for its primary purpose in the refining or petrochemical processing operation. One example of an unutilized heat source is “waste heat.” For example, the unutilized heat or unutilized heat source can be a heat source that is no longer used in refining and/or petrochemical processing operation and would traditionally be discarded. The unutilized heat can be provided as an unutilized heat stream. For example, but not limitation, unutilized heat can include steam that was employed in a heat exchanger used in petroleum and petrochemical processing.

[0035] Reference will now be made to various aspects and embodiments of the disclosed subject matter in view of the definitions above. Reference to the methods will be made in conjunction with, and understood from, the systems disclosed herein.

[0036] For the purpose background and not admission of prior art, an adsorption system 1000 is shown in Figure 1. The system 1000 is disclosed in US Patent Application No. 12/603,243 entitled “System Using Unutilized Heat For Cooling and/or Power Generation”. The disclosure of which is hereby incorporated in its entirety. An adsorption bed (110) is provided, that contains tubes packed with adsorbents (e.g., MOFs/ZIFs/Zeolites/Carbon). The adsorption bed is adapted to receive either a feed of waste heat (120) or cold water (130). During an adsorption stroke, the adsorption bed is provided with a feed of cold water and the adsorbents adsorb working fluid (e.g., CO₂) at a lower temperature, T₃, and lower pressure, P₂. The cold water supply is then valved off, and a feed of waste heat is then fed to the adsorption bed to heat the adsorbent bed to T₁ (>T₂) to release adsorbed working fluid. The heating increases the pressure of the released working fluid P₁ (>P₂). Thus the adsorbent acts as a compressor, and conventional devices, e.g., pumps, are not required to drive the cycle.

[0037] The pressurized working fluid can be introduced to a turboexpander (140) to generate electricity. Downstream of the turboexpander, working fluid is now at a lower pressure, P₂ and lower temperature, T₂. The thermodynamic conditions are such that the working fluid is in an at least a partially condensed phase. After exiting the turboexpander, the condensed working fluid is fed to an evaporator (150) to chill a given process stream in the refinery, which in turn increases the temperature of the working fluid to T₃. The working fluid is again introduced to adsorption bed and the process is repeated.

[0038] The adsorption system shown in Figure 1 is equipped with a second adsorption bed (160), also adapted to receive a feed of either waste heat (170) or cold water (180). Having two adsorption beds in parallel allows one adsorption bed to be regenerated (adsorption stroke) while the other adsorption bed is in desorption mode. Other details regarding sorption systems can be found in U.S. Patent Application No. 12/603,243, which is hereby incorporated by reference in its entirety.

[0039] However, conventional designs have certain disadvantages. For example, the indirect heating and cooling of the adsorbent results in a slower heat transfer rate and longer temperature swing cycle times. Consequently, this design requires bigger beds and/or multiple beds which increases the cost of the adsorption system and the infrastructure footprint. Additionally, such prior art systems can be ineffective and/or cost prohibitive for use with low grade waste heat, i.e., temperature below 300°F.

[0040] One aspect of the disclosed subject matter is directed to a replacement for the conventional adsorption beds. Particularly, a fiber sorption system and method is provided for creating a pressurized working fluid comprising at least one hollow fiber. The hollow fiber can be constructed with an inner coating generally impermeable to a thermal fluid and working fluid, and defining a channel adapted to receive a supply of the thermal fluid. The hollow fiber also includes an outer surface generally posing no resistance to working fluid that defines a chamber between the outer surface and the inner coating. A sorbent material is contained within the chamber between the inner coating and outer surface. In this configuration, a supply of working fluid is introduced to an exterior surface of the fiber, and the thermal fluid, e.g., heating fluid, is introduced to the channel to obtain a pressurized working fluid from the sorbent material.

[0041] Alternatively, the disclosed subject matter provides a fiber sorption system and method for creating a pressurized working fluid wherein the hollow fiber is constructed with an inner surface posing no resistance to working fluid permeation, and defining a channel adapted to receive a supply of the working fluid. The hollow fiber also includes an outer coating generally impermeable to a thermal fluid (e.g., a heating fluid) and working fluid to define a chamber between the outer coating and the inner surface. A sorbent material is contained within the chamber between the inner surface and outer coating. In this configuration, a supply of working fluid is introduced to the

inner channel of the fiber, and the thermal fluid is introduced to the exterior surface of the chamber to obtain a pressurized working fluid from the sorbent material.

[0042] The system and methods of the disclosed subject matter utilize the adsorptive properties of the selected sorbent, such as MPFs/ZIFs/Zeolites, or the like, with respect to the working fluids such as CO₂, or the like. A schematic representation of these adsorptive relationship is illustrated in Figure 2. Particularly, an increase in temperature reduces the amount of CO₂ uptake. Further, an increase in pressure reduces the CO₂ uptake.

[0043] For purpose of illustration and not limitation, reference is now made to several representative embodiments of the present invention.

[0044] Fig. 3 discloses an uncoated fiber 10 for use in a sorbent system in accordance with aspects of the present invention. The fiber 10 includes an adsorbent 11 and a binder 12. In accordance with an aspect of the present invention, the fiber 10 is made from an adsorbent 11 and a binder 12 whose capacity and rate of adsorption and desorption of working fluid is not affected by the presence of thermal fluid. With such an arrangement, the fiber 10 is permeable to both the working fluid and the thermal fluid does not wet the fiber surface. Suitable adsorbents are described in greater detail below. The binder 12 or binding agent may be an inorganic material (including but not limited to clay and silica resin) or a polymeric material (including but not limited to polyimide, polyamide, polyvinylalcohol, and cellulosic). Other binder materials are considered to be well within the scope of the present invention provided such binder materials do not adversely impact the capacity and rate of adsorption and desorption of the working fluid on the adsorbent 11.

[0045] In accordance with an aspect of the present invention utilizing a fiber 10, the sorption system includes a plurality of fibers 10 housed or otherwise contained within a vessel (e.g., adsorption beds 110 and 160). The working fluid and the thermal fluid are capable of mixing within the vessel. While the present invention is being described in connection with the system 1000 illustrated in Fig. 1, the present invention is not intended to be so limited; rather, it is contemplated that the fibers 10 may be utilized in any sorption system permitting the mixing of the working fluid and the thermal fluid.

[0046] Fig. 4 discloses a coated fiber 20 for use in a sorbent system in accordance with aspects of the present invention. The fiber 20 includes an adsorbent 21, a binder 22 and an outer coating 23. The outer coating 23 is permeable to the working fluid, but is impermeable to the thermal fluid. With such an arrangement, the selection of the adsorbent 21 and the binder 22 is not limited to those materials whose capacity and rate of adsorption and desorption of working fluid is not affected by the presence of thermal fluid.

[0047] The outer coating 23 is preferably an organometallic compound. The metallo component of the organometallic compounds is from Groups 4-15 based on the IUPAC format for the Periodic Table having Groups 1-18, preferably Group 14, more preferably silicon and tin, especially silicon. The organo components of the organometallic compounds are hydrocarbyl groups having from 1 to 30 carbon atoms, preferably from 1 to 20 carbon atoms, more preferably 1-10 carbon atoms. The hydrocarbyl group may be aliphatic or aromatic groups which aliphatic or aromatic groups may be substituted with functional groups such as oxygen, halogen, hydroxy and the like. Preferred hydrocarbyl groups include methyl, ethyl, methoxy, ethoxy and phenyl. Preferred organometallic compounds include alkoxysilanes, silanes, silazanes and phenyl siloxanes. Especially preferred compounds include alkoxysilanes having from 1 to 4 alkoxy groups, especially tetraalkoxy compounds such as tetraethoxy-silane, dialkoxysilanes having from 1 to 6 alkoxy groups, especially hexamethyl-disiloxane.

[0048] The outer coating 23 of the organometallic material on the fiber 20 should have a high water contact angle, higher than 90 degrees, preferably higher than 110 degrees. The outer coating 23 may not cover the entire outer surface of the fiber 20. In accordance with the present invention, the outer coating 23 should cover from greater than 25% of the outer surface of the fiber 20 to 100% of the surface, preferably from 50 to 100%, more preferably from 80 to 100%. The amount of the outer surface covered is most preferably 100% or as close to 100% as possible.

[0049] In accordance with an aspect of the present invention utilizing a fiber 20, the sorption system includes a plurality of fibers 20 housed or otherwise contained within a vessel (e.g., adsorption beds 110 and 160). The working fluid and the thermal fluid are capable of mixing within the vessel. The outer coating 23 prevents the thermal fluid

from passing through the fiber 20 into the interior of the fiber 20 to the adsorbent 21 and the binder 22. While the present invention is being described in connection with the system 1000 illustrated in Fig. 1, the present invention is not intended to be so limited; rather, it is contemplated that the fibers 20 may be utilized in any sorption system permitting the mixing of the working fluid and the thermal fluid, which prevents the passage of the thermal fluid into the fiber 20.

[0050] Fig. 5 discloses a hollow fiber 30 for use in a sorbent system in accordance with aspects of the present invention. The hollow fiber 30 includes an adsorbent 31, a binder 32, and an inner coating 33. The hollow fiber 30 contains a hollow interior 34, which extends the length of the fiber 30. The hollow interior 34 is configured to permit the thermal fluid to flow therein. The inner coating 33 separates the hollow interior 34 from the adsorbent 31 and binder 32. The inner coating 33 is impermeable to both the working fluid and the thermal fluid. With such an arrangement, the selection of the adsorbent 31 and the binder 32 is not limited to those materials whose capacity and rate of adsorption and desorption of working fluid is not affected by the presence of thermal fluid. The thermal fluid will not pass from the hollow interior 34 into the interior of the fiber 30. The working fluid is adsorbed into the adsorbent through the exterior of the fiber 30.

[0051] The inner coating 33 can be, for example, poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl fluoride), poly(vinylidene fluoride), ethylene vinyl alcohol copolymer, poly vinyl alcohol, polyamides, polyethylene (preferably high density), polypropylene (preferably high density), polyesters, polyimides, polyacrylonitrile, polysulfone, polyurethane, etc., their combinations and derivatives thereof.

[0052] In accordance with the present invention utilizing a fiber 30, the sorption system includes a plurality of fibers 30 housed or otherwise contained within a vessel (e.g., adsorption beds 110 and 160). The thermal fluid flows through the hollow interiors 34 of the fibers 30. The thermal fluid provides the necessary heat transfer to permit the adsorption and desorption of the working fluid into the adsorbent 31. The working fluid is capable of passing from the fiber 30 into the interior of the vessel without mixing with the thermal fluid. While the present invention is being described in connection with the

system 1000 illustrated in Fig. 1, the present invention is not intended to be so limited; rather, it is contemplated that the fibers 30 may be utilized in any sorption system, which prevents the mixing of the working fluid and the thermal fluid.

[0053] Fig. 6 discloses a hollow fiber 40 for use in a sorbent system in accordance with aspects of the present invention. The hollow fiber 40 includes an adsorbent 41, a binder 42, and an outer coating 43. The hollow fiber 40 contains a hollow interior 44, which extends the length of the fiber 40. The hollow interior 44 is configured to permit the working fluid to flow therein. The working fluid can pass from the hollow interior 44 into the adsorbent 41 and binder 42. The outer coating 43 is impermeable to both the working fluid and the thermal fluid. With such an arrangement, the selection of the adsorbent 41 and the binder 42 is not limited to those materials whose capacity and rate of adsorption and desorption of working fluid is not affected by the presence of thermal fluid. The thermal fluid will not pass into the fiber 40.

[0054] The outer coating 43 can be, for example, poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl fluoride), poly(vinylidene fluoride), ethylene vinyl alcohol copolymer, poly vinyl alcohol, polyamides, polyethylene (preferably high density), polypropylene (preferably high density), polyesters, poly imides, polyacrylonitril, polysulfone, polyurethane, etc. - their combinations and derivatives thereof.

[0055] Fig. 7 depicts a representative embodiment of the fiber sorption system in which at least one hollow fiber 50 is provided with sorbents contained therein. Generally, however, the sorption system includes a plurality of fibers housed or otherwise contained within a vessel. In this non-limiting embodiment, the channel 51 is adapted to receive steam (heating fluid) and water (cooling fluid). The channel 51 is defined by an impermeable inner coating 52, such as polyacrylonitrile (PAN). A chamber 53 is defined between the inner coating 51 and an outer coating 54 and is packed with sorbent particles 55, such as zeolite 13X or mesoporous silica with adhered amines. The chamber also includes polymer support materials 56 to assist in maintaining the structural integrity of the hollow fiber.

[0056] The hollow fibers 56 can be formed in a tubular configuration and include an inner coating 51 and an outer coating 54 defining a chamber 53 there between. In a preferred embodiment, the chamber 53 extends along a length which is coextensive with the inner and outer coating and contains the sorbent material (e.g., zeolite 13X). This maximizes the amount of sorbent material which can be disposed within the chamber. Preferably, the sorbent material is disposed within the chamber in an uniform concentration or density along the length of the hollow fiber. The inner coating defines a channel or bore within each hollow fiber. The channel extends the entire length of the hollow fiber and is adapted to receive a supply fluid for direct contact with the inner coating. Depending on the embodiment of the hollow fiber sorption system, as described further below, the fluid received within the channel can be either a working fluid, or a thermal fluid (e.g., heating/cooling fluid).

[0057] In one embodiment, the inner coating is generally impermeable to a thermal fluid, and the outer coating, which is generally permeable to a working fluid, defines a chamber between the outer coating and the inner coating. In this configuration, a supply of working fluid is introduced to an exterior surface of the outer coating, and the thermal fluid (e.g., heating fluid) is introduced within the channel to obtain a pressurized working fluid from the sorbent material. Alternatively, the inner coating can be generally permeable to a working fluid, and the outer coating can be generally impermeable to a thermal fluid. In this configuration, a supply of working fluid is introduced within the inner channel of the fiber, and the thermal fluid (e.g., heating fluid) is introduced to the exterior surface of the chamber to obtain a pressurized working fluid from the sorbent material.

[0058] In an exemplary embodiment, the hollow fibers of approximately 100 micron inner diameter, and 100 micron chamber thickness. This configuration allows for dense packing of sorbents within the sorption bed. Fibers of this scale are advantageous in that the temperature of the sorption bed can be altered from hot to cold within seconds. Further, such a frequency of temperature swing allows for the size and footprint of the sorption system to be minimized. The channel and the chamber of each hollow fiber preferably circular in cross-section and oriented with a concentric configuration. For

example, the channel is substantially circular and from about 50 microns to about 400 microns in diameter. Additionally, the linear chamber thickness can be from about 50 to about 400 microns.

[0059] In accordance with another aspect of the disclosed subject matter, a plurality of fibers can be arranged in a bundle similar to a shell and tube heat exchanger. The plurality of fibers can be aligned in a generally parallel arrangement. Alternatively, the plurality of fibers can be oriented at an angle with respect to each other. The fibers can be disposed with portions of adjacent fibers in contact with each other, or provided with a uniform space disposed therebetween over the entire length of the fibers. In an exemplary embodiment, with the outer surface posing no resistance to a working fluid and an inner coating impermeable to a thermal and working fluids, the shell side can be in communication with a working fluid (e.g., CO₂) and the bore side can be in communication with heating medium (e.g., steam) or cooling medium.

[0060] In a preferred embodiment, waste heat (e.g., low grade waste heat) is used as a heating fluid to drive the sorption system. In some applications of the disclosed subject matter, the heating is provided by waste heat from a chemical processing or petrochemical refining operation. In one embodiment, the unutilized heat ranges from about 343K to about 573K, or more preferably from about 363K to about 523K.

[0061] While the working fluid is, for purposes of simplicity, largely described in the context of CO₂, other working fluids can be employed. In one embodiment, the working fluid is a gas and is selected from carbon dioxide, methane, ethane, propane, butane, ammonia, chlorofluorocarbons (e.g., FreonTM), other refrigerants, or other suitable fluids. Similarly, the sorbent material is largely described in the context of zeolite 13X, but is not limited thereto. In one embodiment, the sorbent material is selected from zeolites, silicagel, carbon, activated carbon, metal organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs). In one embodiment the working fluid is carbon dioxide and/or the sorbent material is a zeolite. In one embodiment the working fluid is carbon dioxide and the zeolite is a zeolite X, preferably a zeolite 13X.

Sorbent Materials

[0062] As noted above, and as used in this application, the term “sorbent material” refers to a material that reversibly binds the working fluid, in a chemical or physical sense. Sorbent materials include adsorbents.

[0063] Sorbent materials that can be used in embodiments of the disclosed subject matter include, but are not limited to, metal-organic framework-based (MOF-based) sorbents, zeolitic imidazole framework (ZIF) sorbent materials, zeolites and carbon.

[0064] MOF-based sorbents include, but are not limited to, MOF-based sorbents with a plurality of metal, metal oxide, metal cluster or metal oxide cluster building units. As disclosed in International Published Application No. WO 2007/111738, which is hereby incorporated by reference in its entirety, the metal can be selected from the transition metals in the periodic table, and beryllium. Exemplary metals include zinc (Zn), cadmium (Cd), mercury (Hg), and beryllium (Be). The metal building units can be linked by organic compounds to form a porous structure, where the organic compounds for linking the adjacent metal building units can include 1,3,5- benzenetribenzoate (BTB); 1,4-benzenedicarboxylate (BDC); cyclobutyl 1,4-benzenedicarboxylate (CB BDC); 2-amino 1,4 benzenedicarboxylate (H2N BDC); tetrahydropyrene 2,7-dicarboxylate (HPDC); terphenyl dicarboxylate (TPDC); 2,6 naphthalene dicarboxylate (2,6-NDC); pyrene 2,7-dicarboxylate (PDC); biphenyl dicarboxylate (BDC); or any dicarboxylate having phenyl compounds.

[0065] Specific materials MOF-based sorbent materials include: MOF-177, a material having a general formula of $\text{Zn}_4\text{O}(\text{1, 3, 5-benzenetribenzoate})_2$; MOF-5, also known as IRMOF-I, a material having a general formula of $\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$; IRMOF-6, a material having a general formula of $\text{Zn}_4\text{O}(\text{cyclobutyl 1,4-benzenedicarboxylate})$; IRMOF-3, a material having a general formula of $\text{Zn}_4\text{O}(\text{2-amino 1,4 benzenedicarboxylate})_3$; and IRMOF-11, a material having a general formula of $\text{Zn}_4\text{O}(\text{terphenyl dicarboxylate})_3$, or $\text{Zn}_4\text{O}(\text{tetrahydropyrene 2,7-dicarboxylate})_3$; and IRMOF-8, a material having a general formula of $\text{Zn}_4\text{O}(\text{2,6 naphthalene dicarboxylate})_3$.

[0066] Exemplary zeolitic imidazole framework (ZIF) sorbent materials include, but are not limited to, ZIF-68, ZIF-60, ZIF-70, ZIF-95, ZIF-100 developed at the University of California at Los Angeles and generally discussed in Nature 453, 207-211 (8 May 2008), hereby incorporated by reference in its entirety.

[0067] Zeolite adsorbent materials include, but are not limited to, aluminosilicates that are represented by the formula $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$, where y is 2 or greater, M is the charge balancing cation, such as sodium, potassium, magnesium and calcium, N is the cation valence, and w represents the moles of water contained in the zeolitic voids. Examples of zeolites that can be included in the methods and systems of the present application include natural and synthetic zeolites.

[0068] Natural zeolites include, but are not limited to, chabazite (CAS Registry No. 12251-32-0; typical formula $Ca_2[(AlO_2)_4(SiO_2)_8] \cdot 13H_2O$), mordenite (CAS Registry No. 12173-98-7; typical formula $Na_8[(AlO_2)_8(SiO_2)_{40}] \cdot 24H_2O$), erionite (CAS Registry No. 12150-42-8; typical formula $(Ca, Mg, Na_2, K_2)_{4.5}[(AlO_2)_9(SiO_2)_{27}] \cdot 27H_2O$), faujasite (CAS Registry No. 12173-28-3, typical formula $(Ca, Mg, Na_2, K_2)_{29.5}[(AlO_2)_{59}(SiO_2)_{133}] \cdot 235H_2O$), clinoptilolite (CAS Registry No. 12321-85-6, typical formula $Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24H_2O$) and phillipsite (typical formula: $(0.5Ca, Na, K)_3[(AlO_2)_3(SiO_2)_5] \cdot 6H_2O$).

[0069] Synthetic zeolites include, but are not limited to, zeolite A (typical formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$), zeolite X (CAS Registry No. 68989-23-1; typical formula: $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264H_2O$), zeolite Y (typical formula: $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250H_2O$), zeolite L (typical formula: $K_9[(AlO_2)_9(SiO_2)_{27}] \cdot 22H_2O$), zeolite omega (typical formula: $Na_{6.8}TMA_{1.6}[(AlO_2)_8(SiO_2)_{28}] \cdot 21H_2O$, where TMA is tetramethylammonium) and ZSM-5 (typical formula: $(Na, TPA)_3[(AlO_2)_3(SiO_2)_{93}] \cdot 16H_2O$, where TPA is tetrapropylammonium).

[0070] Zeolites that can be used in the embodiments of the present application also include the zeolites disclosed in the Encyclopedia of Chemical Technology by Kirk-Othmer, Volume 16, Fourth Edition, under the heading "Molecular Sieves," which is hereby incorporated by reference in its entirety.

[0071] Synthetic zeolite sorbent materials are commercially available, such as under the Sylosiv[®] brand from W.R. Grace and Co. (Columbia, Md.) and from Chengdu Beyond Chemical (Sichuan, P.R. China). For example, Sylosiv[®] A10 is one commercially available zeolite 13 X product.

Uses of the Fiber Sorbent Systems of the Present Application

[0072] The adsorbent systems of the present application can be used in various applications provided the setting allows for the presence of a vessel that contains a sorbent material, a supply of working fluid, a heat supply and means to effectively direct the desorbed working fluid to an expansion device to provide refrigeration or a driver device to provide electricity or work. For example, the desorbed gas may be directed to a Joule-Thompson expansion valve, to provide refrigeration. Alternatively, the desorbed working fluid can be directed to a turbine to provide electricity or to a shaft to provide work. The sorption systems described herein may be used to provide chilling, power and chilling in combination with power.

[0073] Possible applications for sorption systems of the present application include residential (for generating air conditioning in the summer and a heat pump in the winter), vehicular (where the on-board air conditioning utilizes exhaust heat) and industrial (refining and chemical plants).

[0074] In a preferred embodiment of the present application, the adsorbent system is used within a chemical or petrochemical refining plant, and the desorbed working fluid is used to provide refrigeration to aid in other process areas, particularly areas that rely on temperature differences to separate components of a mixture. For example, the refrigeration can be used to recover liquefied petroleum gas (LPG, C3+) from flue gases going up a stack, or the refrigeration can be used to operate condensers to improve the effectiveness of vacuum distillation columns, particularly in the summer months.

[0075] By proper selection of the adsorbent and working fluid, the sorbent system can make effective use of lower grade heat than previously provided by sorption systems in the prior art. For example, in one embodiment of the present application, the heat supply is “unutilized heat” which has a temperature of from about 70°C to about 300°C, more preferably from about 90°C to about 250 °C. In accordance with the present

invention, it is contemplated that the adsorbent and working fluid may be selected utilizing the pressure index disclosed in US Patent Application No. 12/603,243 entitled "System Using Unutilized Heat For Cooling and/or Power Generation". The disclosure of which is hereby incorporated in its entirety. By proper selection of thermal fluid and coating material the negative effect of capillary action should be kept minimal. By using appropriate surfactant and additives in thermal fluid / coating material to reduce interfacial tension between the thermal fluid and the coating, e.g., for water, detergent and the like and for triethylene glycol, stearic acid and the like.

[0076] This representative embodiment is provided for exemplary purposes; neither the application nor the invention is limited to the specific embodiments discussed above, or elsewhere in the application.

[0077] The disclosed subject matter is not to be limited in scope by the specific embodiments described herein. Indeed, various modifications of the invention in addition to those described herein will become apparent to those skilled in the art from the foregoing description and the accompanying Figures. Such modifications are intended to fall within the scope of the appended claims.

[0078] It is further to be understood that all values are approximate, and are provided for description.

[0079] Patents, patent applications, publications, product descriptions, and protocols are cited throughout this application, the disclosures of each of which is incorporated herein by reference in its entirety for all purposes.

* * *

CLAIMS

1. A fiber sorption system comprising:
 - at least one vessel;
 - a working fluid;
 - at least one thermal fluid;
 - at least one hollow fiber located within the at least one vessel, wherein the hollow fiber including:
 - (a) a sorbent material and binder material forming an elongated body;
 - (b) the elongated body having a hollow interior;
 - (c) the elongated body having an inner surface adjacent the hollow interior and an outer surface;
 - (d) one of the inner surface and the outer surface having a coating layer formed thereon, wherein the coating layer being impermeable to both the working fluid and the thermal fluid.
2. The fiber sorption system according to claim 1, wherein the coating layer is formed on the inner surface, wherein the thermal fluid passing flowing the hollow interior.
3. The fiber sorption system of claim 2, wherein the working fluid is in fluid communication with the outer surface of the hollow fiber.
4. The fiber sorption system according to claim 1, wherein the coating layer is formed on the outer surface, wherein the working fluid passing through the hollow interior such that it is capable of being adsorbed and desorbed by the sorbent material in the elongated body.
5. The fiber sorption system of claim 4, wherein the working fluid is in fluid communication with the inner surface of the hollow fiber.
6. The fiber sorption system according to claims 2 to 5, wherein the coating layer is selected from the group consisting of poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl fluoride), poly(vinylidene fluoride), ethylene vinyl alcohol copolymer, poly vinyl alcohol, polyamides, polyethylene (preferably high density), polypropylene (preferably high density), polyesters, polyimides, polyacrylonitrile, polysulfone, polyurethane, combinations thereof and derivatives thereof.
7. A fiber sorption system comprising:

at least one vessel;
a working fluid;
a thermal fluid;
at least one hollow fiber located within the at least one vessel, wherein the hollow fiber including:

an inner coating defining a channel adapted to receive one of a supply of the thermal fluid and the working fluid therein;

an outer coating defining a chamber between the outer coating and the inner coating ; and

a sorbent material and a binder material contained within the chamber, wherein one of the inner coating and the outer coating is a generally impermeable membrane that is impermeable to a thermal fluid, and

wherein the other of the inner coating and the outer coating is a generally permeable coating that is permeable to a working fluid.

8. The fiber sorption system of claim 7, wherein the permeable coating is selected from a cellulose fiber, a polysulfone, a polyurethane and a polyimide.

9. The fiber sorption system according to any one of the preceding claims, wherein the thermal fluid includes a heating fluid and a cooling fluid.

10. The fiber sorption system of claim 9, wherein the heating fluid comprises steam.

11. The fiber sorption system according to any one of the preceding claims, , wherein the sorbent material is a zeolite.

12. The fiber sorption system of claim 11, wherein the zeolite is zeolite 13X.

13. The fiber sorption system of claim according to any one of the preceding claims, wherein the working fluid comprises carbon dioxide.

14. The fiber sorption system of claim 13, wherein the carbon dioxide is from a process stream within a petrochemical or chemical processing operation.

15. A fiber sorption system comprising:

at least one vessel;
a working fluid;
at least one thermal fluid; and

at least one fiber located within the at least one vessel, wherein each fiber including a sorbent material and binder material forming an elongated body having an outer surface, wherein the working fluid flows past the outer surface and is capable of being adsorbed and desorbed by the sorbent material.

16. The fiber sorption system according to claim 15, wherein the thermal fluid flows past the outer surface and is not wetting the fiber surface.

17. The fiber sorption system according to claim 15 or claim 16, further comprising an outer coating on the outer surface, wherein the outer coating being permeable to the working fluid such that working fluid may pass through the outer coating for adsorption and desorption by the sorbent material, wherein the outer coating being impermeable to the thermal fluid, whereby the thermal fluid is prevented from passing through the outer coating to the sorbent material.

18. The fiber sorption system according to claims 15 to 17, wherein the outer coating is formed from an organometallic compound.