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(71) Applicant: **Nederlandse Organisatie voor
toegepast-**

**natuurwetenschappelijk onderzoek TNO
2595 DA 's-Gravenhage (NL)**

(72) Inventors:

- **Goetheer, Earl Lawrence Vincent
2628 VK Delft (NL)**
- **van der Ham, Leonardus Volkert
2628 VK Delft (NL)**
- **Mourad, Maurice Christian Danho
2628 VK Delft (NL)**

(74) Representative: **Jansen, Cornelis Marinus et al
V.O.**

**Johan de Wittlaan 7
2517 JR Den Haag (NL)**

(54) **Air conditioning**

(57) The invention relates to a method and system for air conditioning, and to a liquid desiccant composition, a use thereof and a process using such composition. In a preferred aspect, the invention relates to an air conditioning method comprising treatment of the air by dehumidification with a liquid hygroscopic desiccant. An conditioning method, comprising a step of a) dehumidifying

an air stream comprising water vapour by contacting said it with a liquid desiccant composition comprising a hygroscopic compound and plasmonic particles; b) regenerating some liquid desiccant composition; c) using some regenerated liquid desiccant composition in said step (a), and d) cooling at least part of a dehumidified air stream.

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Description

[0001] The invention relates to a method and system for air conditioning, and to a liquid desiccant composition, a use thereof and a process using such composition. In a preferred aspect, the invention relates to an air conditioning method comprising treatment of the air by dehumidification with a liquid hygroscopic desiccant.

[0002] Conventional air conditioning methods use most often electricity to cool and dehumidify air. The electricity is mostly generated from fossil fuels. Accordingly, air conditioning systems are a major consumer of electrical energy and cause significant CO₂-emissions. For these reasons air conditioning systems are desired that can be powered with renewable energy sources, preferably locally available energy sources, in particular by solar light.

[0003] A first approach is to convert solar energy into electricity that is then used to power an air conditioning unit. This involves a disadvantageously large number of energy transformations and has accordingly low energy efficiency. It is desired to convert solar energy more efficiently into cooling and/or drying capacity. More generally, regeneration of liquid desiccants, absorption liquids and the like is a critical step in many processes based on spontaneous uptake of components by a liquid and induced release thereof, limiting the energy efficiency of such processes.

[0004] US-A-2012/0 153 621 to Halas et al. describes a method for powering a cooling unit, comprising generating electricity from steam and using the electricity to power the cooling unit. Steam is generated by evaporation by exposing a fluid to electromagnetic radiation. The fluid comprises a complex, for example copper nanoparticles or nanoshells, and water or ethylene glycol as solvent. This method comprises a disadvantageously high number of energy transformations and does not include humidity control.

[0005] US-A-2011/0 138 832 to Al-Hadhrami et al. describes an air drying method using a liquid desiccant. The liquid desiccant is regenerated by heat exchange with oil in a desiccant regeneration system. The oil is in a closed loop and picks up heat in solar collectors. A disadvantage of this method is a low energy efficiency of the desiccant regeneration.

[0006] US-A-2010/0 011 794 to De Lima describes a solar powered air conditioner having a vapour liquid separator and using a desiccant that is contacted with air. For regeneration of the desiccant, a solar boiler provides heated fluid that is heat exchanged with dilute desiccant (CaCl₂) in a water stripper. Dried air is subjected to evaporative cooling. A disadvantage is the low energy efficiency of the desiccant regeneration and the more complex system by use of a separate heating fluid.

[0007] Use of plasmonic particles for heating has recently been reported. Neumann et al. (ACS Nano 2013, 7, 42-49) describe vapour generation using broadly absorbing metal or carbon nanoparticles dispersed in a liq-

uid phase. Neumann et al. (PNAS 2013, 110(29), 11677-11681) describe the use of broadband light-absorbing nanoparticles as solar photo-thermal heaters, which generate high-temperature steam for a standalone, efficient solar autoclave useful for sanitation of instruments in resource-limited, remote locations, in particular for sterilisation.

[0008] An objective of the invention is to provide a more energy efficient regeneration of a liquid desiccant composition, such as in an air conditioning process using a liquid desiccant composition.

[0009] Surprisingly it has been found that this objective can, at least partly, be met by using a liquid desiccant composition comprising plasmonic particles.

[0010] Accordingly, in a first aspect, the invention relates to an air conditioning method, comprising:

- a) dehumidifying an air stream comprising water vapour by contacting said air stream with a liquid desiccant composition, yielding a dehumidified air stream and rich liquid desiccant composition, wherein said liquid desiccant composition comprises a hygroscopic compound and plasmonic particles,
- b) regenerating at least part of said rich liquid desiccant composition by exposing rich liquid desiccant composition to light comprising electromagnetic waves that are at least partially concentrated by the plasmonic particles, thereby causing evaporation of water from said liquid desiccant composition, yielding regenerated liquid desiccant composition and a stream comprising steam,
- c) using at least part of said regenerated liquid desiccant composition in said step (a), and
- d) cooling at least part of said dehumidified air stream.

[0011] Advantages of the air conditioning method of an aspect of the invention include that no greenhouse gasses need to be used as working fluid, that CO₂ emission is reduced, possibly even to zero emission, and that the high energy efficiency allows for low operating costs. A further advantage is that the method allows for a preferred autonomous system that is not dependent on access to electricity or fossil fuel and optionally even relies fully on solar energy.

[0012] The term "liquid desiccant composition" as used herein refers to a composition comprising a liquid phase, wherein the composition is capable of dehumidifying a stream or phase, in particular of a fluid process stream. The composition may comprise a dispersing continuous liquid phase. Suitable forms of the liquid composition include, but are not limited to, a solution, an emulsion, a suspension, a sol, a spray, a mist, an aerosol, and a foam. Such compositions are also known in the art as "liquid hygroscopic desiccants" and may contain one or more solid components, gaseous components, and/or one or more dissolved compounds; in particular it may contain one or more dissolved salts. The term includes

solutions in a liquid solvent of dissolved hygroscopic compounds, in particular of salts. The solvent may be hygroscopic or not hygroscopic, for example the solvent may be water. Typically, a liquid desiccant composition is hygroscopic and has the property of extracting and retaining moisture from air brought into contact with it.

[0013] The term "plasmon" as used in this application is meant to refer to a surface plasmon. By analogy, the term "plasmonic" as used in this application is meant to refer to the presence of surface plasmons. Surface plasmons comprise coherent electron oscillations that exist at the interface between two suitable materials, such as a conductive material and a dielectric.

[0014] The term "plasmonic particle" as used in this application is meant to refer to a surface-plasmon supporting structure. A plasmonic particle typically is a nanoparticle comprising an electric conducting material. Suitable electrically conductive materials include metals and alloys, but for instance also carbon. Rather than by their form, size or chemical composition, plasmonic particles are characterised by exhibiting plasmon resonance. Suitable forms of plasmonic particles include nanostructures and nanoparticles. Nanostructures include nanostructured surfaces. The plasmon resonance can be at one or more specific plasmon resonance wavelengths. Rod-like nanoparticles, for example, can have two distinct plasmon resonance wavelengths. It is also possible that plasmon resonance occurs within a certain spectral range. This may depend, for instance, on the particle size distribution of the plasmon particles. As is conventional, the plasmon resonance is expressed as a wavelength in air, although frequency of electromagnetic radiation is more suitable for nano-scale resonance.

[0015] The term "plasmonic heating" as used in this application is meant to refer to the dissipation of thermal energy from a plasmonic particle to its environment due to surface plasmon resonance. The surface plasmon resonance is generated upon excitation with light comprising electromagnetic waves that are at least partially concentrated by the plasmonic particles.

[0016] The phrase "exposing to light", as used in this application is meant to include both irradiating with electromagnetic radiation and more specifically illuminating with light.

[0017] The phrase "light comprising electromagnetic waves that are at least partially concentrated by the plasmonic particles" as used in this application is meant to include light with a wavelength coinciding with a plasmonic resonance wavelength of the particles. For example, if a plasmonic resonance wavelength exists at 350 nm, monochromatic light of 350 nm would be considered light comprising electromagnetic waves that are at least partially concentrated by the plasmonic particles, but also an ultraviolet light source providing a spectrum of 200-400 nm would be considered such light. If the spectrum of the applied light (for example the spectral output of the light source) encompasses the plasmonic resonance wavelength, then the light can be considered light

comprising the plasmonic resonance wavelength, which is preferred.

[0018] The term "nanoparticles" as used in this application is meant to refer to particles with at least one dimension of from about 1 nm to about 1000 nm, such as from about 1 nm to about 500 nm, from about 2 nm to about 300 nm, or from about 5 nm to about 200 nm, including spherical or approximately spherical (cuboidal, pyramidal) particles with a diameter (or at least two or three dimensions) in these ranges. These dimensions can be measured with laser diffraction as the volume weighted mean (D50) in this range, at least above 10 nm. For particles smaller than 10 nm transmission electron microscopy (TEM) can be used based on number average equivalent sphere diameter.

[0019] In case of spherical particles the one dimension is preferably the diameter of the particles. For non-spherical particles, the one dimension can, for instance, be the equivalent spherical diameter which is defined as the diameter of a sphere of equivalent volume. The term "nanoparticles" is also meant to include rod-like particles, also known as nanorods. Such nanorods typically have an aspect ratio (longest dimension divided by the shortest dimension) in the range of 2-40, more often in the range of 2-20, such as in the range of 3-10. Typically, each of the dimensions of a rod-like nanoparticle is in the range of from about 1 nm to about 1000 nm.

[0020] The air conditioning method of the invention comprises dehumidifying an air stream comprising water vapour. The air stream is typically an outside ambient air stream. The method preferably comprises transporting air into a building and treating the air during this transport. The aim of the method is typically a reduction of the temperature and a reduction of the water vapour content of the air stream. The method is preferably a continuous process.

[0021] The method comprises contacting the air stream with a liquid desiccant composition. The contacting can be carried out using conventional methods, including spraying, bubbling, waterfall and by using wetted fabric material. The liquid desiccant composition preferably has a temperature of 0-40 °C during the contacting with the air stream and preferably a pressure of 1-10 bar absolute. The air typically has a temperature of 10-50 °C, and a relative humidity of more than 50 %, or even more than 70 %.

[0022] Preferably, the air stream is contacted with liquid desiccant composition using a membrane. More preferably, the air stream is contacted with liquid desiccant compositions through a membrane such that the air stream and the liquid desiccant composition are at opposite sides of the membrane. Typically the air stream and the liquid desiccant composition are only contacted through the membrane. Preferably, the air stream and the liquid desiccant flow in a cross-current or counter-current manner through the membrane contactor. The membrane is preferably permeable to gas, in particular to water vapour. The membrane is preferably effectively

impermeable to the desiccant liquid. The membrane is preferably hydrophobic, in case of a polar liquid desiccant composition, and gas-permeable. Advantages of such membrane may include reduced risk of contamination of process streams, a compact contactor design, related to a high amount of contact area per contactor volume, and reduced loss of components of the liquid desiccant composition in the air stream. Preferably the membrane is impermeable for plasmonic particles, to advantageously prevent loss thereof into the air stream. Preferably the membrane allows for independent control over the gas and liquid phase residence times. In addition, an optional feature is that a pressure difference can be maintained between the phases at both sides of the membrane.

[0023] Examples of suitable membranes include polymeric membranes comprising for example poly(1-trimethylsilyl-1-propyne), poly(4-methyl-2-pentyne), poly(1-trimethylgermyl-1-propyne), poly(vinyltrimethylsilane), poly(vinylidimethylsiloxane), poly(tetrafluoroethylene), poly(vinylidene fluoride), poly(carbonate), poly(ethylene), poly(propylene), poly(ethersulphone), poly(sulphone), poly(acrylonitrile), and/or polyamides. Non-polymeric membranes can also be used, such as from ceramic materials such as aluminium oxide, silica, zirconia, perovskites, and metal nitrides. Also possible is to use composite or coated membranes, comprising two or more of the above-mentioned membranes materials.

[0024] Typically, water vapour present in the air stream is taken up by the liquid desiccant composition as a result of the contacting. This yields a dehumidified air stream and a rich liquid desiccant composition. The air stream is dehumidified to at least a certain extent and may still comprise water vapour. The rich liquid desiccant composition has taken up water and has hence a higher water concentration than the liquid desiccant composition directly prior to contacting with the air stream. Taking up of water may comprise absorption of water vapour by physisorption and/or chemisorption, a form of absorption is condensation of water vapour at the gas-liquid interface. As a result of the absorption of water by the liquid desiccant, heat of condensation can be released and the temperature of the liquid desiccant can increase.

[0025] At least a portion of the rich liquid desiccant composition is regenerated. The regeneration comprises exposure of at least part of the liquid desiccant composition to light. While the liquid desiccant composition is regenerated, such as exposed to light, it comprises preferably a hygroscopic compound, dispersed plasmonic particles, and optionally a solvent. For example, the liquid desiccant composition may comprise, during such regeneration, plasmonic particles, solvent, such as water, and one or more dissolved hygroscopic compounds, including metal salts and/or organic compounds.

[0026] The light comprises electromagnetic waves that are at least partially concentrated by the plasmonic particles, thereby causing evaporation of water from said liquid desiccant composition. The regeneration yields regenerated liquid desiccant composition and a stream

comprising steam, typically a stream essentially consisting of steam. At least part of the regenerated liquid desiccant composition is used again for dehumidifying the air stream; preferably the method comprises an essentially closed loop for the liquid desiccant composition. More preferably, the method comprises maintaining a loop for liquid desiccant composition with a pressure that is constant within a range of less than 1 bar, more preferably less than 0.1 bar.

[0027] Optionally, the method comprises adding liquid desiccant composition, or any of its components separately, to compensate for loss thereof, for example into the air stream.

[0028] Optionally, the regenerated liquid desiccant is cooled before it is used again for dehumidifying the air stream, for example with heat exchange against a cooling fluid, such as for example ambient outside air and/or rich liquid desiccant composition.

[0029] An important advantage of the invention is that by virtue of the plasmonic particles, steam is formed with a temperature higher than the boiling point of pure liquid water at the pressure applied in the regeneration step, for example more than 100 °C, while the bulk liquid phase of the liquid desiccant composition, and/or the formed regenerated liquid desiccant composition, has a lower temperature, preferably at least 10 °C lower than the temperature of the formed steam, more preferably at least 20 °C lower or even at least 30 °C lower. For example, the bulk liquid phase can be maintained at 70 °C or less. Accordingly, the regenerated liquid desiccant composition typically has a temperature of 10-70 °C, more preferably 30-50 °C.

[0030] Typically, the method comprises cooling at least part of the regenerated liquid desiccant composition before reusing by contacting with the air stream, preferably by heat exchange with outside or inside ambient air. The advantageously small increase in temperature of liquid desiccant composition during regeneration allows for efficient cooling against ambient air.

[0031] The method comprises cooling at least part of said dehumidified air stream. Preferably, said cooling at least part of said dehumidified air stream comprises evaporating liquid water in contact with at least part of said dehumidified air stream, thereby causing evaporative cooling at least part of said stream. This is especially useful for stand-alone solar powered air conditioning.

[0032] The cooling is typically based on adiabatic evaporative cooling. Because typically the water content of the dehumidified air stream is lower than its equilibrium water vapour pressure, by virtue of the contact with the liquid desiccant composition, some liquid water will evaporate when brought in contact with the dehumidified air stream. This evaporation can contribute to cooling the air stream. Preferably, the method comprises controlling the amount and temperature of the liquid water in order to control the humidity and temperature of the resulting air stream. The resulting cooled and re-humidified air stream is obtained as product and can be distributed into

the building. Evaporative cooling is well known and can be carried out for example by spraying of liquid water in the dehumidified air stream. Another example is by using a membrane contactor similar as described for the dehumidification step. Optionally, said dehumidified air stream is partly cooled using evaporative cooling, and partly by another conventional cooling process, such as for example heat exchange against a cooling fluid.

[0033] Preferably, the dehumidification step is carried out in a central station and the evaporative cooling step is carried out in one or more, typically a plurality, of distributed units. The distributed units are typically placed in or close to the rooms or spaces where the cooled air is received, typically inside the building, for efficient transport of cooled air to where it is needed. This configuration is especially suitable for large buildings, for example wherein the regeneration section can be placed on a roof and the distributed units on the various building levels. For smaller buildings, for example houses, a preferred configuration comprises a single unit comprising parts for dehumidification and for evaporation.

[0034] Optionally, the stream comprising steam is used as working fluid to perform mechanical work, more preferably to drive a generator to generate electricity. For example, the stream can be supplied to a turbine coupled to a generator, for example by a shaft to a rotary generator. In order to maximise the power output of the turbine, steam at an elevated pressure is preferably used. Hence, preferably the solution from which the steam is evaporated is pressurised; accordingly the rich liquid desiccant composition is preferably pressurised at least in a regeneration unit. For example, liquid desiccant composition can be maintained in a pressurised loop in the method, for example using indirect contacting through a membrane. Alternatively, the liquid desiccant composition can be pressurised before the regeneration step, for example by using a pump upstream of and a throttle valve downstream of the regeneration unit in the conduit for liquid desiccant composition. Hence, preferably, the steam has an absolute pressure of at least 1.5 bar, more preferably at least 2 bar, at least 5 bar or even more preferably at least 10 bar. Preferably the pressurised liquid desiccant composition also has such absolute pressure, at least during regeneration, preferably in the entire method.

[0035] An important feature of the present invention is that the obtained steam has a higher temperature than the bulk liquid phase from which it is evaporated. Typically, steam is obtained with a temperature 100-200 °C, pressurised as determined by the temperature. Accordingly, a non-equilibrium state is in some embodiments obtained at the gas-liquid interface during regeneration. Accordingly, steam is separated from the liquid phase by convection, for example towards a turbine and/or condenser downstream of the regeneration step.

[0036] Optionally, the regeneration section comprises a thermally insulating layer that is permeable to steam, such as a membrane. This layer preferably forms the gas-liquid interface of the liquid desiccant composition

with a gaseous phase through which the evaporated water is released. This advantageously reduces re-condensation of steam in the liquid. The separation of steam from the liquid bulk phase is preferably selective against the plasmonic particles, such that the particles remain in the liquid desiccant composition rather than in the stream comprising steam.

[0037] Preferably, the method comprises condensing the steam at some stage, for example with heat exchange against ambient outside air, to yield liquid water. This water can be obtained as a product, is relatively pure and can be used for example at least partly as drinking water.

[0038] Preferably at least part of the obtained liquid water is used for evaporative cooling of the dehumidified air stream. Accordingly, the method preferably comprises condensation of at least part of said stream comprising steam to provide liquid water, and preferably further comprises evaporating at least part of said liquid water in the cooling step. Typically, the amount of water vapour in the cooled air is lower than in the initial air stream and hence more water is produced than is needed for cooling. In case of a dry initial air stream, the method can comprise providing water from an external source for the cooling step.

[0039] The inventors found that plasmons may be advantageously for use in regeneration of a liquid desiccant composition. Directing electromagnetic waves at the interface between an electric conductive material (such as a metal) and a dielectric can induce a resonant interaction between the waves and the mobile electrons at the surface of the conductive material. In a conductive material, the electrons are not strongly attached to individual atoms or molecules. In other words, the oscillations of electrons at the surface match those of the electromagnetic field outside the conductive material. The result is the generation of surface plasmons, *i.e.* density waves of electrons that propagate along the interface.

[0040] The plasmonic particles preferably have a plasmon resonance excitation wavelength in the infrared (700 nm to 10 μ m), near-infrared (700-1400 nm), visible (400-700 nm) and/or ultraviolet spectrum (180-400 nm). The wavelength of such resonances strongly depends on the dimensions and morphology of the plasmonic particle and the refractive index of its environment.

[0041] Preferably the plasmonic particles exhibit a surface plasmon resonance in the range of 180-1500 nm, such as in the range of 300-1500 nm, more preferably 350-1500 nm or 350-1000 nm.

[0042] In particular for solar-light powered evaporation, a broad absorption and an efficient harvesting of the solar spectrum is desired. In such a case it can be advantageous to use a mixture of various plasmonic particles that have a complementary absorption spectrum so that a large part of the solar spectrum is covered.

[0043] Preferred plasmonic particles comprise an electric conductive structure with at least one dimension of from about 1 nm to about 1000 nm, such as from about 1 nm to about 500 nm, from about 2 nm to about 300 nm,

or from about 5 nm to about 200 nm. These dimensions can be measured with laser diffraction as the volume weighted mean (D50) in this range, at least above 10 nm. For particles smaller than 10 nm transmission electron microscopy (TEM) can be used based on number average equivalent sphere diameter. The electric conductive structure can for example comprise one or more metals which form a continuous metallic structure with at least one dimension in the mentioned preferred sizes. Another example is an electric conductive structure formed of an electric conductive form of carbon having such sizes. Preferably, the electric conductive material has a resistivity of 0.1 mΩ·m or less at 20 °C. The electric conductive structure preferably has a surface that interfaces with a dielectric phase. The dielectric phase may be part of the particle or of a medium in which the particle is dispersed. The dielectric phase can for example be solid or liquid. Hence, the surface may be an exposed surface (directly in contact with the liquid phase of the liquid desiccant composition) or an internal surface. For example, a solid dielectric phase may comprise a coating layer (typically 20 nm thick or less) of a dielectric material, such as silica, on a metallic nanoparticle. In case of a solid dielectric phase is typically part of the plasmonic particle. Surface plasmons can for example form at the interface of the electric conductive structure and the dielectric phase. The small dimensions of the particles, relative to the surface plasmon resonance wavelength, contribute to localisation of the formed surface plasmons.

[0044] The plasmonic particles can be free (*viz.* mobile), such as in suspension in a liquid. They can also be immobilised on a support or on a surface of a conduit for liquid desiccant composition. The plasmonic particles can have morphologies including spherical, elongated, rod-like, cuboidal, pyramidal, plate-like, board-like, oblate, spindle, and nanostars; nanoshells, encapsulated nanoshells, encapsulated nanoparticles, and branched nanostructures.

[0045] Some of the suitable types of nanoparticles include metal nanoparticles, nanoparticles comprising a dielectric core and a metallic shell, nanoparticles comprising a metallic core and a dielectric shell, nanoparticles comprising a metallic core and a metallic shell, and hollow metallic nano-shells. In case of a core/shell nanoparticle, the core and the shell have a different chemical composition. The shell may be porous. These types of nanoparticles comprise preferably one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, In, Sn, Zr, Ti, Cr, Ta, W, Fe, Rh, Ir, Ru, Os, and Pb. More preferably, the metals are selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, and Rh. The metals may be present as alloys. As an alternative for the metals, or in addition, the particles may comprise carbon. Carbon is advantageous in terms of costs.

[0046] Examples of suitable plasmonic particles include nanoparticles comprising a SiO₂ core and a metal nanoshell, in particular an gold nanoshell, nanoparticles with a metal core, for example a gold core, and a silica

nanoshell, polymer/silver nanoshells, metal coated chalcogenide II-VI nanoparticles, such as gold coated CdTe nanoparticles and gold coated CdSe nanoparticles. For example, suitable plasmonic particles include SiO₂/Au nanoshells prepared by suspending 120 nm silica nanoparticles (e.g. commercially obtainable from Precision Colloids, Inc.) in ethanol, functionalising with 3-aminopropyltriethoxysilane, adding gold colloidal particles (1-3 nm) which are adsorbed on the amine groups and act as seed for growth of the nanoshell by reacting HAuCl₄ with the seeds in the presence of formaldehyde (Neumann et al., ACS Nano 2013, 7, 42-49). It is further possible that the nanoparticles have a solid metal shell filled with another substance which may be a non-solid, for example a fluid, including a gas-filled core (hollow particles). Examples of substances that can be included in the core, and are hence contained in a preferably conductive shell, are insulators or dielectric materials such as water, gases (such as nitrogen, argon and neon), aqueous gels (such as polyacrylamide gels and gels containing gelatin), and organic substances such as ethanol.

[0047] Further preferred plasmonic particles are gold nanoparticles with a silica shell, typically a porous silica shell. The plasmonic particles can also comprise carbon nanoparticles, for example Carbon black N115 commercially available from Cabot, Inc. Graphitic particles and graphene comprising particles can also be used.

[0048] Preferably, nanoparticles used as plasmonic particles are modified at their exposed surface to increase stability. Preferably, the nanoparticles comprise stabilisers, for example grafted molecules, for example natural or synthetic polymers, for steric stabilisation. The nanoparticles may also comprise, as an alternative or in addition, charged compounds as stabilisers for electrostatic stabilisation. Surfactants are preferably used for stabilisation, in particular in case the liquid desiccant composition comprises metal salts in an amount of for example more than 1 wt. %.

[0049] Preferably, the plasmonic particles comprise one or more selected from the group consisting of:

- (i) metal nanoparticles comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh,
- (ii) core-shell nanoparticles comprising a core comprising a dielectric material and a shell comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh,
- (iii) core-shell nanoparticles comprising a core comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh and a shell comprising a dielectric material, and
- (iv) carbon nanoparticles comprising carbon in an electric conductive form.

[0050] Preferably, these preferred plasmonic particles comprise surfactants for stabilisation, for example one or more carboxylates, phosphines, amines, thiols, and/or

grafted polymer brushes.

[0051] Without wishing to be bound by way of theory, plasmonic heating is believed to contribute to the evaporation. Plasmonic heating refers to the dissipation of thermal energy from a plasmonic particle to its environment due to surface plasmon resonance. Without wishing to be bound by any theory, it is believed that the electromagnetic field of the light can result in excitation of surface plasmons by resonant coupling. The energy not re-radiated through light scattering is dissipated, resulting in a temperature increase in the nano- to micrometer-scale vicinity of the particle surface.

[0052] Preferably, the plasmonic heating results in heating of the direct proximity of the plasmonic particles (for example up to 2 μm around the plasmonic particles or up to 1 μm around the plasmonic particles). This is to say, preferably the temperature of the plasmonic particles is 20 °C or higher than the bulk temperature of the liquid desiccant composition, preferably at least 50 °C higher, more preferably 100 °C higher. The temperature of plasmonic particles, such as nanoparticle, can be estimated by applying Fourier's law at the particle interface ($P = G \cdot S \cdot (T_p - T_s)$, wherein P represents the power absorbed by the particle, G represents the effective interfacial thermal conductance, S represents the surface area of the particle, T_p represents the particle temperature, and T_s represents the surrounding temperature). The temperature can also be obtained from surface-enhanced Raman scattering (SERS) measurements.

[0053] Typically, plasmonic heating comprises the formation of a vapour layer around the plasmonic particles, such that bubbles are formed. Without wishing to be bound by way of theory, the lower thermal conductivity of the vapour is believed to be able to cause thermal insulation of the plasmonic particle, a temperature increase of the plasmonic particle and further evaporation. The formation of a vapour bubble around a plasmonic particle may contribute to transport of the bubble to the gas-liquid interface, at least in case of free dispersed plasmonic particles. The buoyancy and the lower volumetric mass density of the vapour compared to the liquid may cause the bubble to lift. At the gas-liquid interface, the vapour can be released while the particle returns into the liquid phase. The formation of the bubble may provide for thermal insulation of the plasmonic particle from the bulk liquid phase. As a result, steam can be produced at the gas-liquid interface with only very limited heating of the bulk liquid desiccant composition, thereby increasing the energy efficiency of the process, and reducing the need for cooling of the regenerated liquid desiccant.

[0054] Important advantages that can be obtained by using plasmonic heating for the regeneration include that steam with high temperature and pressure can be obtained, that the bulk temperature of the regenerated liquid desiccant composition is relatively low, that the plasmonic particles can be adjusted to match the light spectrum, in particular of solar light, and that the rate of regeneration is high.

[0055] The method comprises exposing rich liquid desiccant composition to light comprising electromagnetic waves that are at least partially concentrated by the plasmonic particles, preferably to light comprising a wavelength in the infrared (700 nm to 10 μm), near-infrared (700-1400 nm), visible (400-700 nm) and/or ultraviolet spectrum (180-400 nm).

[0056] In the regeneration step the liquid desiccant composition is preferably exposed to light of which one or more wavelengths are absorbed by at least a part of the plasmonic particles. Preferably, the light is spatially non-coherent light, in order to allow for homogenous exposure of the liquid desiccant composition and efficient use of the plasmonic particles comprised therein. Laser beams are spatial coherent, spatial non-coherent light includes light from divergent light sources such as sunlight, light emitting diode (LED) light, incandescent and luminescent (fluorescent and/or phosphorescent) light.

[0057] Preferably, the light intensity (irradiance) is preferably 10² W/m² or more, such as 10²-10⁹ W/m², more preferably 10³-10⁸ W/m², at the surface of the interface of the liquid desiccant composition. Preferably, the spectral irradiance is 0.1 Wm⁻² nm⁻¹ or more at a plasmon resonance wavelength of the plasmonic particles; such as 0.1-10 Wm⁻² nm⁻¹, preferably 0.4-2 Wm⁻² nm⁻¹. Herein the spectral irradiance is measured at the surface of the interface of the liquid desiccant composition. Preferably, the liquid desiccant is exposed to such light at least 1 s, such as at least 10 s, more preferably at least 1 minute or at least 5 minutes.

[0058] Preferably, the regeneration of liquid desiccant composition comprises exposure of the composition to solar light. This provides an advantage that the air conditioning method can be carried out in a stand-alone unit, which does not need to be connected to an external power source, such as the electric grid.

[0059] In that case, the method preferably comprises providing buffer volumes of the lean and of the rich liquid desiccant compositions and of liquid water to be evaporated, that can be used when not sufficient solar light is provided, for example during the night. In addition, the method preferably comprises focussing solar light, for example by using a (Fresnel) lens, a parabolic trough or a mirror.

[0060] In an aspect the invention relates to a liquid desiccant composition. Such compositions are preferably used in the air conditioning method of an aspect of the invention. The liquid desiccant composition comprises a hygroscopic compound and dispersed plasmonic particles, preferably a hygroscopic compound and plasmonic particles as described hereinbefore. The liquid desiccant composition may comprise one or more hygroscopic compounds and/or one or more types of plasmonic particles.

[0061] The liquid desiccant composition optionally comprises a liquid component, which can be the same or different as the hygroscopic compound. For example, the liquid component can be a solvent for the hygroscopic

compound. The plasmonic particles are typically dispersed in a liquid phase, such as in the optional liquid component. For example, the liquid desiccant composition may comprise as liquid component such as water, ethanol, ethylene glycol and tri-ethylene glycol.

[0062] Preferably, the liquid desiccant composition comprises 0.01-10 wt.% of plasmonic particles, more preferably 0.1-5 wt.%, based on the total weight of the liquid desiccant composition, and/or based on the weight of liquid desiccant composition minus any optional solvent.

[0063] Preferred hygroscopic compounds include organic compounds comprising one or more hydroxyl groups, more preferably polyols such as glycerine, in particular diols, even more preferably ethylene glycol and propylene glycol compounds. Further preferred hygroscopic compounds include propylene carbonate, alkanolamines, and sulfolane. Preferably the liquid desiccant compositions comprises one or more of these compounds in at least 20 wt.%, based on total weight of these compounds and total weight of the liquid desiccant composition.

[0064] Preferred hygroscopic compounds are in particular ethylene glycol compounds. Preferably, the composition comprises one or more compounds having the formula $H-(O-CH_2-CH_2)_n-OH$ with $n = 1$ to 10, or $n = 2$ to 10, more preferably $n = 1$ to 4, even more preferably $n = 2, 3$ or 4. Preferably, the liquid desiccant compositions comprises such ethylene glycol compounds in an amount of at least 20 wt.%, based on total weight of ethylene glycol compounds and total weight of the liquid desiccant composition, more preferably at least 40 wt.%, at least 60 wt.% or most preferably at least 80 wt.%; preferably at least directly prior to contacting with the air stream.

[0065] Further preferred hygroscopic compound are metal halide compounds. Preferably, the liquid desiccant composition comprises an aqueous solution of one or more metal halides, preferably at least 20 wt.% (based on total weight of dissolved metal halides and total weight of the liquid desiccant composition), even more preferably at least 40 wt.% or at least 60 wt.%, typically up to the solubility limit of the one or more metal halides. Preferred metal halides include the chlorides, bromides and iodides of the alkali metals, more preferably, Li, Na and K; and of the earth alkali metals, more preferably magnesium and calcium; fluorides are also possible. Most preferred are calcium chloride, lithium chloride, magnesium chloride and lithium bromide.

[0066] Other suitable hygroscopic compounds include but are not limited to metal hydroxides, sulphates and acetates, for example of Na, K, Ca, Mg, more in particular NaOH, Na_2SO_4 and $KC_2H_3O_2$. Ionic liquids are also suitable as hygroscopic compounds, including ionic liquids comprising cation parts such as 1-alkyl-3-alkyl imidazolium, for example 1-ethyl-3-methyl imidazolium, and/or anion parts such as tetrafluoro borate or alkylsulfates, for example ethylsulphate.

[0067] Accordingly, preferably the liquid desiccant

composition comprises one or more selected from the group consisting of:

- (1) metal nanoparticles comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh,
- (2) core-shell nanoparticles comprising a core comprising a dielectric material and a shell comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh,
- (3) core-shell nanoparticles comprising a core comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh and a shell comprising a dielectric material, and
- (4) carbon nanoparticles comprising carbon in an electric conductive form and wherein the hygroscopic compound comprises, in an amount of 20 wt.% or more based on total weight of the liquid desiccant composition,

(a) one or more compounds having the formula $H-(O-CH_2-CH_2)_n-OH$ with $n = 1-10$, more preferably 2-10, and/or

(b) one or more dissolved metal halides, in combination with said conductive surface nanoparticles.

[0068] Specifically disclosed is the embodiment comprising (a) and plasmonic particles 1, 2, 3 or 4, and the embodiment comprising (b) and plasmonic particles 1, 2, 3 or 4.

[0069] In a further aspect, the invention relates to an air conditioning system, preferably for an air conditioning method as described. The system comprises

- a contactor for contacting an air stream to be treated with a liquid desiccant composition, said contactor comprising an inlet and an outlet for said air stream and an inlet and an outlet for said liquid desiccant composition,
- a regeneration unit for regenerating said liquid desiccant composition connected with said inlet and said outlet for said liquid desiccant of said contactor, wherein said regeneration unit comprises an outlet for steam and a conduit for liquid desiccant composition that is configured to receive solar light through a transparent part of a wall of said conduit,
- an evaporation unit connected to said outlet for said air stream of said membrane contactor and an inlet for a liquid stream, allowing for evaporation of liquid from said liquid stream in contact into said air stream, further comprising an outlet for said air stream.

[0070] Accordingly, the system allows for direct contact of liquid desiccant composition with the air stream, such as through a membrane, and direct exposure of liquid desiccant composition to solar light. This provides a simpler system compared to systems comprising sep-

arate conduits for heating fluids and liquid desiccants and contributes to energy efficiency.

[0071] The transparent part of said wall is typically transparent to light with a wavelength in at least part of the range of 350-1500 nm, preferably has a transmittance for such light of at least 90 %, more preferably has a transmittance of at least 90 % over the entire range of 350-1500 nm. Suitable materials include a colourless glass slab and colourless plastic window.

[0072] Preferably, the regeneration unit comprises a reflective inner surface on parts of the wall that are not transparent to visible light. This allows for light that not absorbed by the reaction mixture to be reflected back. Preferably, the regeneration unit comprises a volume for steam provided with an outlet for said steam above (with respect to gravity) a volume for flow of a liquid desiccant stream, said volume comprising an inlet and an outlet for said fluid stream defining the direction of flow of said liquid desiccant stream. Preferably, the regeneration unit has a plate-like or membrane-like form and comprises a reaction channel for receiving liquid desiccant composition and a wall comprising a part that is arranged for receiving solar light and configured for passing through solar light to said reaction volume. Accordingly, preferably the regeneration unit comprises such part having a surface area and an adjacent reaction channel having an average thickness (in the direction perpendicular to the surface part) of less than 10 % of the square root of said area of said surface part, more preferably less than 5 %.

[0073] Preferably, the system comprises a concentrator for solar light, for example a Fresnel lens, a parabolic through or a dish mirror, configured to receive solar light and to provide concentrated solar light to the regeneration unit.

[0074] Preferably, the regeneration unit comprises a conduit for liquid desiccant composition comprising a wall comprising an inner surface part, that is in operation in contact with liquid desiccant composition, and that is provided with plasmonic particles and/or plasmonic structures.

[0075] Preferably the system comprises a condenser connected to an outlet for steam configured to convert steam to liquid water, more preferably in heat exchange with a stream to be heated or with ambient air.

[0076] The contactor preferably comprises a gas/liquid membrane contacting unit comprising a membrane as described hereinbefore. Suitable constructions involve stacked membranes, spirally wound, tubular membranes and hollow fibre membranes.

[0077] Optionally, the system comprises a turbine provided with a connection for receiving steam from said regeneration unit to perform mechanical work using said steam as working fluid. Preferably the turbine is coupled to a generator to generate electricity. For example the turbine can be connected to the shaft of a rotary generator.

[0078] In yet a further aspect, the invention relates to use as desiccant of a liquid desiccant composition as

described. The composition can be used as desiccant for any material to be dehumidified, for example a fluid process stream or a stationary atmosphere. The fluid process stream can for example be gaseous, for example a natural gas stream.

[0079] The use as desiccant of the liquid desiccant compositions, which comprise plasmonic particles, allows for a use that comprises regeneration by exposure to electromagnetic radiation comprising electromagnetic waves that are at least partially concentrated by at least part of the plasmonic particles.

[0080] Accordingly, in yet a further aspect the invention relates to more general process for separating at least part of a component from a fluid stream, comprising contacting said fluid stream with a liquid desiccant composition as described, thereby causing said composition to take up at least some of said component, and regenerating at least part of said composition by release of at least some said component from said composition by exposing at least part of said composition to electromagnetic radiation that is at least partially concentrated by plasmonic particles in said composition, and reusing at least part of the regenerated composition in step (a).

[0081] Herein, the composition comprises plasmonic particles and a hygroscopic compound, or more generally a compound with a high affinity for the component to be separated from the fluid stream, and optionally a liquid component. The hygroscopic compound and the optional liquid component can be the same or can be different. Typically, the component to be separated is water. Typically, the fluid stream and the composition with component transported therein are separated from each other, in this way effecting that the component is separated from the fluid stream. Typically, the taking up of the component by the composition comprises absorption, adsorption and/or condensation into the composition, for example by physisorption and/or chemisorption.

[0082] For example the process can involve glycol dehydration for the removal of water from natural gas and natural gas liquids. Regeneration of the glycol desiccant has been a critical issue in such processes. The method of the invention can be more energy efficient and is for example suitable for remote gas wells, in particular in places with often abundant solar light.

[0083] Figure 1 shows a schematic process scheme of an exemplary air conditioning method and system according to an aspect of the invention. Air stream 1 is hot and moist and is passed in contactor A. In contactor A, it is dehumidified by contacting with liquid desiccant composition to yield air stream 2 that is hot and dry and a rich liquid desiccant composition 4 that is rich in water. Rich liquid desiccant composition 4 is regenerated in regeneration unit B by exposing it to light 11. Light 11 is in this case solar light. Light 11 enters regeneration unit B through a transparent wall part of B (indicated with dotted lines). This yields steam 6 and regenerated liquid desiccant composition 5. Regenerated liquid desiccant composition 5 is passed back to contactor A and reused for

dehumidifying air stream 1. Steam 6 is pressurised and passed to turbine C to perform mechanical work that is converted by a generator (not shown) to electricity 8. Steam stream 7 is then passed to condensation unit D for heat exchange with a cooling fluid. Condensate 9 is formed in condensation unit D and comprises water. A part of condensate 9 is obtained as drinking water 10 and a part is passed to evaporation unit E. In evaporation unit E, the liquid stream of water 9 is evaporated in dehumidified air stream 2, which is thereby cooled to yield cool and moist air stream 3. Air stream 3 is provided in a room where air conditioning is desired.

[0084] The invention will now be further illustrated by the following nonlimiting example.

Examples

Example 1

[0085] For an example method with 1 ton of cooling capacity, which equals 12000 BTU/hr or 3.5 kW, the following properties are calculated.

[0086] *Evaporative cooling:* Adiabatic evaporative cooling of 30 °C air (outdoors temperature) to a relative humidity of 90 % results in an air temperature of 11 °C and a water vapor content of 9.2 gram per m³ of air (which is well within the indoor comfort range). With the enthalpy of evaporation for water being 2.3 kJ/g, the corresponding cooling capacity per m³ of treated air is 21 kJ. So for 1 ton of cooling capacity, which equals 12000 BTU/hr or 3.5 kW, the cool air flow will be about 630 m³/hr.

[0087] *Solution regeneration:* Assuming 80 % relative humidity for the incoming outdoors air, 24 gram of water needs to be removed per m³ of air in order to dry it. Evaporating this amount of water from the liquid desiccant, which is needed to completely regenerate the solution and establish a closed loop, requires 55 kJ of evaporation energy per m³ of incoming air. Taking into account the change in molar volume of air, 670 m³/hr of incoming air is required per ton of cooling capacity, resulting in a required evaporative energy input of 10 kW. With an solar irradiance of 5 kWh/day/m², 12 sun hours per day, and all solar energy translated into evaporation as advantage of the use of the plasmonics particles, as approximation, a solar surface of 24 m² is required per ton of cooling capacity.

[0088] *Electricity generation:* For heat source and heat sink temperatures of 150 and 50 °C, the maximum theoretical efficiency for the conversion of heat into electricity is 24 %. Assuming that 50 % of this efficiency can be achieved with a small-scale turbine (large-scale turbines can achieve up to 90 %) results in an overall efficiency of 12 %. So for per ton of cooling capacity, 1.2 kW of electricity can be produced. Compared to a conventional electrically driven air conditioning unit having a coefficient-of-performance of 3, an additional 1.2 kW of electricity can be prevented per ton of cooling capacity.

[0089] *Water production:* The difference between the

amount of water removed from the incoming air during drying and the amount of water added during evaporative cooling is 10 kg/hr of water per ton of cooling capacity.

Claims

1. Air conditioning method, comprising:

- a) dehumidifying an air stream comprising water vapour by contacting said air stream with a liquid desiccant composition, yielding a dehumidified air stream and rich liquid desiccant composition, wherein said liquid desiccant composition comprises a hygroscopic compound and plasmonic particles,
- b) regenerating at least part of said rich liquid desiccant composition by exposing rich liquid desiccant composition to light comprising electromagnetic waves that are at least partially concentrated by the plasmonic particles, thereby causing evaporation of water from said liquid desiccant composition, yielding regenerated liquid desiccant composition and a stream comprising steam,
- c) using at least part of said regenerated liquid desiccant composition in said step (a), and
- d) cooling at least part of said dehumidified air stream.

2. Air conditioning method according to claim 1, wherein said light comprises solar light and wherein said cooling at least part of said dehumidified air stream comprises evaporating liquid water in contact with at least part of said dehumidified air stream, thereby causing evaporative cooling at least part of said stream.

3. Air conditioning method according to claim 1 or 2, further comprising generating electricity by driving a generator by performing mechanical work using said stream comprising steam as working fluid.

4. Air conditioning method according to any one of claims 1-3, further comprising condensation of at least part of said stream comprising steam to provide liquid water and evaporating at least part of said liquid water in step d).

5. Air conditioning method according to any one of claims 1-4, wherein said contacting comprises contacting said air stream with liquid desiccant composition through a hydrophobic gas-permeable membrane.

6. Air conditioning method according to any one of claims 1-5, wherein said plasmonic particles exhibit a plasmon resonance excitation wavelength in the

range of 180-1500 nm.

7. Air conditioning method according to any one of claims 1-6, wherein said plasmonic particles comprise one or more selected from the group consisting of:

- metal nanoparticles comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh,
- core-shell nanoparticles comprising a core comprising a dielectric material and a shell comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh,
- core-shell nanoparticles comprising a core comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh and a shell comprising a dielectric material, and
- carbon nanoparticles comprising carbon in an electric conductive form.

8. Air conditioning method according to any one of claims 1-7, wherein said hygroscopic compound comprises, in an amount of 20 wt.% or more based on total weight of the liquid desiccant composition, one or more compounds having the formula $H-(O-CH_2-CH_2)_n-OH$ with $n = 1-10$.

9. Air conditioning method according to any one of claims 1-7, wherein said liquid desiccant composition comprises an aqueous solution of a metal halide.

10. Air conditioning system, preferably for a method according to any one of claims 1-9, the system comprising

- a contactor for contacting an air stream to be treated with a liquid desiccant composition, said contactor comprising an inlet and an outlet for said air stream and an inlet and an outlet for said liquid desiccant composition,
- a regeneration unit for regenerating said liquid desiccant composition connected with said inlet and said outlet for said liquid desiccant of said contactor, wherein said regeneration unit comprises an outlet for steam and a conduit for liquid desiccant composition that is configured to receive solar light through a transparent part of a wall of said conduit,
- an evaporation unit connected to said outlet for said air stream of said membrane contactor and comprising an inlet for a liquid, configured for evaporation of liquid in contact with said air stream, further comprising an outlet for said air stream.

11. Air conditioning system according to claim 10, further comprising

- a turbine provided with a connection for receiving steam from said regeneration unit to perform mechanical work using said steam as working fluid.

12. Liquid desiccant composition comprising a hygroscopic compound and dispersed plasmonic particles, preferably as defined in any one of claims 6-9.

13. Liquid desiccant composition according to claim 12, wherein said plasmonic particles comprise one or more selected from the group consisting of:

- metal nanoparticles comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh,
- core-shell nanoparticles comprising a core comprising a dielectric material and a shell comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh,
- core-shell nanoparticles comprising a core comprising one or more metals selected from the group consisting of Ag, Al, Au, Cu, Ni, Co, Pd, Pt, Rh and a shell comprising a dielectric material, and
- carbon nanoparticles comprising carbon in an electric conductive form and wherein the hygroscopic compound comprises, in an amount of 20 wt.% or more based on total weight of the liquid desiccant composition, one or more compounds having the formula $H-(O-CH_2-CH_2)_n-OH$ with $n = 2-10$, and/or one or more dissolved metal halides, in combination with said plasmonic particles.

14. Use of a composition according to claim 12 or 13 as desiccant.

15. Process for separating at least part of a component from a fluid stream, comprising

- a) contacting said fluid stream with a composition according to claim 12 or 13, thereby causing said composition to take up at least some of said component,
- b) regenerating at least part of said composition by release of at least some said component from said composition by exposing at least part of said composition to electromagnetic radiation that is at least partially concentrated by plasmonic particles in said composition, and
- c) reusing at least part of the regenerated composition in step (a).

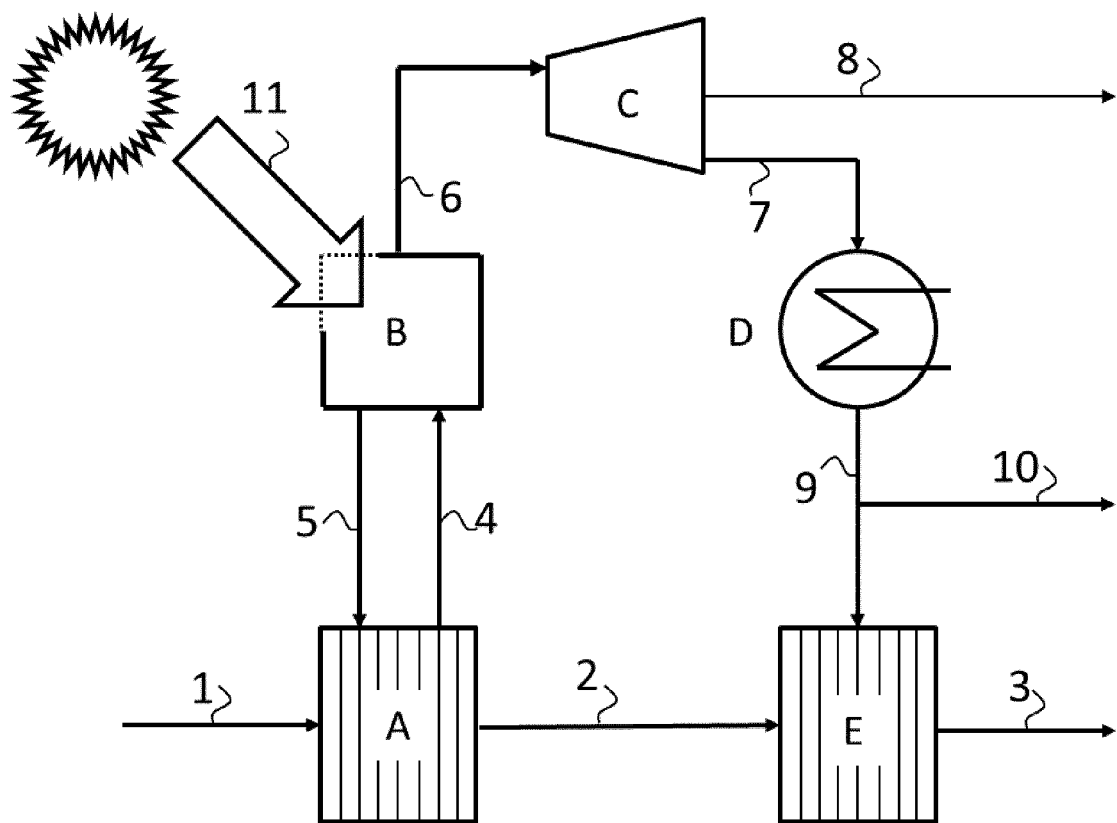


Figure 1



EUROPEAN SEARCH REPORT

Application Number
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
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Place of search		Date of completion of the search	Examiner
Munich		23 September 2014	Vuc, Arianda
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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