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(54) **REFRIGERANT STORAGE IN SECONDARY LOOP REFRIGERATION SYSTEMS**

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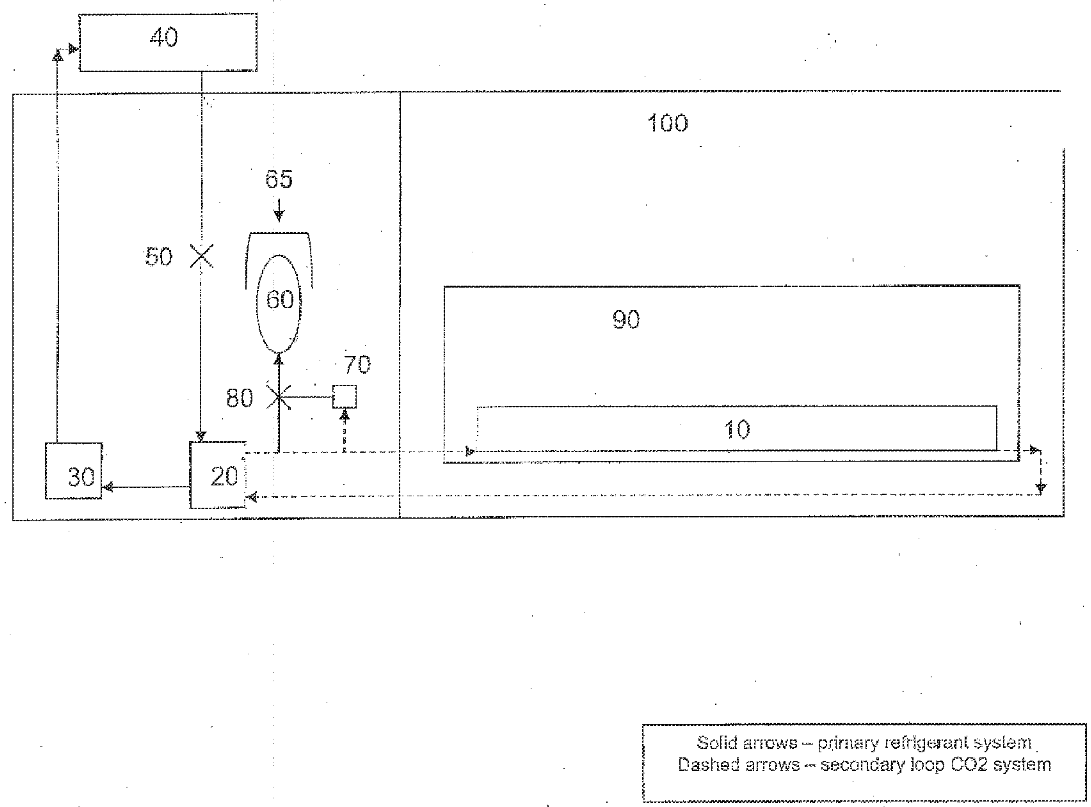
(57) **ABSTRACT**

A process and system for storing and recovering a secondary refrigerant such as carbon dioxide in a secondary loop refrigeration system after a shutdown of the primary refrigeration system using ionic liquids is described. The process eliminates the release of the secondary refrigerant into the environment and the need to recharge the secondary loop after a shutdown of the primary refrigeration system.



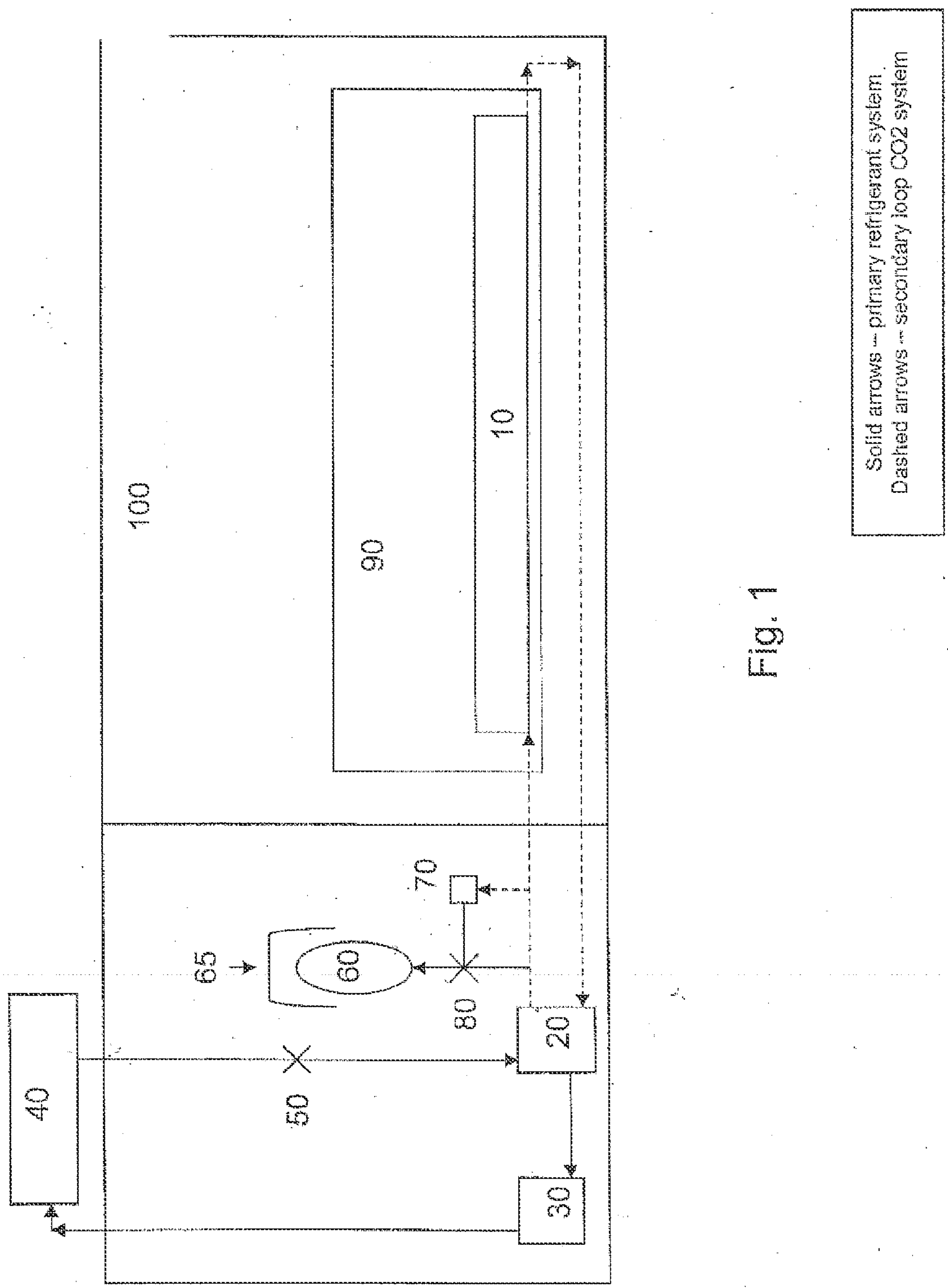

100
90
10
70
65
60
80
20
50
40
30
Solid arrows -- primary refrigerant system
Dashed arrows -- secondary loop CO2 system

Fig. 1

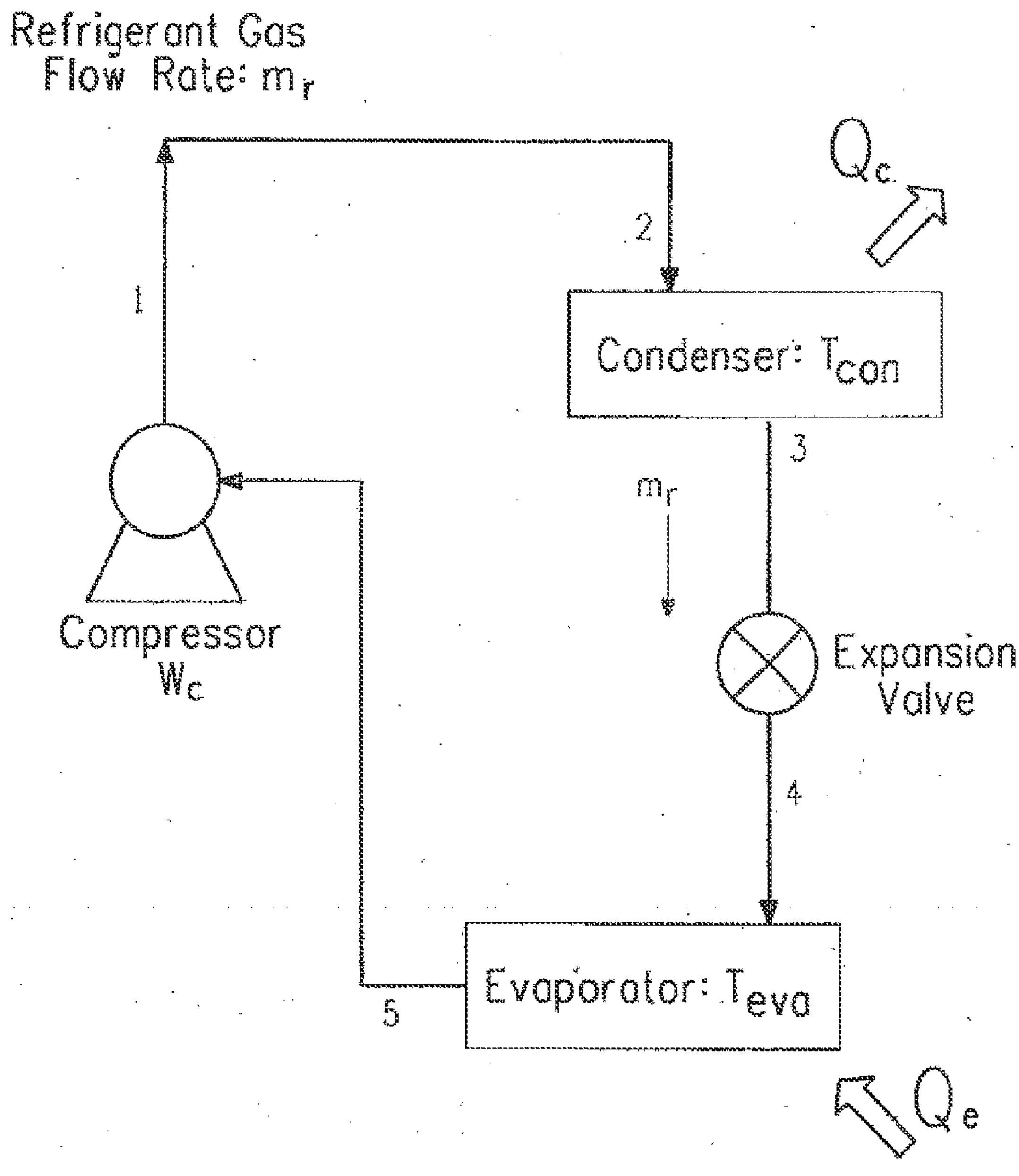

Refrigerant Gas
Flow Rate: m_r
Q_c
2
1
Condenser: T_{con}
3
m_r
Compressor
W_c
Expansion
Valve
4
Evaporator: T_{eva}
5
Q_e

Figure 2

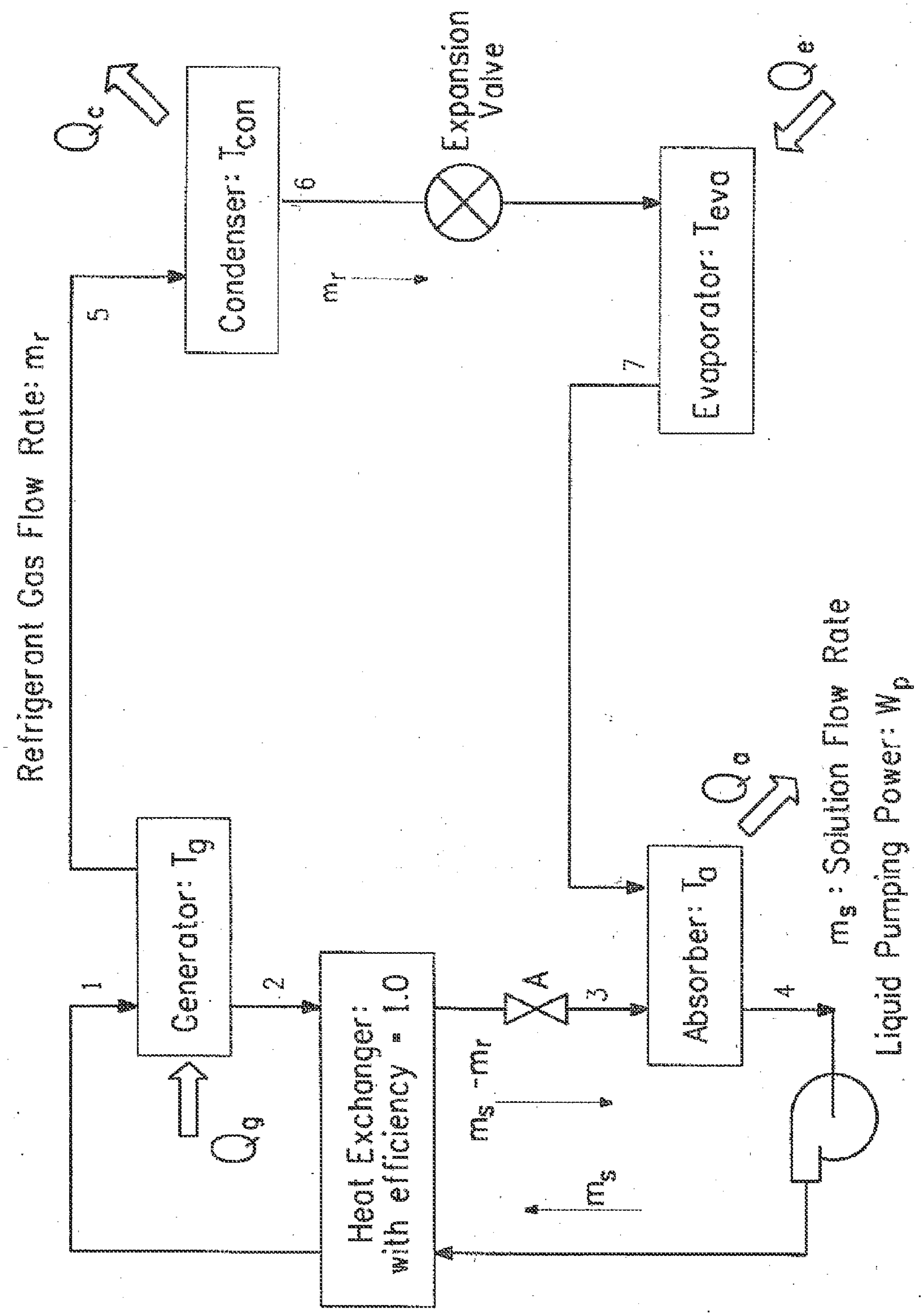

Refrigerant Gas Flow Rate: m_r
Condenser: T_con
Q_c
Expansion Valve
Q_e
Evaporator: T_evo
Generator: T_g
Heat Exchanger: with efficiency = 1.0
Absorber: T_a
Q_a
Q_g
A
1
2
3
4
5
6
7
m_r
m_s - m_r
m_s
m_s : Solution Flow Rate
Liquid Pumping Power: W_p

Figure 3

REFRIGERANT STORAGE IN SECONDARY LOOP REFRIGERATION SYSTEMS

[0001] This application claims priority under 35 U.S.C. §119(e) from, and claims the benefit of, U.S. Provisional Application No. 61/260,369, filed Nov. 11, 2009, which is by this reference incorporated in its entirety as a part hereof for all purposes.

TECHNICAL FIELD

[0002] This invention relates to the field of refrigeration systems. More specifically, the invention relates to a process and system for storing a secondary refrigerant such as carbon dioxide in a secondary loop refrigeration system using ionic liquids.

BACKGROUND

[0003] Secondary loop refrigeration systems have found widespread use in supermarkets and storage warehouses. This type of refrigeration system incorporates a primary refrigeration system and a secondary loop. The primary refrigeration system is often a traditional direct expansion design that uses a phase change refrigerant and a compressor to circulate a primary refrigerant. The secondary loop contains a nontoxic and nonflammable refrigerant such as carbon dioxide or propylene glycol. A heat exchanger is used to transfer energy between the primary refrigerant and the refrigerant in the secondary loop. In use, the primary refrigeration system is typically restricted to an isolated location, e.g. a machine room or roof top, and the secondary loop runs through the storage compartments for storing refrigerated goods, e.g. supermarket display cases. Secondary loop refrigeration systems offer many advantages over conventional refrigeration systems, one of the most important being a significant improvement in energy efficiency. Additionally, secondary loop refrigeration systems are more compact, operate with a small charge of refrigerant, and minimize the effects of refrigerant leakage.

[0004] Carbon dioxide is widely used as the secondary refrigerant in the secondary loop of these refrigeration systems. A problem arises when there is a shutdown of the primary refrigeration system, e.g. due to a loss of electrical power. The secondary refrigerant in the secondary loop increases in pressure, which can lead to very high pressures, such that the secondary refrigerant may need to be vented to prevent rupture of the secondary loop. Typically, a safety relief device is used in these systems so that when the pressure reaches the set point of the relief device, the device opens to the atmosphere, releasing the secondary refrigerant. The loss of the secondary refrigerant requires the system to be recharged when operation is restarted in order for the secondary loop to function properly.

[0005] Ionic liquids are known to absorb refrigerants such as carbon dioxide, and have been used to remove carbon dioxide from gas mixtures. For example, Moriya (US 2007/0084344) describes a gas collection method for selectively absorbing a gas, such as carbon dioxide, from a gas mixture using an ionic liquid. Additionally, Tonkovich (US 2009/0071335) describes methods for separating methane and carbon dioxide from a gas mixture using an ionic liquid. However, ionic liquids have not been used as storage media for a secondary refrigerant such as carbon dioxide in secondary loop refrigeration systems.

[0006] Therefore, the need still exits for a method to store and recover carbon dioxide in a secondary loop refrigeration system after a shutdown of the primary refrigeration system.

SUMMARY

[0007] This invention solves the stated problem by providing a method and apparatus for storing and recovering a secondary refrigerant, such as carbon dioxide, in a secondary loop refrigeration system using ionic liquids.

[0008] In one embodiment, this invention provides, in a secondary loop refrigeration system that comprises a primary refrigeration loop containing a primary refrigerant, a secondary refrigeration loop containing a secondary refrigerant, and a heat exchanger contacted by both the primary and secondary refrigeration loops, a method of storing secondary refrigerant, comprising (a) flowing at least a portion of the secondary refrigerant from the secondary loop to an auxiliary container; and (b) absorbing at least a portion of the flowed secondary refrigerant with an ionic liquid in the auxiliary container to form a mixture thereof.

[0009] In another embodiment, this invention provides an apparatus for adjusting the temperature of an object, medium or space, comprising (a) a primary refrigeration module that comprises a primary refrigeration loop containing a primary refrigerant, a condenser and an expansion valve; (b) a secondary refrigeration module that comprises a secondary refrigeration loop containing a secondary refrigerant, and an evaporator; (c) and a heat exchanger contacted by both the primary and secondary refrigeration loops; and (d) an auxiliary container in fluid communication with the secondary refrigeration loop through a flow interrupter, said auxiliary container containing at least one ionic liquid; wherein the condenser is located in proximity to an object, medium or space to be heated, or the evaporator is located in proximity to an object, medium or space to be cooled.

[0010] In a further embodiment, this invention provides a process for storing carbon dioxide in a secondary loop refrigeration system comprising the steps of (a) providing a secondary loop refrigeration system comprising a secondary loop containing carbon dioxide; (b) releasing the carbon dioxide from the secondary loop; and (c) contacting the carbon dioxide released from the secondary loop with at least one ionic liquid, whereby at least a portion of the carbon dioxide is absorbed by the ionic liquid.

[0011] In yet another embodiment, this invention provides a refrigeration system comprising (a) an object, space or medium to be cooled; (b) a primary refrigeration system containing a primary refrigerant, said primary refrigeration system comprising a compressor, a condenser, and an expansion valve; (c) a second refrigeration loop containing carbon dioxide; (d) an evaporator in open communication with the second refrigeration loop for transferring heat from said object, space or medium to the carbon dioxide; (e) a heat exchanger for transferring heat from the carbon dioxide in the second refrigeration loop to said primary refrigerant in the primary refrigeration system; and (f) an expansion tank in fluid communication with the second refrigeration loop through a flow interrupter, said expansion tank containing at least one ionic liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. **1** is a schematic drawing of an exemplary secondary loop refrigeration system for use with the process disclosed herein.

[0013] FIG. 2 is a layout of the components of a vapor compression cycle.

[0014] FIG. 3 is a layout of the components of an absorption cycle.

DETAILED DESCRIPTION

[0015] As used above and throughout the description of the invention, the following terms, unless otherwise indicated, shall be defined as follows:

[0016] The term "secondary loop refrigeration system" refers to a refrigeration system in which a thermal energy transfer medium contained in a secondary loop is used to transport thermal energy from a heat source to a primary refrigeration system.

[0017] The term "secondary loop" refers to the path over which the thermal energy transfer medium travels while it is being cycled between the heat source and the primary refrigeration system.

[0018] The term "secondary refrigerant" refers to the thermal energy transfer medium in the secondary loop.

[0019] The term "primary refrigeration system" refers to the part of a secondary loop refrigeration system where heat is transferred to an object, medium or space, such as the external environment, by way of a compressor or an absorber/generator system.

[0020] The term "primary refrigerant" refers to the thermal energy transfer medium in the primary refrigeration system.

[0021] The term "ionic liquid" refers to an organic salt that is fluid at or below about 100° C.

[0022] The term "refrigerant" refers to a fluidic substance such as a fluorocarbon (FC), hydrofluorocarbon (HFC), chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), or ammonia, alkanes, alkenes, aromatics, carbon dioxide, or other gas such as hydrogen, oxygen, nitrogen, and argon that may be used as a thermal energy transfer medium. A refrigerant, when it changes phase from liquid to vapor (evaporates), removes heat from the surroundings; and when it changes phase from vapor to liquid (condenses), it adds heat to the surroundings. Although the term refrigerant may carry the connotation of a substance used only for cooling, the term is used herein in the generic sense of a thermal energy transfer medium that is applicable for use in a method, apparatus or system that may be used for heating or cooling.

[0023] Disclosed herein are a method and apparatus for storing and recovering a secondary refrigerant, such as carbon dioxide, in a secondary loop refrigeration system using one or more ionic liquids to absorb the secondary refrigerant. The inventions hereof may be used in situations where, for example, there is a shutdown of the primary refrigeration system. The methods and apparatus hereof eliminate the release of a secondary refrigerant into the environment and the need to recharge the secondary loop after a shutdown of the primary refrigeration system. Secondary loop refrigeration systems find utility in refrigeration applications such as supermarket display cases and warehouse storage containers.

Secondary Loop Refrigeration Systems

[0024] Secondary loop refrigeration systems are well known in the art [see for example, U.S. Pat. Nos. 5,524,442 and 5,819,549 (each of which is by this reference incorporated in its entirety as a part hereof for all purposes)]. Briefly, a secondary loop refrigeration system comprises a primary refrigeration system and a secondary loop. The primary refrigeration system is a traditional direct expansion design that uses a phase change refrigerant and a compressor, or an absorber/generator system, to circulate the refrigerant.

[0025] Any suitable phase change refrigerant may be used as the primary refrigerant. Examples of suitable primary refrigerants include without limitation ammonia, fluorocarbons such as tetrafluoromethane (Freon 14), fluoroform (Freon 23), and hexafluoroethane (Freon 116); hydrofluorocarbons such as difluoromethane (HFC-32), 1,1-difluoroethane, 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a), fluoroethane (HFC-161), pentafluoroethane (HFC-125), 1,1,1,3,3-pentafluoropropane (HFC-245fa), and 1,1,1,3,3-pentafluorobutane (HFC-365mfc); fluoro-olefins such as 2,3,3,3-tetrafluoroprop-1-ene (HFO-1234yf); and mixtures thereof.

[0026] The primary refrigeration system is typically contained in an isolated location, e.g. a machine room or roof top, when the system is used for cooling and it is desired to reject heat to the atmosphere. In other embodiments, however, the system may be used for heating, and the condenser is located in proximity to an object, medium or space to be heated. The secondary loop contains a secondary refrigerant, which is frequently carbon dioxide. Other suitable secondary refrigerants, however, include nitrogen, argon, helium, ammonia, perfluoroalkanes, ethylene glycols, and hydrofluoroethers. When the system is used for cooling, such as when the secondary loop runs through a storage compartment for storing refrigerated goods (e.g. a supermarket display case), the evaporator is located in proximity to an object, medium or space to be cooled.

[0027] In operation of the cooling embodiment, heat energy from a food storage compartment is transferred to the secondary refrigerant in the secondary loop by way of an evaporator containing refrigeration coils. The heat transfer to the secondary refrigerant may be facilitated by the use of fans, which circulate the air in the storage compartment. The secondary refrigerant is circulated in the secondary loop to a heat exchanger by a circulating pump. In the heat exchanger, the thermal energy from the secondary refrigerant is transferred to the primary refrigerant contained in the primary refrigeration system. The cooled secondary refrigerant is returned to the storage compartment by way of the secondary loop. The warmed primary refrigerant is circulated through a compressor, or an absorber/generator system, to a condenser where the primary refrigerant is liquefied and cooled. By this process, the thermal energy is extracted from the primary refrigerant and rejected into the environment. The primary refrigerant is then expanded through an expansion valve and returned to the heat exchanger.

[0028] The primary refrigerant may be routed to the condenser by either a vapor compression cycle or an absorption cycle. Vapor compression and absorption cycles, and systems in which they are run, are described in Application Guide for Absorption Cooling/Refrigeration Using Recovered Heat [Dorgan et al (American Society of Heating, Refrigeration and Air Conditioning Engineers, Inc., 1995, Atlanta, Ga., Chapter 5)]. A schematic diagram for a system in which a simple vapor compression cycle is run is shown in FIG. 2. The system is composed of condenser and evaporator units with an expansion valve, and a vapor compressor that is capable of mechanically increasing the pressure of a refrigerant vapor. A schematic diagram for a simple absorption cycle is shown in FIG. 3. The system is composed of condenser and evaporator units with an expansion valve similar to an ordinary vapor compression cycle shown in FIG. **2**, but an absorber-generator solution circuit replaces the compressor. The circuit may be composed of an absorber, a generator, a heat exchanger, a pressure control device (A) and a pump for circulating the solution. In some embodiments, the heat released by the absorber upon the absorption of the refrigerant by the absorbent may be used to heat a mixture of refrigerant and absorbent in the generator to separate the refrigerant in vapor form from the absorbent. In various embodiments, the absorbent can be any ionic liquid.

[0029] This invention thus involves an apparatus for adjusting the temperature of an object, medium or space wherein the refrigerant is routed to the condenser by either a vapor compression cycle or an absorption cycle, as described herein, to cool or heat an object (for example a conduit or a container), a medium (for example a fluid such as air or water) or a space. The apparatus may thus be composed of a mechanical compressor, a condenser and evaporator units with an expansion valve; or it may include components such as an absorber-generator solution circuit (which by the outflow and inflow of heat increases the pressure of refrigerant vapor as a compressor does mechanically) where the circuit may be composed of an absorber, a generator, a heat exchanger, a pressure control device and a pump for circulating the solution.

[0030] Vapor compression and absorption systems are further described in US 2006/0197053 and US2007/0019708, each of which is by this reference incorporated in its entirety as a part hereof for all purposes.

[0031] An apparatus of this invention may be deployed for use in, or fabricated or operated as, a refrigerator, a freezer, an ice machine, an air conditioner, an industrial cooling system, a heater or heat pump. Each of these instruments may be situated in a residential, commercial or industrial setting, or may be incorporated into a mobilized device such as a car, truck, bus, train, airplane, or other device for transportation, or may be incorporated into a piece of equipment such as a medical instrument.

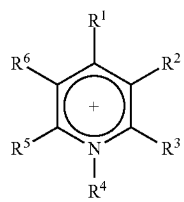
Ionic Liquids

[0032] Ionic liquids suitable for use as disclosed herein can, in principle, be any ionic liquid that absorbs a secondary refrigerant such as carbon dioxide; however, ionic liquids that have minimal absorption of the refrigerant will be less effective. Ideally, ionic liquids having high absorption of the selected refrigerant are desired for efficient use as described herein. Additionally, mixtures of two or more ionic liquids may be used.

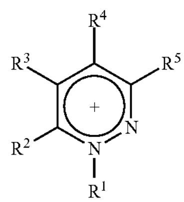
[0033] Many ionic liquids are formed by reacting a nitrogen-containing heterocyclic ring, preferably a heteroaromatic ring, with an alkylating agent (for example, an alkyl halide) to form a quaternary ammonium salt, and performing ion exchange or other suitable reactions with various Lewis acids or their conjugate bases to form the ionic liquid. Examples of suitable heteroaromatic rings include substituted pyridines, imidazole, substituted imidazole, pyrrole and substituted pyrroles. These rings can be alkylated with virtually any straight, branched or cyclic C_{1-20} alkyl group, but preferably, the alkyl groups are C_{1-16} groups. Various triarylphosphines, thioethers and cyclic and non-cyclic quaternary ammonium salts may also be used for this purpose. Ionic liquids suitable for use herein may also be synthesized by salt metathesis, by an acid-base neutralization reaction or by quaternizing a selected nitrogen-containing compound; or they may be obtained commercially from several companies such as Merck (Darmstadt, Germany), BASF (Mount Olive, N.J.), Fluka Chemical Corp. (Milwaukee, Wis.), and Sigma-Aldrich (St. Louis, Mo.).

[0034] Representative examples of ionic liquids suitable for use herein are included among those that are described in sources such as *J. Chem. Tech. Biotechnol.*, 68:351-356 (1997); *Chem. Ind.*, 68:249-263 (1996); *J. Phys. Condensed Matter*, 5: (supp 34B):B99-B106 (1993); *Chemical and Engineering News*, *Mar.* 30, 1998, 32-37; *J. Mater. Chem.*, 8:2627-2636 (1998); *Chem. Rev.*, 99:2071-2084 (1999); and US 2008/0028777 (which is by this reference incorporated in its entirety as a part hereof for all purposes), and references cited therein. In one embodiment, a library, i.e. a combinatorial library, of ionic liquids may be prepared, for example, by preparing various alkyl derivatives of a quaternary ammonium cation, and varying the associated anions. The acidity of the ionic liquids can be adjusted by varying the molar equivalents and type and combinations of Lewis acids.

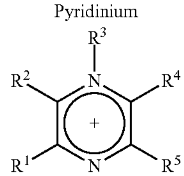
[0035] Ionic liquids suitable for use herein comprise an anion and a cation. In various different embodiments, the cation is selected from the group consisting of cations represented by the structures of the following formulae:



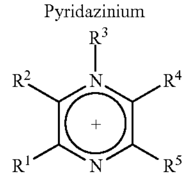
Pyridinium



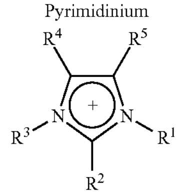
Pyridazinium



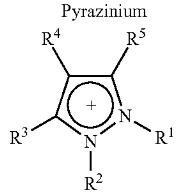
Pyrimidinium



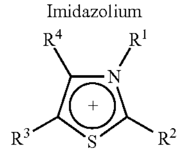
Pyrazinium



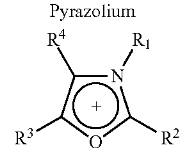
Imidazolium



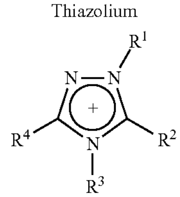
Pyrazolium



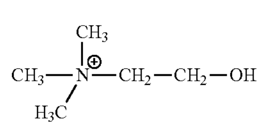
Thiazolium



Oxazolium

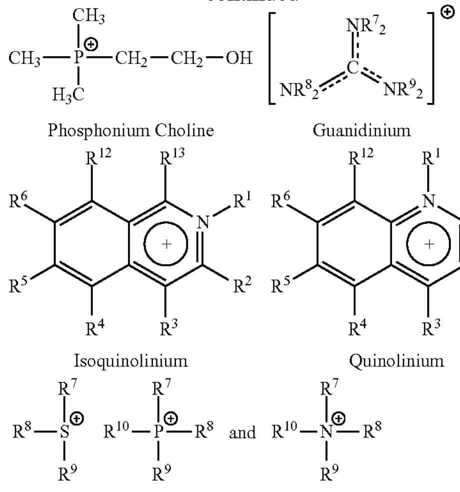


Triazolium



Choline

-continued



Phosphonium Choline Guanidinium

Isoquinolinium Quinolinium

Sulfonium Phosphonium and Ammonium

wherein:

[0036] a) R^1, R^2, R^3, R^4, R^5, R^6, R^{12} and R^{13} are independently selected from the group consisting of:

[0037] (i) H,

[0038] (ii) halogen,

[0039] (iii) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

[0040] (iv) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

[0041] (v) C_6 to C_{20} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S;

[0042] (vi) C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

[0043] (A) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,

[0044] (B) OH,

[0045] (C) NH_2, and

[0046] (D) SH; and

[0047] (vii) —$(CH_2)_nSi(CH_2)_mCH_3$, —$(CH_2)_nSi(CH_3)_3$, —$(CH_2)_nOSi(CH_3)_m$, where n is independently 1-4 and m is independently 0-4;

[0048] b) R^7, R^8, R^9, and R^{10} are independently selected from the group consisting of:

[0049] (viii) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

[0050] (ix) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

[0051] (x) C_6 to C_{25} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

[0052] (E) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,

[0053] (F) OH,

[0054] (G) NH_2, and

[0055] (H) SH; and

[0056] (xi) —$(CH_2)_nSi(CH_2)_mCH_3$, —$(CH_2)_nSi(CH_3)_3$, —$(CH_2)_nOSi(CH_3)_m$, where n is independently 1-4 and m is independently 0-4;

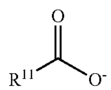
[0057] c) optionally at least two of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, and R^{10} can together form a cyclic or bicyclic alkanyl or alkenyl group

[0058] In one embodiment, the ionic liquid comprises an anion selected from one or more members of the group consisting of: $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_3]^{3-}$, $[HPO_3]^{2-}$, $[H_2PO_3]^{1-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, carborates optionally substituted with alkyl or substituted alkyl; carboranes optionally substituted with alkylamine, substituted alkylamine, alkyl or substituted alkyl; and a fluorinated anion.

[0059] In one embodiment, the ionic liquid comprises a cation selected from one or more members of the group consisting of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, phosphonium, ammonium, benzyltrimethylammonium, choline, dim ethylimidazolium, guanidinium, phosphonium choline, tetramethylammonium, and tetramethylphosphonium.

[0060] In another embodiment, the ionic liquid comprises an anion selected from one or more members of the group consisting of aminoacetate, ascorbate, benzoate, catecholate, citrate, dimethylphosphate, formate, fumarate, gallate, glycolate, glyoxylate, iminodiacetate, isobutyrate, kojate, lactate, levulinate, oxalate, pivalate, propionate, pyruvate, salicylate, succinamate, succinate, tiglate, tetrafluoroborate, tetrafluoroethanesulfonate, tropolonate, $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, $[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[HCF_2CF_2SO_3]^-$, $[CF_3HFCCF_2SO_3]^-$, $[HCClFCF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(CF_3CF_2SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[CF_3CO_2]^-$, $[CF_3OCFHCF_2SO_3]^-$, $[CF_3CF_2OCFHCF_2SO_3]^-$, $[CF_3CFHOCF_2CF_2SO_3]^-$, $[CF_2HCF_2OCF_2CF_2SO_3]_-$, $[CF_{21}CF_2OCF_2CF_2SO_3]$, $[CF_3CF_2OCF_2CF_2SO_3]^-$,

$[(CF_2HCF_2SO_2)_2N]^-$, $[(CF_3CFHCF_2SO_2)_2N]^-$, F^-, and anions represented by the structure of the following formula:



[0061] wherein R^{11} is selected from the group consisting of:

[0062] (i) —CH_3, —C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

[0063] (ii) —CH_3, —C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

[0064] (iii) C_6 to C_{10} unsubstituted aryl, or C_3 to C_{10} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and

[0065] (iv) C_6 to C_{10} substituted aryl, or C_3 to C_{10} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

[0066] (A) —CH_3, —C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,

[0067] (B) OH,

[0068] (C) NH_2, and

[0069] (D) SH.

[0070] In one embodiment, the ionic liquid is selected from the group consisting of 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4], 1-hexyl-3-methylimidazolium bistrifluoromethylsulfonylimide [hmim][Tf_2N], and 1-butyl-3-methylimidazolium acetate [bmim][acetate].

Method and Apparatus for Storing Secondary Refrigerant in a Secondary Loop Refrigeration System

[0071] The method disclosed herein for storing a secondary refrigerant in a secondary loop refrigeration system comprises the following steps. The first step is providing a secondary loop refrigeration system, as described above. When there is a shutdown of the primary refrigeration system, e.g. due to a loss of electrical power, the secondary refrigerant is released from the secondary loop and contacted with at least one ionic liquid, as described above, whereby at least a portion of the secondary refrigerant is absorbed by the ionic liquid. The portion of the secondary refrigerant absorbed is sufficient to relieve the pressure in the secondary loop. The amount of ionic liquid needed will depend on the amount of secondary refrigerant contained in the secondary loop and the absorption capability of the ionic liquid used. When operation of the primary refrigeration system resumes; the absorbed secondary refrigerant may be released from the ionic liquid back into the secondary loop. The secondary refrigerant can be released from the ionic liquid most conveniently by heating the ionic liquid containing the secondary refrigerant.

[0072] The inventions hereof can be better understood by reference to FIG. **1**., which shows a schematic drawing of an exemplary secondary loop refrigeration system in cooling mode that may be used to practice the method disclosed herein. The secondary loop refrigeration system illustrated in FIG. **1** is suitable for use, for example, in a supermarket or grocery store. Similar systems may be useful for other applications, e.g. storage warehouses.

[0073] Referring to FIG. **1**, the secondary loop containing the secondary refrigerant is depicted by dashed arrows and runs through an evaporator **10** in a refrigerated display case **90** (an example of a storage compartment for storing refrigerated goods), which is located in the interior of the store **100**. The evaporator is in open communication with the secondary loop for transferring heat from the display case to the secondary refrigerant. In FIG. **1**, the primary refrigeration system is depicted by solid arrows and comprises a compressor **30**, a condenser **40**, and an expansion valve **50**. The heat exchanger **20** serves to transfer heat energy from the secondary refrigerant in the secondary loop to the primary refrigerant in the primary refrigeration system, as described above.

[0074] In the event of a shutdown of the primary refrigeration system, pressure in the secondary loop increases. This pressure increase may be sensed by a pressure sensor **70** in fluid communication with the secondary loop. When the pressure in the secondary loop exceeds a predetermined value, a flow interrupter, for example a valve such as a pressure relief valve **80** depicted in FIG. **1**, is opened, thereby releasing the secondary refrigerant from the secondary loop. The released secondary refrigerant enters an expansion tank **60**, which is in fluid communication with the secondary loop, where it is contacted with at least one ionic liquid contained in the tank, whereby at least a portion of the released secondary refrigerant is absorbed by the ionic liquid. When operation of the primary refrigeration system resumes, the absorbed secondary refrigerant may be released from the ionic liquid back into the secondary loop by heating the ionic liquid using a heat source **65**, such as an electrical heating element, a natural gas or oil fueled heat source, that is in thermal contact with the expansion tank.

EXAMPLES

[0075] This invention is further defined in the following examples. It should be understood that these examples, while indicating preferred embodiments of the invention, are given by way of illustration only. From the above discussion and these examples, the essential characteristics of this invention can be ascertained, and without departing from the spirit and scope thereof, various changes and modifications of the invention can be made to adapt it to various uses and conditions.

[0076] The meaning of abbreviations used is as follows: "min" means minute(s), "hr" means hour(s), "mL" means milliliter(s), "μL" means microliter(s), "g" means gram(s), "mg" means milligram(s), "μg" means microgram(s), "Pa" means pascal(s), "kPa" means kilopascal(s), and "MPa" means megapascal(s).

Materials

[0077] 1-Butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] (Lot No. 1055432, Filling Code

31304010), 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] (Lot No. 1080045, Filling Code 11304079), and 1-butyl-3-methylimidazolium acetate [bmim][Ac] (Lot No. S25803, Filling Code 444041302) were purchased from Fluka Chemika (Buchs, Switzerland) with a purity of >96%, >97%, >95% respectively. The 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyflimide [hmim][Tf_2N] (Lot EQ500831 632) was purchased from EMD Chemicals, Inc. (Gibbstown, N.J.) with a purity of >99%. Coleman grade CO_2 was obtained from MG Industries (Malvern, Pa.), with a minimum purity of 99.99%. A molecular sieve trap was installed to remove trace amounts of water from the CO_2.

Example 1

Solubility of Carbon Dioxide in 1-Butyl-3-Methylimidazolium Hexafluorophosphate

[0078] This example illustrates the solubility of carbon dioxide in 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] at temperatures of 283.15° K, 298.15° K, 323.15° K, and 348.15° K.

[0079] The gas solubility measurements were made using a gravimetric microbalance (IGA-003 Multicomponent Analyzer, Hiden Isochema Ltd., Warrington WAS 7TN UK). The IGA design integrates precise computer-control and measurement of weight change, pressure and temperature to enable fully automatic and reproducible determination of gas absorption isotherms and isobars. The microbalance consists of an electrobalance with sample and counterweight components inside a stainless steel pressure-vessel. The balance has a weigh range of 0-100 mg with a resolution of 0.1 μg. An enhanced pressure stainless steel (SS316LN) reactor capable of operation to 2.0 MPa and 773.15° K was installed. Approximately 60 mg of the [bmim][PF_6] ionic liquid sample was added to the sample container and the reactor was sealed. The sample was dried and degassed by first pulling a course vacuum on the sample with a diaphragm pump (model MVP055-3, Pfeiffer Vacuum Inc., Nashua, N.H.) and then fully evacuating the reactor to 10^{-9} M Pa with a turbopump (model TSH-071, Pfeiffer Vacuum Inc.). While under deep vacuum, the sample was heated to 348.15° K for 10 hr with an external water jacket connected to a remote-controlled constant-temperature bath (Ministat, model cc-S3, Huber-USA, Northport, N.Y.). A mixture of 30% ethylene glycol and 70% water by volume was used as the recirculating fluid with a temperature range from 278.15 to 363.15° K. The sample mass slowly decreased as residual water and gases were removed. Once the mass had stabilized for at least 60 min, the sample dry mass was recorded. The percent weight loss for the ionic liquid was about 1-3%. This weight loss can be attributed to the loss of residual water.

[0080] The IGA-003 can operate in both dynamic and static modes. All absorption measurements were performed in static mode. Static mode operation introduces gas into the top of the balance away from the sample, and both the admittance and exhaust valves control the set-point pressure. The sample temperature was measured with a type K thermocouple with an accuracy of ±0.1° K. The thermocouple was located inside the reactor next to the sample container. The water jacket maintained the set-point temperature automatically to within an accuracy of ±0.1° K. Four isotherms (at 283.15, 298.15, 323.15, and 348.15° K) were measured beginning with 283.15° K. Once the desired temperature was achieved and stabilized, the admittance and exhaust valves automatically opened and closed to adjust the pressure to the first set-point. Pressures from 10^{-10} to 10^{-2} MPa were measured using a capacitance manometer (model PKR25, Pfeiffer Vacuum Inc.), and pressures from 10^{-2} to 2.0 MPa were measured using a piezo-resistive strain gauge (model PDCR4010, Druck, New Faifield, Conn.). The reactor pressure set-point was maintained to within ±0.4 to 0.8 kPa. The pressure ramp rate was set at 20 kPa/min and the temperature ramp rate was set at 1° K/min. The upper pressure limit of the stainless steel reactor was 2.0 MPa, and several isobars up to 2.0 MPa (0.01, 0.05, 0.1, 0.4, 0.7, 1.0, 1.3, 1.5, and 2.0 MPa) were measured. To ensure sufficient time for gas-liquid equilibrium, the ionic liquid sample was maintained at set-point for a minimum of 3 hr with a maximum time-out of 20 hr.

[0081] The IGA method exploits the relaxation behavior following pressure and temperature changes to simultaneously evaluate the time-dependent absorption and asymptotic uptake. The real-time processor was used to determine the end-point for each isotherm. The percent relaxation used as an end point for the real-time analysis was 99 percent. The minimum weight change for real-time analysis was set at 1 μg, the acceptable average deviation of the model from the acquired data was set at 7 μg, and the target interval for weight acquisition was set at a typical value of 1 μg. The temperature variation during an isotherm was maintained less than 0.1μ° K/min.

[0082] The solubility data for carbon dioxide in [bmim][PF_6] is given in Table 1. The results demonstrate that the ionic liquid [bmim][PF_6] absorbs significant quantities of carbon dioxide at various temperatures and pressures and that the absorbed carbon dioxide can be released by increasing the temperature of the ionic liquid. These results suggest that the ionic liquid [bmim][PF_6] could be used as a storage medium for carbon dioxide in a secondary loop refrigeration system.

TABLE 1

Solubility of Carbon Dioxide in [bmim][PF_6]

Temperature (° K)	Pressure (MPa)	CO_2 (mass %)
283.05	0.05009	0.24
283.05	0.10018	0.46
283.55	0.39956	1.72
283.75	0.69959	2.97
283.65	0.99996	4.22
283.05	1.99975	8.35
298.05	0.05015	0.14
298.05	0.10020	0.29
298.15	0.39963	1.19
298.15	0.70000	2.07
298.05	0.99941	2.95
298.05	1.29990	3.80
298.05	1.49942	4.41
298.05	1.99919	5.80
323.25	0.01020	0.03
323.15	0.05026	0.09
323.15	0.10020	0.19
323.25	0.39961	0.76
323.15	0.70004	1.29
323.15	0.99979	1.81
323.15	1.30023	2.34
323.25	1.50027	2.70
323.25	1.99978	3.56
348.05	0.05008	0.04
348.05	0.10003	0.11
348.05	0.39969	0.51

TABLE 1-continued

Solubility of Carbon Dioxide in [bmim][PF_6]		
Temperature (° K)	Pressure (MPa)	CO_2 (mass %)
348.05	0.70001	0.89
348.25	1.99951	2.45

Example 2

Solubility of Carbon Dioxide in 1-Butyl-3-methylimidazolium Tetrafluoroborate

[0083] This example illustrates the solubility of carbon dioxide in 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] at temperatures of 283.15° K, 298.15° K, 323.15° K, and 348.15° K.

[0084] The method and the apparatus used to make the solubility measurements were the same as described in Example 1. The results of the solubility measurements are given in Table 2. The results demonstrate that the ionic liquid [bmim][BF_4] absorbs significant quantities of carbon dioxide at various temperatures and pressures and that the absorbed carbon dioxide can be released by increasing the temperature of the ionic liquid. These results suggest that the ionic liquid [bmim][BF_4] could be used as a storage medium for carbon dioxide in a secondary loop refrigeration system.

TABLE 2

Solubility of Carbon Dioxide in [bmim][BF_4]		
Temperature (° K)	Pressure (MPa)	CO_2 (mass %)
282.75	0.01017	0.04
282.95	0.05015	0.24
283.05	0.10010	0.46
283.05	0.40010	1.88
283.25	0.69962	3.25
283.05	0.99967	4.64
283.05	1.30019	5.93
283.15	1.50006	6.79
283.05	2.00019	8.97
298.15	0.05002	0.19
298.05	0.10013	0.36
298.15	0.39956	1.42
298.15	0.70022	2.45
297.95	0.99967	3.46
298.15	1.30022	4.44
297.95	1.50008	5.09
298.05	2.00020	6.66
323.25	0.01015	0.06
323.15	0.05011	0.13
323.15	0.10014	0.23
323.15	0.39970	0.88
323.15	0.69962	1.49
323.15	1.00020	2.09
323.15	1.29965	2.69
323.15	1.50011	3.07
323.15	2.00000	4.02
348.15	0.01020	0.04
348.15	0.05013	0.07
348.05	0.10018	0.15
348.05	0.40018	0.60
348.15	0.69956	1.01
347.95	1.00027	1.43
348.15	1.30000	1.83

TABLE 2-continued

Solubility of Carbon Dioxide in [bmim][BF_4]		
Temperature (° K)	Pressure (MPa)	CO_2 (mass %)
348.15	1.50024	2.11
348.05	1.99990	2.77

Example 3

Solubility of Carbon Dioxide in 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

[0085] This example illustrates the solubility of carbon dioxide in 1-hexyl-3-methylimidazolium bistrifluoromethylsulfonylimide [hmim][Tf_2N] at temperatures of 283.15° K, 298.15° K, 323.15° K, and 348.15° K.

[0086] The method and the apparatus used to make the solubility measurements were the same as described in Example 1. The results of the solubility measurements are given in Table 3. The results demonstrate that the ionic liquid [hmim][Tf_2N] absorbs significant quantities of carbon dioxide at various temperatures and pressures and that the absorbed carbon dioxide can be released by increasing the temperature of the ionic liquid. These results suggest that the ionic liquid [hmim][Tf_2N] could be used as a storage medium for carbon dioxide in a secondary loop refrigeration system.

TABLE 3

Solubility of Carbon Dioxide in [hmim][Tf2N]		
Temperature (° K)	Pressure (MPa)	CO_2 (mass %)
283.04	0.0103	0.08
283.08	0.0499	0.27
283.09	0.1000	0.51
283.17	0.3994	1.93
283.23	0.7003	3.39
283.10	0.9996	4.87
283.12	1.2993	6.35
283.08	1.4996	7.29
283.08	2.0002	9.79
298.25	0.0105	0.07
298.17	0.0504	0.20
298.11	0.1004	0.38
298.25	0.3993	1.38
298.08	0.7003	2.41
298.22	1.0004	3.43
298.24	1.2997	4.42
298.14	1.4993	5.06
323.12	0.0104	0.02
323.09	0.0504	0.10
323.12	0.1000	0.20
323.16	0.3999	0.85
323.13	0.6994	1.49
323.00	0.9995	2.15
323.08	1.3002	2.80
323.09	1.4994	3.19
323.12	1.9998	4.23
348.13	0.0105	0.04
348.11	0.0502	0.08
348.09	0.1002	0.18
348.14	0.4002	0.64
348.09	0.6995	1.10
348.20	1.0002	1.57
348.09	1.3003	1.99
348.18	1.5004	2.28
348.15	1.9994	2.97

Example 4

Solubility of Carbon Dioxide in 1-Butyl-3-methylimidazolium Acetate

[0087] This example illustrates the solubility of carbon dioxide in 1-butyl-3-methylimidazolium acetate [bmim][acetate] at temperatures of 283.15° K, 298.15° K, 323.15° K, and 348.15° K.

[0088] The method and the apparatus used to make the solubility measurements were the same as described in Example 1. The results of the solubility measurements are given in Table 4. The results demonstrate that the ionic liquid [bmim][acetate] absorbs significant quantities of carbon dioxide at various temperatures and pressures and that the absorbed carbon dioxide can be released by increasing the temperature of the ionic liquid. These results suggest that the ionic liquid [bmim][acetate] could be used as a storage medium for carbon dioxide in a secondary loop refrigeration system.

TABLE 4

Solubility of Carbon Dioxide in [bmim][acetate]

Temperature (° K)	Pressure (MPa)	CO_2 (mass %)
283.16	0.0103	1.73
283.10	0.0503	4.64
283.06	0.1001	7.07
283.14	0.3993	9.84
283.09	0.7000	11.70
283.09	0.9993	13.33
283.08	1.3016	14.85
282.99	1.4999	15.69
283.06	1.9999	17.93
298.09	0.0102	4.12
298.04	0.0503	6.91
298.18	0.1003	7.76
298.10	0.3994	9.61
298.13	0.7001	10.79
298.14	0.9996	11.83
298.25	1.3002	12.78
298.14	1.5000	13.39
298.13	1.9994	14.92
323.09	0.0104	2.61
323.11	0.0504	4.52
323.06	0.1004	5.38
323.11	0.3995	7.26
323.15	0.7003	8.27
323.05	1.0001	9.08
323.09	1.3002	9.75
323.08	1.4995	10.15
323.20	1.9993	11.13
348.09	0.0104	1.47
348.07	0.0505	3.19
348.15	0.1000	4.07
348.09	0.4002	6.04
348.12	0.6994	6.88
348.10	1.0003	7.51
348.12	1.2994	7.98
348.13	1.4997	8.21
348.18	1.9993	8.91

[0089] The term "invention" as used herein is a non-limiting term, and is not intended to refer to any single embodiment of the various inventions hereof to the exclusion of others, but encompasses all possible embodiments as described in the specification and the claims.

[0090] In this specification, unless explicitly stated otherwise or indicated to the contrary by the context of usage, where an embodiment of the subject matter to hereof is stated or described as comprising, including, containing, having, being composed of or being constituted by or of certain features or elements, one or more features or elements in addition to those explicitly stated or described may be present in the embodiment. An alternative embodiment of the subject matter hereof, however, may be stated or described as consisting essentially of certain features or elements, in which embodiment features or elements that would materially alter the principle of operation or the distinguishing characteristics of the embodiment are not present therein. A further alternative embodiment of the subject matter hereof may be stated or described as consisting of certain features or elements, in which embodiment, or in insubstantial variations thereof, only the features or elements specifically stated or described are present.

What is claimed is:

1. In a secondary loop refrigeration system that comprises a primary refrigeration loop containing a primary refrigerant, a secondary refrigeration loop containing a secondary refrigerant, and a heat exchanger contacted by both the primary and secondary refrigeration loops, a method of storing secondary refrigerant, comprising (a) flowing at least a portion of the secondary refrigerant from the secondary loop to an auxiliary container; and (b) absorbing at least a portion of the flowed secondary refrigerant with an ionic liquid in the auxiliary container to form a mixture thereof.

2. A method according to claim **1** further comprising a step of separating the second refrigerant from an ionic liquid, and flowing the separated secondary refrigerant from the auxiliary container back into the secondary loop.

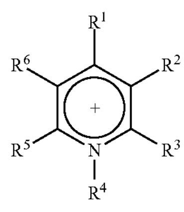
3. A method according to claim **1** wherein separating the secondary refrigerant from an ionic liquid comprises heating the mixture of the ionic liquid and absorbed secondary refrigerant.

4. A method according to claim **1** further comprising a step of compressing the primary refrigerant.

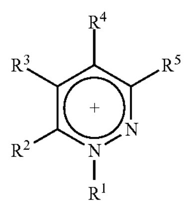
5. A method according to claim **1** further comprising a step of absorbing the prim ref in an ionic liquid.

6. A method according to claim **1** wherein the secondary refrigerant comprises carbon dioxide.

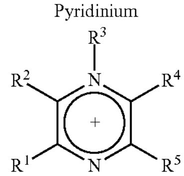
7. A method according to claim **1** wherein an ionic liquid comprises a cation selected from the group consisting of cations represented by the structures of the following formulae:



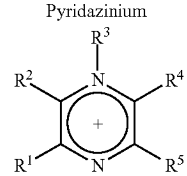
Pyridinium



Pyridazinium

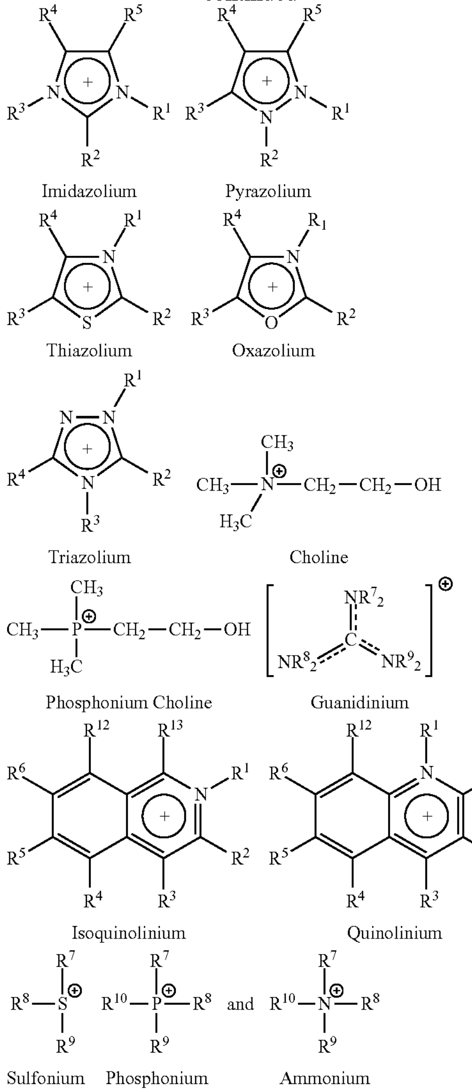


Pyrimidinium



Pyrazinium

-continued



wherein:

A) R^1, R^2, R^3, R^4, R^5, R^6, R^{12} and R^{13} are independently selected from the group consisting of:

(vii) H,

(viii) halogen,

(ix) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(x) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(xi) C_6 to C_{20} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S;

(xii) C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(A) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,

(B) OH,

(C) NH_2, and

(D) SH; and

(vii) —$(CH_2)_nSi(CH_2)_mCH_3$, —$(CH_2)_nSi(CH_3)_3$, —$(CH_2)_nOSi(CH_3)_m$, where n is independently 1-4 and m is independently 0-4;

B) R^7, R^8, R^9, and R^{10} are independently selected from the group consisting of:

(viii) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(ix) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(x) C_6 to C_{25} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(E) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,

(F) OH,

(G) NH_2, and

(H) SH; and

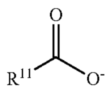
(xi) —$(CH_2)_nSi(CH_2)_mCH_3$, —$(CH_2)_nSi(CH_3)_3$, —$(CH_2)_nOSi(CH_3)_m$, where n is independently 1-4 and m is independently 0-4; and

C) optionally at least two of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, and R^{10} can together form a cyclic or bicyclic alkanyl or alkenyl group.

8. A method according to claim **1** wherein an ionic liquid comprises an anion selected from one or more members of the group consisting of: $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_3]^{3-}$, $[HPO_3]^{2-}$, $[H_2PO_3]^{1-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, carborates optionally substituted with alkyl or substituted alkyl; carboranes optionally substituted with alkylamine, substituted alkylamine, alkyl or substituted alkyl; and a fluorinated anion.

9. A method according to claim **1** wherein an ionic liquid comprises a cation selected from one or more members of the group consisting of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, phosphonium, ammonium, benzyltrimethylammonium, choline, dimethylimidazolium, guanidinium, phosphonium choline, tetramethylammonium, and tetramethylphosphonium.

10. A method according to claim **1** wherein an ionic liquid comprises an anion selected from one or more members of the group consisting of aminoacetate, ascorbate, benzoate, catecholate, citrate, dimethylphosphate, formate, fumarate, gallate, glycolate, glyoxylate, iminodiacetate, isobutyrate, kojate, lactate, levulinate, oxalate, pivalate, propionate, pyruvate, salicylate, succinamate, succinate, tiglate, tetrafluoroborate, tetrafluoroethanesulfonate, tropolonate, $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, $[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[HCF_2CF_2SO_3]^-$, $[CF_3HFCCF_2SO_3]^-$, $[HCClFCF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(CF_3CF_2SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[CF_3CO_2]^-$, $[CF_3OCFHCF_2SO_3]^-$, $[CF_3CF_2OCFHCF_2SO_3]^-$, $[CF_3CFHOCF_2CF_2SO_3]^-$, $[CF_2HCF_2OCF_2CF_2SO_3]^-$, $[CF_2ICF_2OCF_2CF_2SO_3]^-$, $[CF_3CF_2OCF_2CF_2SO_3]^-$, $[(CF_2HCF_2SO_2)_2N]^-$, $[(CF_3CFHCF_2SO_2)_2N]^-$, F^-, and anions represented by the structure of the following formula:



wherein R^{11} is selected from the group consisting of:

(v) —CH_3, —C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(vi) —CH_3, —C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(vii) C_6 to C_{10} unsubstituted aryl, or C_3 to C_{10} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and

(viii) C_6 to C_{10} substituted aryl, or C_3 to C_{10} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(A) —CH_3, —C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,

(B) OH,

(C) NH_2, and

(D) SH.

11. A method according to claim **1** wherein an ionic liquid is selected from the group consisting of 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4], 1-hexyl-3-methylimidazolium bistrifluoromethylsulfonylimide [hmim][Tf_2N], and 1-butyl-3-methylimidazolium acetate [bmim][acetate].

12. An apparatus for adjusting the temperature of an object, medium or space, comprising:

(a) a primary refrigeration module that comprises a primary refrigeration loop containing a primary refrigerant, a condenser and an expansion valve;

(b) a secondary refrigeration module that comprises a secondary refrigeration loop containing a secondary refrigerant, and an evaporator;

(c) and a heat exchanger contacted by both the primary and secondary refrigeration loops; and

(d) an auxiliary container in fluid communication with the secondary refrigeration loop through a flow interrupter, said auxiliary container containing at least one ionic liquid;

wherein the condenser is located in proximity to an object, medium or space to be heated, or the evaporator is located in proximity to an object, medium or space to be cooled.

13. An apparatus according to claim **12** wherein the condenser is located in proximity to an object, medium or space to be heated.

14. An apparatus according to claim **12** wherein the evaporator is located in proximity to an object, medium or space to be cooled.

15. An apparatus according to claim **12** further comprising a compressor to compress the primary refrigerant.

16. An apparatus according to claim **12** further comprising an absorber to absorb the primary refrigerant in an ionic liquid.

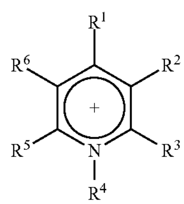
17. An apparatus according to claim **12** further comprising a heat source in thermal contact with the auxiliary container.

18. An apparatus according to claim **12** wherein the flow interrupter comprises a valve.

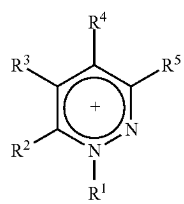
19. An apparatus according to claim **18** wherein the valve comprises a pressure relief valve.

20. An apparatus according to claim **12** wherein the secondary refrigerant comprises carbon dioxide.

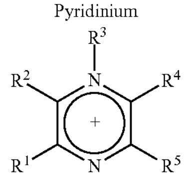
21. An apparatus according to claim **12** wherein an ionic liquid comprises a cation selected from the group consisting of cations represented by the structures of the following formulae:



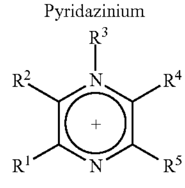
Pyridinium



Pyridazinium

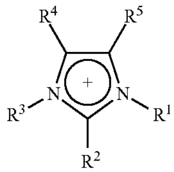


Pyrimidinium

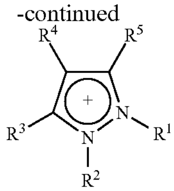


Pyrazinium

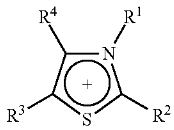
-continued



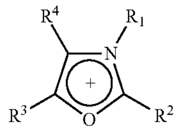
Imidazolium



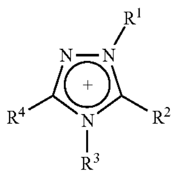
Pyrazolium



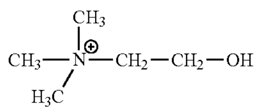
Thiazolium



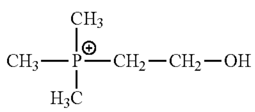
Oxazolium



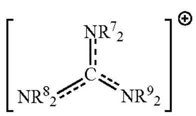
Triazolium



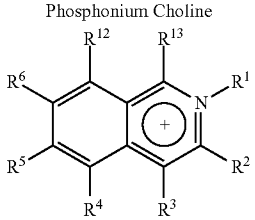
Choline



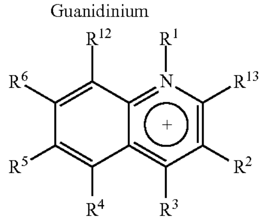
Phosphonium Choline



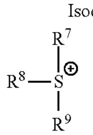
Guanidinium



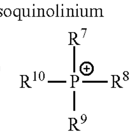
Isoquinolinium



Quinolinium

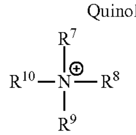


Sulfonium



Phosphonium

and



Ammonium

wherein:

A) R^1, R^2, R^3, R^4, R^5, R^6, R^{12} and R^{13} are independently selected from the group consisting of:

(xiii) H,

(xiv) halogen,

(xv) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(xvi) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(xvii) C_6 to C_{20} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S;

(xviii) C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(A) —CH_3, —C_2H_5, or C_3 to CM straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,

(B) OH,

(C) NH_2, and

(D) SH; and

(vii) —$(CH_2)_nSi(CH_2)_mCH_3$, —$(CH_2)_nSi(CH_3)_3$, —$(CH_2)_nOSi(CH_3)_m$, where n is independently 1-4 and m is independently 0-4;

B) R^7, R^8, R^9, and R^{10} are independently selected from the group consisting of:

(viii) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(ix) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(x) C_6 to C_{25} unsubstituted aryl, or C_3 to C_{25} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and C_6 to C_{25} substituted aryl, or C_3 to C_{25} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(E) —CH_3, —C_2H_5, or C_3 to C_{25} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,

(F) OH,

(G) NH_2, and

(H) SH; and

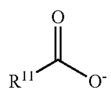
(xi) —$(CH_2)_nSi(CH_2)_mCH_3$, —$(CH_2)_nSi(CH_3)_3$, —$(CH_2)_nOSi(CH_3)_m$, where n is independently 1-4 and m is independently 0-4; and

C) optionally at least two of R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, and R^{10} can together form a cyclic or bicyclic alkanyl or alkenyl group.

22. An apparatus according to claim **12** wherein an ionic liquid comprises an anion selected from one or more members of the group consisting of: $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_3]^{3-}$, $[HPO_3]^{2-}$, $[H_2PO_3]^{1-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CuCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, carborates optionally substituted with alkyl or substituted alkyl; carboranes optionally substituted with alkylamine, substituted alkylamine, alkyl or substituted alkyl; and a fluorinated anion.

23. An apparatus according to claim **12** wherein an ionic liquid comprises a cation selected from one or more members of the group consisting of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, phosphonium, ammonium, benzyltrimethylammonium, choline, dimethylimidazolium, guanidinium, phosphonium choline, tetramethylammonium, and tetramethylphosphonium.

24. An apparatus according to claim **12** wherein an ionic liquid comprises an anion selected from one or more members of the group consisting of aminoacetate, ascorbate, benzoate, catecholate, citrate, dimethylphosphate, formate, fumarate, gallate, glycolate, glyoxylate, iminodiacetate, isobutyrate, kojate, lactate, levulinate, oxalate, pivalate, propionate, pyruvate, salicylate, succinamate, succinate, tiglate, tetrafluoroborate, tetrafluoroethanesulfonate, tropolonate, $[CH_3CO_2]^-$, $[HSO_4]^-$, $[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[AlCl_4]^-$, $[CO_3]^{2-}$, $[HCO_3]^-$, $[NO_2]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, $[PO_4]^{3-}$, $[HPO_4]^{2-}$, $[H_2PO_4]^-$, $[HSO_3]^-$, $[CUCl_2]^-$, Cl^-, Br^-, I^-, SCN^-, $[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[CF_3SO_3]^-$, $[HCF_2CF_2SO_3]^-$, $[CF_3HFCCF_2SO_3]^-$, $[HCClFCF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(CF_3CF_2SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[CF_3CO_2]^-$, $[CF_3OCPHCF_2SO_3]^-$, $[CF_3CF_2OCFHCF_2SO_3]^-$, $[CF_3CFHOCF_2CF_2SO_3]^-$, $[CF_2HCF_2OCF_2CF_2SO_3]^-$, $[CF_2ICF_2OCF_2CF_2SO_3]^-$, $[CF_3CF_2OCF_2CF_2SO_3]^-$, $[(CF_2HCF_2SO_2)_2N]_{-}$, $[(CF_3CFHCF_2SO_2)_2N]^-$, F^-, and anions represented by the structure of the following formula:



wherein R^{11} is selected from the group consisting of:

(ix) —CH_3, —C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(x) —CH_3, —C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene comprising one to three heteroatoms selected from the group consisting of O, N, Si and S, and optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH;

(xi) C_6 to C_{10} unsubstituted aryl, or C_3 to C_{10} unsubstituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and

(xii) C_6 to C_{10} substituted aryl, or C_3 to C_{10} substituted heteroaryl having one to three heteroatoms independently selected from the group consisting of O, N, Si and S; and wherein said substituted aryl or substituted heteroaryl has one to three substituents independently selected from the group consisting of:

(A) —CH_3, —C_2H_5, or C_3 to C_{10} straight-chain, branched or cyclic alkane or alkene, optionally substituted with at least one member selected from the group consisting of Cl, Br, F, I, OH, NH_2 and SH,

(B) OH,

(C) NH_2, and

(D) SH.

25. An apparatus according to claim **12** wherein an ionic liquid is selected from the group consisting of 1-butyl-3-methylimidazolium is hexafluorophosphate $[bmim][PF_6]$, 1-butyl-3-methylimidazolium tetrafluoroborate $[bmim][BF_4]$, 1-hexyl-3-methylimidazolium bistrifluoromethylsulfonylimide $[hmim][Tf_2N]$, and 1-butyl-3-methylimidazolium acetate [bmim][acetate].

* * * * *