

Absorption refrigeration machine

The invention is related to an absorption refrigeration machine having a reduced mechanical energy requirement.

5

Classical refrigeration machines are based on a circuit in which a refrigerant is vaporized and cooling is achieved as a result of the heat of vaporization taken up by the refrigerant. The vaporized refrigerant is then brought to a higher pressure by means of a compressor and condensed at a higher temperature than in the vaporization, resulting in the heat of vaporization being liberated again. The liquefied refrigerant is subsequently depressurized again to the pressure of the vaporizer.

15

The classical refrigeration machines have the disadvantage that they consume a large amount of mechanical energy for compression of the gaseous refrigerant.

20

In comparison, absorption refrigeration machines have a reduced mechanical energy requirement. Absorption refrigeration machines have, in addition to the refrigerant, the vaporizer and the condenser of a classical refrigeration machine, a sorption medium, an absorber and a desorber. In the absorber, the vaporized refrigerant is absorbed at the pressure of the vaporization in the sorption medium and is subsequently desorbed again from the sorption medium in the desorber at the higher pressure of the condensation by introduction of heat. The compression of the liquid working medium composed of refrigerant and sorption medium requires less mechanical energy than the compression of the refrigerant vapor in a classical refrigeration machine; the consumption of mechanical energy is replaced by the thermal energy used for desorption of the refrigerant.

35

US 1,882,258 discloses an absorption refrigeration machine in which a liquid phase composed of the absorption medium water and the refrigerant ammonia is separated in the absorber by a porous permeable wall from a gas phase containing gaseous ammonia and an inert gas. The machine described in this document is intended to be operated without supply of mechanical energy. In the machine described in this document, absorber, desorber, condenser and vaporizer are all operated at the same pressure, which results in a low efficiency. In addition, not only ammonia but also water vapor can get from the liquid phase through the porous wall into the vaporizer and lead to malfunctions there, e.g. as a result of ice formation.

The same problem occurs in the process proposed in DE 633 146, in which the absorber is provided with a diaphragm through which the absorption medium water can likewise get in vapor form into the absorber, and also the process proposed in WO 2004/104496 which likewise uses water as sorption medium.

DE 195 11 709 discloses an absorption refrigeration machine having a working medium containing LiBr or LiBr/ZnBr₂ as nonvolatile sorption medium and water or methanol as volatile refrigerant. Condensation and vaporization of the refrigerant do not occur in this machine. Instead, cooling is effected by pervaporation of refrigerant from a refrigerant-rich working medium, coming from the absorber, through a hydrophobic membrane into a refrigerant-deficient working medium, coming from the desorber. In this machine, the membrane is not located in the absorber.

US 4,152,9001 and US 5,873,260 disclose absorption refrigeration machines in which the desorber is provided with a membrane through which desorption of refrigerant from the working medium occurs. In the

process of US 4,152,9001, sorption medium passes through the membrane and gets into the vaporizer. In US 5,873,260, too, it is stated that the sorption medium water passes as vapor through the membrane.

5

Accordingly, there continues to be a need to further reduce the mechanical energy requirement compared to prior art absorption refrigeration machines, without malfunctions occurring as a result of absorption medium getting into the vaporizer of the refrigeration machine.

The invention provides an absorption refrigeration machine having a 'working medium, containing a nonvolatile sorption medium and a volatile refrigerant, and an absorber, in which a vapor phase containing refrigerant and a liquid phase containing sorption medium are separated from one another by a membrane, wherein the membrane is a semipermeable membrane which is permeable to the refrigerant and impermeable to the sorption medium.

Arrangement of a semipermeable membrane, which separates the gaseous refrigerant from the liquid working medium, in the absorber in combination with a nonvolatile sorption medium allows absorption even against a pressure difference between the gaseous refrigerant and the liquid working medium, without sorption medium being able to get into the vapor space of the absorber and into the vaporizer. As a result, the refrigerant can be absorbed even at a pressure of the liquid working medium which is significantly higher than the pressure of the vaporization without any compression of the gaseous refrigerant being necessary and without malfunctions occurring as a result of sorption medium getting into the vaporizer. The mechanical energy requirement for compression of the liquid working medium can be reduced compared to the

absorption refrigeration machines known from the prior art by an increase in the pressure of the liquid working medium in the absorber.

5 The absorption refrigeration machine of the invention comprises a working medium, containing a nonvolatile sorption medium and a volatile refrigerant, and a semipermeable membrane which is permeable to the refrigerant and impermeable to the sorption medium. In
10 principle, it is possible to use all working media, having a nonvolatile sorption medium and a volatile refrigerant, which are known from the prior art for absorption refrigeration machines, in combination with a suitable semipermeable membrane.

15

The working medium preferably contains water, ammonia or carbon dioxide as volatile refrigerant. Water is particularly preferably used as refrigerant.

20 The working medium additionally contains a nonvolatile sorption medium. In this context, the term nonvolatile sorption medium refers to a sorption medium whose vapor pressure is a factor of more than 10 000 lower than the vapor pressure of the refrigerant. Preference is given
25 to sorption media which at 20°C have a vapor pressure of less than 10^{-3} mbar, particularly preferably less than 10^{-6} mbar. Preference is given to using polymeric or salt-like sorption media as nonvolatile sorption media.

30

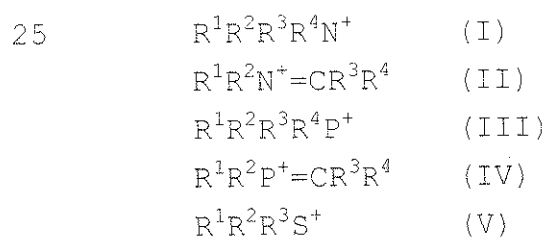
A working medium which is known from the prior art and is suitable for the absorption refrigeration machine of the invention is an aqueous solution of lithium bromide with water as refrigerant and lithium bromide as
35 nonvolatile sorption medium.

A sorption medium comprising one or more ionic liquids is preferably used in the absorption refrigeration

machine of the invention. In this context, the term ionic liquid refers to a salt or a mixture of salts composed of anions and cations, where the salt or the mixture of salts has a melting point of less than 100°C. Compared to conventional sorption media such as lithium bromide, ionic liquids have the advantage that a larger proportion of the refrigerant can be driven off in the desorber without solidification of the sorption medium. Using an ionic liquid as sorption medium, the absorption refrigeration machine can therefore be operated without malfunctions at a higher capacity of the working medium for the refrigerant, which allows more compact construction of the absorption refrigeration machine.

The ionic liquid preferably consists of one or more salts of organic cations with organic or inorganic anions. Mixtures of a plurality of salts having different organic cations and the same anion are particularly preferred.

Suitable organic cations are, in particular, cations of the general formulae (I) to (V):



30

where

R^1 , R^2 , R^3 , R^4 are identical or different and are each hydrogen, a linear or branched aliphatic or olefinic hydrocarbon radical having from 1 to 30 carbon atoms, a cycloaliphatic or cycloolefinic hydrocarbon radical having from 5 to 40 carbon atoms, an aromatic hydrocarbon radical having from 6 to 40 carbon atoms,

an alkylaryl radical having from 7 to 40 carbon atoms,
a linear or branched aliphatic or olefinic hydrocarbon
radical which has from 2 to 30 carbon atoms and is
interrupted by one or more -O-, -NH-, -NR'-, -O-C(O)-,
5 - (O)C-O-, -NH-C(O)-, - (O)C-NH-, - (CH₃)N-C(O)-,
- (O)C-N(CH₃)-, -S(O₂)-O-, -O-S(O₂)-, -S(O₂)-NH-,
-NH-S(O₂)-, -S(O₂)-N(CH₃)- or -N(CH₃)-S(O₂)- groups, a
linear or branched aliphatic or olefinic hydrocarbon
radical which has from 1 to 30 carbon atoms and is
10 terminally functionalized by OH, OR', NH₂, N(H)R' or
N(R')₂ or a polyether radical of the formula -(R⁵-O)_n-R⁶
having a block or random structure,

R' is an aliphatic or olefinic hydrocarbon radical
15 having from 1 to 30 carbon atoms,

R⁵ is a linear or branched hydrocarbon radical
containing from 2 to 4 carbon atoms,

20 n is from 1 to 200, preferably from 2 to 60,

R⁶ is hydrogen, a linear or branched aliphatic or
olefinic hydrocarbon radical having from 1 to 30 carbon
atoms, a cycloaliphatic or cycloolefinic hydrocarbon
25 radical having from 5 to 40 carbon atoms, an aromatic
hydrocarbon radical having from 6 to 40 carbon atoms,
an alkylaryl radical having from 7 to 40 carbon atoms
or a -C(O)-R⁷ radical,

30 R⁷ is a linear or branched aliphatic or olefinic
hydrocarbon radical having from 1 to 30 carbon atoms, a
cycloaliphatic or cycloolefinic hydrocarbon radical
having from 5 to 40 carbon atoms, an aromatic
hydrocarbon radical having from 6 to 40 carbon atoms or
35 an alkylaryl radical having from 7 to 40 carbon atoms,

where at least one and preferably all of the radicals
R¹, R², R³ and R⁴ is different from hydrogen.

Cations of the formulae (I) to (V) in which the radicals R^1 and R^3 together form a 4- to 10-membered, preferably 5- to 6-membered, ring are likewise
5 suitable.

Heteroaromatic cations having in the ring at least one quaternary nitrogen atom bearing a radical R^1 as defined above, preferably derivatives of pyrrole, pyrazole,
10 imidazole, oxazole, isoxazole, thiazole, isothiazole, pyridine, pyrimidine, pyrazine, indole, quinoline, isoquinoline, cinnoline, quinoxaline or phthalazine substituted on the nitrogen atom, are likewise suitable.

15 Suitable inorganic anions are, in particular, tetrafluoroborate, hexafluorophosphate, nitrate, sulfate, hydrogensulfate, phosphate, hydrogenphosphate, dihydrogenphosphate, hydroxide, carbonate,
20 hydrogencarbonate and the halides, preferably chloride.

Suitable organic anions are, in particular, $R^aOSO_3^-$, $R^aSO_3^-$, $R^aOPO_3^{2-}$, $(R^aO)_2PO_2^-$, $R^aPO_3^{2-}$, R^aCOO^- , R^aO^- , $(R^aCO)_2N^-$, $(R^aSO_2)_2N^-$ and NCN^- where R^a is a linear or branched
25 aliphatic hydrocarbon radical having from 1 to 30 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 40 carbon atoms, an aromatic hydrocarbon radical having from 6 to 40 carbon atoms, an alkylaryl radical having from 7 to 40 carbon atoms
30 or a linear or branched perfluoroalkyl radical having from 1 to 30 carbon atoms.

In a preferred embodiment, the ionic liquid comprises one or more 1,3-dialkylimidazolium salts, where the
35 alkyl groups are particularly preferably selected independently from among methyl, ethyl, n-propyl, n-butyl and n-hexyl. Particularly preferred ionic liquids are salts of one or more of the cations

1,3-dimethylimidazolium, 1-ethyl-3-methylimidazolium,
1-(n-butyl)-3-methylimidazolium, 1-(n-butyl)-
3-ethylimidazolium, 1-(n-hexyl)-3-methylimidazolium,
1-(n-hexyl)-3-ethylimidazolium and 1-(n-hexyl)-
5 3-butylimidazolium with one of the anions chloride,
acetate, methylsulfate, ethylsulfate, dimethylphosphate
or methylsulfonate.

10 In a further preferred embodiment, the ionic liquid
comprises one or more quaternary ammonium salts having
a monovalent anion and cations of the general
formula (I) in which

R^1 is an alkyl radical having from 1 to 20 carbon atoms,
 R^2 is an alkyl radical having from 1 to 4 carbon atoms,
15 R^3 is a $(CH_2CHRO)_n-H$ radical where n is from 1 to 200
and $R = H$ or CH_3 and

R^4 is an alkyl radical having from 1 to 4 carbon atoms
or a $(CH_2CHRO)_n-H$ radical where n is from 1 to 200 and
 $R = H$ or CH_3 .

20 Particular preference is given to chloride, acetate,
methylsulfate, ethylsulfate, dimethylphosphate or
methylsulfonate as anion.

Processes for preparing the ionic liquids are known to
25 those skilled in the art from the prior art.

Preference is given to using ionic liquids which are
stable at a temperature of 150°C as sorption media.
When water is used as refrigerant, preference is given
30 to using an ionic liquid which is stable to hydrolysis.
Ionic liquids stable to hydrolysis display less than 5%
degradation by hydrolysis in a mixture with 50% by
weight of water on storage at 80°C for 8000 h.

35 Ionic liquids forming a nonideal mixture with the
refrigerant with lowering of the vapor pressure of the
refrigerant are preferably used as sorption media.

The working medium can contain further additives in addition to the sorption medium and the refrigerant. The working medium preferably further contains one or more corrosion inhibitors. Here, it is possible to use
5 all nonvolatile corrosion inhibitors which are known from the prior art to be suitable for the materials used in the absorption refrigeration machine.

In a preferred embodiment of the absorption
10 refrigeration machine of the invention, the semipermeable membrane in the absorber is a solution diffusion membrane. A solution diffusion membrane has virtually no pores. With a solution diffusion membrane, the selective permeability of the membrane for the
15 refrigerant is based on the refrigerant dissolving in the material of the membrane and diffusing through the membrane, while the sorption medium is insoluble in the material of the membrane. The suitability of a
20 dissolution diffusion membrane for the absorption refrigeration machine of the invention can therefore be determined by a person skilled in the art by simple experiments on the solubility of refrigerant and sorption medium in the material of the membrane.

25 In the case of the preferred embodiment using water as refrigerant and a salt-like sorption medium, it is possible to use as the solution diffusion membrane any pore-free membrane which is known to those skilled in the art as suitable for desalination of aqueous salt
30 solutions from the technical fields of dialysis, reverse osmosis and pervaporation.

The material used for the solution diffusion membrane is preferably a hydrophilic or hydrophilically
35 functionalized polymer containing polyvinyl alcohol, polyimide, polybenzimidazole, polybenzimidazolone, polyamide hydrazide, cellulose ester, cellulose acetate, cellulose diacetate, cellulose triacetate,

cellulose butyrate, cellulose nitrate, polyurea, polyfuran, polyethylene glycol, poly(octylmethylsiloxane), polysiloxane, polyalkylsiloxane, polydialkylsiloxane, polyester-polyether block
5 copolymer, polysulfone, sulfonated polysulfone, polyamide, in particular aromatic polyamide, polyether, polyether ether ketone, polyester, polyether-urea composite, polyamide-urea composite, polyether sulfone, polycarbonate, polymethyl methacrylate, polyacrylic
10 acid or polyacrylonitrile. It is likewise possible to use mixtures or copolymers of two or more of these polymers. Particular preference is given to solution diffusion membranes composed of cellulose acetate, crosslinked polyethylene glycol, crosslinked
15 polydimethylsiloxane or a polyester-polyether block copolymer.

In a preferred embodiment of the absorption refrigeration machine of the invention, the
20 semipermeable membrane in the absorber is a microporous membrane. For the purposes of the invention, microporous membranes are membranes which have pores extending through the membrane having a minimum diameter in the range from 0.3 nm to 100 μm . The
25 membrane preferably has pores in the range from 0.3 nm to 0.1 μm .

Preference is given to using a microporous membrane which is not wetted by the working medium composed of
30 sorption medium and refrigerant in the absorber. For the present purposes, the term wetting means a contact angle between working medium and microporous membrane of less than 90° , which leads to intrusion of working medium into pores of the membrane as a result of
35 capillary forces. The contact angle between working medium and microporous membrane is preferably more than 120 degrees, particularly preferably more than 140 degrees. By use of a nonwetting microporous

membrane, a flow of the liquid working medium through the pores of the membrane to the vapor side of the membrane can be prevented even for a pressure on the side of the liquid working medium which is higher than
5 that on the vapor side. A person skilled in the art can therefore determine the suitability of a microporous membrane for the absorption refrigeration machine of the invention by determining the contact angle between the working medium and the membrane.

10

In the preferred embodiment using water as refrigerant, preference is given to using a hydrophobic microporous membrane as semipermeable membrane. Suitable hydrophobic microporous membranes are known to those
15 skilled in the art as waterproof membranes which are permeable to water vapor in the technical field of functional clothing.

Preference is given to using hydrophobic microporous
20 membranes composed of polyethylene, polypropylene, polytetrafluoroethylene, polyvinylidene fluoride or fluoroalkyl-modified polymers. It is likewise possible to use mixtures or copolymers of two or more of these polymers. Inorganic hydrophobic microporous membranes
25 or composite membranes comprising an inorganic hydrophobic microporous material, for example membranes whose pores are formed by silicalite or hydrophobicized silica, are likewise suitable.

30 The semipermeable membrane is preferably arranged on a porous support layer. Arrangement on a porous support layer enables a mechanically stable membrane unit to be achieved even when a thin semipermeable membrane is
35 used. This allows more rapid mass transfer through the membrane and thus a smaller and more compact design of the absorber. The support layer is preferably arranged on the side of the semipermeable membrane which is in contact with the vapor phase. Such an arrangement of

the support layer leads to a reduced mass transfer resistance than an arrangement of the support layer on the side of the membrane facing the liquid working medium.

5

The porous support layer can comprise either inorganic or organic materials. The membrane is preferably arranged on a porous support layer composed of a hydrophobic polymer, in particular a polyolefin, a polyester or polyvinylidene fluoride. The support layer
10 can additionally contain reinforcement, e.g. by layers of fabric.

In a preferred embodiment, the semipermeable membrane
15 is arranged in the absorber in the form of hollow fibers. The configuration of the membrane in the form of hollow fibers allows a particularly compact construction of the absorber and operation of the absorber at a higher pressure difference between the
20 vapor phase and the liquid phase in the absorber.

The absorption refrigeration machine of the invention can additionally contain a membrane in the desorber, through which desorption of refrigerant from the
25 working medium occurs. In the desorber, it is in principle possible to use all membranes which are suitable as semipermeable membrane for the absorber of the absorption refrigeration machine of the invention. The use of a membrane in the desorber also makes it
30 possible to use working media which tend to foam during desorption.

The absorption refrigeration machine of the invention can also be configured in the form of a multistage
35 refrigeration machine, as described in F. Ziegler, R. Kahn, F. Summerer, G. Alefeld "Multi-Effect absorption chillers", Rev. Int. Froid 16 (1993) 301-311.

Owing to the compact construction and the low mechanical energy requirement, the absorption refrigeration machine of the invention is particularly suitable for mobile use, in particular in motor vehicles and ships. Furthermore, the absorption refrigeration machine of the invention is also particularly suitable for the air-conditioning of buildings since it can be operated with particularly low noise and allows for efficient air-conditioning using solar energy.

Claims:

1. An absorption refrigeration machine comprising a working medium, containing a nonvolatile sorption medium and a volatile refrigerant, and an absorber in which a vapor phase containing refrigerant and a liquid phase containing sorption medium are separated from one another by a membrane, characterized in that the membrane is a semipermeable membrane which is permeable to the refrigerant and impermeable to the sorption medium.
2. The absorption refrigeration machine as claimed in claim 1, characterized in that the refrigerant is water.
3. The absorption refrigeration machine as claimed in claim 1 or 2, characterized in that the sorption medium comprises one or more ionic liquids.
4. The absorption refrigeration machine as claimed in claim 3, characterized in that the ionic liquid consists of salts of organic cations with organic or inorganic anions.
5. The absorption refrigeration machine as claimed in claim 4, characterized in that the ionic liquid comprises one or more 1,3-dialkylimidazolium salts.
6. The absorption refrigeration machine as claimed in claim 4, characterized in that the ionic liquid comprises one or more quaternary ammonium salts of the general formula $R^1R^2R^3R^4N^+A^-$, where
 R^1 is an alkyl radical having from 1 to 20 carbon atoms,
 R^2 is an alkyl radical having from 1 to 4 carbon atoms,
 R^3 is a $(CH_2CHRO)_n-H$ radical where n is from 1 to 200
and $R = H$ or CH_3 ,

R^4 is an alkyl radical having from 1 to 4 carbon atoms or a $(CH_2CHRO)_n-H$ radical where n is from 1 to 200 and $R = H$ or CH_3 and A^- is a monovalent anion.

5

7. The absorption refrigeration machine as claimed in any one of the preceding claims, characterized in that the semipermeable membrane is a solution diffusion membrane.

10

8. The absorption refrigeration machine as claimed in any one of the preceding claims, characterized in that the semipermeable membrane is a microporous membrane which is not wetted by the working medium.

15

9. The absorption refrigeration machine as claimed in claim 8, characterized in that the refrigerant is water and the semipermeable membrane is a hydrophobic microporous membrane.

20

10. The absorption refrigeration machine as claimed in any one of the preceding claims, characterized in that the semipermeable membrane is arranged on a porous support layer.

25

11. The absorption refrigeration machine as claimed in claim 10, characterized in that the support layer is arranged on the side of the semipermeable membrane which is in contact with the vapor phase.

30

12. The absorption refrigeration machine as claimed in any one of the preceding claims, characterized in that the semipermeable membrane is arranged in the absorber in the form of hollow fibers.