

REFRIGERANT COMPOSITIONS AND USE THEREOF

The present invention relates to a refrigerant composition and more particularly a refrigerant composition comprising 1,1-difluoroethylene (R-1132a), which is suitable for use as a refrigerant in liquid chiller systems, such as in liquid chiller systems which are incorporated into or are thermal management systems of vehicles, especially electric vehicles.

The listing or a discussion of a prior-published document or any background in the specification should not necessarily be taken as an acknowledgement that a document or background is part of the state of the art or is common general knowledge.

Unless otherwise stated, it is to be understood that the term "electric vehicle" as used herein refers to both purely electric vehicles as well as vehicles which use electricity as one of several means of propulsion, such as hybrid vehicles.

The simple vapour compression cycle used for air-conditioning in internal combustion engine (ICE) vehicles is conventionally arranged with warm air being cooled and dehumidified by flowing in cross-flow over an evaporator heat exchanger in which the refrigerant evaporates inside the tubes of the evaporator. Similarly, heat is rejected outside the vehicle by flowing external air in cross-flow over the tubes of the condenser and condensing refrigerant inside the tubes. The air flowing over the evaporator drops in temperature and the air flowing over the condenser increases in temperature.

In this geometry, the refrigerant evaporation temperature must be below that of the air for heat exchange to occur in the evaporator; at the same time, it must be above that of the air for heat exchange to occur in the condenser. This is shown in Figure 1 for a single component refrigerant (or equivalently an azeotropic or nearly-azeotropic mixed refrigerant). In any real heat exchanger, there is a minimum economic temperature difference between hot and cold fluids, termed the "approach temperature" or "approach", as shown in Figures 1 to 3.

A non-azeotropic refrigerant used in the crossflow arrangement must also obey these constraints. However, in this case, the situation is made more complex by the existence of "temperature glide" (a phenomenon that a non-azeotropic refrigerant's temperature increases as it evaporates and decreases as it condenses). The total temperature change in evaporation or condensation is the temperature glide. This means that in an extreme case of pure crossflow, the refrigerant dewpoint temperature in the evaporator needs to be below the temperature of air leaving the evaporator, and the refrigerant bubble point in the condenser

needs to be above the air temperature. This situation is shown in Figure 2. It is evident from inspection of Figures 1 and 2 together that it is possible for the combined effect of temperature approach and glide to result in average evaporating and condensing temperatures for the non-azeotropic refrigerant that are quite different than would be the case if the fluid had no glide. This has the effect of penalizing the performance of the refrigerant relative to a fluid with no glide.

Increasingly, in electric vehicles (whether pure battery electric vehicles (BEV) or hybrid vehicles (HEV)), the air-conditioning system arrangement common to ICE is being supplanted or augmented by use of liquid coolant loops to recover waste heat from components that need cooling, notably the drivetrain battery, but also other electronic components. There are many configurations possible, ranging from a conventional air-conditioning system which also can feed refrigerant to a "chiller" to remove heat from the coolant loop, to an air-conditioning system that can be run in reverse as a heat pump to warm a passenger cabin, to a full "secondary loop" configuration. In the latter, the refrigerant is no longer used directly to warm or cool passenger air but instead is used to move heat between a reservoir of hot liquid and cold liquid; this allows use of the hot and cold liquids to heat/cool the passenger cabin air.

While the architectures are varied, a common feature of such thermal management systems involving secondary liquid heat transfer fluid circuits is that the heat exchangers for moving heat between refrigerant in the chiller system and the hot and cold liquids will be arranged so that the fluids are in counter-current flow. The effect of this arrangement is shown in Figure 3 for a non-azeotropic refrigerant (Figure 1 is still valid for refrigerants with no glide). It can be seen that in this arrangement, the glide now will have no adverse effect on performance. Furthermore, the average evaporating temperature can rise (relative to that of a fluid with no glide) and the average condensing temperature can fall (relative to that of a fluid with no glide). This means that the glide allows the refrigerant cycle to operate over a lower temperature range than the fluid with no glide and, consequently, to gain in relative capacity and energy efficiency.

It is an object of the present invention to address the above deficiencies.

According to a first aspect of the present invention, there is provided a use as a refrigerant of a composition comprising 1,1-difluoroethylene (R-1132a) in a liquid chiller system.

The present inventors have unexpectedly found that compositions comprising 1,1-difluoroethylene (R-1132a) (and especially the compositions comprising R-1132a,

difluoromethane (R-32) and 2,3,3,3-tetrafluoropropene (R-1234yf) can exploit their temperature glide to benefit in performance in liquid chiller systems (particularly the liquid chiller systems comprising one or more counter-flow heat exchangers) when compared to R-1234yf or binary mixtures of R-32 and R-1234yf used in similar systems. Particularly useful applications of the liquid chiller systems utilising such compositions include thermal management systems of vehicles, especially those of electric vehicles.

Liquid chiller systems which employ a vapour-compression cycle are known in the art. When used in such liquid chiller systems (particularly the liquid chiller systems comprising one or more counter-flow heat exchangers), the compositions disclosed herein exhibit superior refrigeration performance as compared to R-1234yf or binary mixtures of R-1234yf and R-32 (e.g. R-454C).

Specifically, the performance of the compositions disclosed herein is markedly improved when the compositions are used in a liquid chiller system employing a counter-flow heat exchanger geometry as compared to a cross-flow geometry. This is in direct contrast to the corresponding use of R-1234yf and binary compositions of R-1234yf and R-32 (e.g. R-454C), wherein such an improvement is not observed (in the case of R-1234yf) or is not substantial (in the case of R-454C).

In the use of the present invention, the composition typically comprises a second component selected from difluoromethane (R-32), 2,3,3,3-tetrafluoropropene (R-1234yf), *trans*-1,3,3,3-tetrafluoropropene (R-1234ze(E)), 1,1-difluoroethane (R-152a) and mixtures thereof.

Conveniently, the composition comprises at least about 1 or about 1.5 weight % R-1132a, such as at least 2 weight %, such as at least about 3 or about 4 weight %, for example at least about 5 weight %.

Advantageously, the composition comprises from about 1 to about 20 weight % R-1132a, such as from about 2 to about 15 weight %, for example from about 3 to about 12 weight %, optionally from about 4 to about 9 weight %

Typically, the second component is present in the composition in an amount from about 80 to about 99 weight %, such as from about 85 to about 98 weight %, for example from about 88 to about 97 weight %, optionally from about 91 to about 96 weight %.

Advantageously, the second component is R-32 and/or R-1234yf, preferably wherein the second component is R-32 and R-1234yf.

Conveniently, the R-32 is present in the composition in an amount of from about 1 to about 30 weight %, such as from about 2 to about 25 weight %, for example from about 3 to about 21 weight %, optionally from about 4 to about 19 weight %.

Typically, the R-1234yf is present in the composition in an amount of about 50 to about 98 weight %, such as from about 55 to about 97 weight %, for example from about 60 to about 96 weight %, optionally from about 65 to about 95 weight % or from about 70 to about 94 or about 92 weight %.

Conveniently, the composition comprises from about 1 to about 20 weight % R-1132a, from about 1 to about 30 weight % R-32 and from about 50 to about 98 weight % R-1234yf, such as wherein the composition comprises from about 2 to about 15 weight % R-1132a, from about 2 to about 25 weight % R-32 and from about 60 to about 96 weight % R-1234yf, for example wherein the composition comprises from about 3 to about 12 weight % R-1132a, from about 3 to about 21 weight % R-32 and from about 67 to about 94 weight % R-1234yf, optionally wherein the composition comprises from about 4 to about 9 weight % R-1132a, from about 4 to about 19 weight % R-32 and from about 72 to about 92 weight % R-1234yf.

In the use of the present invention, the composition is advantageously a non-azeotropic composition.

It is believed that the compositions disclosed herein exhibit a completely unexpected combination of low/non-flammability, low GWP, improved lubricant miscibility and improved refrigeration performance properties in the claimed use, liquid chiller system and thermal management system. Some of these properties are explained in more detail below.

The compositions of the present invention have zero ozone depletion potential.

Conveniently, the composition has a Global Warming Potential (GWP) of less than about 300, such as less than about 200, for example less than about 150.

Flammability may be determined in accordance with ASHRAE Standard 34 (e.g. ASHRAE Standard 34:2019) incorporating the ASTM Standard E-681, the entire content of which is incorporated herein by reference.

In one embodiment, the compositions have one or more of (a) a higher lower flammable limit; (b) a higher ignition energy (c) a higher auto-ignition temperature; or (d) a lower burning velocity compared to R-1132a alone.

Preferably, the compositions of the invention are less flammable compared to R-1132a in one or more of the following respects: lower flammable limit at 23°C; lower flammable limit at 60°C; breadth of flammable range at 23°C or 60°C; auto-ignition temperature (thermal decomposition temperature); minimum ignition energy in dry air or burning velocity. The flammable limits and burning velocity being determined according to the methods specified in ASHRAE-34 and the auto-ignition temperature being determined in a 500ml glass flask by the method of ASTM E659-78.

Typically, the composition is classified as "weakly flammable" (Class 2L) in accordance with ASHRAE Standard 34:2019 or ISO Standard 817.

Advantageously, the composition as formulated has a laminar burning velocity of less than about 10 cm/s, such as less than about 7 cm/s, for example less than about 5 cm/s.

The compositions disclosed herein are typically compatible with all classes of lubricants currently used with established HFC refrigerants. They may be optionally stabilized or compatibilized with mineral oils by the use of appropriate additives.

Typically, in the use of the present invention, the composition is combined with a lubricant.

The lubricant is conveniently selected from of mineral oil, silicone oil, polyalkyl benzenes (PABs), polyol esters (POEs), polyalkylene glycols (PAGs), polyalkylene glycol esters (PAG esters), polyvinyl ethers (PVEs), poly (alpha-olefins) and combinations thereof, preferably wherein the lubricant is selected from PAGs, POEs and mixtures thereof.

Typically, the composition has a coefficient of performance (COP) which is higher than that of R-1234yf or R-454C.

Conveniently, the composition has a volumetric cooling capacity which is higher than that of R-1234yf or R-454C.

In one embodiment, the composition may consist essentially of the stated components. By the term "consist essentially of", we include the meaning that the compositions contain substantially no other components, particularly no further (hydro)(fluoro)compounds (e.g. (hydro)(fluoro)alkanes or (hydro)(fluoro)alkenes) known to be used in heat transfer compositions. The term "consist of" is included within the meaning of "consist essentially of".

In an embodiment, the compositions are substantially free of any component that has heat transfer properties (other than the components specified). For instance, the compositions of the invention may be substantially free of any other hydrofluorocarbon compound.

In one embodiment, the compositions contain substantially no trifluoroiodomethane (CF_3I).

By "substantially no" and "substantially free of" we include the meaning that the compositions contain 0.5% by weight or less of the stated component, preferably 0.4%, 0.3%, 0.2%, 0.1% or less, based on the total weight of the compositions.

As used herein, all % amounts mentioned in the compositions herein, including in the claims, are by weight based on the total weight of the composition, unless otherwise stated.

By the term "about", as used in connection with numerical values of amounts of component in % by weight, we include the meaning of ± 0.5 weight %, for example ± 0.2 weight %.

For the avoidance of doubt, it is to be understood that the stated upper and lower values for ranges of the amounts of components in the compositions disclosed herein may be interchanged in any way, provided that the resulting ranges fall within the broadest scope of the invention.

The compositions may be prepared by simply mixing the R-1132a and the optional components, such as the second component (e.g. R-32 and R-1234yf) and/or a lubricant.

All of the chemicals described herein are commercially available. For example, the fluorochemicals may be obtained from Apollo Scientific (UK).

In the use of the present invention, the compositions are used as refrigerants in a liquid chiller system. Some of the preferred features of the liquid chiller system are discussed below.

Advantageously, the liquid chiller system comprises at least one counter-flow heat exchanger for exchanging heat between the refrigerant and the liquid.

The counter-flow heat exchanger allows the refrigerant and the liquid to flow in a counter-current flow relative to each other when the refrigerant and the liquid pass through the counter-flow heat exchanger. This is in contrast to a cross-flow heat exchanger, in which the liquid and the refrigerant flow roughly perpendicularly to each other when passing through the heat exchanger.

Typically, the liquid chiller system utilizes a vapour compression refrigeration cycle.

Conveniently, the at least one counter-flow heat exchanger comprises at least one compact-plate type counter-flow heat exchanger.

Advantageously, the liquid chiller system is a water chiller system or a water/glycol chiller system. Typically, the glycol can be ethylene glycol or propylene glycol (propane-1,2-diol). The liquid employed in the liquid chiller system may also be a synthetic hydrocarbon fluid, a silicone-based fluid or wholly or partially fluorinated fluid, for example a fluorinated ether or ketone.

Optionally, the liquid chiller system is a secondary loop liquid chiller system. In such systems, the refrigerant is used to transfer heat between "cold" and "hot" loops containing the liquid circulated in the liquid chiller system. It may also be used to provide direct cooling of the battery in parallel with providing conventional air-conditioning cooling.

Preferably, the liquid chiller system is incorporated into or is a thermal management system of a vehicle, preferably a thermal management system of an electric vehicle. Conveniently, the thermal management system of a vehicle is a heat pump and/or air-conditioning system.

Conveniently, the liquid chiller system is a liquid chiller system adapted for heating and/or cooling a battery and/or a passenger cabin of a vehicle, preferably of an electric vehicle. For example, the liquid chiller system may be adapted for cooling and/or heating the passenger cabin of a vehicle and may be adapted for cooling the battery of a vehicle. The liquid chiller system may also be adapted for cooling other sources of potentially useful waste heat such as power electronics, instrument displays or braking systems.

In a second aspect of the present invention, there is provided a liquid chiller system comprising at least one counter-flow heat exchanger for exchanging heat between a refrigerant composition and the liquid, said at least one counter-flow heat exchanger allowing the refrigerant composition and the liquid to flow in a counter-current flow relative to each other when the refrigerant composition and the liquid pass through the counter-flow heat exchanger, wherein the refrigerant composition is a composition comprising 1,1-difluoroethylene (R-1132a) and, optionally, a second component selected from difluoromethane (R-32), 2,3,3,3-tetrafluoropropene (R-1234yf), *trans*-1,3,3,3-tetrafluoropropene (R-1234ze(E)), 1,1-difluoroethane (R-152a).

It is to be understood that the preferred and optional features disclosed in respect of the first aspect of the invention shall analogously apply to the second aspect of the present invention.

Conveniently, the liquid chiller system is incorporated into or is a thermal management system of a vehicle, preferably a thermal management system of an electric vehicle. The thermal management system of a vehicle is typically a heat pump and/or air-conditioning system.

Typically, liquid chiller system is a liquid chiller system adapted for heating and/or cooling a battery and/or a passenger cabin of a vehicle, preferably of an electric vehicle. For example, the liquid chiller system may be adapted for cooling and/or heating the passenger cabin of a vehicle and may be adapted for cooling the battery of a vehicle. The liquid chiller system may also be adapted for cooling other sources of potentially useful waste heat such as power electronics, instrument displays or braking systems.

According to a third aspect of the present invention, there is provided a thermal management system of a vehicle comprising a liquid chiller system comprising at least one counter-flow heat exchanger for exchanging heat between a refrigerant composition and the liquid, said counter-flow heat exchanger allowing the refrigerant composition and the liquid to flow in a counter-current flow relative to each other when the refrigerant composition and the liquid pass through the counter-flow heat exchanger, wherein the refrigerant composition is a composition comprising 1,1-difluoroethylene (R-1132a) and, optionally, a second component selected from difluoromethane (R-32), 2,3,3,3-tetrafluoropropene (R-1234yf), *trans*-1,3,3,3-tetrafluoropropene (R-1234ze(E)), 1,1-difluoroethane (R-152a), preferably wherein the vehicle is an electric vehicle.

It is to be understood that the preferred and optional features disclosed in respect of the first and second aspects of the invention shall analogously apply to the second aspect of the present invention.

Conveniently, the liquid chiller system is a liquid chiller system adapted for heating and/or cooling a battery and/or a passenger cabin of a vehicle. For example, the liquid chiller system may be adapted for cooling and/or heating the passenger cabin of a vehicle and may be adapted for cooling the battery of a vehicle. The liquid chiller system may also be adapted for cooling other sources of potentially useful waste heat such as power electronics, instrument displays or braking systems.

Typically, the thermal management system further comprises at least one of the following: a vapor injection system, a high side receiver and/or a low side accumulator for storing the refrigerant composition.

The invention is illustrated by reference to the following non-limiting Figures, in which:

Figure 1 shows the temperature changes in heat exchangers for a single refrigerant or an azeotropic refrigerant.

Figure 2 shows the temperature changes in cross-flow heat exchangers for a non-azeotropic refrigerant.

Figure 3 shows the temperature changes in counter-flow heat exchangers for a non-azeotropic refrigerant.

The invention is illustrated by the following non-limiting examples.

EXAMPLES

- A thermodynamic model of the R-1132a/R-32/R-1234yf fluid system was built using the Span-Wagner equation of state as implemented in NIST REFPROP9.1 software. A pure fluid model
- 5 for R-1132a was derived by measuring its vapour pressure from boiling point to critical point, determining the critical point, measuring compressed liquid and vapour densities and measuring enthalpy content and heat capacity of the fluid in liquid and vapour states. Next, the vapour-liquid equilibrium behaviour of the binary mixtures of R-1132a with R-32 and R-1234yf was measured using constant-volume apparatus to measure the vapour pressure of a
- 10 series of binary compositions over a range of temperatures and pressures from about -50°C to $+70^{\circ}\text{C}$. These data were then regressed to provide binary interaction parameters suitable for use in modelling performance of ternary mixtures as refrigerants using standard cycle modelling techniques.
- 15 Subsequently, two refrigeration/heat pump cycle models were constructed in Microsoft Excel, linked to the REFPROP software to provide thermodynamic property data for the mixtures. In one model the heat exchanger geometry was assumed to be pure cross-flow, with a minimum temperature approach constraining the refrigerant phase change temperatures as shown in Figure 1 (for a fluid with zero glide) and Figure 2 (for the fluids with glide). In the other model
- 20 the heat exchanger geometry was assumed to be counter-current flow so that the same minimum temperature approach was used but was implemented to constrain phase change temperatures as shown in Figure 3. The performance of R-1234yf and a selected composition R-1132a/R-32/R-1234yf (6%/20%/74% by weight) was then simulated in both models and the results were compared. As a comparative example, the performance of refrigerant R-454C
- 25 (R-32/R-1234yf in proportions 21.5/78.5%) was also simulated. This refrigerant has a similar GWP to the ternary composition but has a smaller temperature glide.

The following cycle input conditions were assumed for the modelling:

Data Input Section		R1234yf
Target cooling capacity	kW	5
temperature approach in evaporator	K	3
temperature approach in condenser	K	3
Condenser glycol inlet temperature	°C	35
Condenser glycol temperature rise	K	10
Evaporator glycol inlet temperature	°C	15
Evaporator glycol temperature drop	K	8
Condenser subcooling	K	3.0
Evaporator superheat	K	1.0
Evaporator pressure drop	bar	0.50
Suction line pressure drop	bar	0.30
Condenser pressure drop	bar	0.30
Compressor suction superheat	K	10.0
Isentropic efficiency		65.0%

Table 1: Cycle input conditions

5 The modelling results are shown in Tables 2 and 3 below:

Table 2 Summary Results - Crossflow	Units	R1234yf	R1132a/R32/R1234yf 6/20/74%	R454C
Cooling COP		2.35	2.18	2.36
Volumetric cooling capacity	kJ/m ³	1518	2724	2640
Compressor suction pressure	bar	2.81	5.42	5.04
Compressor discharge pressure	bar	12.4	23.6	20.8
Pressure ratio		4.42	4.36	4.14
Compressor discharge temperature	°C	70.4	92.1	87.8
Compressor displacement	m ³ /hr	11.9	6.6	6.8

Table 3 Summary Results - Counterflow	Units	R1234yf	R1132a/R32/R1234yf 6/20/74%	R454C
Cooling COP		2.35	3.67	3.41
Volumetric cooling capacity	kJ/m ³	1518	4018	3463
Compressor suction pressure	bar	2.81	6.88	5.95
Compressor discharge pressure	bar	12.4	19.14	17.81
Pressure ratio		4.42	2.78	2.99
Compressor discharge temperature	°C	70.4	76.1	76.2
Compressor displacement	m ³ /hr	11.9	4.48	5.20

From the performance data, it can be seen that although the change in heat exchanger geometry does not affect the performance of R1234yf, it makes a significant difference to the performance of the ternary composition selected to illustrate the use of the invention.

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In crossflow, the selected blend exhibits slightly reduced COP compared to R-1234yf. However, in counter-flow, it exhibits significantly enhanced COP, reduced compressor displacement, reduced compression ratio and reduced compressor discharge temperature.

- 10 Furthermore, it can be seen from the performance data that although R-454C gains some performance benefit when used in conjunction with a counter-flow heat exchanger as compared to cross-flow heat exchanger, it does not gain as much as does the ternary composition.