

COMPOSITIONS

The present invention relates to compositions suitable for use as working fluids in air-conditioning and refrigeration applications. The compositions disclosed herein are especially
5 useful in heat pump water heaters, air-conditioning systems for trains, buses, cars and trucks, commercial refrigeration systems including supermarket display systems and cold rooms (such as walk-in fridges and freezers), and transportation refrigeration systems.

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

Carbon dioxide (CO₂, R-744) is finding favour as a low Global Warming Potential (GWP) refrigerant for applications where non-flammability of refrigerant is required. These
15 applications include air-conditioning systems for trains, buses, cars and trucks; heat pump-water heater systems; commercial refrigeration systems including supermarket display systems and cold-rooms, and transportation refrigeration systems fitted to refrigerated shipping containers or trucks.

CO₂ has two main disadvantages compared to other fluorocarbon refrigerants in use in the same applications. Firstly, it suffers from low energy efficiency in ambient temperatures of above about 25 to 30°C. Secondly, its operating pressures are much higher than those of traditional fluorocarbon-based systems.

25 Non-flammable refrigerant mixtures comprising difluoromethane (R-32) and CO₂ have been proposed (see Adams *et al.* (J. Chem. Eng. Data 16 (1971) 146-149) and US7238299, the contents of which are incorporated herein by reference in their entirety). Such non-flammable compositions can contain up to about 60% R-32 by weight.

30 However, such binary refrigerant compositions, whilst non-flammable as formulated, would still be considered as flammable according to ASHRAE Standard 34 (2019). This is because the mixtures are non-azeotropic. ASHRAE Standard 34 requires that the outcome of a series of vapour leakage experiments at a range of temperatures from -40°C to 60°C is considered to identify whether leakage can generate a more flammable composition than the "as-formulated"
35 composition. When this is done for non-flammable binary mixtures of R-32 with CO₂, a vapour leakage at -40°C will result in generation of a flammable composition, as the more volatile CO₂

is preferentially removed from the system, causing fractionation of the remaining material so that it contains more than 60% R-32.

Therefore, it would be desirable to identify refrigerant compositions which address these problems, whilst preferably retaining the non-flammability of pure CO₂. Such compositions should preferably also have a low GWP. In particular, a GWP of about 150 or less would be required under the European Union F-Gas Regulations for certain applications, such as air-conditioning systems in passenger cars or self-contained refrigeration appliances.

5 The present invention addresses the above and other deficiencies, and the above needs, by the provision of a composition comprising carbon dioxide (CO₂, R-744), difluoromethane (R-32), trifluoroiodomethane (CF₃I), and, optionally, 1,1-difluoroethylene (R-1132a). Such compositions will be referred to hereinafter as “the compositions of the (present) invention”.

15 The present inventor has found that relatively minor amounts of CF₃I may be added to R-744 and R-32 to ensure that the resulting mixture will not fractionate to a flammable composition when analysed according to the ASHRAE Standard 34 protocol. Furthermore, minor amounts of a flammable species (e.g. R-1132a) may also be added to the mixtures of the present invention without generating a flammable composition.

20

The compositions of the present invention are believed to be especially useful in heat transfer systems (e.g. refrigeration, air-conditioning and heat pump systems) utilising a transcritical refrigeration cycle. The basic transcritical cycle consists of the following steps:

- 25 (a) Evaporation of a liquid refrigerant at low pressure to remove heat from a low temperature source fluid (such as air);
- (b) Compression of the resultant refrigerant vapour in a compressor to yield a hot, high pressure gas;
- (c) Cooling of the high-pressure gas by heat exchange with a sink fluid, at higher temperature than the source, to yield a cooler, dense refrigerant gas at high pressure. This gas is said to be a “supercritical” fluid, since it is above its critical temperature; and
- 30 (d) Expansion of the supercritical fluid through an expansion valve or other restriction device to give a two-phase mixture of liquid refrigerant with vaporised refrigerant vapour at low pressure; this mixture is then fed back to the evaporator stage (a) to complete the cycle.

35

Optionally, in such a cycle there occurs an internal heat exchange process between the warm high-pressure gas leaving the gas cooler, and the cool vapour flowing from the evaporator to

the compressor. This process takes place in an "internal heat exchanger" ("IHX") and has the effect of boosting the refrigeration capacity and efficiency of the cycle.

5 Conveniently, such a transcritical refrigeration cycle may contain a liquid accumulator positioned after the evaporator (and before the IHX, if one is used). This serves to hold excess charge of refrigerant when the external ambient temperature is such that the gas cooler pressure is reduced.

10 The compositions of the present invention have also been found to be suitable for use in such cycles, whether incorporating IHX or accumulator features or not.

The compositions of the present invention will now be described in detail.

15 According to the present invention, there is provided a composition comprising CO₂, R-32 and CF₃I.

20 Typically, the compositions of the present invention comprise from about 50 to about 98 weight % CO₂, such as from about 52 or about 55 to about 95 weight %, for example from about 59 to about 92 weight %, preferably from about 65 or 70 to about 90 weight %, optionally from about 75 to about 87 weight %.

25 Conveniently, the compositions of the invention comprise from about 1 to about 30 weight % R-32, such as from about 2 to about 25 weight %, for example from about 3 to about 21 weight %, optionally from about 3 to about 15 weight %.

Advantageously, the compositions of the invention comprise from about 1 or 2 to about 20 weight % CF₃I, such as from about 3 to about 15 or about 13 weight %.

30 Typically, the compositions of the present invention comprise from about 50 to about 98 weight % CO₂, from about 1 to about 30 weight % R-32 and from about 1 to about 20 weight % CF₃I, such as from about 55 to about 90 weight % CO₂, from about 2 to about 28 weight % R-32 and from about 2 to about 17 weight % CF₃I, for example from about 57 to about 85 weight % CO₂, from about 2 to about 26 weight % R-32 and from about 3 to about 17 weight % CF₃I.

35 The compositions of the present invention may additionally comprise R-1132a.

When present, the compositions of the present invention typically comprise from about 1 or about 2 to about 20 weight % R-1132a, such as from about 4 to about 17 weight %, for example from about 7 to about 16 weight %, optionally from about 10 to about 15 weight %.

- 5 Advantageously, the amount of R-1132a is selected so that the compositions of the present invention comprise R-32 and R-1132a in a combined amount of less than about 37 weight %, such as less than about 35 weight %.

- 10 Conveniently, the compositions of the present invention comprise R-32 and CF₃I in a weight ratio of R-32 to CF₃I of less than about 2:1, such as less than about 1.8:1.

- 15 The compositions of the invention may additionally comprise a further component selected from 1,1,1,2-tetrafluoroethane (R-134a), *trans*-1,3,3,3-tetrafluoropropene (R-1234ze(E)), 2,3,3,3-tetrafluoropropene (R-1234yf), 1,1,1,2,3,3,3-heptafluoropropane (R-227ea) and mixtures thereof.

- Typically, the further component is R-134a or R-134a and one or more of R-1234yf and R-1234ze(E). Alternatively, the compositions may additionally comprise one or more of R-1234yf and R-1234ze(E) as a further component.
- 20

Conveniently, the compositions of the present invention comprise from about 1 about 15 weight % of the further component(s), such as from about 3 to about 12 weight %, for example from about 4 or about 5 to about 10 weight %.

- 25 In one embodiment, the compositions of the present invention consist essentially of the stated components. By the term "consist essentially of", we include the meaning that the compositions of the invention 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
- 30 "consist essentially of".

- In one embodiment, the compositions of the invention 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.
- 35

By “substantially no” and “substantially free of” we include the meaning that the compositions of the invention 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.

- 5 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 %.

10

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

15

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

- Typically, the compositions of the present invention have a Global Warming Potential (GWP) which is less than 220, such as less than about 210 or less than about 200, for example less than about 150, preferably less than about 140.

- Conveniently, the compositions of the invention are non-flammable as determined by ASHRAE Standard 34:2019. For example, the compositions of the invention are non-flammable at a test temperature of 60°C using the ASHRAE-34 methodology. Advantageously, the mixtures of vapour that exist in equilibrium with the compositions of the invention at any temperature between about -20°C and 60°C are also non-flammable.

- It is believed that the compositions of the invention exhibit a completely unexpected combination of low/non-flammability, low GWP, improved lubricant miscibility and improved performance properties when used in refrigeration systems, especially in air-conditioning systems. Some of these properties are explained in more detail below.

- Typically, the compositions of the present invention have a coefficient of performance (COP) which is greater than or about equal to that of CO₂.

35

Conveniently, the compositions of the present invention have a temperature glide in a condenser or an evaporator of less than about 11K, such as less than about 9K, for example less than about 7K.

- 5 Advantageously, the compositions of the invention have a volumetric refrigeration capacity which is within about 25% of that of CO₂, such as within about 20%, for example within about 15%.

Typically, the compositions of the invention have an operating pressure in a condenser or an
10 evaporator which is lower than that of CO₂.

The compositions of the invention are typically suitable for use in existing designs of equipment and are believed to be compatible with all classes of lubricants and currently used with established HFC refrigerants. They may be optionally stabilized or compatibilized with mineral
15 oils by the use of appropriate additives.

Preferably, the lubricant is selected from mineral oil, silicon 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
20 lubricant is selected from PAGs, POEs and combinations thereof.

Conveniently, a stabiliser is selected from diene-based compounds, phosphates, phenol compounds and epoxides, and mixtures thereof.

- 25 In another aspect of the present invention, there is provided a use of a composition of the present invention as a working fluid in a heat transfer system.

Typically, the heat transfer system is a refrigeration, heat pump or air-conditioning system.

- 30 Preferably, the refrigeration system comprises a commercial refrigeration system (such as a supermarket display refrigeration system, beverage cooler refrigeration system, warehouse refrigeration system or a cold-room refrigeration system), or a transportation refrigeration system (for example a refrigeration system fitted to a refrigerating shipping container or a refrigeration system fitted to a vehicle).

35

Conveniently, the heat pump system comprises a water heater heat pump system.

Preferably, the air-conditioning system comprises a transportation air-conditioning system, such as a bus, car, train or truck air-conditioning system.

Advantageously, the heat transfer (e.g. refrigeration, heat pump and/or air-conditioning) systems defined above operate as transcritical heat transfer systems for at least part of the year.

In some of the applications of transcritical cycle technology, a vapour compression cycle used is a single compression cycle as is typical in mobile air-conditioning applications. In other applications, the gas compression is carried out in two stages, which permits efficient operation over a large temperature difference between heat source and heat sink temperatures. It is believed that the compositions of the invention are suitable for use in a single and dual compression stage cycles.

In one aspect of the present invention, there is provided a use of the composition of the invention as an alternative for an existing working fluid in a heat transfer device, such as a new heat transfer device designed to meet the same application requirements.

Conveniently, the existing working fluid is R-410A. Alternatively, the existing working fluid may be R-407C.

In another aspect of the present invention, there is provided a heat transfer device comprising a composition of the present invention.

Preferably, the heat transfer device is a transcritical heat transfer device, such as a transcritical refrigeration, heat pump or air-conditioning device.

Optionally, the transcritical heat transfer device comprises an internal heat exchanger (IHX) system.

The transcritical heat transfer device may also comprise a liquid accumulator positioned after the evaporator, or, if the IHX is present, between the evaporator and the IHX.

According to another aspect of the invention, there is provided a method of producing heating which comprises condensing a composition of the invention in the vicinity of a body to be heated.

According to another aspect of the invention, there is provided a method of producing cooling which comprises evaporating a composition of the invention in the vicinity of a body to be cooled.

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

- The compositions of the invention may be prepared by simply mixing CO₂, R-32 and CF₃I (and optional components, such as R-1132a and/or a lubricant) in the desired proportions. The
10 compositions can then be added to a heat transfer device or used in any other way as described herein.

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

EXAMPLES

The vapour liquid equilibrium behaviour of CO₂ with CF₃I and with R-32 is described in the academic literature and the available data was used to generate interaction parameters for use with the NIST REFPROP9.1 software. The vapour liquid equilibrium behaviour of CF₃I with R-32 and R-1132a, and of R-1132a with CO₂ and R-32 was studied experimentally in the temperature range –40°C to 70°C using a constant-volume equilibrium apparatus, and the resulting data also used to fit binary interaction parameters for each binary pair. The principle of measurement of this experimental work was the determination of vapour pressure for a series of known compositions over a range of temperatures, followed by regression to the thermodynamic model to minimise the difference between calculated and observed pressure over the data set.

The interaction parameters thus obtained were used with the NIST REFLEAK5.1 computer program to simulate the fractionation of ternary CO₂/R-32/CF₃I mixtures and quaternary R-744/R-1132a/R-32/CF₃I mixtures at –40°C. The compositions studied had 1-30% R-32 and the quaternary compositions had up to 15% by weight R-1132a. The initial fill composition for these simulations was taken as 90% of maximum allowable liquid fill, where the allowable liquid fill was calculated according to the requirements of ASHRAE Standard 34 (2019). The fractionation was run from the initial fill to 95% mass loss for each composition.

Modelling of a series of compositions led to the following observations

- If the total amount of R-1132a + R-32 in the blend is less than about 35% then the initial vapour and liquid compositions are non-flammable.
 - If the mass ratio of R-32 to CF₃I in the composition is less than or equal to about 2:1 then the final liquid and vapour compositions will be substantially free of CO₂ and R-1132a and will contain less than 58% by weight of R-32, ensuring they will be non-flammable
- Standard refrigeration cycle modelling techniques were then used to estimate the performance of selected compositions of the invention. The performance of R-744 was also calculated as a comparative example. Where the cycle conditions resulted in the high-pressure side of the cycle operating above the fluid critical temperature (a “transcritical” cycle) then the compressor discharge pressure was varied to optimise the cycle efficiency (Coefficient of Performance -

COP). The cycle modelled was a transcritical cycle using an internal heat exchanger (IHX) to exchange heat between the gas leaving the gas cooler and the low-pressure vapour leaving the evaporator.

- 5 The following conditions were assumed for the modelling purposes:

Air temperature rise over gas cooler	10	K
Air on temperature	33	°C
Air off temperature	43	°C
Temperature approach in gas cooler	4	K
Capacity	6	kW
Mean evaporation temperature	7	°C
Evaporator superheat	0	K
Suction line heat gain across IHX	20	K
isentropic efficiency	65%	

Table 1: Model input conditions

- 10 The performance data for the selected compositions of the invention is shown in Table 2 below.

It can be seen from the performance data that the compositions of the invention have superior energy efficiency and reduced operating pressures compared to CO₂. In addition, the GWP of the compositions is less than about 210.

15

From the performance data, it can be seen that is not desirable to include more than about 30 weight % R-32 in these compositions because the temperature glide in the evaporator becomes greater than 11K. R-32 content of 21% or lower ensures the GWP of the composition will be lower than 150, which is required for some applications under the EU F-Gas Regulation.

20

The compositions of the invention can be further augmented by the addition of R-1132a, for example by substitution of a portion of the R-744 content with R-1132a, so that the R-1132a content is between 1% and 15% by weight without generating a flammable composition during fractionation. Addition of R-1132a reduces compressor discharge temperature and reduces the temperature glide in the evaporator. Such compositions also have higher energy efficiency and reduced operating pressures compared to R-744.

25

Table 2: Compositions comprising CO₂, R-32, CF₃I and, optionally, R-1132a.

	R744	R1132a	R32	CF3I	100%	59%	58%	54%	52%	55%	62%	68%	70%	76%
					0%	10%	10%	15%	10%	0%	0%	0%	0%	0%
					0%	21%	21%	21%	25%	30%	25%	21%	20%	16%
					0%	10%	11%	10%	13%	15%	13%	11%	10%	8%
Coefficient of Performance	2.69	3.12	3.12	3.10	3.21	3.30	3.22	3.16	3.14	3.04				
Volumetric cooling capacity	14497	11646	11591	11333	11288	11364	11852	12208	12312	12497				
Compressor discharge temperature	102.6	105.6	105.9	103.7	107.7	113.5	111.8	109.7	109.0	106.5				
Evaporator pressure	41.8	28.1	27.8	27.7	25.8	24.2	26.5	28.5	29.2	31.4				
Gas cooler pressure	90.2	62.8	62.4	61.7	58.9	56.9	61.0	64.4	65.5	68.9				
Evaporator glide	0.0	7.8	8.0	7.7	9.1	10.4	9.4	8.3	7.8	6.4				
COP	100.0%	116.1%	116.2%	115.5%	119.4%	122.9%	120.0%	117.5%	116.8%	113.3%				
Q _{vol}	100.0%	80.3%	79.9%	78.2%	77.9%	78.4%	81.8%	84.2%	84.9%	86.2%				
GWP	1	142	142	142	169	203	169	142	136	109				